Design, Synthesis and Characterization of
Functional Metal-Organic Framework Materials

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of Master of Science in Chemical Science

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ABSTRACT


Badriah J. Alamer

Over the past few decades, vast majority of industrial and academic research throughout the world has witnessed the emergence of materials that can serve as ideal candidates for potential utility in desired applications, and these materials are known as Metal Organic Framework (MOFs). This exceptional new family of porous materials is fabricated by linkage of metal ions or clusters and organic linkers via strong bonds. MOFs have been awarded with remarkable interest and widely studied due to their inherent structural methodology (e.g. use of various metals, expanded library of organic building blocks with different geometry and functionality particularly frameworks designed from carboxylate organic linkers) and unquestionably unique structural and chemical features for many practical applications. (i.e. gas storage/separation, catalysis, drug delivery etc). Simply, metal organic frameworks epitomize the beauty of porous chemical structures. From a design perspective, the introduction of the Molecular Building Block (MBB) approach is actively being pursued pathway by researchers toward the construction of MOFs by employing inorganic building blocks and organic linkers and taking advantage of not only their multiple coordination modes and geometries but also the way in which they are reticulated to generate final framework. In this thesis, research studies will be directed toward (i) the investigation of the relationship between experimental parameters and synthesis of well-known fcu –MOF, (ii) rational design and synthesis of new rare
earth (RE) based MOFs, (ii) isoreticular materials based on particular MBB ([M₃O(RCO₂)₆]), M= p- and d-block metals, and (iv) zeolite- like metal organic framework assembled from single-metal ion based MBB ([MN₂(CO₂)₄]) via 2-, 3-, and 4-connected organic linkers. Consequently, the porosity, chemical and thermal stability, and gas sorption properties will be evaluated and detailed.
ACKNOWLEDGEMENTS

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<td>$^\circ$C</td>
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<tr>
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CHAPTER 1: INTRODUCTION

1.1 Preamble

“Synthesis is the process of making a natural product, or some other substance, artificially, in the lab, one step at a time, from extremely simple building blocks”

Gregory Petsko

The quest for designing novel materials for particular applications has become a great challenge for researchers aiming to address the urgent real-world demands. To meet this target, significant attention has been paid to develop new routes toward designing and synthesizing of materials owning desirable properties. Hence, in this direction, efforts have been undertaken to introduce superior functionality materials based upon combination of multiple components. Metal organic framework (MOFs) emerged as new class of hybrid porous materials built up from metal ions or cluster and organic linkers which are linked through coordination bonds to form networks in one-, two-, three dimensions and proven to possess unprecedented potential for a large number of applications i.e. storage media, gas separation, catalysis, drug delivery, selective sensing etc…

MOFs are very attractive because of their tunability and remarkable degree of diversity in the inorganic and organic units they can possess in their structures. The advantages of having accurate control of inorganic-organic components during the assembly process coupled with their unique physical properties are expected to drive this field further into new realms of synthetic chemistry where astonishing materials can be achieved.
Moreover, the possibility to be able to predict coordination geometries, to some extent, by carefully choosing the metal ions and organic ligands gives rise to generate a varied ambit of framework architectures. Many of fruitful rational design approaches have been developed and arisen to facilitate the construction of desired materials. This chapter will give a brief historical perspective of MOFs along with some useful terminologies.

1.2 Overview of History:

As early as 1943, examples of crystalline materials generated using metal centers and nitrogen organic linkers emerged namely, Werner-type complexes. This class of compounds has the general formula \( \text{MX}_2\text{L}_4 \) where \( M \) is assigned to divalent metal in an octahedral geometry (e.g., Zn, Cu), \( X \) is assigned to an anionic ligand (e.g. \( \text{NCO}^- \), \( \text{CN}^- \), \( \text{NO}_3^- \)), and \( L \) is assigned to pyridine coordinated molecule (Figure 1.1).  

![Figure 1.1: a fragment of Werner complex, Ni(SCN)_2(4-methylpyridine). Color code: Ni= green, C= gray, S= yellow and N= blue.](image)

At the end of 1960s, other examples that involved compounds of Hofmann-type clathrate were discovered and fully investigated by Iwamoto and co-workers, and these
compounds were extracted from original compound that possessed the formula Ni(NH$_3$)$_2$(CN)$_4$(C$_6$H$_6$) and discovered first by K.A. Hofmann (Figure 1.2).\textsuperscript{14,15}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{hofmann_clathrate.png}
\caption{example of Hofmann clathrate structure. Color code: Cu = green, Ni = yellow, N = blue and C = gray. H atoms omitted for clarity.}
\end{figure}

Another early family of inclusion compounds, known as Prussian blue consists of mixed valence Fe ions bridged via cyano-entity, and identified by X-ray technique in 1970 (Figure 1.3).\textsuperscript{16}
In 1756, Axel Frederik Cronstedt discovered the first natural Zeolites, namely stilbite, and since then, research on this class of porous material has rapidly increased. Functional microporous materials began to appear in 1990 when Robson and co-workers recorded porous coordination polymers which displayed ion exchange properties. In the meantime, Omar M. Yaghi and co-workers prepared a revolutionary compound that has been reported to be the first robust and highly porous material, MOF-5 as compared to zeolite and activated carbon. MOF-5 is synthesized from zinc acetate building block and benzene-1,4-dicarboxylic acid, having a **pecu**-topology (Figure 1.4).
Since the 1990s, MOFs have become one of the hottest topics in material chemistry, which have experienced a unique growth. The variability in the potential geometry, size, permanent porosity, adjusted pore size, and functionality has opened the door for more than 20,000 various MOFs to be synthesized and studies over the past few decades.\textsuperscript{11}

1.3 Metal Organic Frameworks Constructed from Carboxylate Ligands:

The extended library of organic ligands (ditopic, tritopic, tetratopic ligand etc) that coordinate metal ions in different fashion (i.e. monodentate, bidentate) can give rise to an infinite combination of both organic and inorganic parts leading to the formation of different MOFs. The carboxylate functionality allows chelation of metal ions to yield rigid and geometrically determined clusters. However, the major challenge is finding the appropriate conditions that permit the formation of metal clusters.
1.4 Topological Perspective

The analysis of reported materials has allowed the MOF community to identify different Building Units that can be used to describe the obtained materials. Indeed, only few symmetrical geometrical figures are employed to describe most of the MOFs that have been synthesized as shown in figure 1.5.\textsuperscript{18}

![Image](image_url)

*Figure 1.5: High symmetry inorganic molecular building block (MBBs) (left) and organic molecular building block (right) and their related secondary building units (SBUs)*

For example, the well-known tetrazine acetate cluster of MOF-5 can be simplified as an octahedral building unit if we consider carbons of carboxylate moieties as points of extension. Following the same reasoning, the copper paddle wheel cluster is considered as a square building block (Figure 1.5).

The utilization of appropriate organic and inorganic building units allows the chemist to design and target specific structures that display an interesting topology. For example, the combination of ditopic organic building block such as benzene dicarboxylic acid and 12-
connected inorganic building unit such as lanthanide based hexanuclear cluster give rise to a face cubic structure (\textbf{fcu} topology, Figure 1.6).

![Figure 1.6: left, 12-connected building unit. Right, \textbf{fcu} topology based on 12-connected cluster and ditopic ligand.](image)

1.5 Molecular Building Block Approach

The molecular building approach can be defined as the utilization of specific molecular species that forms in solution prior to be combined by organic species. Established by Eddaoudi \textit{et al}, this very powerful approach allows the chemist to design materials with specific structural characteristics. Eddaoudi \textit{et al}, among others have developed strategies to synthesize very interesting MOF based on trimer building unit with the following formula $\text{M}_3\text{O(CO}_2\text{)}_3$ (M= In$^{3+}$, Fe$^{3+}$, Al$^{3+}$). More recently, Eddaoudi \textit{et al}. have discovered a very interesting modulator namely 2-fluorobenzoic acid that has the
property to be able to participate in the formation of a unique new building block based on lanthanide. In solution, perfect control of the hexanuclear cluster formation allows the fabrication of a new series of interesting materials for gas sorption-separation applications (fcu-MOF, ftw-MOF…).

1.6 Crystal Structure, Purity and Thermal Stability

Prior to examining and pinpointing the capabilities of materials for various applications, thorough characterization is needed to draw a good conclusion about their structural properties. Numerous state-of-art techniques have been used here to confirm the structures and features of prepared MOFs. Techniques were utilized for this purposes include: powder X-ray Diffraction (PXRD), single-crystal X-ray Diffraction (SCXRD), Thermogravimetric Analysis (TGA), Infrared Spectroscopy (IR), Elemental Analysis and Adsorption-Desorption measurements. Herein, we will discuss the basic principles of each technique, and what kind of structural information is relevant to each one.

**Powder X-Ray Diffraction (PXRD):**

Powder X-ray diffraction (PXRD) reveals information about the purity of the material as the X-ray powder pattern is considered as a fingerprint of the sample. The measurements were carried out on a PANalytical X’Pert X-ray diffractometer using for CuKa (λ=1.5418 Å) with scan speed of 20/min and step size of 0.032°.

**Single-Crystal X-Ray Diffraction (SCXRD):**

Single-Crystal X-Ray diffraction provides data used to determine the structure of a material. A suitable amount of the crystalline solid is put on glass fiber where X-ray
diffraction intensities were collected with a Bruker-AXS SMART-APEX2 CCD diffractometer (Cu Kα = 1.54178Å) at 150K. The substantial redundancy in the data allowed a semi-empirical absorption correction (SADABS) to be applied, on the basis of multiple measurements of equivalent reflections. The structures were solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least squares on all F² data using SHELXTL.

**Thermogravimetric Analysis (TGA):**

Thermogravimetric analysis probes the changes in the mass of the material as a function of temperature. It gives quantitative measurement related to weight changes accompanied with the transition of the material and thermal degradation. Hence, it can be used to determine the thermal stability of the material. Here, thermogravimetric analysis was performed on a TA Q500 apparatus with samples held in a platinum pan following a specific program (heating rate of 10°C under air atmosphere).

**Fourier-Transform Infrared (FT-IR):**

The principle behind Fourier-Transform Infrared is based on the fact that molecules absorb particular frequencies that are assigned to specific type of functional group existing among the material. The IR spectra (4000-600 cm⁻¹) were performed on powdered samples and were collected on a Thermo Scientific Nicolet 6700 apparatus.

**Elemental Analysis:**

In order to confirm the experimental formula of the material, the elemental analysis technique is the most common method. Samples are burned in the presence of excess oxygen. The analysis of volatile combustion product is utilized to calculate the
composition of the material by means of chromatography. These CHN analyses were conducted with a Thermo Scientific Flash 2000 instrument.

**Brunauer- Emmett- Teller (BET) and Pore Analysis:**

Brunauer- Emmett- Teller (BET) and Pore Analysis studies were recorded and calculated on a fully microspore gas analyzer at 77K using an Autosorb 6B (Quantachrome Instruments) at relative pressure up to 1 atm. Total pore volume and specific surface areas were calculated according to BET method at relative pressure of P/Po of 0.988.

**1.7 Investigation of MOFs Porosity and Protocol for Sample Activation:**

It is of essential importance to fully activate porous MOFs prior to sorption studies. However, identifying the suitable protocol is ongoing challenge. Indeed, MOFs that possess permanent porosity are mostly activated through solvent exchange. In other words, guest molecules of higher boiling points which occupy cavities or channels of as-synthesized MOF are exchanged with volatile solvent such as EtOH, CH₂CN, (CH₃)₂CO etc at RT. For example, Eddaoudi and co-workers stated that host molecules in MOF-5 can be completely exchanged with chloroform, and easily evacuated from the void spaces without losing the crystallinity.¹⁸ This method was evident to be successful for numerous porous MOFs but still sometimes not proper for many compounds.

To overcome this challenge, some alternative methods have been suggested. One method offered by Hupp and co-workers¹⁹ based upon liquids that have a specific critical point at specific pressure and temperature where the densities of liquids which have a specific critical point at a specific pressure and temperature where densities of liquid and gas phase of the transitional fluid are same. For this, CO₂ is considered as favorable solvent
since its critical pressure reaches 1072 psi, and its lower critical temperature of 31°C. When the critical points transition appears, the gas phase can be completely removed from the sample with no affect on the framework. Supercritical CO₂ activation is an appropriate method to avoid the damage of many MOFs.

1.7 Principles and Fundamentals of Adsorption

Adsorption systems can be described as plots of the mass of adsorbate as a function of partial pressure at constant temperature. Adsorption is attributed to the process where adsorbate molecules are accumulated onto the surface of adsorbent, the reverse process, where adsorbate molecules are removed from a surface is termed as desorption. Based upon the interactions between the adsorbate and adsorbent, the adsorption can be divided into two principle mechanisms chemisorption and physisorption and the differences between them as shown in table 1.1.
Table 1.1: schematic representation of the differences between Chemisorption and Physisorption.

<table>
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<th>Chemisorption</th>
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<td>Occurs only at the temperature below the boiling point of the adsorbate. (molecule)</td>
<td>Can occur at all temperatures</td>
</tr>
<tr>
<td>Heat of adsorption is less than 40KJmol⁻¹</td>
<td>Heat of adsorption can be more than 200 KJmol⁻¹</td>
</tr>
<tr>
<td>The adsorbed amount increases when the pressure of adsorbate is increasing.</td>
<td>Pressure is Insignificant.</td>
</tr>
<tr>
<td>The adsorbed amount depends more on the nature of the adsorbate than the adsorbent (surface).</td>
<td>The adsorbed amount depends on both the nature of the adsorbent and the adsorbate.</td>
</tr>
<tr>
<td>No appreciable activation energy is required.</td>
<td>An appreciable activation energy maybe involved in the process.</td>
</tr>
<tr>
<td>Multilayer adsorption occurs.</td>
<td>Only the monolayer adsorption occurs.</td>
</tr>
</tbody>
</table>

To better understand how sorption isotherms behave, IUPAC classified the pore size according to the diameter of pore. (i) Microspores ≤ 2 n.m, (ii) Mesopores 2 n.m to 50 n.m, and Macropores > 50 n.m. There are six types of adsorption isotherms and porous material should fall into one of them as shown in figure 1.7.
Type I is typical for adsorbents with characteristics of microporous solid where the adsorption process is limited to few molecular layers. This is the case in many of MOFs, zeolites and activated carbon.

Type II is observed for non-porous or macroporous solids, and it indicates to a monolayer coverage followed by multilayers at high relative pressure.

Type III is observed as a curve convex with relative pressure axis, and it is characteristic of non-porous or micropores materials where weak adsorbate-adsorbent interactions occur which leads to low uptake at low relative pressures.
Type IV is distinguished by appearance of hysteresis loop, which is common character associated with existence of mesoporosity. This isotherm shows a restricted uptake at high relative pressures.

Type V is combination of type III and IV isotherms and it is indicative of microporous and mesoporous materials.

Type VI is unique because each adsorbed layer is represented via stepwise multilayer adsorption on homogenous non-porous solid.
CHAPTER 2: RARE-EARTH BASED METAL ORGANIC FRAMEWORK
MATERIALS

2.1 Introduction

Features as high coordination number and connectivity led to fascinating growth of lanthanide based metal organic frameworks (Ln-MOFs) in recent years. These promising materials have shown unique applications compared to transition metals, in sorption and catalyst, optical magnetic etc. By implementing judicious metal-containing component and organic linkers and employing distinctive design strategies such as MBB approach, furnish novel porous materials can be obtained. In this chapter, the majority of research studies will be highlighting mainly by the investigation of different parameters on well-defined fcu-MOF, synthesis of new rare earth RE based MOFs by using ditopic such as aminoterephalic acid, 2-NH₂BDC and 3-amino-3′-fluoro-[1,1′-biphenyl]-4,4′dicarboxylic acid, NH₂FPC as well as flexible tetratopic ligand such as benzoimidephenanthroline tetracarboxylic acid, H₄BIPA-TC. The synthesis and characterization of all compounds will be described.

2.2 Evaluation of The Impact of Different Parameters on The Synthesis RE Based MOFs with fcu-Topology

2.2.1 Introduction

Rational construction of made-to-order materials with programmable and modular features has propelled chemists to dedicate more effort to design and discover ideal
materials that can be considered as crucial in the sense of addressing energetic societal challenges and for environmental sustainability issues. Consequently, many conceptual approaches have been developed. One of the most important concepts, introduced by our group, is the Molecular Building Block (MBB) approach. This concept is based on inserting desired properties and functionalities in preselected modular building block at the design step before the assembly process. The successful enforcement of MBB approach relies on the selection of an ideal blueprint net that belongs solely to its corresponding basic building unit, and then establishing the reaction conditions that allow the in situ generation of desired MBB.\textsuperscript{20-23}

Metal Organic Frameworks constructed from Rare Earth (RE) polynuclear carboxylate based cluster are of prime interest because of their distinguished properties (i.e. gas storage, gas separation, catalysis). Interestingly, based on aforementioned approach (MBB), our group has succeeded for the first time to isolate the reaction conditions that allow the formation of series of MOFs constructed of a hexanuclear RE-based MBB and thus possessing the face centered cubic topology (fccu) by using fluorinated ligands or 2-flourobenzoic acid as modulator.\textsuperscript{24}
This fascinating discovery inspired us to further explore the parameters that control the formation of above-mentioned system and in particular to validate the fact that fluorinated modulator are mandatory for the in-situ generation of the specific hexanuclear cluster. Intentionally, we opted to investigate the impact of changing different synthetic conditions (modulator, concentration of metal, metal/ligand ratio) on the synthesis of the fcu-MOF platform. Different modulators have been used to evaluate their impact on the in-situ formation of hexanuclear clusters. 2-chlorobenzoic acid, 2-nitrobenzoic acid, benzoic acid, fluoroacetic acid and chloroacetic acid have been chosen because their pKa values are close to the one of 2-fluorobenzoic acid (pKa =3.27) and also to evaluate the impact of different functionalities such chlorine or nitro instead of fluorine. Chloroacetic acid and fluoroacetic acid have also been tested to determine if (i) an aliphatic acid could allow the formation of such new cluster and (ii) any fluorinated modulator can play the same role as 2-fluorobenzoic acid.
2.2.2 Experimental Conditions

A typical reaction involves a mixture of 2-aminoterephthalic acid, Tb(NO$_3$)$_3$.5H$_2$O in DMF (1mL), EtOH (0.5 mL), and chlorobenzene (0.5mL) heated at 115°C for 72h. All the synthetic reactions conditions were summarized in the following table.

<table>
<thead>
<tr>
<th>Modulator [1M]</th>
<th>pKa</th>
<th>M/L</th>
<th>M/MD</th>
<th>M (0.087M)</th>
<th>L [0.087M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorobenzoic acid (0.348mmol)</td>
<td>2.92</td>
<td>1:2</td>
<td>1:8</td>
<td>0.0435mmol</td>
<td>0.087mmol</td>
</tr>
<tr>
<td>2-Nitrobenzoic acid (0.348mmol)</td>
<td>2.16</td>
<td>1:2</td>
<td>1:8</td>
<td>0.0435mmol</td>
<td>0.087mmol</td>
</tr>
<tr>
<td>Benzoic acid (0.348mmol)</td>
<td>4.19</td>
<td>1:2</td>
<td>1:8</td>
<td>0.0435mmol</td>
<td>0.087mmol</td>
</tr>
<tr>
<td>Chloroacetic acid (0.348mmol)</td>
<td>2.86</td>
<td>1:2</td>
<td>1:8</td>
<td>0.0435mmol</td>
<td>0.087mmol</td>
</tr>
<tr>
<td>Fluoroacetic acid (0.348mmol)</td>
<td>2.59</td>
<td>1:2</td>
<td>1:8</td>
<td>0.0435mmol</td>
<td>0.087mmol</td>
</tr>
</tbody>
</table>

Table 2: Summary of the experimental condition for the study of the effect of different modulator on the fcu-MOF synthetic conditions.
2.2.3 Results and Discussion

The different chemical systems were investigated along a large range of concentration and at different metal/ligand ratio (Figure 2.2).

![Figure 2.2: Summary of experimental condition applied to different chemical system.](image)

The investigation over this large range of concentration using non-fluorinated modulators shows clearly that it is not possible to synthesize the targeted fcu-MOF. Either the concentration of the mixture or either the metal/ligand ratio have an impact on the in-situ formation of this specific hexanuclear cluster. Consequently, we decided to evaluate the effect of another fluorinated modulator to confirm the need of using fluorine-based modulator. Accordingly, we decided to use fluoroacetic acid that has pKa 2.59 which is different from 2-fluorobenzoic acid one. As expected, we could manage to synthesize the targeted fcu-MOF without any problem. To further confirm our conclusion, we decided to test this new modulator on another platform from our group namely gea-MOF that has
another type of cluster (nonannuclear). Successfully, we could obtain this new material using this new modulator.

The scientific explanation of the phenomena is not clearly evidenced to date. Many hypotheses can be formulated in order to try to explain the easy formation of cluster instead of chains of Rare Earth but all of them are related to the presence of fluorine atoms. Accordingly, it can be due to the repelling effect of fluorine atoms, as it is well known that fluorinated materials are hydrophobic. Fluorine atom is also the most electronegative element on Earth. Consequently, it can help in stabilizing the formation of cluster using hydrogen bond. Further experiments will be conducted in the future to elucidate this important phenomenon that allow us to fabricate a very interesting new class of materials.

2.3 Synthesis of New RE Based MOFs Using Ditopic and Tetratopic Ligands

2.3.1 Introduction

The investigation of factors governing the synthesis of fcu-MOF platform allowed us to clearly establish the essential role of 2-fluorobenzoic acid. During this study, two new materials have been isolated using 2-chlorobenzoic and 2-fluorobenzoic acid respectively. These results encouraged us also to evaluate the impact of 2-fluorobenzoic acid on a new chemical system displaying this time a tetracarboxylic acid, namely benzoimidephenanthroline tetracarboxylic acid.
2.3.2 Experimental Section

2.3.2.1 Materials

All chemical and solvents were used in the preparation of compounds as received from Fisher Scientific and Sigma-Aldrich.

2.3.2.2 Synthesis of Organic Linkers

2.3.2.2.1 Synthesis of 3-amino-3'-fluoro-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H$_2$NH$_2$FPDC)

![Figure 2.3: Structure of 3-amino-3'-fluoro-[1,1'-biphenyl]-4,4'-dicarboxylic acid](image)

3-amino-3'-fluoro-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H$_2$NH$_2$FPDC):

A solution of 18-crown-6 (0.66 g, 2.5 mmol) in THF (60 ml) and absolute EtOH (30 ml) was degassed by bubbling argon through for 60 minutes. Then, methyl 2-amino-4-bromobenzoate (2.3 g, 10 mmol), 3-fluoro-4-methoxycarbonylphenylboronic acid (2.18 g, 11 mmol) [1,1'-bis (diphenylphosphino)ferrocene]dichloropalladium(II) (0.220 g, 0.3 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 0.246 g, 0.6 mmol) and finely grounded K$_3$PO$_4$ (4.24 g, 20 mmol) were added, the whole was stirred under argon atmosphere at 90 °C for 22 h. The reaction mixture was then filtered through Celite® and the solvent evaporated. The residue was absorbed on silica gel and subjected
to column chromatography (100% hexane to 100% ethyl acetate) to yield the product as yellow solid (2.71 g, 74%), consisting of a mixture of ethyl/methyl esters, as evidenced by $^1$H NMR (Appendix). It was taken into the next step without further purification. 3-amino-3'-fluoro-[1,1'-biphenyl]-4,4'-dicarboxylic acid: the intermediate triester was dissolved in 7:1 THF/MeOH mixture (80 ml). An aqueous NaOH solution (2 g in 100 ml H$_2$O, 50 mmol) was added to this mixture and then stirred at RT for 18 h. The solution was washed with diethyl ether (50 ml, discarded), then acidified to pH = 4 using 2N HCl. The precipitate was separated by filtration, washed thoroughly with water and air-dried to yield 1.755 g (64% in 2 steps) of dark yellow solid. $^1$H NMR (600MHz, DMSO-d$_6$): $\delta =$ 7.95 (m, 3H), 7.79 (d, $J$=8.3, 1H), 7.54 (m, 2H), 7.11 (d, $J$=1.7, 1H), 6.88 (dd, $J_1$=8.3, $J_2$=1.8, 1H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta =$ 169.2, 164.80, 164.78, 162.3, 160.6, 151.7, 145.84, 145.77, 142.5, 132.5, 122.44, 122.42, 118.6, 114.9, 114.7, 114.5, 113.4, 109.9. $^{19}$F NMR (376.7 MHz, DMSO-d$_6$): -109.8 (m, 3F).

2.3.2.2.2 Synthesis of benzoimidephenanthroline tetracarboxylic acid

![Synthesis of benzoimidephenanthroline tetracarboxylic acid](image)

Figure 2.4: Synthesis of benzoimidephenanthroline tetracarboxylic

The benzoimidephenanthroline tetracarboxylic acid, H$_4$BIPA-TC was synthesized according to optimized procedure from the literature.$^{26}$ 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.769 g, 2.8674 mmol), 5-aminoisophthalic acid
(0.536 g, 2.9588 mmol) and DMF (15mL) were mixed and refluxed in a round bottom flask at 180\(^\circ\)C for 1 h. The temperature was reduced to 160\(^\circ\)C for roughly 4 h and then cooled to room temperature to obtain a homogenous light brown precipitate that was separated by filtration, washed thoroughly with MeOH and DMF and finally air-dried.

**2.3.2.3 Synthesis of New MOFs**

2.3.2.3.1 \{(DMA)\(_2\)Tb\(_3\)(HCO\(_2\))\(_2\)(NH\(_2\)BDC)\(_4\)\}, 1

A mixture of Tb(NO\(_3\))\(_5\)H\(_2\)O (9.78 mg, 0.0225 mmol), 2-aminoterephthalic acid (2-NH\(_2\)BDC) (4.07 mg, 0.0225 mmol), 2-chlorobenzoic acid (28.18 mg, 0.18 mmol), H\(_2\)O (0.511 mL), DMF (1.019 mL), was prepared in a 20-mL scintillation vial and subsequently heated to 115\(^\circ\)C for 72 h and cooled to room temperature to give brown needle crystals. Crystals of 1 were harvested and washed with DMF.

2.3.2.3.2 \{(DMA)\(_2\)Tb\(_6\)(OH)\(_8\)(H\(_2\)O)\(_6\)(NH\(_2\)FPDC)\(_6\)\(_{\text{solv}}\)\}, 2

A mixture of Y(NO\(_3\))\(_6\)H\(_2\)O (16.66 mg, 0.0435 mmol), ligand (11.96 mg, 0.0435 mmol), 2-fluorobenzoic acid (49.04 mg, 0.35 mmol), H\(_2\)O (0.5 mL), DMF (1.5 mL), was prepared in 20-mL scintillation vial and subsequently heated to 105 \(^\circ\)C for 72 h and cooled to room temperature to give brown polyhedral crystals. Crystals of 2 were harvested and washed with DMF. The formula has been confirmed by elemental analysis.

Calculated %C, N, H: 43.53; 4.62; 3.30. Experimental %C, N, H: 42.03; 5.24; 3.57.
2.3.2.3.3 \{(Tb_{2}(HCO_{2})_{2}(BIPA-TC))_{1.5}\}, 3

A mixture of Tb(NO_{3})_{3}.5H_{2}O (18.92 mg, 0.0435 mmol), H_{4}BIPA-TC (12.93 mg, 0.0217 mmol), 2-fluorobenzoic acid (97.52 mg, 0.696 mmol), and DMF (1.152 mL), was prepared in a 20-mL scintillation vial and subsequently heated to 115 °C for 12 h and cooled to room temperature to give pure brown square crystals. Crystals of 3 were harvested and washed with DMF. The formula has been confirmed by elemental analysis. Calculated %C, N, H: 36.54; 4.90; 2.79. Experimental %C, N, H: 32.66; 2.54; 1.15. The slight difference between experimental and calculated values is attributed to solvent molecules present within cavities.

2.3.3 Results and Discussion:

2.3.3.1 \{(DMA)_{2}Tb_{3}(HCO_{2})_{2}(NH_{2}BDC)_{4}\}

Compound 1 is obtained after heating a reaction mixture of Tb(NO_{3})_{3}.5H_{2}O and (2-NH{sub}2BDC) in a DMF/H_{2}O solution, resulting in brown needles crystals. The single-crystal X-ray crystallography studies reveals that the compound 1 is formulated as \{(DMA)_{2}Tb_{3}(HCO_{2})_{2}(NH_{2}BDC)_{4}\} and crystallizes in an orthorhombic space group \textit{Pmmn}. The crystal structure of 1 reveals a 3- periodic framework built-up from trimer secondary building unit consisting of three crystallographically equivalent Terbium cations, and each two adjacent metal ions are bridged through three-deprotonated 2-aminoterephtalate moieties. The coordination spheres of terbium cation are completed by one water molecule (d_{Tb-O}= 2.834 Å) and two formate anions (Figure 2.5). The presence of formate anions allows the connection between trimers that forms infinite chains along the [010]
direction; these chains are connected via organic linker to generate a 3D porous material displaying channels with an aperture of 6 Å (Figure 2.5).

The purity of the compound was confirmed by similarities between the experimental and calculated powder X-ray diffraction patterns (Figure 2.6).
Figure 2.6. Comparison between the calculated and experimental Powder X-ray diffraction patterns of 1 showing the purity of the material.

The confirmation of the porosity and the evaluation of gas storage performance have not been performed because of a problem of reproducibility. Although different starting materials and different reaction conditions were tested, we could not synthesize more material for further characterization.

2.3.3.2 \{(DMA)₂Tb₆(OH)₈(H₂O)₆(NH₂FPDC)₆.(solv)ₓ\}

The reaction of NH₂FPDC with Y(NO₃)₃.6H₂O under solvothermal conditions yields colorless homogenous crystals having a polyhedral morphology and crystallizing in cubic space group \(Fm\overline{3}m\) (compound 2). The microcrystalline material was characterized and formulated by single-crystal X-ray diffraction studies as \{(DMA)₂Y₆(OH)₈(H₂O)₆(NH₂FPDC)₆.(solv)ₓ\}. The single crystal structure of 2 is a 3-
periodic feu-MOF constructed from \([(Y_6(\mu_3-OH)_8(O_2C^-)_{12})\)] inorganic MBBs linked by heterofunctional dicarboxylate organic MBBs, namely \(\text{NH}_2\text{FPDC}\). Obviously, each Y metal ion is coordinated to eight (\(\mu_3\)-OH) groups belonging to carboxylate moieties, and ninth coordinated site is occupied with a water molecule. In the same time, adjacent Y ions are linked via \(\mu_3\)-OH and deprotonated carboxylate in a bis-monodentate fashion to result in a \([(Y_6(\mu_3-OH)_8(O_2C^-)_{12})\)] MBB.

The powder X-ray diffraction pattern of as-synthesized compound is in a good agreement with calculated pattern and thus proves the purity of the compound (Figure 2.7).

Figure 2.7. Comparison between the calculated and experimental Powder X-ray diffraction patterns of 2 showing the purity of the material

Thermal stability of 2 has been evaluated using thermogravimetric analysis. The first loss mass occurs starts from 50 °C and is attributed to the departure of DMF molecules. The material retains its stability until 275 °C (Figure 2.8).
Detailed knowledge of thermal behavior of compound 2 can be understood by using \textit{in situ} variable temperature X-ray diffractometry to probe reaction kinetics in crystalline sample. Practically, we collected a number of scans at different temperature ranging from 25 °C to 400 °C. The structural insights from these measurements indicate that this material is thermally stable up to 275 °C as depicted in Figure 2.9.
In terms of chemical stability, we used different solvents such as H₂O, Acetone, Acetonitrile, Chloroform, Ethanol, and Methanol separately for 24 h. We run the PXRD and observed that the compound is stable in all solvents. In addition to that, we exposed the sample to air for 24h, and it was stable as well. That means the framework of our material is not affected by changing the mother solvent, which allow us to have an idea about the most suitable solvent to study gas sorption-adsorption (Figure 2.10).
The permanent porosity study of compound 2 was operated on an activated acetonitrile-exchanged sample under nitrogen ambience at 77K. The uptake of nitrogen adsorbent follows a fully reversible type I isotherm (Figure 2.11). The effective BET was deduced to be 2432.70 m$^2$g$^{-1}$ with a corresponding empirical pore volume of 0.959 cc/g. These values agree perfectly with the theoretical value (2450 m$^2$g$^{-1}$, 0.965 cc/g).
2.3.3.3 \{\text{(DMA)}_2\text{\(\text{Tb}_2\text{(HCO}_2\text{)}_2\text{(BIPA-TC)}_{1.5}\text{(solv)}_x\)}_x\}\)

Solvothermal reaction between \(\text{Tb(NO}_3\text{)}_3\cdot.5\text{H}_2\text{O}\) and benzoimidephenanthroline tetracarboxylic acid (\(\text{H}_4\text{BIPA-TC}\)) in an \(\text{N},\text{N}'\)-dimethylformamide solution and in the presence of 2-FBA as modulator yielded brownish square crystals, formulated by single-crystal X-ray diffraction study (SCXRD) studies as: \{\text{(DMA)}_2\text{\(\text{Tb}_2\text{(HCO}_2\text{)}_2\text{(BIPA-TC)}_{1.5}\text{(solv)}_x\)}_x\}_3.

Compound 3 crystallizes in a monoclinic space group \(\text{C2/m}\). The structural analysis of resulting crystal discloses the \textit{in situ} generation of Terbium dimer building blocks. Analysis of the Tb dimer reveals that each two Tb\textsuperscript{3+} cations are surrounded by eight oxygen atoms belonging to three carboxylates from three independent (\(\text{H}_4\text{BIPA-TC}\)) ligands connected in a monodentate fashion, and one carboxylate connected to the metal
ion in a bidentate fashion, whereby other three coordination sites are occupied by water molecules. Accordingly, these dimers gives rise to a 4-connected inorganic MBB $[\text{Tb}_2(\text{O}_2\text{C}-)_4]$ (Figure 2.12), where the carbon atoms of carboxylate moieties acts as points of extension (Figure 2.12). Each inorganic MBB are bridged together via four separate organic linkers leading to the formation of novel compound displaying an 4,4-c \textit{lvt} topology. The generated 3-periodic structure possesses cavities with size estimated to be 10Å.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.12.png}
\caption{Left, connection between Terbium based dimer and tetratopic organic linker. Middle, pillaring of square-grid via tetratopic organic ligand. Right, schematic representation of the \textit{lvt} topology}
\end{figure}
The phase purity of crystalline material for 3 was confirmed by similarities between as-synthesized and calculated PXRDs (Figure 2.13).

![Figure 2.13. Comparison between the calculated and experimental Powder X-ray diffraction patterns of 3 showing the purity of the material](image)

The stability of the 3 has been investigated by immersing the product in different solvents such as Methanol, Ethanol, Acetone, Acetonitrile, and Chloroform for 24 h while one sample was exposed to air for the same time. Markedly, the peaks of samples in Chloroform, Acetonitrile, and Acetone were matching the powder X-ray diffraction pattern of the as-synthesized material whereby the peaks of the samples in the rest of the solvents were slightly shifted, and this observation could be correlated to the nature of the solvent that may induce a slight change of the framework of the foregoing MOF. However, the exposure of the material to air reveals that the material is not stable as confirmed by the experimental Powder X-ray diffraction (Figure 2.14).
The thermal stability of the material has been evaluated using thermogravimetric analyses as shown in Figure 2.15. The continuous weight loss of around 25% is observed before 400 °C attributed to the departure of DMF molecules located within cavities.

![Thermogravimetric analysis of compound 3](image)

> Figure 2.15. Thermogravimetric analysis of compound 3
Nitrogen gas adsorption studies performed on activated acetonitrile exchanged sample at 77 K, showed fully reversible type-I isotherm, which is characteristic of microporous materials. The apparent BET and pore volume were estimated to be 0.643 cc/g and 148.23 m$^2$ g$^{-1}$, respectively. In fact, compound 3 has a very moderate free volume and low surface area as compared to the theoretical values (Figure 2.16). Consequently, the experimentally obtained total pore volume is lower than the associated theoretical value derived from SCXRD data, i.e. 858.5 m$^2$ g$^{-1}$ and 1.28cc/g.

![Nitrogen sorption isotherm for compound 3 at 77K](image)

*Figure 2.16: Nitrogen sorption isotherm for compound 3 at 77K*

A plausible explanation of this phenomenon could be due to either framework collapse resulting from removing some guest molecules or improper solvent exchange protocol. Further investigations on the activation process are in progress.
2.3.4 Summary

To sum up, we have successfully synthesized dimer, trimer, and hexanuclear rare earth based metal organic framework by involving multi-carboxylate organic ligands. Those structures exemplify the power of Molecular Building Block MBB to target a specific net. In conjugation with that, the gas sorption properties were investigated. Some of studied materials exhibit a good capability to uptake nitrogen adsorbent in contrast to others which have lower values than the anticipated ones and consequently the future work will be toward identifying the suitable synthetic and activation protocol.
CHAPTER 3: ASSEMBLY OF METEL ORGANIC FREAMWORK BASED ON TRIMER BUILDING BLOCK VIA SINGULAR AND MIXED POLYCARBOXYLTE LIGANDS

3.1 Introduction

The search for new porous MOFs with high thermal and chemical stability has been one of the main objectives for several research groups. So far, most of isolated MOFs are based on divalent metal ions (i.e. Cu$^{+2}$, Zn$^{+2}$, Ni$^{+2}$); however, recent studies have shown that chemical stability, especially toward hydrolysis can be improved through using trivalent metal ions instead. Furthermore, tremendous efforts have been made on construction of MOFs with trivalent cations since Fêrey et al published the first report on the family of Cr-MIL-88 platform. These materials are built from trimeric building units and versatility of ditopic linkers and have exhibited amazing features in terms of stability and fully reversible swelling amplitudes. This cluster with the formula $[M_3(\mu_3-O)(O_2CR)_6]$ can be exemplified as trigonal prism, which is one of the most high symmetrical MBBs and usually its surface is decorated by six binding carboxylate moieties. Iron (III) and indium (III) are considered as highly promising candidates to obtain such kind of MBBs conjugated with their unique features especially iron owing to its redox properties, low toxicity, cheap component etc. This chapter is devoted to describe the synthesis, characterizations of 3D open frameworks based on Indium- or iron-trigonal prismatic building block and single or mix organic linkers following the mix-ligand approach.
3.2 Experimental Method of Synthesis

3.2.1 Materials

All chemical and solvents were used in the preparation of compounds as received from Fisher Scientific and Sigma-Aldrich.

3.2.2 Synthesis of New MOFs

3.2.2.1 \( \{\text{Fe}_3\text{O}(\text{H}_2\text{O})_3(\text{BTB})_2(\text{Cl})(\text{solv})_x\} \), 4

FeCl\(_3\).6H\(_2\)O (29.19 mg, 0.108 mmol) and 1,3,5-Tris(carboxyphenyl)benzene, BTB (7.01 mg, 0.016 mmol) were added to a solution of DEF (2mL) and trifluoroacetic acid (0.08 mL, 2M in DEF) in a 20 mL scintillation vial, heated at 130 °C for 20 h and then cooled. The as-synthesized orange octahedral crystals were collected and washed with DEF. The crystals of 4 were found to be insoluble in water and other common organic solvents. The formula has been confirmed by elemental analysis. Calculated %C, H: 55.42; 4.33. Experimental % C, H: 58.46; 3.25. The slight difference between experimental and calculated values is attributed to solvent molecules present within cavities.

3.2.2.2 \( \{\text{In}_3\text{O}(\text{H}_2\text{O})_3(\text{PIBA-TC})_3(\text{BTB})_2(\text{NO}_3)_3(\text{solv})_x\} \), 5.

In(NO\(_3\))\(_3\).5H\(_2\)O (32.4032 mg, 0.108 mmol), BTB (7.01 mg, 0.016 mmol) and H\(_4\)PIBA-TC (14.31 mg, 0.024 mmol) were added to a solution of DEF (2mL) and HNO\(_3\) (0.3 mL, 3.5 M in DMF) in a 20 mL scintillation vial, heated at 105 °C for 24 h and then cooled to RT to produce a cubic orange crystals which were harvested and washed with DEF. The crystals of 5 were found to be insoluble in water and common organic solvents. The
formula has been confirmed by elemental analysis. Calculated % C, N, H: 43.69; 5.04; 3.85. Experimental % C, N, H: 44.5; 2.16; 2.0. The slight difference between experimental and calculated is attributed to solvent molecules present within cavities.

3.2.2.3 \{Fe_3O(H_2O)_3\}[PIBA-TC]_3(BTB)_2(Cl)_3(solv)_x\}, 6.

FeCl$_3$.6H$_2$O (27.03 mg, 0.1mmol), BTB (14.47mg, 0.033mmol) and H$_4$PIBA-TC (29.82 mg, 0.05 mmol) were added to a solution of DMF (3mL) and trifluoroacetic acid (0.06 mL, 2M in DMF) in a 20 mL Teflon lined autoclave, heated up to 150°C for 48 h and then cooled gradually to RT to give dark brown cubic crystals, which were harvested and washed with DMF. The crystals of 6 were found to be insoluble in water and common organic solvents. The formula has been confirmed by elemental analysis. Calculated % C, N, H: 42.80; 4.65; 3.97. Experimental % C, N, H: 51.5; 2.5; 2.32. The slight difference between experimental and calculated values is attributed to solvent molecules present within cavities.

3.3 Results and Discussion

3.3.1 \{Fe_3O(H_2O)_3(BTB)_2(Cl)(solv)_x\}, 4

Solvothermal reaction between BTB and FeCl$_3$.6H$_2$O in DEF/CF$_3$CO$_2$H solution yielded homogenous crystals of, compound 4. The as-synthesized material, characterized by single crystal X-ray diffraction as \[Fe_3O(H_2O)_3(BTB)_2(Cl)(solv)_x\], crystallizes in orthorhombic space group Pca2$_1$. The study of its crystal structure reveals that compound 4 is constructed from oxo-bridged ternary iron- carboxylate cluster and possess the formula \[Fe_3O(O_2C^-)_6.(H_2O)_3\]. In mentioned trimer, there are three iron metal ions; each
iron cation is coordinated to six oxygen atoms to adopt an octahedral shape with the following formula \([\text{FeO}_5(\text{H}_2\text{O})]\). Concurrently, all three iron cations are connected through one central \(\mu_3\)-oxo anion. Crystallographic analysis exhibit that each trimer is bridged via six crystallographic independent organic linkers leaving the three apical positions occupied by terminal water molecules (Figure 3.1). Topological interpenetration indicates that components of 4 can be described as the assembly of three connected nodes (organic linker) and 6- connected nodes (iron trimer) resulting in the formation of periodic network having \((3,6)\)-c topology.

Figure 3.1. Assembly of iron based trimer inorganic building block and tritopic organic building block to generate a material with a \((3,6)\)-c topology.
The purity is confirmed by similarities between experimental and simulated X-ray powder diffraction (PXRD) patterns (Figure 3.2).

![Graph showing PXRD patterns](image)

*Figure 3.2. Comparison between the calculated and experimental Powder X-ray diffraction patterns of 4.*

The chemical stability of compound 4 has been investigated by soaking the product in diverse solvents such as H₂O, Acetone, Acetonitrile, Chloroform, Ethanol, and Methanol for 24h. The product showed a good stability as proved by comparison of theoretical and experimental powder X-ray patterns. The air stability has been evaluated but unfortunately the material is air sensitive, behavior attributed to the breakdown of iron-carboxylate chemical bond upon normal drying at RT (Figure 3.3).
Figure 3.3 Comparison between the calculated and experimental Powder X-ray diffraction patterns of 4 showing the stability of the material in different solvent.

In order to assess the sorption properties, solvent molecules present in cavities were exchanged with acetonitrile for 24h. The material was then loaded into sample cell and outgassed for roughly 8 h at RT. The crystallographic perspective reinforces the fact that this material is highly porous since it has two well-defined types of channels running along the a and b crystallographic directions displaying an aperture of approximately 7 Å. However, the activation attempts using common low boiling solvents were unsuccessful. Indeed, the values of BET and pore volume values were lower than anticipated ones. This is assigned to the framework collapse upon removal of the exchanged solvent. Consequently, an alternative method to avoid this problematic issue is to use supercritical CO₂ as defined in chapter 1. The successful use of supercritical CO₂ allows us to access
the porosity of the material. Indeed, the recorded nitrogen isotherm at 77 K shows a fully reversible type I isotherm (Figure 3.4). The apparent BET surface area was evaluated to be 1581 m$^2$g$^{-1}$ and total pore volume 0.65 cc/g respectively. However, the results do not match with the theoretical pore value that is estimated to be 1.6 cc/g.

![Graph showing nitrogen sorption isotherms for compound 4 at 77K](image)

*Figure 3.4 Nitrogen sorption isotherms for compound 4 at 77K*

Thermogravimetric analysis of 4 points out two essential weight variations, which are situated around 100°C and 400°C. The first loss is due to the departure of coordinated water and solvent molecules; the second loss comes from the decomposition of material (Figure 3.5).
3.3.2 \{\text{In}_3\text{O}(\text{H}_2\text{O})_3\text{(PIBA-TC)}_3\text{(BTB)}_2\text{(NO}_3)_3\text{(solv)}_x\}, \text{5}

Reaction between \text{In(NO}_3)_3, \text{BTB, and H}_4\text{PIBA-TC in N,N’-diethylformamide under solvothermal conditions result in unprecedented MOF based on mixed organic building block, compound 5. This material formulated by single crystal X-ray diffraction study as \{\text{In}_3\text{O}(\text{H}_2\text{O})_3\text{(PIBA-TC)}_3\text{(BTB)}_2\text{(solv)}_x\} crystallized in the cubic space group \text{Fm}-3\text{m}. Analysis of the resultant crystal structure reveals the formation of specific building unit, namely iron based trimer. This building unit comprised of three-iron cations, which are located in the same plane and share one oxo-center that possesses three-fold rotation axis. The analysis of the trimer cluster shows that these inorganic building units are connected by two tritopic and four tetratopic ligands in a bis-monodentate fashion through carboxylate moieties leaving the three apical sites coordinated to terminal aqua
molecules. The generated 3-periodic structure encloses two interesting kinds of octahedral cages (Figure 3.6). The biggest cage delimited by four BTB and six trimmers, and it has an octahedral shape with porosity of 12 Å.

Figure 3.6: Assembly of indium based trimer, tritopic organic building block and tetratopic organic building unit to generate a new material with 3,4,6-c topology
The second cage displaying also an octahedral shape delimited by six trimer and twelve isophtalic moieties belonging to BIPA ligand shows a smaller cavity of 7 Å. The topology analysis allows us to consider the BTB ligand as 3-connected node, the BIPA-TC ligand as 4-connected node, and the inorganic building block as 6-connected node. Consequently, the 3-periodic compound can be simplified as the assembly of 3, 4, and 6 connected nodes resulting in the generation of a new 3,4,6-connected topology.

The powder X-ray diffraction of as-synthesized material matches exactly with the simulated pattern. Consequently the compound 5 does not contain any impurities (Figure 3.7).

![Figure 3.7 Comparison between the calculated and experimental Powder X-ray diffraction patterns of compound 5](image)

To evaluate the thermal stability of compound 5, a thermogravimetric analysis has been performed under N₂ with a heating rate of 1°C/min. Two weight losses steps occur around 80°C and 480°C. The first one is assigned to the departure of the solvent (DEF)
followed by a second one, which is assigned, to the decomposition of the material (Figure 3.8).

Figure 3.8. Thermogravimetric analysis of compound 5

In order to establish the activation conditions, we dispersed the same amount of the product in several polar or apolar solvents including Water, Acetone, Acetonitrile, Chloroform, N-methylpyrrolidone, Ethanol and Methanol for 24 h. The powder X-ray diffraction analysis shows that the material retained its stability in acetone, n-methylpyrrolidone, and chloroforms while it lost its stability in other solvents (Figure 3.9). In parallel, the air stability at RT has also been evaluated and it was found that unfortunately, the material is air sensitive. The objective of this study was to determine
which solvent has to be chosen properly to activate properly the material before adsorption measurements.

![Comparison between the calculated and experimental Powder X-ray diffraction patterns of 4 showing the stability of the material in different solvent](image)

To evaluate the activation temperature, the thermal stability of compound 5 has been tested under vacuum at different temperature ranging from $25\,^\circ\mathrm{C}$ to $375\,^\circ\mathrm{C}$. The analysis of the diffraction patterns reveals clearly that the material retains its stability up to $250\,^\circ\mathrm{C}$ (Figure 3.10).
Owing to its gas sorption properties, the sample was exchanged with acetonitrile for 48 h and loaded into a sample cell and outgassed for 12 h at 55 °C. Its nitrogen adsorption can be regarded as a type I isotherm, and confirmed permanent microporosity. The experimental BET and total pore volume reached 1762 m²/g and 0.7 cc/g respectively, and these results are in excellent qualitative agreement with the theoretical values extracted from crystal structure data, (1770 m²/g and 0.72 cc/g; Figure 3.11).

*Figure 3.10 Variable Temperature PXRD patterns for compound 5*
The reaction of FeCl$_3$·6H$_2$O with BTB and H$_4$BIPA-TC in acidic solution containing trifluoroacetic acid/DMF under solvothermal conditions produces homogenous dark brown cubic-like shape crystals with the following formula \{(In$_3$O(H$_2$O)$_3$)$_3$(PIBA-TC)$_3$(BTB)$_2$(Cl)$_3$(solv)$_x$\} determined by SCXRD analysis. The unit cell values and the space group allow us to clearly confirm that compound 6 is isoreticular to compound 5, previously described. Consequently, the structure of 6 is constructed from the same carboxylic organic moieties (BTB and BIPA-TC) as used in 5 but each indium metal ion in inorganic building block was replaced by iron metal cation.
The purity of compound 6 was confirmed by a good agreement between the as-synthesized and calculated PXRD patterns (Figure 3.12).

![Figure 3.12 comparison between theoretical and experimental powder x-ray patterns of 5 and 6](image)

The investigation of the thermal stability of compound 6 has been conducted by running a thermogravimetric analysis under N₂ atmosphere and with a heating rate of 10°C/min. As expected (Figure 3.13), there are two distinct thermal events. The first one is attributed to the departure of DMF molecules, and other one accounts for decomposition of the material.
According to thermal stability, the experiment has been conducted by X-ray thermodiffractometry. Similar calculated and experimental patterns are observed at various temperatures. As expected, this solid showed very high thermal stability up to 375 °C under vacuum, since the iron is more stable than indium.
In the light of porosity investigation, as anticipated, compound 6 displays a permanent porosity similar to 5. This feature was achieved by using an acetonitrile-exchanged sample, outgassed for 12 h at RT. The corresponding BET and associated total pore volume were estimated as 1609.4 m$^2$g$^{-1}$ and 0.67 cc/g sequentially and they are in good agreement with the theoretical ones i.e. 1630 m$^2$g$^{-1}$ and 0.70 cc/g.

![Figure 3.15 Nitrogen isotherm of compound 6](image)

**3.4 Summary**

In conclusion, we have successfully isolated promising novel metal organic frameworks platforms that obtain unique features based on iron (III) and indium (III) trimeric clusters and either individual or mixture of tri and tetracarboxylate organic linkers via systematic exploration. Moreover, the outstanding sorption studies data have shown that these materials could be interesting candidates for gas storage and thus, these findings open the door for us to practice more isoreticular chemistry by designing and synthesizing other
materials in the future, including several lighter metals such as Al, Cr, etc which are known for its high thermal and chemical stability.
CHAPTER 4: ASSEMBLY of ZEOLITIC LIKE METAL ORGANIC FRAMEWORK MATERIAL

As a well-defined class of solid-state material, zeolites are of essential significance for myriad industrial applications.\(^{33}\) They are typically pure inorganic microporous structures that occur naturally and are produced industrially as well. Generally speaking, zeolites are constructed from TO\(_4\) (SiO\(_4\) and/or AlO\(_4\)) tetrahedral bridged via oxygen atom to at roughly 145° T-O-T angle, and possess a general formula of M\(_{n+x/n}\)\((\text{AlO}_2_x\text{SiO}_2)_y\)\(_x\)-wH\(_2\)O. The assembly of tetrahedral building units tends to generate numerous of astonishing open and rigid 3D structures (over 225 recorded by IZA) that are differentiated based on several criteria i.e. cage dimension, aperture opening, ring size, topology, etc.\(^{34}\) They possess suitable characteristics for separation and catalysis due to the presence of regular nanocavities, which can accommodate a wide variety of cations. In addition to that, these materials can act as molecular sieves\(^{35}\) i.e. they have the ability to selectively sort molecules based primarily on a size exclusion process. However, their applications are limited and attributed to small cavities size that can be effective solely toward small molecules and impurities that accompanies the main product. To address this issue, many efforts have been made in order to discover new strategies able to provide materials with decorated and expanded tetrahedral open networks. In recent years, our group among others have been pursuing the goal of to establishing a new class of metal organic framework that display zeolitic topologies as so-called Zeolite- like metal organic framework (ZMOFs) with good tunable features that outperform conventional purely inorganic zeolites.\(^{36}\)
4.1 Design Strategies Toward the Construction of Zeolite-like Metal Organic Frameworks:

In attempt to expand further the scope of ZMOFs, multiple rational design strategies have been designed, discovered and systematically developed in order to synthesize such astounding subset of MOFs with desirable properties for specific applications. One strategy consists of using the so-called single-metal-ion molecular building block. This approach offers a prospective route where demanded functionalities and directionalities can be incorporated into molecular building block prior to assembly processes. Practically, this approach requires several stipulations: (i) angular hetero atomic organic ligands contain O- and N-donors to generate heterochelating agents. For instance, nitrogen atom is located on aromatic particles to allow sufficient placement of tetrahedral building units as angle akin to zeolite (e.g.145°) whereas oxygen atom is positioned in α-position comparatively to nitrogen to lock metal ion in its position. (ii) the metal ion coordination sphere allows the formation of prerequisite MBBs e.g. MN₄O₄ or MN₂O₄, which consider as robust and directional, and it can vary from 6 to as many as 8. According to above-mentioned criteria, the ligands of imidazole-dicarboxylate and pyrimidinecarboxylate are well-suited candidates to target MOFs with zeolitic topology.
4.2 Metal-Ligand Directed Assembly of MOFs from Gallium and 2-amino-4,6-PmDC

Significant interest has been paid to synthesis ZMOFs. Therefore, the work conducted in this section represents the implementation of single-metal-ion MBB approach. The ligand 2-amino-4,6-PmDC was employed as organic linker since it is rigid and owns the necessary binding and chelating characteristics to generate ZMOFs.

4.2.1 Experimental Section

4.2.1.1. Synthesis of 2-amino-4,6-Pyrimidinedicarboxylic Acid:

Figure 4.2: representation of 2-Amino-4,6-pyrimidinedicarboxylic acid
2-Amino-4,6-dimethylpyrimidine (2 g; 16.3 mmol) was dissolved in pyridine (80 ml) in a 250 ml round-bottom flask, and selenium dioxide (7.2 g; 65 mmol) was added in one portion, the flask was sealed with septum and heated at 80 °C for 3 - 5 days with vigorous stirring. The reaction mixture was then cooled, diluted with aq. NH₃ (200 ml), followed by water (100 ml), filtered through Celite®, washing additionally with aq. NH₃, and concentrated on rotovap to ± 150 ml vol. It was acidified using 2N HCl to produce orange precipitate, that was filtered, washed with DI water and dried on air to give product as brown solid (2.47 g, 83%). \(^1\)H NMR (700 MHz, DMSO-d₆): δ = 7.45 (s, 1H), 7.27 (br s, 2H). \(^{13}\)C NMR (176 MHz, DMSO-d₆): δ = 165.6 (Cq), 164.4 (Cq), 159.3 (Cq), 107.8.

4.2.1.2 \{[Ga(2-amino-4,6- PmDC)₂] \}, 7.

Reaction between Ga(NO₃)₃xH₂O (5.55 mg, 0.0217 mmol) and 2-amino-4,6- PmDC (7.9 mg, 0.0435 mmol) in the presence of H₂O (0.75mL), HNO₃ (0.1 mL, 3.5 M) and DMA (1mL) was heated up to 85 °C for 12h, followed by additional heating to 105°C for 24 h and 115 °C for 24h to finally cooled to room temperature. The reaction afforded colorless homogeneous polyhedral crystals.

4.2.2 Results and Discussion

In the crystal structure of 7, \{[Ga(2-amino-4,6-PmDC)₂]\}, each Gallium metal ion is surrounded by four 2-amino-4,-6 PmDC entities to complete the coordination sphere of the metal ion. Two of them are coordinated in bis-bidentate fashion via O and N atoms to lock the center metal in its position and enhance the solidity of TBUs while the other two are binding in bis-monodentate fashion giving rise to generate in situ (GaN₂(CO₂)₄)
MBB. The building units is assembled in the way that leads to the formation of octahedral $\beta$-cage, which has both four- and six-membered rings. The topological analysis reveals that the overall structure possesses a sod- zeolite net. The diameter of the sphere that can fit into the cage considering the van der waals forces (vdW) is estimated to be 12 Å.

*Figure 4.3. Implementation of single-ion methodology to generate a gallium based ZMOF compound*

The purity of this material was confirmed by similarities between calculated and experimental powder X-ray diffraction (Figure 4.4). The thermal stability has been investigated using thermogravimetric analysis. The stability of this material is difficult to evaluate precisely as the TGA has no clear phase transitions (figure 4.4).
Figure 4.4 top, comparison between calculated and experimental powder x-ray diffraction. Bottom, thermogravimetric analysis of compound 7.
4.2.3 Summary

The objective of this study was to use a single-metal-ion strategy to synthesize novel ZMOFs based on heterofunctional organic ligand such as 2-amino-4,6-PmDC to target robust and directional TBUs. The ongoing study is to explore the unique sorption properties and construct further ZMOFs by employing different metals.
CHAPTER 5: CONCLUSION AND PERSPECTIVE

The findings in this thesis are focused primarily upon design, synthesis, and characterization of novel metal organic framework through employing unique rational construction approach like molecular building block (MBB), which encompasses introducing the desired properties at the design step before actual assembly process. The most significant achievement was the capability to target networks, which is exclusive to an incorporation of MBBs and can present a great scope toward forecasting and synthesis of consequent structures.

Concisely, this study dealt with several tasks (i) investigate the influence of several parameters on fcu-MOF system (i.e. modulators, ratio of metal to ligand, and concentration of metal), and finally we found that fluorinated modulators such as fluoroacetic acid or 2-fluorobenzoic acid are indispensable to the formation of high connectivity clusters which gives rise to effective materials for gas sorption applications. (ii) Synthesis of novel RE materials and with emphasis on ditopic and tertratopic ligands coupled with probing their gas sorption properties. In this regard, we were capable of successfully studying tetracarboxylate based MOF system, but on the other hand; we were unable to study ditopic one since it was not reproducible.(iii) Establishing and characterizing an isostructural cationic platforms from the self-assembly of In- and Fe-trimer building units with 3- and 4-connected organic linkers. These materials show exceptional chemical and structural properties. (iv) the implementation of the single-metal-ion approach via usage of angular heterofunctional ligand (2-amino-4,6- PmDC) lead to the assembly of zeolite -like topology MOF. It is therefore considered worthwhile
to point out that due to changes in the experimental conditions, the variation in the orientation of chelation and connectivity in MBBs has a structure-directing impact on networks.

Overall, this work can be further expanded in the future by completing the full studies of all the mentioned structures by conducting extensive and systematic adsorption measurements to assess the uptake capacity utilizing different sorts of sorbate molecules such as H$_2$, CO$_2$, and CH$_4$ through a broad range of pressures and temperatures. It would be also of interesting to employ different metals especially with mixed-ligand system to enfold RE-metals and other lighter metals such as Al and Cr. The concluding point is that, without any doubt, metal organic frameworks would change the future to make our world’s technology more energy efficient, making it possible for industries to excel in becoming environmentally friendly if the modeling and production of these materials are further developed.
REFERENCES


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APPENDIX A. INFRA-RED FOR SELECTED COMPOUNDS

Figure A1. Infra-red for compound 2

Figure A2. Infra-red for compound 3
Figure A3. Infra-red for compound 4

Figure A4. Infra-red for compound 5
Figure A5. Infra-red for compound 6
APPENDIX B. NMR SPECTRA

Figure B1: $^1$H-NMR of benzoimidephenathroline tetracarboxylic acid

Figure B2: $^1$H-NMR of 3-amino-3'-fluoro-[1,1'-biphenyl]-4,4'-dicarboxylic acid
Figure B3: $^1$H-NMR of 2-amino-4,6-pyrimidinedicarboxylate