Crystals Growth Study of Microporous Metal-Organic Frameworks by Atomic Force Microscopy

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Table of Contents

Table of contents ........................................................................................................... 2
List of tables .................................................................................................................. 6
List of figures .................................................................................................................. 7
List of abbreviations ...................................................................................................... 12
Abstract ......................................................................................................................... 13
Declaration ...................................................................................................................... 14
Copyright statement ...................................................................................................... 15
Dedication ....................................................................................................................... 16
Acknowledgement .......................................................................................................... 17

CHAPTER ONE

1.1 Porous Crystalline Materials .................................................................................. 18
1.2 Metal-Organic Framework (MOF) .......................................................................... 19
1.3 Topology of MOFs .................................................................................................. 21
1.4 Flexibility in MOF structure ................................................................................... 23
1.5 Properties and applications of MOFs ..................................................................... 24
1.6 Synthesis of MOFs .................................................................................................. 29
1.7 Zn(tbip) MOF ......................................................................................................... 31
1.8 UiO-66 family .......................................................................................................... 34
1.9 MOF-801-SC ............................................................................................................ 36
1.10 Objective of the research work .............................................................................. 38
1.11 Nucleation and crystal growth .............................................................................. 39
1.12 Crystals and crystallization ................................................................................... 39
1.13 Solubility ................................................................................................................ 40
<table>
<thead>
<tr>
<th>Page</th>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td></td>
<td>2.8 Gas Adsorption..............................85</td>
</tr>
<tr>
<td>2.9</td>
<td></td>
<td>2.9 References...................................87</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>CHAPTER THREE</strong></td>
</tr>
<tr>
<td>3.1</td>
<td></td>
<td>3.1 MOF-801-SC Results and Discussion........89</td>
</tr>
<tr>
<td>3.2</td>
<td></td>
<td>3.2 Powder X-ray Results........................91</td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td>3.3 SEM Results................................92</td>
</tr>
<tr>
<td>3.4</td>
<td></td>
<td>3.4 AFM Results................................93</td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td>3.5 References..................................98</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>CHAPTER FOUR</strong></td>
</tr>
<tr>
<td>4.1</td>
<td></td>
<td>4.1 Zn(tbip) Results and Discussion..........99</td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td>4.2 Powder X-ray Results........................101</td>
</tr>
<tr>
<td>4.3</td>
<td></td>
<td>4.3 SEM Results................................103</td>
</tr>
<tr>
<td>4.4</td>
<td></td>
<td>4.4 TGA Results................................104</td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>4.5 N&lt;sub&gt;2&lt;/sub&gt; Adsorption Results..........106</td>
</tr>
<tr>
<td>4.6</td>
<td></td>
<td>4.6 Single crystal Results......................108</td>
</tr>
<tr>
<td>4.6.1</td>
<td></td>
<td>4.6.1 Single crystal without Methanol.........111</td>
</tr>
<tr>
<td>4.7</td>
<td></td>
<td>4.7 Solid State C&lt;sup&gt;13&lt;/sup&gt; NMR Results.....113</td>
</tr>
<tr>
<td>4.8</td>
<td></td>
<td>4.8 Single crystal with Methanol..............114</td>
</tr>
<tr>
<td>4.9</td>
<td></td>
<td>4.9 AFM Results................................115</td>
</tr>
<tr>
<td>4.10</td>
<td></td>
<td>4.10 References................................122</td>
</tr>
</tbody>
</table>
CHAPTER FIVE

5.1 Conclusion ......................................................................................................................123
List of tables

**Table 2.1:** Grade and suppliers of all Materials used…………………………………58

**Table 2.2:** Seven Crystal System and Bravais Lattices……………………………………61

**Table 4.1:** Crystal data and structure refinement parameters for Zn(tbip) at 100K………108

**Table 4.2:** Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters
(Å² x 10³) for Zn(tbip) at 100K………………………………………………………………………108

**Table 4.3:** Bond lengths (Å) and bond angles (°) for Zn(tbip) at 100K…………………..109

**Table 4.4:** Anisotropic displacement parameters (Å² x 10³) for Zn(tbip)………………..111
List of figures

**Fig. 1.1:** General Classification of Porous Solid Materials……………………………….19

**Fig. 1.2:** Metal-organic framework structures (1D, 2D, and 3D) reported in the Cambridge Structural Database (CSD) from 1971 to 2011………………………………………20

**Fig. 1.3:** Inorganic SBUs (A) and Organic Linkers (B)………………………………………21

**Fig. 1.4:** Single-crystal X-ray structure of MOF-5 (a), hydrogen gas-sorption isotherm for MOF-5 at 78 K (b) and 298 K (c). Single-crystal X-ray structure of MOF-177 (d) and hydrogen gas-sorption isotherm for MOF-177 at 78 K and high pressure (e)…………….25

**Fig. 1.5:** Gas-sorption isotherms of JUC-61a at 77K (hydrogen, green/circle; nitrogen, blue/square)……………………………………………………………………27

**Fig. 1.6:** H₂tbip (ligand) structure………………………………………………………………32

**Fig. 1.7:** Crystal Structure of Zn(tbip) MOF………………………………………………32

**Fig. 1.8:** Adsorption isotherms for Zn(tbip) MOF: (a) Ar (87 K) and N₂ (77 K); (b) H₂ (77 and 87 K)………………………………………………………………………………33

**Fig. 1.9:** (a): MeOH adsorption isotherms at different temperatures, (b): Adsorption of DME at 30 °C followed by MeOH on Zn(tbip) MOF………………………………….33

**Fig. 1.10:** Schematic of the Zr-O cluster (a), UiO-66 structure formed from benzene-1,4-dicarboxylate (BDC) linker (b), showing octahedral (large yellow) and tetrahedral (pink) sites respectively……………………………………………………………………34

**Fig. 1.11:** UiO-66 MOF structure with tetrahedron cage (a), with octahedron cage (b), with one octahedron cage and two adjacent tetrahedron cages (c)…………………………..35

**Fig. 1.12:** Zr-MOF with BDC as linker, UiO-66 (a), Zr-MOF with BPDC as linker, UiO-67 (b), Zr-MOF with TPDC as linker, UiO-68………………………………………………35
Fig. 1.13: Structure of the non-linear linker fumarate (a), structural model for the MOF-801-SC showing; (b) the outlined cubic unit cell, (c) the unit cell central octahedron with the fumarate linkers’ double bonds shown in green………………………………………37

Fig. 1.14: Water isotherms of MOF-801-SC and other related MOFs measured at 25 °C..38

Fig. 1.15: Solubility of KNO₃, CuSO₄ and NaCl in aqueous solution……………………..41

Fig. 1.16: Solubility of hexamethylenetetramine in different solvents.........................42

Fig. 1.17: Solubility-Supersolubility diagram.................................................................43

Fig. 1.18: Free energy diagram for nucleation showing a ‘critical nucleus’……………….48

Fig. 1.19: Temperature effect on size and critical nucleus energy of formation (T₁ < T₂).47

Fig. 1.20: Nucleation rate as a function of supersaturation........................................48

Fig. 1.21: Growing crystal-solution interface...............................................................50

Fig. 1.22: The supersaturation effect of crystal mechanism........................................51

Fig. 1.23: Layer-by-layer growth mechanism..............................................................52

Fig. 1.24: Mechanism of spiral growth........................................................................53

Fig. 2.1: A defined unit cell.............................................................................................60

Fig. 2.2: The 14 Bravais lattices....................................................................................62

Fig. 2.3: Schematic representation of the Bragg condition...........................................64

Fig. 2.4: The main components of a single crystal X-ray diffractometer.......................66

Fig. 2.5: Scheme of SEM Principle................................................................................72

Fig. 2.6: SEM interactions types between electrons and a sample...............................73

Fig. 2.7: CRT for electron beam size intensification and regulation during SEM sample scan for image display.................................................................74

Fig. 2.8: AFM Images showing structural details on solid surfaces captured at different magnifications.................................................................75
Fig. 2.9: A schematic diagram showing the major parts of AFM machine.................76
Fig. 2.10: The components of a photodetector of an AFM machine .....................77
Fig. 2.11: The Main Imaging Modes of an AFM showing the cantilever interaction with the sample surface.................................................................78
Fig. 2.12: NMR basic principle showing energy transfer high and low spin nucleus.....80
Fig. 2.13: The $^{13}$C Liquid and Solid-state NMR spectra.....................................81
Fig. 2.14: Schematic diagram of the Solid-state NMR spectrometer showing the interconnection of its main components.....................................................82
Fig. 2.15: Schematic diagram showing gas path through the components of a TGA Machine.................................................................83
Fig. 2.16: The thermograph of CaC$_2$O$_4$.H$_2$O showing degradation of the sample constituents at different temperature.........................................................85
Fig. 2.17: Types of Adsorption Isotherms.............................................................86

Fig. 3.1: SEM images of UiO-66 captured at different magnifications.......................89
Fig. 3.2: UiO-66 SEM images captured at different magnifications.........................90
Fig. 3.3: The combined powder XRD of three different synthesised samples of MOF-801-SC.................................................................91
Fig. 3.4: The powder XRD pattern of Zn(tbip) with the calculated peaks..................92
Fig. 3.5: MOF-801-SC scanning electron micrographs captured at different magnifications.................................................................93
Fig. 3.6: The AFM deflection images of the {$\{111\}$ facets of MOF-801-SC showing layer-by-layer growth.................................................................94
Fig. 3.7: MOF-801-SC crystal structure showing height of the growth steps.............95
Fig. 3.8: The AFM height images of MOF-801-SC crystal surfaces.........................96
Fig. 3.9: Cross-sectional analyses of a developing growth step on a \{111\} face of MOF-801-SC crystal surfaces

Fig. 3.10: Cross-sectional analyses of a developing growth step on a \{111\} face of MOF-801-SC crystal surfaces

Fig. 4.1: SEM micrographs of initial Zn(tbip) captured at different magnifications

Fig. 4.2: AFM micrographs of initial Zn(tbip)

Fig. 4.3: The combined powder XRD of three different synthesised samples of Zn(tbip)

Fig. 4.4: The powder XRD pattern of Zn(tbip) with the calculated peak

Fig. 4.5: Zn(tbip) scanning electron micrographs captured at different magnifications

Fig. 4.6: The Thermogravimetric profile of Zn(tbip) under N\textsubscript{2}

Fig. 4.7: N\textsubscript{2} adsorption-desorption isotherm for Zn(tbip) at 77K

Fig. 4.8: Zn(tbip) BET surface area plot

Fig. 4.9: Zn(tbip) Langmuir surface area plot

Fig. 4.10: Asymmetric unit of Zn(tbip) without methanol

Fig. 4.11: Structure of Zn(tbip) without methanol viewed along c-direction

Fig. 4.12: Zn(tbip) solid state C\textsuperscript{13} NMR spectrum

Fig. 4.13: Asymmetric unit of Zn(tbip) after absorbing methanol

Fig. 4.14: Structure of Zn(tbip) after absorbing methanol viewed along c-direction

Fig. 4.15: Zn(tbip) atomic force micrographs captured at different magnifications

Fig. 4.16: Zn(tbip) optical microscope images (a and b), and SEM image (c) showing large anisotropic growth

Fig. 4.17: Zn(tbip) crystal structure showing height of the growth steps

Fig. 4.18: The AFM height images of Zn(tbip) crystal surfaces

Fig. 4.19: AFM height images of Zn(tbip) crystal surfaces
**Fig. 4.20:** Cross-sectional analyses of a developing growth step on a Zn(tbip) crystal surface………………………………………………………………………………………………121

**Fig. 4.21:** Cross-sectional analyses of developing growth steps on a Zn(tbip) crystal surfaces………………………………………………………………………………………………122
List of Abbreviation

IUPAC International Union of Pure and Applied Chemistry
MOF Metal Organic Framework
SBU Secondary Building Unit
CSD Cambridge Structural Database
MTV Multivariate
BET Branauer-Emmett-Teller
DA Dubinin-Astakhov
GFMMOF Guest-Free Microporous Metal Organic Framework
DME Dimethyl Ether
Atm Atmosphere
BPDC Biphenyl Dicarboxylate
TPDC Terphenyl Dicarboxylate
BDC Benzene Dicarboxylate
PIZOF Porous Interpenetrated Zr-Organic Frameworks
1D One-Dimensional
2D Two-Dimensional
3D Three-Dimensional
PCP Porous Coordination Polymer
Abstract

Porous materials are one of the extensively used class of solid mostly useful for adsorption, catalysis, separation, storage and ion exchange. Microporous materials have received a rapidly growing rate of interest with regards to their syntheses, characterisation and applications.

In the current study ex-situ atomic force microscopy (AFM) was used to investigate the crystal surfaces of MOF-801-SC and Zn(tbip) crystals to provide information concerning the crystal growth of the materials.

MOF-801-SC is a novel porous coordination polymer (PCP) and a member of the Zr-based UiO-66 series as seen by powder X-ray diffraction (PXRD), composed of zirconium (iv) oxychloride octahydrate (ZrOCl₂.8H₂O), and fumarate (O₂C(CH)₂CO₂⁻) linkers has been synthesised by a modulated synthesis approach. MOF-801-SC further characterised by scanning electron microscopy (SEM) revealing that the crystals have octahedral cubic morphology with crystal sizes ranging from 7.0 µm to 9.0 µm. The AFM height images analyses revealed that most of the growth steps are 1.0 ± 0.1 nm high.

Zn(tbip) is a novel guest-free Microporous metal-organic framework (GFMMOF) composed of Zn-based secondary building units (SBUs), [Zn(NO₃)₆H₂O], and 5-tert-butyl isophthalate (tbip²⁻) ligands has been synthesised and characterised structurally robust with an extraordinary thermal stability. The PXRD pattern of the sample indicated that a monophasic sample had been prepared. The SEM revealed that the crystals have elongated hexagonal prism morphology with crystals sizes ranging from 300 µm to 500 µm. Thermogravimetric analysis (TGA) showed that the crystal is thermally stable up to 420 °C and is guest molecule free. Single crystals were determined by single crystal X-ray diffraction (SXRD). Solid-state NMR proved that the crystals are guest-free. SXRD showed that methanol addition to the single crystals proved that a molecule can go into the crystal pores. A multilayer growth features were observed in the AFM micrographs of Zn(tbip) crystals.
Declaration

I declare that no portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Samaila Audu Jovial

The University of Manchester, 2014
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Dedication

I dedicated this thesis to my beloved parents and children.
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1.0 CHAPTER ONE

1.1 POROUS CRystalline materials

Porous materials are one of the extensively used group of solids mostly useful for adsorption, catalysis, separation and ion exchange. Research in the area of porous materials is rapidly developing producing a lot of new materials, changes, characteristics and applications being recognised and improved.\(^1\) Porous materials were classified by the International Union of Pure and Applied Chemistry (IUPAC) into three different groups – microporous having less than 2 nm pore diameters, mesoporous with pore diameters between 2 – 50 nm, and macroporous having pores larger than 50 nm.\(^2-4\) Nanoporous materials are those porous materials whose pore diameters are less than 100 nm.\(^3, 5\) The coverage of this literature review is limited to microporous materials, which have received a rapidly increasing rate of interest with regards to their syntheses, characterisations and applications. Microporous materials are crystalline framework materials possessing channels and cavities of molecular dimension, and with very narrow pore sizes.\(^1\) Microporous solid materials encompass a very wide range, from organic to inorganic,\(^6\) which are categorized into porous organic, porous inorganic, and porous organic-inorganic hybrid. Typical crystalline porous inorganic solids are zeolites and zeotypes, with pores in the range of 0.4 to 1.3 nm, whereas the organic porous materials are amorphous polymers, and a recently existed group of porous organic-inorganic hybrid,\(^6\) metal-organic frameworks (MOFs) as seen in Fig. 1.1.
1.2 METAL-ORGANIC FRAMEWORKS (MOFs)

It should be noted that MOFs are called with different names (porous coordination polymers, porous coordination networks, etc.); nevertheless all share attributes of the same general type of material. The nomenclature difference simply manifests the framework type and the researchers who created it. MOFs have received a tremendous research interest in the past decade, and are generally prepared by linking the metal containing units [secondary building units (SBUs)] with the organic linkers to build open crystalline frameworks with high pore volumes and surface areas formed through strong bonds. The variation of the organic linkers and the metal SBUs has led to thousands of compounds being synthesised and investigated every year as seen in Figs. 1.2 and 1.3.

The outstanding porosity of MOFs has given them a broad range of important applications in catalysis, gas storage, separations and so forth. Specifically, the versatile
applications of MOFs in these applications and large-scale manufacture have attracted great attention\(^8\) into their syntheses, modifications, as well as their potential applications.

**Fig. 1.2:** Metal-organic framework structures (1D, 2D, and 3D) reported in the Cambridge Structural Database (CSD) from 1971 to 2011.\(^8\)
Fig. 1.3: Inorganic SBUs (A) and Organic Linkers (B).^8

1.3 TOPOLOGY OF MOFs

Research on MOFs for over a decade now have gone deeply into the conformation of new functional materials with interesting structural topologies. MOFs are receiving uninterrupted interest from material researchers due to their versatile material.
characteristics, and varied structural topology.\textsuperscript{15} An effective means for varying the reactivity of the MOFs pores is the post synthetic integration of metal-organic complexes and organic units by reactions with linkers.\textsuperscript{16} It is important to understand the SBUs, which determine the final structure of the framework, and the organic linkers whose structure can be varied during assembly of the MOFs.\textsuperscript{7} The geometric principle of building is achieved by connecting the stable SBUs, rather than the building of earlier coordination networks through joining single atoms with ditopic coordinating linkers.\textsuperscript{8} A lot of work was eventually reported through the normal use of SBUs on the use of isoreticular principle in the MOFs of superior porosity and extraordinary bigger pore openings.\textsuperscript{8} Multivariate MOFs (MTV-MOFs) provide options for linking different functionalities, designing a complex and controllable single framework within the MOFs pores\textsuperscript{17} as seen in Scheme 1.
1.4 FLEXIBILITY IN MOF STRUCTURE

Flexibility (responsiveness) of MOFs evolved from a curiosity to an integral part of MOFs, which demonstrates a wide range of conformational effects, like negative thermal expansion, breathing effect and swelling. Flexible MOFs are commonly bistable thermodynamically, exhibiting guest-induced framework breathing with change in structure amplitude much bigger than commonly known materials, with very few bigger than 40%. Flexibility is a remarkable feature of MOFs and direct researchers in developing
stimuli-responsive MOFs for applications in chemical sensing, drug release control and medical therapy.\textsuperscript{15, 19, 21, 22} Proper experimentation development is the main practice for flexibility discovery of the novel structures, which depends on the materials, thermal, chemical or mechanical stimuli applied for deformations, coupled with required techniques used to understand the elastic response of MOFs.\textsuperscript{19} The MOFs flexibility can be modified with a great variability in the pore shapes and size, through varying the nature of the metal-oxide part and that of the organic linkers,\textsuperscript{2, 23} and other factors like temperature, solvents and stoichiometry of the reaction.\textsuperscript{15}

1.5 PROPERTIES AND APPLICATIONS OF MOFs

Reticular chemistry gave room for the construction of MOFs of interesting structures, chemical compositions and applications in hydrogen storage, sieving of quantum liquids, and for fuel cell membranes.\textsuperscript{24} The capacity to modify the chemistry of the functional group and windows, openings and channels of the organic structure generate chances for definite gas intake, with related applications in storage and separation with real technological necessity in fuel gases.\textsuperscript{25}

1.5.1 Energy Storage

One of the most favourable applications of MOFs is gas storage. The gas sorption features of MOFs are centred on increasing their intake of fuel gases like hydrogen and methane.\textsuperscript{25-27} Hydrogen is a perfect energy carrier with nearly three times the gasoline gravimetric heat of combustion (120 MJ/kg \textit{vs} 44.5 MJ/kg), and the primary by-product after release of energy is water, making hydrogen a better choice for on-board fuel.\textsuperscript{7} Yaghi \textit{et al.} reported the first observed hydrogen adsorption measurement on Zn\textsubscript{4}O(BDC)\textsubscript{3} (MOF-5), which was 4.5 wt\% at 77 K and 1 atm, and 1.0 wt\% at room temperature and 20 bars. Yaghi also reported a different MOF of great porosity, Zn\textsubscript{4}O(BTB)\textsubscript{2} (MOF-177), with a higher total
gravimetric intake, 7.5 wt% at 77 K and 78 bar (Fig. 1.4). More than 200 special MOFs have been investigated for their hydrogen storage capacity. However, MOFs display distinct H₂ intake by mass but are also distinguished by very light H₂ adsorption energies (typically 3-10 kJ/mol), such that extremely low temperatures are needed to notice reasonable H₂ storage. Various design standards have been suggested to increase the characteristics of hydrogen storage in their frameworks: including a high porosity framework for high hydrogen saturation intake; dependence of adsorption enthalpy on the pore size in which intake of hydrogen is more effective in narrow pores than in the larger ones; and partial charges on the MOFs surface, which strengthen the H₂ binding through dipole interaction.

**Fig. 1.4:** Single-crystal X-ray structure of MOF-5 (a), hydrogen gas-sorption isotherm for MOF-5 at 78 K (b) and 298 K (c). Single-crystal X-ray structure of MOF-177 (d) and hydrogen gas-sorption isotherm for MOF-177 at 78 K and high pressure (e).
1.5.2 Separation

Porous MOFs allow their pore sizes and volumes, and pore wall chemical usefulness to be systematically tuned by the wise choice of the metal and ligand components, and synthesis method that makes these porous materials important for molecular separations.\textsuperscript{27} Chen et al. showed the usability of a microporous MOF, MOF-508, in the gas chromatography separation of alkanes on the basis of size and shape-selective matching.\textsuperscript{28} Pore surface functionality is among the MOFs’ importance for molecular separations. Kitagawa et al. in 2005 demonstrated the sorption of high levels of acetylene molecules, on to the MOF, \( \text{Cu}_2(\text{pzdc})_2(\text{pyz}) \). This high level was thought to occur when the molecules of acetylene are kept at a fixed repeat distance from each other by hydrogen bonding with two non-coordinated oxygen atoms in the pore wall of the framework.\textsuperscript{27} JUC-61 is a triply permeated structure that has a confined pore size for gas separation. A significant amount of hydrogen (117 cm\(^3\)/g) is taken up by activated JUC-61, but only very small amount of nitrogen (\textbf{Fig. 1.5}) showing the separation ability of JUC-61 for \( \text{N}_2/\text{H}_2 \) separation.\textsuperscript{27}
Fig. 1.5: Gas-sorption isotherms of JUC-61a at 77K (hydrogen, green/circle; nitrogen, blue/square).  

1.5.3 Adsorption

With the rising need for cheap and more environmentally friendly industrial applications, industrial processes for selective adsorption of gases depend strongly on very low temperature conditions and membrane- and adsorption based techniques. Adsorbent selectivity for an adsorbate and adsorption capacity of the adsorbate are the two principal criteria for choosing exclusive gas adsorption materials, which are determined by the nature and chemical make-up of the adsorbent, the equilibrium temperature and pressure at the time of adsorption. The main chemical processes on which exclusive gas adsorption is accomplished in MOFs are interactions of the adsorbate surface and size-inclusion (effect of molecular sieve), where interactions of the adsorbate-surface include the physical and
chemical interaction of the adsorbate and the adsorbent, while size-exclusion rely on the shape and framework pores structure.\(^7\)

### 1.5.4 Catalysis

Porous materials have been extensively studied with a view to technical utilization as catalysts and catalyst backups. MOFs usage as solid catalysts is especially interesting in that the pore size and framework functionality can be altered over a broad range for various catalytic reactions. Even though many MOFs are known but only a few have been tested in catalytic reactions so far. It is still a tremendous problem to figure out whether the interactions of metal-ligand, metal centres, functionalised ligands or size of particles, causes the unusual catalytic properties.\(^27\) The catalytic activity of the sodalite type chemical compound \(\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{CH}_3\text{OH})_{10}]_2\) was investigated by Long et al. demonstrating that the chemical compound is a thermally stable microporous solid exhibiting a cubic structure of 7 and 10 Å pores that affords a BET surface area of 2100 m\(^2\)/g, and Mn\(^{2+}\) ions exposed on the surface of the model might serve as potent Lewis acids. This chemical compound catalyses the cyanosilylation of aromatic aldehydes and ketones, as well as the more demanding Mukaiyama aldehyde alcohol reaction, and moreover, in each case, a noticeable size selectivity effect consistent with the pore features is observed.\(^27\)

### 1.5.5 Sensing

MOFs with specificity in terms of shapes or functionalities have been identified through quantitative exchange studies. These observations have suggested that with correct tailoring, MOFs can be generated to function as extremely selective molecular sieves, catalysts or sensors. The sensor potentiality of MOFs containing luminescent lanthanides or paramagnetic transition metals was realized through changing the optical, electronic or
magnetic properties of the framework by the interactions with guest molecules. MOFs possessing magnetic and luminescence features together with shape- or size-selective sorption are potentially used in sensor devices. In 2009, Qiu and Zhu reported that Cu$_3$(PTMTC)$_2$(py)$_6$(CH$_3$CH$_2$OH)$_2$(H$_2$O)/(MOROF-1), exhibits a reversible and extremely discriminating solvent-induced ‘shrinking-breathing’ method that intensely affects the material’s magnetic properties. This magnetic absorbent feature could be a way towards magnetic solvent sensors. However, the guest dependent magnetic features of MOROF-1 and the majority of porous magnets are as a result of changes in the metal coordination environment induced by guest surface assimilation or permutation rather than through magnetic exchange with a paramagnetic adsorbate. Surveys of MOFs as potential sensing elements with luminescent properties are very common. These show that by combining mixtures of luminescent organic building blocks or luminescent metal building blocks or luminescent systems can be produced.

Other application areas of MOFs include drug storage and delivery, ion exchange, electrical and magnetic properties and so on.

1.6 SYNTHESIS OF MOFs

Several factors must be considered when designing MOF syntheses, such as geometric principles during design and the maintenance of the building blocks’ integrity, as it is often essential that a great deal of effort has to be in place for effective MOF synthesis and the conditions should be moderate enough to maintain the conformation and functionality of the MOF. This should be reactive enough to form the metal-organic bonds. It is obvious that structural control is an essential requirement for optimizing the ability to naturally design and synthesize functional MOFs. Studies in this area is centred on the design and construction of novel MOFs, and their structures and properties relationships.
assembly and preservation of the joining parts and the appropriate synthetic conditions must be consistent for in situ generation of desired SBU. This is done by product precipitation to form a precursor solution. The predominant goal of MOF synthesis is to produce high quality single crystals for structural analysis, before enough knowledge base was developed to start elaborating the root concepts of reticular synthesis. It is therefore not surprising that early attempts was focused on solutions of simple, more soluble precursor solution with late transition metal ions. The solubility difference of inorganic and organic elements of potential MOFs has been a barrier to synthesis, but has been solved through two-phase solvothermal synthesis in which the inorganic part dissolved in water, while the organic part in an immiscible alcohol. Solvothermal synthesis is a suitable technique that substituted the older, more time-demanding approach involving slow joining of the coordinating units. The dilute solutions of the precursors are actually mixed in polar solvents, like water, acetone, and alcohols and heated in closed vessels, producing autogenous pressure. MOFs are usually synthesized by mixing metal salts and organic linkers in solvothermal reactions vessel at comparatively low temperature (less than 300°C). The features of the ligand (bulkiness, bond angle, chirality, ligand length, etc.) are very important in determining what the resultant framework will be, and the likelihood of the metal ion to accept certain geometries also direct the MOFs structure. The choice and synthesis of the organic bridging ligands always have a great effect on the construction of the suitable frameworks. Changes in length, flexibility, and symmetry of the organic ligands can generate MOFs with diverse frameworks and functions. The most significant factors of solvothermal synthesis of MOF are temperature, the ligand and metal salt concentrations (which differ across a wide range), the pH of the solution, and the magnitude of the reactants solubility in the solvent. Even though experience always
determines the best conditions for growing the MOFs, experimentation and trial-and-error methods are quite essential.\textsuperscript{7}

1.7 Zn(tbip) MOF

H\textsubscript{2}tbip simply means 5-tert-Butyl Isophthalic Acid (Fig. 1.6). Zn(tbip), a novel guest-free microporous metal organic framework (GFMMOF) is synthesized and characterized structurally with an extraordinary thermal stability, possessing special ability for separating methanol (MeOH) from dimethyl ether (DME) and from water. It is also one of the microporous MOFs possessing the highest take-up at hydrogen (0.054 g/cm\textsuperscript{3} at 77 K and 1 atm).\textsuperscript{30} Zn(tbip) single crystals were produced by hydrothermal synthesis. Due to the massive aliphatic group of H\textsubscript{2}tbip ligand, a hydrophobic and solvent-free channel structure is built using water as a solvent. A three dimensional structure was then generated by joining zinc tetrahedral centres to tbip ligands. A 2-fold rotation symmetry position is occupied by tetrahedral Zn\textsuperscript{2+}. All the neighbouring zinc nodes are bridged along c axis by two carboxylic groups to produce a 3\textsubscript{1} spiral chain of 15.875 Å pitch along the crystallographic c axis (screw axis) with a 3.38 Å of zinc-zinc intrachain shortest distance. Each chain links to three similar adjacent chains via tbip, producing the nearest interchain distance of 7.212 Å. This generates a 3D framework structure incorporating 1D closed-packed open channels with a pore diameter of 4.5 Å along the c direction, and the ligand three methyl groups are disordered and projected into the channels. GFMMOFs are highly stable guest-free molecules due to their adequately small channels diameter as seen in Fig. 1.7 with a 3.56 (slab) and 3.26 Å (vertical) distance between the phenyl rings forming the channel wall.\textsuperscript{30}
Zn(tbip) MOF pore characteristics and hydrogen adsorption abilities were described by the gas sorption study using the formerly described method by Jing Li et al., and Fig 1.8a shows the DA (Dubinin-Astakhov) calculated pore volume of Zn(tbip) MOF as 0.15 and 0.14 cm$^3$/g based on Ar and N$_2$ sorption data collected at 87 and 77 K, respectively. Also, a gravimetric density of 0.52 and 0.75 wt % of hydrogen was obtained at 87 and 77 K and 1 atm, respectively (Fig. 1.8b).
Zn(tbip) MOF is highly hydrophobic in nature, showing essentially zero water adsorption (< ~ 1 mg/g at $P/P^0 = 0.65$) but adsorbing large volumes of methanol, 110 mg/g at 24.5 °C and 90 Torr MeOH ($P/P^0 = 0.73$)\(^{30}\) as seen in Fig. 1.9a below. Zn(tbip) MOF also shows potential for DME separation from MeOH, and the DME adsorption followed by MeOH adsorption, as seen in Fig. 1.9b. 30 mg/g of DME is quickly adsorbed on Zn(tbip) MOF at 30 °C and 650 Torr ($P/P^0 = 0.13$), and after 30 min, concurrently, the DME pressure is set to zero and MeOH is introduced at 85 Torr. As DME desorps ($P = 0$) it is replaced by MeOH and rapidly reaches the 105 mg/g adsorption level.\(^{30}\)
1.8 UiO-66 Family

The stability of MOFs is mainly measured by the framework nature of the inorganic building units and that of the chemical bonds they form with the organic linkers. Many MOFs have shown that they are weakly stable mechanically, chemically and thermally which have restricted their usage in so many applications.\textsuperscript{31, 32} The high organic-inorganic number of coordination (12) of the Zr-based MOF (Fig. 1.10) indicates that this MOF can have a better mechanical and thermal stabilities due to higher order of its organic-inorganic structural frameworks.\textsuperscript{32}

UiO-66 is one of the few MOFs for which the structural foundation is based on a Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4} octahedron producing lattices by 12-fold linkage via a 1,4-benzenedicarboxylate (BDC) organic linker as seen in Fig. 1.11. Substitution of the organic linker with 4,4’ biphenyldicarboxylate (BPDC) or terphenyldicarboxylate (TPDC) generates isoreticular UiO-67 and UiO-68 frameworks (Fig. 1.12) This MOFs series is distinguished by great surface area and by unparallel stability.\textsuperscript{9, 31, 33}

![Fig. 1.10: Schematic of the Zr-O cluster (a), UiO-66 structure formed from benzebe-1,4-dicarbaryl (BDC) linker (b), showing octahedral (large yellow) and tetrahedral (pink) sites respectively.\textsuperscript{32}](image.png)
Fig. 1.11: UiO-66 MOF structure with tetrahedron cage (a), with octahedron cage (b), with one octahedron cage and two adjacent tetrahedron cages (c).\textsuperscript{9}

Fig. 1.12: Zr-MOF with BDC as linker, UiO-66 (a), Zr-MOF with BPDC as linker, UiO-67 (b), Zr-MOF with TPDC as linker, UiO-68.\textsuperscript{33}

This great stability is due to the fact that each Zr octahedron is 12-fold linked to the adjacent octahedral. This is a common connection for metals producing a well packed face-centred cubic structure, though it is peculiar in the topologies of MOFs.\textsuperscript{9, 31} The Zr-O linkages produced between organic carboxylate ligand and inorganic cluster is the reason for high stability of Zr-based MOFs. More especially, the strong Zr-O linkages together with the capability of the inner Zr\textsubscript{6}-cluster to reconfigure on addition or removal of µ\textsubscript{3}-OH group causing no alteration in the linking organic carboxylate contributed to the higher stability of UiO-66. The UiO-66 series is highly stable to thermal treatments and capable
of maintaining their crystalline structures on reaction with aggressive chemicals. These outstanding features made UiO-66 to have a wide range of potential applications, mostly in catalysis.31,33

1.9 MOF-801-SC

More stable MOFs are those containing Zr$^{4+}$ cation, and the early members of the class are the UiO-66 to 68 series which are isostructural with cubic-close packing similar topology. MOF-801-SC was first reported by Wißmann et al.34 as Zr-fum MOF. It has a crystal topology similar to that of UiO-66, but possesses a primitive cubic lattice instead of a face-centred cubic one. The framework of this MOF has a similar two fold interpenetrated version of the UiO-66 topology. This is observed from the longer organic linkers used to construct them. Despite the interpenetration, they have high surface areas and larger pore volumes, and hence are named “porous interpenetrated Zr-organic frameworks” (PIZOFs). UiO-66 and PIZOFs are very resistant to temperature and are stable in atmospheric moisture. The higher stability of Zr-based MOFs is due to stronger Zr–O bonds within the Zr-MOFs and the high degree of interlinkages between their SBUs.34

MOF-801-SC is one of the members of the Zr-based UiO-66 series that allowed the evaluation of the influence of framework topologies, pore sizes, surface areas and possession of hydrophilic functional groups upon the water adsorption characteristics of the materials. It rapidly captures water at lower relative pressure and shows higher uptake and stability due to optimum interactions between the water molecules. MOF-801-SC is prepared using fumarate organic linker (Fig. 1.13a). It belongs to the cubic space group $Pn\bar{3}$, which has two tetrahedral cavities of slightly different sizes (5.6 Å and 4.8 Å) and an octahedral cavity (7.4 Å) as seen in Fig. 1.11. Whereas, the popular UiO-66 produced from
BDC linker ([Fig. 1.10b](#)) has octahedral and tetrahedral cavities of 8.4 Å and 7.4 Å respectively.\(^{35}\)

![Diagram of MOF-801-SC structure](image)

**Fig. 1.13:** Structure of the non-linear linker fumarate (a), structural model for the MOF-801-SC showing; (b) the outlined cubic unit cell, (c) the unit cell central octahedron with the fumarate linkers’ double bonds shown in green.\(^{34}\)

At 25\(^0\)C, the MOF-801-SC water isotherm is seen in [Fig. 1.14](#). The increase in the amount of water adsorption is gradual and proportional to the pressure \(p/p_0 = 0.05\), followed by rapid water uptake between the pressure range of \(p/p_0 = 0.05\) to 0.10, and the highest uptake is 350 cm\(^3\)/g at \(p/p_0 = 0.90\). This shows that MOF-801-SC has higher affinity for water due to its low step pressure than UiO-66.\(^{35}\)
Fig. 1.14: Water isotherms of MOF-801-SC and other related MOFs measured at 25 °C.35

1.10 OBJECTIVES OF THE RESEARCH WORK

The various potential applications of MOFs, coupled with their previously proven properties such as catalysis, gas storage, separation, sensing, magnetic properties and electrical conductivity stimulates the curiosity for better understanding of their crystal structure and growth mechanisms. Due to the large number of reports on application capacities of different types of MOFs, an interest was developed on Zn(tbip) for its special separation ability as a guest free MOF. Another interest was developed to study MOF-801-SC for its complex cluster network, high thermal and aggressive chemical stability.

This research work focuses on investigating the crystal growth mechanism of the MOFs, Zn(tbip) MOF, and MOF-801-SC. Atomic Force Microscopy (AFM) is the suitable method employed to study the crystal growth mechanism on the surfaces of these crystals.
Ex-situ AFM technique will be used in this research work in order to provide new information about the crystal growth on the surfaces of these microporous MOFs.

1.11 NUCLEATION AND CRYSTAL GROWTH

Nucleation and growth of crystals is at the center of the growth of all crystalline solid materials. Not unexpectedly there is a vast interest across many fields to gain a profound understanding of these processes with a view to controlling and developing them and their consequence, and to possibly predict their outcomes. The main focus is crystallization at the earliest stages, which is a major structural determinant of the resulting product. In spite of all the interest, the mechanism of the crystallization at the earlier stages still remains as an important fundamental problem.36

1.12 CRYSTALS AND CRYSTALLIZATION

The products of crystallization have their constituent atoms, ions or molecules regularly packed producing an infinite three dimensional lattice called a crystal or crystalline solid.37 38 Crystallization is a process from which solid crystals are produced and settled from a solution at the appropriate chemical and physical conditions.37 39 Crystallization process is promoted through the different available methods of synthesis, ranging from the easiest technique such as evaporation of the solution mixture, to the more complicated ones such as microwave synthesis, coupled with correct reaction mixtures formation, reaction conditions and thermodynamic conditions of the system.38 40

Crystals can have different sizes, and their growth is always directionally dependent. They grow larger in an orderly way without altering their functionality, topology or chemical composition when the same building unit species are joined with the available crystals under monitored and consistent chemical and physical conditions. Most crystals are
anisotropic due to their different ordered crystalline structures, with their mechanical, thermal, magnetic, electrical and optical properties varying if measured from different directions.\textsuperscript{37,38}

\section*{1.13 SOLUBILITY}

All crystallization processes occur in solution (in this context, a homogeneous mixture of liquid when one or more solutes dissolve in a solvent) under the correct thermodynamic conditions.\textsuperscript{41} At a steady temperature, a solute can dissolve in a given volume of solvent until it attains saturation, that is, a point when no more solute will dissolve in a solvent. The maximum amount of solute that can make a saturated solution at a given set of conditions and often increases with the solution temperature is termed as solubility.\textsuperscript{39} The solubility of materials depends on temperature. In most cases the solubility increases with increasing temperature, although the rate of increase varies broadly from one compound to another. The solubility of different inorganic compounds as a function of temperature is seen in Fig. 1.15. Sodium chloride is observed to have relatively weak temperature dependence with the solubility changing from 35.7 to 39.8 g/100 g water over a 100 °C range. Potassium nitrate, on the other hand, changes from 13.4 to 247 g/100 g water over the same temperature range.\textsuperscript{42} This kind of information is very important in crystallization processes since it will determine the amount of cooling required to yield a given amount of product and will in fact determine if cooling will provide a reasonable product yield. Solubility curves are useful for the crystallization of pure solids from a single-solute solution, because they provide information about the amount of a solute that can be dissolved in a given volume of solvent and solution temperature to achieve saturation.
Fig. 1.15: Solubility of KNO₃, CuSO₄ and NaCl in aqueous solution\textsuperscript{42}

When dealing with organic compounds (or inorganic compounds in non-aqueous solvents) a wide collection of solvent mixtures can usually be used, and the solute-solvent interaction determines the differences in solubility commonly observed for a given organic species in a number of different solvents.\textsuperscript{42} This is illustrated in Fig. 1.16.
1.14 SUPERSATURATION

Crystallization of a compound from a solution mixture is possible when it is more concentrated than would usually be, that is, when it is in a state of supersaturation – above equilibrium saturation. This is normally accomplished by increasing the temperature and/or pressure of the solution above ambient conditions to allow for more dissolution of solute and then slowly cooling it. MOF solvothermal synthesis, for example, require heating of the organic-inorganic reaction mixture in an oven, which essentially raises the rate of the reaction and the vapour pressure of the system, which favour the organic-inorganic reaction. Supersaturation of the reactant solution is necessary for crystallization as it provides the driving force for the subsequent formation of active clusters, nucleation and growth of the crystals. The four most common means to generate supersaturation
are; change in solvent composition, change in temperature of the system, change in chemical reaction, and evaporation of solvent.\textsuperscript{42}

The solubility-supersolubility diagram (Fig. 1.17) provides an important starting point for considering why crystallization takes place and what kind of process might be most suitable for formation of a particular substance. It is divided into three regions; \textit{undersaturated} - crystals present at this level will dissolve, \textit{metastable} - a supersaturated region in which crystal will grow, and \textit{labile} - a region where spontaneous nucleation of the solution take place.\textsuperscript{39}

![Solubility-Supersolubility diagram](image)

\textbf{Fig. 1.17:} Solubility-Supersolubility diagram.\textsuperscript{39}

The driving force in terms of the chemical potential differences that are related to the temperature and concentration differences during transporting processes, heat and mass transfer, are coupled in crystal growth.\textsuperscript{41} The driving force can be expressed in different
ways, but the most common for supersaturation are the concentration driving force, $\Delta c,$ supersaturation ratio, $S,$ and relative supersaturation, $\sigma.$\textsuperscript{38}

\[
\Delta c = c_{ss} - c_{eq} \quad 1.1
\]

\[
S = \frac{c_{ss}}{c_{eq}} \quad 1.2
\]

\[
\sigma = \frac{\Delta c}{c_{eq}} = S - 1 \quad 1.3
\]

where $c_{ss}$ is the supersaturated solution concentration, and $c_{eq}$ is the equilibrium saturation concentration at a given temperature.

The difference between a chemical potential of a substance, $\mu,$ in the transferring and transferred states, in solution ($\mu_s$) and on the crystal surface ($\mu_c$) is the central driving force for crystallization as seen below.\textsuperscript{38}

\[
\Delta \mu = \mu_s - \mu_c \quad 1.4
\]

The chemical potential, $\mu,$ is defined in terms of standard potential, $\mu^o,$ and the activity, $a,$ by

\[
\mu = \mu^o + RT \ln a \quad 1.5
\]

where $R$ is the gas constant and $T$ is the absolute temperature.

The fundamental dimensionless driving force for crystallization can be expressed as

\[
\frac{\Delta \mu}{RT} = \ln(a/a^*) = \ln S \quad 1.6
\]

where $a^*$ is the activity of a saturated solution and $S$ is the fundamental supersaturation,\textsuperscript{38} i.e.

\[
S = \exp(\Delta \mu/RT) \quad 1.7
\]
1.15 NUCLEATION

Nucleation is the initial phase of crystal growth and the name for the production of new solid nuclei from the mother solution. Nuclei can be considered as stable clusters of molecules that are arranged in an ordered lattice structure. The two main types of nucleation are primary and secondary nucleation. Primary nucleation simply means the formation of nuclei that occur in both homogeneous and heterogeneous systems, while secondary nucleation refers to the formation of nuclei induced by the crystals present in the system.

1.15.1 PRIMARY NUCLEATION

*Homogeneous Nucleation*

In primary homogeneous nucleation the nuclei are formed spontaneously, that is, without requiring any external factor, from the precursor solution. These nuclei are formed in solution by addition of molecules to the surface of the clusters until reaching a critical size, which is more stable with an identity arrangement that allow more attachment of nuclei to form a crystal block according to molecular addition mechanism seen below.

\[
\begin{align*}
A + A & \rightleftharpoons A_2 \\
A_2 + A & \rightleftharpoons A_3 \\
A_{n-1} + A & \rightleftharpoons A_n \text{ (critical-size cluster)} \\
A_n + A & \rightleftharpoons C \text{ (crystal growth)}
\end{align*}
\]

The interaction of these molecules with the cluster is monitored by cluster free energy, which is directly related to the size of the cluster. Assuming the cluster to be a sphere of radius \(r\), the total free energy, \(\Delta G\), sum of surface excess free energy, \(\Delta G_s\) (the free energy change between the particle surface and the particle bulk), and the volume of excess free energy, \(\Delta G_V\) (free energy between a large cluster of radius \(r = \infty\) and solute in the solution...
resulting from the phase transformation). $\Delta G_s$ has a positive magnitude which is proportional to $r^2$. $\Delta G_V$ has a negative magnitude in a saturated solution which is proportional to $r^3$ (Fig. 1.18).\(^3^8\)

$$\Delta G = \Delta G_s + \Delta G_V$$

$$= 4\pi r^2 \gamma + 3/4\pi r^3 \Delta G_V$$

$$= 4\pi r^2 \gamma + 3/4\pi r^3 / v \Delta \mu$$

\(1.8\)

**Fig. 1.18:** Free energy diagram for nucleation showing a ‘critical nucleus’.\(^3^8\)

Where $\Delta G_V$ is the change in free energy for modification per unit volume, $\gamma$ is the tension of interface between crystal surface and supersaturated solution, and $\Delta \mu$ is the chemical potential with a negative value. **Fig. 1.19** shows how free energy, $\Delta G$ depends on cluster size, $r$, that is, the higher the supersaturation the lower the free energy barrier value and therefore the size of the critical nucleus. With a higher supersaturation the free energy barrier becomes low enough for spontaneous nucleation to take place.\(^3^7, ^3^8\)
Fig. 1.19: Temperature effect on size and critical nucleus energy of formation ($T_1 < T_2$).\textsuperscript{38}

The promotion of crystal growth depends on the system having enough driving force to overcome the energy barrier\textsuperscript{38,44} as seen in Fig 1.20, which is inversely proportional to the square of the supersaturation.\textsuperscript{45}

The nucleation rate is monitored by three major factors; these include supersaturation ratio, $S$, temperature, $T$, and tension of interface, $\gamma$. The effect of each of these factors is described in Equation 1.9 which is derived from the Arrhenius equation.\textsuperscript{38} This indicates that the nucleation rate decreases with decreasing temperature and supersaturation, and with an increasing surface energy.

$$J = A \exp[- \frac{16\pi \gamma^3 \nu^2}{3kT^2} (\ln S)^2]$$ \hspace{1cm} 1.9

where $J$ is the rate of nucleation, $A$ is the molecules in critical cluster, $\nu$ is the nucleus volume and $k$, the Boltzmann constant.
**Heterogeneous Nucleation**

This is the second type of primary nucleation, where the nucleation is favoured due to the presence of impurities within the system, such as trace amount of foreign particles, or scratches on the surface of the vessel wall.\(^{41, 45}\) This type of nucleation is sometimes undesirable and generates incorrect products; nevertheless it can be very useful, for instance in the membrane production. Heterogeneous nucleation has a lower Gibb’s free energy than homogeneous nucleation. This is because the impurity surface can favour adsorption of the crystalline material, which means that to achieve successful heterogeneous nucleation the required supersaturation is lower than for homogeneous nucleation as the free energy barrier is lower.\(^{37, 42}\)

1.15.2 SECONDARY NUCLEATION

Secondary nucleation takes place when there is crystalline material present within a reaction vessel, and this is referred to as *seeding* in terms of synthesis. In this type of nucleation a small quantity of desired crystalline product is added to the reactants to
promote the growth of the material. In effect, seeding avoids the early stage of the nucleation process as crystals with a critical size being present already in the mixture of the reaction.\textsuperscript{38, 41} The most essential and usually encountered mechanism of secondary nucleation is \textit{contact nucleation}, or sometimes called \textit{collision breeding}, which is the most useful nucleation mechanism as it is recognised as having significance for materials of high or moderate solubility.\textsuperscript{37} The processes governing the secondary nucleation rate include, generation of secondary nuclei as a solid phase, removal of clusters, and formation of new solid phase through growth.\textsuperscript{42}

There are two main advantages to secondary nucleation over primary nucleation; these are, low free energy barrier, that is, crystallization occurs at lower supersaturation, and allows for greater control over the crystalline structure of the product.\textsuperscript{38}

1.16 CRYSTAL GROWTH

Crystal growth is a process including diffusion and integration, optimized by the solid surfaces effect on which it takes place (\textbf{Fig. 1.21}), and the solid ions or molecules attain the growing faces of a crystal by diffusion through the phase of the liquid. They have to become organized at the surface via an adsorbed layer. This proceeds only when the solution is supersaturated. The growth of crystals from solution requires two important processes; mass transport from the solution to the crystal surface by diffusion and convection mechanisms, and integration of materials into the crystal lattice by surface reaction process.\textsuperscript{39} Once the nuclei have attained the critical size, then crystal growth takes place, which is the subsequent stage of crystallization. This happens when the nuclei are covered by the supersaturated solution and thus the number of growth units adding to the crystal surface is higher than the one leaving.\textsuperscript{45} Crystal growth normally requires determination of the reactants’ solubility, supersaturation condition, nucleation, growth of
clusters that attained critical size, and crystal growth at supersaturation condition. The main purpose of crystal growth study is to get a full understanding of the growth mechanism.46

Fig. 1.21: Growing crystal-solution interface.39

1.17 GROWTH MECHANISMS

Fig. 1.22 indicates the rate of growth $R$ versus the driving force for $\Delta \mu / kT$ for the three forms of mechanism of growth. The figure illustrate that as driving force increases, an interface becomes rougher, and that two bending points emerges at $\Delta \mu / kT^*$ and $\Delta \mu / kT^{**}$, because the relating growth mechanism models change. The mechanism of growth becomes sticky-type over $\Delta \mu / kT^{**}$ and the interface becomes rough, whereas the growth becomes mainly monitored by the spiral-type growth mechanism below $\Delta \mu / kT^*$ and the interface becomes smooth. Between $\Delta \mu / kT^*$ and $\Delta \mu / kT^{**}$, the interface becomes smooth, but the mechanism of growth becomes mainly by two-dimensional nucleation, also known as layer-by-layer growth or ‘birth and spread growth.’41
1.17.1 LAYER-BY-LAYER GROWTH MECHANISM

This is the type of crystal growth that takes place at higher supersaturation level in order to overcome the necessary free energy barriers. It initiates on the crystal surface when the growth units are absorbed onto the surface of the crystal, where the particles migrate freely on the surface through surface diffusion and attach to kink sites in the step as seen in Fig. 1.23a. Fig. 1.23b shows the advancement of the step to the edge of the face. Subsequently, a new two-dimensional nucleus will be produced on the surface of the crystal as seen in Fig. 1.23c.44
1.17.2 SPIRAL GROWTH MECHANISM

Spiral growth takes place in the presence of a dislocation at the crystal surface called a screw dislocation, which can promote the spiral growth to build upward and finally form a ‘hillock’ on the surface of the crystal as seen in Fig. 1.24. Spiral growth mostly occurs on smooth surfaces and has a lower driving force compared to layer-by-layer growth which occurs at relatively high supersaturation levels. The first step is generated by dislocation (Fig. 1.24a), a second step is generated only when length reaches $2r_{2D}^*$ as seen in Fig. 1.24b, the third step is generated from second step on reaching $2r_{2D}^*$ length (Fig. 1.24c), then the fourth step comes up and so forth (d).\(^{44}\) Hence, a spiral pattern is produced around the core of the dislocation.

**Fig. 1.23:** Layer-by-layer growth mechanism.\(^{44}\)
Crystal growth kinetics is essential to provide information about the solution species interactions that generate the crystal aggregates during the nucleation process and their attachment to the successive crystals. Crystals with lower free energy of nucleation are generally the first crystals to be produced in a solution system, that is, crystals are produced due to the nucleation ease but are smaller at first as the reactants are consumed before they grow into larger sizes with time to become thermodynamically favoured products having a low free energy. The crystals aggregate and then dissolve back into the solution and recrystallise onto the larger crystals making them to increase in size. This is called ‘Ostwald ripening’. Ostwald ripening takes place due to the high surface energy and overall free energy of the smaller crystals than the larger ones that are thermodynamically less stable.
1.19 References


2.0 CHAPTER TWO

2.1 SYNTHESIS AND INSTRUMENTAL TECHNIQUES

The materials used in this research work are listed in Table 2.1.

Table 2.1: Grade and supplier of all Materials used

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<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>Supplier</th>
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<tbody>
<tr>
<td>5-tertbutyl isophthalic acid</td>
<td>98%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>99.8%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethanol</td>
<td>≥99.8%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>≥99.5%</td>
<td>Fluka Analytical</td>
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<td>98/100%</td>
<td>Fisher Scientific</td>
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<td>Fumaric acid</td>
<td>99%</td>
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<td>99.8%</td>
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<tr>
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<tr>
<td>Zinc (II) nitrate hexahydrate</td>
<td>98%</td>
<td>Alfa Aesar</td>
</tr>
</tbody>
</table>

2.2 SYNTHESIS

A summary of the equipment and experimental methods used for all the synthetic procedures in this research work is provided in this section.

2.2.1 Zn(tbip) MOF

A procedure adapted from L. Pan et al. was used. A hydrothermal reaction of 98.5 mg of zinc (II) nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and 74 mg of 5-tertbutyl isophthalic acid (H₂tbip) dissolved in a solution mixture of 6.5 mL of water and 1.5 mL of ethylene glycol. The solution mixture was placed in a 20 mL Teflon line steel autoclave and heated in a
stable oven at 180 °C for 84 hours. Uniform brown column crystals were obtained by filtering the sample and thoroughly washing it with distilled water followed by ethanol. The sample was then dried at room temperature.

2.2.2 MOF-801-SC [Zr₆O₄(OH)₄(fumarate)₆]

A procedure adapted from H Furakawa et al² was used. 27 mg of fumaric acid [HO₂C(CH)₂CO₂H] and 76.7 mg of zirconium (iv) oxychloride octahydrate (ZrOCl₂·8H₂O) were dissolved in a solvent mixture of 11.7 mL of dimethylformamide (DMF) and 1.8 mL of formic acid (HCO₂H) in a 20 mL screw-capped glass jar rinsed with a Sigmacote siliconizing reagent followed by rinsing three times with acetone and dried in the oven. This is to reduce nucleation in the growth of the MOF single crystals. The solution mixture was then heated in a stable oven at 120 °C for 24 hours. Octahedral colourless crystals were obtained by filtering the sample and washing with anhydrous DMF. The sample was then dried at room temperature.

2.3 ANALYTICAL TECHNIQUES

2.3.1 X-RAY DIFFRACTION (XRD)

X-ray crystallography is a technique used to understand the structure of simple crystals and the forces holding them together. This technique depends on the fact that the interatomic distances in crystals have the same order of magnitude as X-ray wavelength (1 Å). A crystal can thus serve as a 3-dimensional diffraction grating to the X-ray beam. The diffraction pattern produced is then interpreted to get the precise internal locations of the atoms in the crystals, thus showing the distances and the angles between them. Crystals are solid particles of regular shape and shiny surfaces. A crystal is produced from a basic ‘building unit’ that repeats continuously in every direction, in a regular manner. This
building unit is called the unit cell. The unit cell of a 3-dimensional lattice is a parallelepiped described by three lengths $a$, $b$, and $c$ and three angles $\alpha$, $\beta$, and $\gamma$ as seen in Fig. 2.1 below.$^3$

![Diagram of a unit cell](image)

**Fig. 2.1: A defined unit cell$^1$**

Since unit cells are the crystal’s basic building units, they must be space filling. All the different unit cell shapes fulfil this condition are called the seven crystal systems as seen in Table 2.2 below. The four different types of a 3-dimensional unit cells are Primitive (P), Body-centred (I), Face-centred (F), and base-centred (A, B, or C).$^3$
<table>
<thead>
<tr>
<th>Seven systems</th>
<th>Axes and angles</th>
<th>14 Bravais Lattices</th>
<th>Lattice symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Body centered</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face centered</td>
<td>F</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Body centered</td>
<td>I</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Body centered</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Base face centered</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face centered</td>
<td>F</td>
</tr>
<tr>
<td>Trigonal or rhombohedral</td>
<td>$a = b = c$</td>
<td>Primitive</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
<td>Base face centered</td>
<td>B or C</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = 90^\circ$</td>
<td>Base face centered</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 120^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = 90^\circ \neq \gamma$</td>
<td>Base face centered</td>
<td>B or C</td>
</tr>
<tr>
<td></td>
<td>$or (a = \beta = 90^\circ \neq \gamma)$</td>
<td>Base face centered</td>
<td>B or C</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>Primitive</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The combination of the seven possible unit cell shapes and the four types of lattices, produce the 14 permissible Bravais lattices shown in **Fig. 2.2** below.
2.3.1.1 POWDER X-RAY DIFFRACTION (PXRD)

Powder X-ray diffraction is a very powerful technique for investigating a range of chemical and physical features of solid materials. Powder X-ray diffraction is the most commonly used technique in solid state inorganic chemistry and has many applications from phase purity assessment analysis to structure determination. X-ray diffraction comes from X-ray and atomic electron interactions. Depending on the atomic arrangements, when the difference in the path between two diffracted rays varies by a whole number of wavelengths the interference of the scattered rays is constructive. This
exclusive condition is explained by the Bragg equation. W. L. Bragg formulated a law which is very important in powder x-ray diffraction that establishes a good relationship between the diffraction angles (Bragg angle), interplanar distance, and wavelength. According to Bragg, the diffraction of crystalline sample can be viewed and explained by a mirror reflection notion of the incident beam of X-rays from a set of crystallographic planes.$^7$

Fig. 2.3 shows the Bragg condition for the X-rays reflection by a solid crystal. The black points array stands for a crystal section and the lines linking the dots label a parallel planes set with Miller indices $hkl$ and interplanar length $d_{hkl}$. The parallel beam emanating from the X-ray source (A and D) are ‘reflected’ from different but parallel crystal planes (B and F) and arrive at the X-ray detector in phase with one another (C and H). This is called constructive interference, and for it to occur, the path lengths of the beams interfering must differ by wavelengths of a whole number. For BE and BF drawn at right angle to the beam,

Path length difference = EF + FG

But $EF = FG + d_{hkl} \sin \theta_{hkl}$

So, path length difference = $2d_{hkl} \sin \theta_{hkl}$ \hspace{1cm} 1.10

This must be equal to an integral number, $n$ of wavelengths. As X-rays wavelength is $\lambda$, then $n \lambda = 2d_{hkl} \sin \theta_{hkl}$ (Bragg equation).$^3$ This allows the calculation of d-spacing between the crystal planes giving the peak in powder XRD pattern from the angle between the source and the detector ($2\theta$).
In this research project, all the PXRD analyses were performed on PANalytical X’Pert HighScore Plus diffractometer with Cu Kα X-rays (wavelength 1.5406 Å). Crystals were ground into powder for the analysis. The tube voltage was 40 kV and the current was 30 mA. The crystals were scanned between 3 and 60° 20 with a step size of 0.0167° at 42.545 s/step.

2.3.1.2 SINGLE CRYSTAL X-RAY DIFFRACTION

Single crystal X-ray diffraction provides crystal structures on which the explanation of most of the data from powder X-ray diffraction is based. From a single crystal, it is possible to determine the location and intensity of the hkl reflections correctly and from the data measured not only the unit cell dimensions determine the space group of the structure, but also the definite atomic locations. In most instances, this is achieved very rapidly and accurately, and serves as a powerful technique to a chemist.
Single crystal X-ray diffraction data is at present collected with the use of a diffractometer controlled by a computer, which determines the Bragg angle $\theta$ and intensity $I$ for every $hkl$ reflection. Most contemporary single crystal X-ray diffractometers use a flat-plate detector in order to collect and measure all the reflections concurrently. A complete set of data (thousands of reflections) is gathered in few hours.\(^3\)

After single crystals have been grown, a suitable single crystal is first chosen using a polarising microscope for the single crystal X-ray analysis. The crystal is immersed in oil, which holds the crystal by surface tension and protects it. Imperfections in the crystals if any are seen when viewed between cross polarisers. The chosen crystal is put onto the goniometer head in the centre of the diffractometer. The crystal is cooled by a stream of nitrogen gas (100 K), which prevents the crystal from X-ray damage and also freezes the oil to attach the crystal firmly to the fibre. The crystal is then centred manually with the help of in-built telescope and the x,y,z adjustments of the goniometer head. The diffractometer has been set so that the telescope crosswires coincide with the point where the X-ray beam intersects the centre of the circles.\(^8\)
Fig.2.4: The main components of a single crystal X-ray diffractometer.

Three important circles are used for rotating the crystal (φ, κ, and ω), in which κ is fixed and the other two (φ and ω) are varied. Another circle of rotation is used for moving the detector 2θ. The CCD detector is used to record different images at various crystal angles. The images are processed to get the reflection angles, which are used to calculate the unit cell dimension and class of crystal system. The full set of reflections (h,k,l intensity) is measured and the number depends on the unit cell dimensions and crystal system. Correction of the raw intensity data is then performed to correct the various physical effects associated with the data collection mode.

Corrected intensity = $F^2(hkl) = I(hkl)/[Lp \times (Dec) \times (Abs)]$
where \( I(hkl) \) is the raw intensity, \( F(hkl) \) is the structure factor, \( Dec \) is a decomposition correction obtained by scaling between X-ray images using common reflections, \( Abs \) is the absorption correction and is calculated from the variations in intensity of the same reflection measured at different psi-angles, known as a multi-scan correction, and \( Lp \) is the Lorentz and polarisation corrections. The Lorentz factor \( L \), is related to the time taken by the reflection in its diffracting position, which depends on the geometry of the diffractometer and hence method of data collection. The polarisation factor \( p \), allows for partial polarisation of the X-ray beam when it is reflected off the crystal. Both Lorentz and polarisation effects are \( \theta \) dependent and a correction is easily calculated. The space group is then assigned.\(^8\)

The Bragg equation provides information mainly about the angular distribution of reflections but says nothing about their intensities. This is because “point atoms” sitting on lattice points are used i.e. all the atoms coincide with Bragg planes and scatter constantly at all \( \theta \) values.

In real crystals, X-rays are scattered by electrons so that the scattering factor, \( f_j \), for a real atom is equal to \( Z \), but only for \( \theta = 0 \). X-ray falls off with increasing angle due to destructive interference within the atom’s electron shells. Atoms are distributed across the unit cell \( x_1, y_1, z_1; \ldots; x_j, y_j, z_j \), not just in the Bragg planes. The fractional distance of atom \( j \) from a Bragg plane is given by \( hx_j + ky_j + lz_j \). As there is a shift in the phase of the reflected wave by \( 2\pi \) in traversing from one Bragg plane to the next, atom \( j \)'s phase will be shifted by \( \Phi_j = 2\pi(hx_j + ky_j + lz_j) \). The scattered waves must therefore be summed taking the phase shifts into consideration - vector addition. For example, using the following equation;

\[
F(hkl) = \sum f_j [\cos 2\pi(hx_j + ky_j + lz_j) + isin 2\pi(hx_j + ky_j + lz_j)]
\]
or its equivalent $F(hkl) = \sum f_j \exp 2\pi i (hx_j + ky_j + lz_j)$

If the structure is centrosymmetric the vector sum is made up of two mirror images sets. This means that the equation for the vector addition for centrosymmetric structures reduces to:

$F(hkl) = \sum f_j \cos 2\pi (hx_j + ky_j + lz_j)$

Importantly, the phase, $\alpha(hkl)$, of the resulting vector $F(hkl)$ has got to be either 0° or 180° or $F(hkl)$ is either $+|F(hkl)|$ or $-|F(hkl)|$.

The $F(hkl)$ equation is a Fourier series and as such can be inverse Fourier transformed.

$\rho(xyz) = \Sigma_{all \ hkl} F(hkl) \exp[-2\pi i (hx + ky + lz)]$

where $\rho(xyz)$ is the electron density at point x, y, z within the unit-cell. The peaks in the electron density map will correspond to atoms, with the biggest peaks representing the atoms with high Z values.

As $\rho(xyz)$ is overwhelmingly real the above can be simplified to:

$\rho(xyz) = \Sigma_{all \ hkl} |F(hkl)| \cos(\alpha(hkl) - 2\pi (hx + ky + lz))$

where $\alpha(hkl)$ is the phase of $F(hkl)$ and is 0 or 180° for centrosymmetric structures i.e.

$\rho(xyz) = \Sigma_{all \ hkl} \pm |F(hkl)| \cos(-2\pi (hx + ky + lz))$

Unfortunately we only know $|F(hkl)|$ i.e. we’ve lost the phase information. Recovering the sign or phase of $F(hkl)$ is known as solving the phase problem and has, by now, become routine.

After solving the structure using direct method it is then possible to produce a Fourier Map of the electron density $\rho(xyz)$ within the unit cell. The Fourier map is not normally plotted but searched automatically to produce a list of peak heights and their locations in fractional atomic coordinates $x_j y_j z_j$. 

68
Molecular graphics packages are then used to display the results in the form of molecules on the computer screen. The crystallographer is able to interact at this stage to name atoms and remove any weak peaks from the atom list.  

**Least-Squares Refinement**

Least-Squares refinement is an efficient method of minimizing the difference between calculated and observed structure factors by progressively adjusting the input atomic parameters. The function minimized is:

\[ Q = \sum_{\text{All hkl}} w [ |F_{\text{obs}}| - |F_{\text{calc}}| ]^2 \]

Unfortunately, \( F_{\text{calc}} \) is not linear with respect to atomic parameters, so that the optimum structure cannot be calculated immediately. However, if a reasonable trial structure is available it will be possible to derive the shifts needed to improve the model.

The parameter shifts thus obtained are then applied to the starting parameters \( x_1, y_1 \) etc., and the process repeated. Many cycles of refinement are usually needed before convergence is achieved. When the input parameters have stopped shifting it is necessary to look for further atoms such as hydrogen using difference Fourier maps. Any newly discovered atoms is added to the list and further cycles of refinement performed.

In addition to fractional atomic coordinates, least-squares refinement provides two other types of important information.

1. Estimated standard deviations or standard uncertainties for all the parameters are calculated as part of the least-squares process, making it possible to determine the accuracy of molecular parameters, such as bond lengths.

2. Vibrational parameters - Each atom is described by three positional and a vibrational parameter for isotropic refinement (total 4) or three positional and six vibrational parameters for anisotropic refinement (total 9). Isotropic refinement describes
vibration as a sphere and requires only one parameter, the radius of the sphere. While anisotropic vibration is represented by an ellipsoid, which has to be described by six parameters; three independent radii and three tilt angles. Atomic vibration makes an atom look more spread out so that it scatters less at higher θ values than a stationary atom.

**R-factors**

Once the peaks in the Fourier map have been assigned to atoms it is possible to start refining the structure. Substitution of the fractional atomic coordinates \((x_j, y_j, z_j)\) and scattering factors \((f_j)\) into the following equation enables the structure factors \(F(hkl)\) to be calculated.

\[
F(hkl) = \sum f_j \exp 2\pi i(hx_j + ky_j + lz_j)
\]

Comparison of calculated and observed \(|F|\) values provides a measure of how accurate the proposed atomic parameters are. Formally this is done using \(R\) factors.

\[
R = \sum_{\text{All hkl}} \left| F_{\text{obs}} - |F_{\text{calc}}| \right| / \sum |F_{\text{obs}}|
\]

\(wR\) similar to \(R\) except \(F_{\text{obs}}\) weighted according to accuracy. Other types of \(R\) factors use \(F^2\) but they are all low for good agreement between observed and calculated structure factors.

Clearly adjusting \(x_j, y_j\) and \(z_j\) so that \(R\) is minimized will produce the optimal molecular geometry.

Once there are no significant features left in the Difference Fourier map and the least-squares refinement has converged the final parameters are written to a Crystallographic Information File (CIF). A CIF is written in plain text and each item is preceded by an internationally agreed key word e.g. \(_\text{cell_length_a}\) for a unit cell parameter. When a structure is published the CIF is properly checked, deposited and made available through
the crystallographic databases. The data contained in this file is compatible with molecular graphics and electronic publishing packages.\textsuperscript{8}

In this research works a very high Cu brightness and sensitive Prospector X8 single crystal diffractometer was used to collect data at 100 K and wavelength of 1. 542Å. Data were refined using full-matrix least-square on $F^2$.

\section*{2.4 SCANNING ELECTRON MICROSCOPY (SEM)}

Nowadays, SEM is certainly the most broadly used technique of all the electron beam instruments\textsuperscript{9} and has become a versatile technique employed in many research laboratories. SEM is very useful in material science for revealing the microscopic structure and distinguishes many phases from one another due to its high resolution, great focus, user friendliness, high automation level, ease of acquired images interpretation and microanalysis capabilities.\textsuperscript{9,10} The beam of electron scans sample surfaces line - by - line and generates signals due to sample and electron beam interactions in the evacuated column of the microscope, which are detected electronically and intensified by appropriate instrument.\textsuperscript{10} Primarily, the response signal is seen as a brightness modulation on a cathode ray tube (CRT) where the beam of the electron is moved concurrently to the column beam, as seen in \textbf{Fig. 2.5} of SEM principle scheme below.
SEM image resolution is mainly obtained by the sample interaction with primary electrons interaction and the diameter of the electron probe centred on the face of the sample. In SEM signal production depends on the energy of the beam, as a result of interaction the beam of incident electron with the sample surface (Fig. 2.6). The primary charged electrons interact highly with the samples’ charged particles. The interaction is *inelastic* if at the time of interaction the primary electron lost some of its energy, and if the primary electron lost no energy the interaction is *elastic*.10

**Fig. 2.5:** Scheme of SEM Principle10
SEM is now considered a device for mapping. A suitable electron probe in SEM instrument which is produced by the use of higher objective lens to reduce the size of a small source of electron is scanned on a sample in 2-D raster. Signals produced from the sample are detected, intensified, and regulate the size of the beam brightness of the second electron that is scanned synchronously with electron probe of SEM across the CRT display. Hence, a sample image is mapped for investigation on the CRT display (Fig. 2.7).
In this research project, a FEI Quanta 200 SEM Environmental operating in high vacuum mode was used to obtain all the images of the morphology of the crystals. Samples were mounted on sticky carbon tape and coated with gold to prevent charging of the sample. Secondary electrons were used with an accelerating voltage of 20 kV with a working distance of 10 mm.

2.5 ATOMIC FORCE MICROSCOPY (AFM)

It has been a familiar practice in the last few years to complement electron microscopy with AFM, as AFM permits direct characterization of the surface of solid materials and gives more insight into the surface features of these materials. It also gives high resolution imaging of the sample surface between a few nanometers and a hundred micrometers as seen in Fig. 2.8 below. AFM serves as a tool for measurement of sensitive force. AFM belongs to a family of scanning probe microscopes (SPMs) with a common feature of using extremely sharp probe to scan across a sample surface and produce a desired
AFM is a technique for imaging consisting of mechanical device capable of measuring extremely small forces as molecules or atoms are very close together. AFM has a unique advantage over STM (scanning tunnelling microscope) for being able to image non-conductive samples in a low vacuum condition, and can equally operate under different environmental conditions such as air, fluid and variable temperatures.

**Fig. 2.8:** AFM Images showing structural details on solid surfaces captured at different magnifications

**Fig. 2.9** shows the major parts of a commercial AFM, which has been used in an ambient environment. The major components include laser source, photodetector, optical microscope, sample stage, scanner and controller. The tip of the AFM is capable of
probing a very small contact surface (of radius between 5-50 nm), and this makes it a highly sensitivity to little forces.

**Fig. 2.9:** A schematic diagram showing the major parts of AFM machine.\(^{12}\)

The cantilever is a flexible plate spring, which is the crucial part of the instrument which is fixed at one end, and supports the pointed tip at the other end to measure the force between the tip and the sample. The tip approaches the sample and moves over its surface. The cantilever deflection as it scans is measured by the instrument, converted into electrical signal and a 3-dimensional image of the sample is built up. The forces of attraction or repulsion between the sample and the tip, moves cantilever away from or close to the sample. The cantilever deflection alters the laser beam reflected angle, making the spot to
fall on another side of the photodetector. The deflection signal is obtained by comparing the four quadrant signals (Fig. 2.10). The position of laser spot is also calculated through either vertical deflection (comparing “top” and “bottom” signals) or lateral deflection (comparing “left” and “right” signals). \(^ {11} \)

**Fig. 2.10:** The components of a photodetector of an AFM machine.\(^ {11} \)

### 2.5.1 Imaging Modes

There are many different imaging modes by which AFM is operated for investigation of different sample types. AFM scans can be recorded for each of these modes listed below laterally over a sample surface without changing the cantilever height to measure deflection signal, “constant height” imaging (feedback mechanism is not used), or at
“constant force”, where a constant force is applied to the sample surface and a feedback mechanism is used to adjust the height accordingly and the sample damage is avoided. The main AFM imaging modes are;

1. **Contact mode:** In this mode, the tip of the probe is in contact with the sample surface (Fig. 2.11) and the cantilever deflection is used as the feedback signal. Thus, the image of the microscope uses “constant force” rather than “constant height”. At a defined cantilever deflection value the cantilever height is adjusted by the feedback system keeping the deflection constant as the scan progresses.

2. **Intermittent contact mode:** In this mode, a repulsive contact is made by the tip with the sample surface at the cantilever’s lowest point of oscillation (Fig. 2.11). This has a lower lateral force than contact mode as a result of very low time of contact between tip and sample surface. However, when tip and sample surface are in contact high normal force may be experienced.

3. **Non-contact mode:** In this mode, the cantilever, without making contact, oscillates close to the surface of the sample as seen in Fig 2.11. There is tendency of the tip and sample surface coming into contact, and capillary force puts difficulty in controlling the ambient conditions. Highly rigid cantilevers are required to prevent attraction from overcoming cantilever spring constant.

![Fig.2.11: The Main Imaging Modes of an AFM showing the cantilever interaction with the sample surface](image)
In this research project, a Nanowizard II Bio-AFM from JPK instrument A.G was used to image the crystal surfaces. The AFM was mounted on an inverted Axiovert 200 MAT optical microscope from Carl Zeiss Microimaging GmbH, which was used to locate appropriate crystals (i.e. larger, flat crystals). Contact mode was used with a set point of 0.5 V and scan rates of 1 – 4.0 Hz. Silicon tips (Veeco probes NP-10), with a nominal spring constant of 0.50 Nm$^{-1}$ were used. Image analysis was performed using the JPK data Processing software. Height images were treated with a first order line by line fit to level the images. Step heights are accurate to 0.1 nm.

2.6 NUCLEAR MAGNETIC RESONANCE (NMR)

NMR is the study of structure of molecules by determination of electromagnetic field (of radio frequency oscillation) interactions with a collection of nuclei present in a strong magnetic field. NMR in solids and liquids is mainly detected by measuring the total dipole-dipole magnetic field outside the spin-polarised sample. But the measured magnetic field gives little spatial or structural details about the sample. Hence, many NMR techniques depend on a more detailed method form of spectroscopy known as spin correlation or gradient encoding of magnetic field. Both liquid and solid-state NMR are perfect techniques for investigating chemical compositions of materials. Chemical shift usually permits differentiation of chemical sites and NMR line intensities are proportional to the number of sites present.

Solid-state NMR is a powerful technique for solid materials characterization more especially if the sample is not soluble or molecular change occurs when it is dissolved. Solid state NMR has a good ability of unequivocal identification and distinguishing distinct polymorphs.
The principle of solid state and liquid state NMR is that all nuclei are charged and most are spinned. Introduction of external magnetic field transfers energy from ground state to a higher level. The transfer of energy occurs at a wavelength corresponding to a radio frequency and when spin returns to ground level, energy is emitted at the same frequency.\textsuperscript{15} \textbf{Fig. 2.12} shows the solid-state NMR basic principle.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nmr_principle.png}
\caption{NMR basic principle showing energy transfer of high and low spin nucleus.\textsuperscript{15}}
\end{figure}

Solid-state NMR gives important information on the molecule number in the asymmetric unit and on the molecule site symmetry in the lattice to help in powder XRD data refinement. Solid-state NMR spectra are distinctively made of wider lines arising from different interactions acting on the nuclear spins: dipolar coupling, quadrupolar coupling, Zeeman interaction and anisotropic shielding. By contrast, in liquid-state NMR molecules
speedy random tumbling limits the interactions to zero, and their effects on the NMR spectrum is rarely seen.\textsuperscript{15, 16} (Fig. 2.13)

![Solution $^{13}$C NMR](image1.png)

![Solid State $^{13}$C NMR](image2.png)

**Fig. 2.13:** The $^{13}$C Liquid and Solid-state NMR spectra\textsuperscript{15}

Some methods were developed and considered for minimizing huge anisotropic interactions of nuclei and to increase signal to noise ratio (S/N) in rare spin NMR spectra. These are:

**Magic Angle Spinning (MAS):** This forms artificial movement through placing sample rotor axis at 54.74° (magic angle) with respect to $B_0$. It averages the chemical shift anisotropy ($\omega$). $\omega \propto \frac{1}{2} (3\cos^2\theta - 1)$. The term $3\cos^2\theta - 1 = 0$ when $\theta = 54.74^\circ$. MAS rate has to be higher than or equal to anisotropic interaction magnitude to average it to null.

**Cross Polarization (CP):** This generates a 4-fold enhancement in $^{13}$C experiment. Here, there is transfer of polarization from abundant spins ($^1$H or $^{19}$F) to dilute spins ($^{13}$C or $^{15}$N),
aiming to enhance S/N and to induce relaxation at the nuclei. At “contact time”, CP bridges heteronuclei into a dipolar thermal contact by the adjustment of their precession rate.

**Dilution:** This method minimizes anisotropic interactions and increases S/N ratio of the rare spin NMR spectra which lead to “high-resolution” spectra in the absence of heteronuclear dipole interactions.

**Multi-Pulse Series:** This imposes induced movement on the spin operators intact. It is relevant to both heteronuclear and homonuclear decoupling.

**Fig. 2.14** shows the schematic diagram of the Solid-state NMR spectrometer and its main components.

![Schematic diagram of the Solid-state NMR spectrometer](image)

**Fig. 2.14:** Schematic diagram of the Solid-state NMR spectrometer showing the interconnection of its main components.¹⁵

In this research project, solid-state NMR spectra were obtained on a Bruker Avance III 400 MHz solid state NMR spectrometer using a 4 mm probe. Software used was TopSpin 2.1. All sample used were ground into powder and put into a zirconia rotor and inserted into the
NMR spectrometer. Adamantane as a standard was used to calibrate the NMR spectrometer prior to data collection. ACS/NMR processor was used to process the data.

2.7 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA is a technique of thermal analysis in which variations in chemical and physical characteristics of materials are determined as a function of increasing temperature (at constant rate of heating), or as a function of time (at constant temperature/mass loss). TGA gives details of chemical processes such as decomposition, chemisorptions, and solid-gas interactions. Equally, TGA provides details of physical processes including vaporization, and adsorption and desorption. TGA is mostly used for determination of peculiar characteristics of materials showing either loss or gain in mass due to decomposition, or loss of volatile substances. The analysis is usually conducted up to the degradation temperature of the samples.\textsuperscript{17}

Fig. 2.15: Schematic diagram showing gas path through the components of a TGA Machine.\textsuperscript{18}
TGA depends on a high degree of accuracy in the measurement of heat change and change of mass. Hence, the primary instrumental requisites for TGA are an accurate balance with a pan carrying the sample, and a programmable furnace with either constant rate of heating (most commonly used) or with constant loss of mass with time of heating. The sample is put in an electrically heated furnace provided with a thermocouple to record exact temperature measurements by comparing its output voltage with the computer preinstalled one. Oxidation and other unwanted reactions are prevented by purging an inert gas such as nitrogen (Fig. 2.15) into the sample chamber atmosphere.\(^{17}\)

The sample in TGA equipment is weighed continuously as it is heated to temperature of about 2000 °C. As the temperature rises, different sample constituents are degraded and the percentage mass from the changes is determined. The results are then plotted with the horizontal axis bearing the temperature values, while the vertical axis bearing the values of the mass loss respectively.\(^{17}\) This is seen in Fig. 2.16 for decomposition of CaC\(_2\)O\(_4\).H\(_2\)O from 0 – 1000 °C at the rate of 20°C/min.
Fig. 2.16: The thermograph of CaC$_2$O$_4$·H$_2$O showing degradation of the sample constituents at different temperature.\textsuperscript{19}

In this research work, all TGA data were obtained under nitrogen gas atmosphere using TGA/DSC1, Thermogravimetric Machine manufactured by METTLER TOLEDO. The rate of heating is varied based on the samples nature. The temperature range used was 25 $^\circ$C to 1000 $^\circ$C.

2.8 GAS ADSORPTION

Adsorption of gas on solid surfaces and in pore spaces is a complex process that involves interactions of mass and energy, and changes in phase. The physical adsorption of gases by solid materials is inversely proportional to temperature, but directly proportional to pressure. This process usually gives out heat, it is an exothermic process. Most recently the experiments are performed at an extremely low temperature, usually that of liquid nitrogen at its boiling point (77.35 K) and a pressure of one atmosphere. It has been established that
the quantity of absorbed gas is expressed as its volume at standard temperature and pressure (STP) conditions (0 °C and 760 mmHg), while the pressure is expressed as a relative, that is, ratio of actual pressure $P$ to vapour pressure $P_0$ of the adsorbing gas at the experimental temperature. The plot of volume ($V_a$) on the vertical axis against the relative pressure ($P/P_0$) on the horizontal axis tells much about the adsorbing solid materials including their shape.

![Fig. 2.17: Types of Adsorption Isotherms](image-url)

**Fig. 2.17** shows the six basic types of adsorption isotherms. Type I shows that the adsorbent has pores which are extremely small. Type II and IV show that the adsorbent has either large pores or nonporous. Type III and V show that the molecules have greater affinity for each other than for the solid in pore and surface analysis, that is, they have weak interaction than the adsorbent. Type VI shows rare nonporous solids with homogeneous surface.
In this research work, a Micromeritics ASAP 2010 adsorption analyser was used to collect the adsorption isotherms under liquid nitrogen at approximately 77 K. BET methods was used to calculate the internal surface area over the relative pressure range of 0.001 to 0.90.

2.9 References


18. NETZSCH, TG_209_F3_Tarsus_E_0313.pdf.
3.0 CHAPTER THREE

3.1 MOF-801-SC RESULTS AND DISCUSSION

Some UiO-66 samples including Karl Petter Lillerud et al\textsuperscript{1} and Peter Behrens et al\textsuperscript{2} were synthesised with a hope to study the intergrown on their crystal surfaces using AFM but due to their smaller single crystals nature and their aggregation together (Fig. 3.1 and 3.2), the effective AFM study of their surfaces was not possible.

Fig. 3.1: SEM images of UiO-66 captured at different magnifications\textsuperscript{1}
For MOF-801-SC synthesis, a Sigmacote siliconizing reagent was used to rinse the inner surface of the glass reaction bottle followed by rinsing three times with acetone and dried in the oven. This is to reduce nucleation in the growth of the MOF single crystals. The crystals synthesised using the Sigmacote siliconizing reagent are bigger than those synthesised without the reagent (Fig. 3.5).
3.2 POWDER X-RAY RESULTS

A sample of MOF-801-SC crystals was successfully synthesized. The powder X-ray diffraction pattern of MOF-801-SC crystals indicated that a monophasic sample had been prepared as shown in Fig. 3.3 below where three different sample prepared matched one another when compared, which is very similar to the calculated peak positions of the structure reported by H. Furukawa *et al.* A good match confirmed that the prepared sample was MOF-801-SC as seen in Fig. 3.4 below. The unit cell lengths, angles and space group of the crystal cell are \(a = 17.8348(17) \, \text{Å}, \quad b = 17.8348(17) \, \text{Å}, \quad c = 17.8348(17) \, \text{Å}, \quad \alpha = 90^0, \quad \beta = 90^0, \quad \gamma = 90^0 \) and \(Pn-3\).

![Graph](image)

**Fig. 3.3:** The combined powder XRD of three different synthesised samples of MOF-801-SC.
3.3 SEM RESULTS

Scanning electron micrographs revealed that the MOF-801-SC crystals generally have octahedral cubic morphology with crystal sizes ranging from 7.0 to 9.0 µm. Some intergrown crystals were also observed on the crystals as seen in Fig. 3.5 below, which is showing the images of MOF-801-SC crystals captured at different magnifications by SEM.
Fig. 3.5: MOF-801-SC scanning electron micrographs captured at different magnifications.

3.4 AFM RESULTS

The \{111\} facets of the octahedral cubic crystals of MOF-801-SC were imaged using \textit{ex-situ} AFM. The AFM deflection images showed that the crystal growth occurred by a layer-by-layer growth mechanism. It was observed that terraces are due to the layer-by-layer
growth as seen in Fig. 3.6 below. The edges of the terraces are observed to be a bit rough and not straight and sharp. This could relate to the chemical potential which relates to the supersaturation state ($\Delta \mu$). If the $\Delta \mu$ is higher than the surface energy of the edge sites then both edge and kink growth will be fast which will produce straight and sharp terraces.

**Fig. 3.6:** The AFM deflection images of the {111} facets of MOF-801-SC showing layer-by-layer growth.

MOF-801-SC crystals are observed to have some jagged terraces on the crystal surfaces. The cross-sectional analyses of the height images of MOF-801-SC crystals revealed that most of the growth steps are $1.0 \pm 0.1$ nm high as seen in Fig. 3.8. This step height corresponds to the $d_{111}$-crystal spacing of the MOF-801-SC crystal structure (calculated 1.0...
nm) as seen in Fig. 3.7. The result indicates that the extended structural units are stabilised on the MOF-801-SC crystal surface.

**Fig. 3.7:** MOF-801-SC crystal structure showing height of the growth steps.
Fig. 3.8: The AFM height images of MOF-801-SC crystal surfaces.

It can be observed that the heights measured at the peak points of the nuclei are 0.70 nm (a) and 0.67 nm (b) (Fig. 3.9), and 0.72 nm (a), 0.7 nm (b) and 0.71 nm (c) (Fig. 3.10) which all do not correspond to the height of 1.0 nm. These values show development of
cluster in layers and also show that the surface is not linker. The growing step height was chosen as that measured at its peak point in each image.

**Fig. 3.9:** Cross-sectional analyses of a developing growth step on a \{111\} face of MOF-801-SC crystal surfaces.
Fig. 3.10: Cross-sectional analyses of a developing growth step on a {111} face of MOF-801-SC crystal surfaces.

3.5 References


4.0 CHAPTER FOUR

4.1 Zn(tbip) RESULTS AND DISCUSSION

Great interest was developed to study the crystal growth mechanism on the surface of Zn(tbip) crystals because, it is a guest-free MOF, highly thermally stable, uniqueness in gas separation and is up to 700µm to 1.0mm in size. Initially, Zn(tbip) was synthesised following the procedure of L. Pan et al\textsuperscript{1}, and the crystals (Fig. 4.1) were found to contain a fibre-like materials in them and are a bit soft indicating that the crystallisation process was not complete. Ex-situ AFM studies revealed that the elongated hexagonal prism of Zn(tbip) crystal surface has a large anisotropic growth features as seen in the AFM micrographs (Fig. 4.2). This is indicating much more rapid growth of the crystals in the direction parallel to the channel system than perpendicular to it.
Fig. 4.1: SEM micrographs of initial Zn(tbip) captured at different magnifications.
Subsequently, another set of crystals using similar preparations and procedure but with additional 12 hours to the reaction time was prepared. Robust crystals were produced with the same morphology (Fig. 4.5) as the previously prepared ones. The analyses below were carried out on the latter crystals.

### 4.2 POWDER X-RAY RESULTS

Crystals of Zn(tbip) were successfully synthesized. The powder X-ray diffraction pattern of Zn(tbip) crystals indicated that a monophasic sample had been prepared as shown in
Fig. 4.3 below, where three different samples prepared matched one another when compared, which is very similar to the calculated peak positions of the structure reported by L. Pan et al\textsuperscript{1}. A good match confirmed that the prepared sample was Zn(tbip) as seen in Fig. 4.4 below. The unit cell lengths, angles and the space group of the reported structure are $a = 28.8574(11)$ Å, $b = 28.8574(11)$ Å, $c = 15.8751(6)$ Å, $\alpha = 90^0$, $\beta = 90^0$, $\gamma = 120^0$ and R-3c.

Fig. 4.3: The combined powder XRD of three different synthesised samples of Zn(tbip).
Fig. 4.4: The powder XRD pattern of Zn(tbip) with the calculated peaks.

4.3 SEM RESULTS

The scanning electron micrographs revealed that the Zn(tbip) crystals have an elongated hexagonal prism morphology with crystal sizes ranging from 300 µm to 500 µm in diameter and 1 to 2 mm in length as shown in Fig. 4.5. Some small crystallites are observed within the images of Zn(tbip) (crystal surfaces) captured at different magnifications.
4.4 TGA RESULTS

Thermogravimetric analysis of Zn(tbip) conducted at 350 °C for a prolong period of time of over 24 hours indicated the absence of weight loss.\textsuperscript{1} The full crystallinity of the material structure is maintained during this period. This was ascertained by powder XRD analysis.
followed as soon as the thermogravimetric analysis was stopped. This outstanding feature shows that Zn(tbip) can be suitable for applications requiring repeated adsorption-desorption cycles for longer period of time.\textsuperscript{1}

The thermogravimetric analysis performed on the synthesised Zn(tbip) sample in this work showed that the on-set of mass loss took place at approximately $440 \, ^0\text{C}$, which is about $30 \, ^0\text{C}$ higher than the reported one ($410 \, ^0\text{C}$) as seen in Fig. 4.6 below. This indicates that Zn(tbip) is a guest free MOF as there was no sign of anything coming out of it and is stable to heat treatment within this temperature limit (0 to $430 \, ^0\text{C}$) which is an exception with regards to most MOFs that were investigated to be incapable of withstanding prolonged and repeated heating.\textsuperscript{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Zn_tbip_TGA.png}
\caption{The Thermogravimetric profile of Zn(tbip) under N\textsubscript{2}.}
\end{figure}
4.5  N₂ ADSORPTION RESULTS

The N₂ adsorption-desorption isotherm data were collected at 77K and low relative pressure range of 0.001 – 0.90 for Zn(tbip) (Fig. 4.7) showed a Type I isotherm, which is an indication that Zn(tbip) is microporous. Zn(tbip) seems to exhibit a strong adsorbent-adsorbate interactions in micropores or monolayer adsorption, suitable for small gas molecules separation and hydrogen storage due to its small pore diameter.¹ The surface area of Zn(tbip) (433.0 m²/g) is based on Branauer-Emmett-Teller (BET) equation, which is higher than the reported one (256.0 m²/g) and has a pore volume of 0.21 cm³/g and that of the reported one is 0.14 cm³/g.

Fig. 4.7: N₂ adsorption-desorption isotherm for Zn(tbip) at 77K
Fig. 4.8: Zn(tbip) BET surface area plot

Fig. 4.9: Zn(tbip) Langmuir surface area plot
4.6 SINGLE CRYSTAL RESULT

Table 4.1: Crystal data and structure refinement parameters for Zn(tbip) at 100K

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<td>c = 15.8751(6) Å  γ = 120°</td>
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<td>Largest diff. peak and hole</td>
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Table 4.2: Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for Zn(tbip) at 100K

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Table 4.3: Bond lengths (Å) and bond angles (°) for Zn(tbip) at 100K

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109
C8 – C7 – C10 107.94(14)
C8 – C7 – C9 109.20(14)
C10 – C7 – C9 108.81(14)
C8 – C7 – C1 112.36(12)
C10 – C7 – C1 109.78(13)
C9 – C7 – C1 108.69(13)
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H8A – C8 – C8B 109.5
C7 – C8 – C8C 109.5
H8A – C8 – C8C 109.5
H8B – C8 – C8C 109.5
C7 – C9 – C9A 109.5
C7 – C9 – C9B 109.5
H9A – C9 – C9B 109.5
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H9A – C9 – C9C 109.5
H9B – C9 – C9C 109.5
C7 – C10 – C10A 109.5
C7 – C10 – C10B 109.5
H10A – C10 – C10A 109.5
C7 – C10 – C10C 109.5
H10A – C10 – C10C 109.5
H10B – C10 – C10C 109.5

The symmetry transformation used to generate equivalent atoms:

(1)  x-y+2/3, -y+4/3, -z+11/6;  (2)  -x+1, -y+1, -z+2;  (3)  x-1/3, x-y+1/3, z-1/6;
(4)  x+1/3, x-y+1/3, z-1/6
Table 4.4: Anisotropic displacement parameters (Å² x 10³) for Zn(tbip)

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4.6.1 SINGLE CRYSTAL WITHOUT METHANOL

Fig. 4.10: Asymmetric unit of Zn(tbip) without methanol
4.6.1.1 Data analysis of Zn(tbip)

The model of Zn(tbip) reported by L. Pan et al. in the literature has a trigonal crystal system and the following cell parameters: space group (R-3m), cell dimension \(a = 28.863(4) \text{ Å}, c = 7.977(2) \text{ Å}\), volume \((5755.1(18) \text{ Å}^3, Z(18) \text{ and } F(000)(2628)\). While the one produced from this work also has a trigonal crystal system and the following cell parameters; space group (R-3c), cell dimension \((a = 28.857(11) \text{ Å}, c = 15.875(6) \text{ Å}\), volume \((11448.8(18) \text{ Å}^3, Z(36) \text{ and } F(000)(5258)\). It is observed from these data that the edge length \(c\) of the synthesized Zn(tbip) with space group, R-3c and trigonal crystal system is doubled that of the reported one which also has a trigonal crystal system but R-3m space group. This means that additional reflection is seen of which was not seen by the previous researchers on the sample. This might be due to the fact that an alternating configuration of the molecules in the sample due to c-glide, and that the diffractometer is
very reliable, has very high Cu brightness, low temperature and most sensitive 16 Mega pixel CCD detectors.

4.7 SOLID STATE $^{13}$C NMR RESULT

Zn(tbip) solid state $^{13}$C NMR analysis, which has not been done before revealed that all the peaks (Fig. 4.12) are due to the atoms present in the Zn(tbip) crystal and proving that there is nothing in the pores. This also confirms that Zn(tbip) is a guest free MOF.

Fig. 4.12: Zn(tbip) solid state $^{13}$C NMR spectrum
4.8 SINGLE CRYSTAL WITH METHANOL

Fig. 4.13: Asymmetric unit of Zn(tbip) after absorbing methanol

Fig. 4.14: Structure of Zn(tbip) after absorbing methanol viewed along c-direction
After the sample was put into a methanol solution for three days, the single crystal diffraction pattern has changed completely from the one without methanol. The values of the cell parameters becomes; space group (R-3), cell dimension \( (a = 28.924(11) \, \text{Å}, \, c = 8.101(3) \, \text{Å}) \), volume \( (5869.3(4) \, \text{Å}^3) \), \( Z \, (18) \) and \( F(000) \, (2952) \). This shows that the edge length of c-axis is reduced to half its original length as a result of the disorder in the molecule caused by methanol introduction. This means a reflection has been destroyed by methanol introduction reducing its length to half its original which is not a characteristic of the larger c-axis, and hence the c-glide is no longer possible because of the reduction in order. The crystal quality has been reduced as weak reflections are no more visible. Hence, it is now proved that molecules can go into the Zn(tbip) crystal pores (Fig. 4.14).

### 4.9 AFM RESULTS

*Ex-situ* AFM was used to investigate the Zn(tbip) crystal surfaces to provide information concerning the crystal growth mechanism of the material. Large anisotropic growth features were observed in the AFM micrographs (Fig. 4.15) which are similar to those observed in the optical microscope images and SEM images as seen in Fig. 4.16 below, indicating much more rapid growth of the crystals.
Fig. 4.15: Zn(tbip) atomic force micrographs captured at different magnifications.
Fig. 4.16: Zn(tbip) optical microscope images (a and b), and SEM image (c) showing large anisotropic growth.

The facets of the elongated hexagonal crystals of Zn(tbip) were imaged by \textit{ex-situ} AFM. The AFM deflection images showed that the crystal growth occurred by a layer-by-layer growth mechanism. It was observed that terraces are due to the layer-by-layer growth as seen from Fig. 4.15 above. The edges of the terraces are observed to be a bit straight and
sharp. This could be related to the chemical potential which relates to the supersaturation state ($\Delta \mu$). If the $\Delta \mu$ is higher than the surface energy of the edge sites then both edge and kink growth will be fast and that will produce straight and sharp terraces.

The cross-sectional analyses of the height images of Zn(tbip) crystals revealed that the growth steps are found to be within 40-54 nm ($\pm$ 1 nm) high as seen in Fig. 4.18 below. This means that the steps are multilayer high when compared to the unit cell edge length of the Zn(tbip) MOF (Fig. 4.17). The result indicates that the extended structural units are stabilised on the Zn(tbip) crystal surface.

![Zn(tbip) crystal structure showing height of the growth steps.](image)

**Fig. 1.17:** Zn(tbip) crystal structure showing height of the growth steps.
Fig. 4.18: The AFM height images of Zn(tbip) crystal surfaces.
Fig. 4.19: AFM height images of Zn(tbip) crystal surfaces

From Fig. 4.20 and Fig. 4.21 below, it can be observed that the heights measured at the peak points of the nuclei are 19 nm (Fig. 4.20a), 36 nm (Fig. 4.20b), 14 nm (Fig. 4.21a), 28 nm (Fig. 4.21b), 32 nm (Fig. 4.21c) and 19 nm (Fig. 4.21d). The growing step height was chosen as that measured at its peak point in each image.
Fig. 4.20: Cross-sectional analysis of a developing growth step on a Zn(tbip) crystal surfaces.
**Fig. 4.21:** Cross-sectional analyses of developing growth steps on a Zn(tbip) crystal surfaces

### 4.10 Reference

CHAPTER FIVE

CONCLUSION

This work demonstrated the use of AFM to provide new information on the surface structure and crystal growth of a cubic MOF, MOF-801-SC, and a non-cubic MOF, Zn(tbip). *Ex-situ* AFM showed that the terraces on MOF-801-SC crystals are rough and sharp with an average height of 1.0 ± 0.1 nm corresponding to the $d_{111}$ crystal spacing of the crystal structure. Whereas the terraces on Zn(tbip) crystals grow rapidly with an average height of 50 nm indicating a multilayer growth.