



**UNIVERSITI PUTRA MALAYSIA**

**SYNTHESIS AND STRUCTURAL STUDY OF AZOLE CONTAINING  
CADMIUM-BASED METAL ORGANIC FRAMEWORKS FOR  
ELECTROCHEMICAL DETECTION OF NITROBENZENE**

**NURUL NABIHAH BINTI MOHAMAD ISHAK**

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By

**NURUL NABIHAH BINTI MOHAMAD ISHAK**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra  
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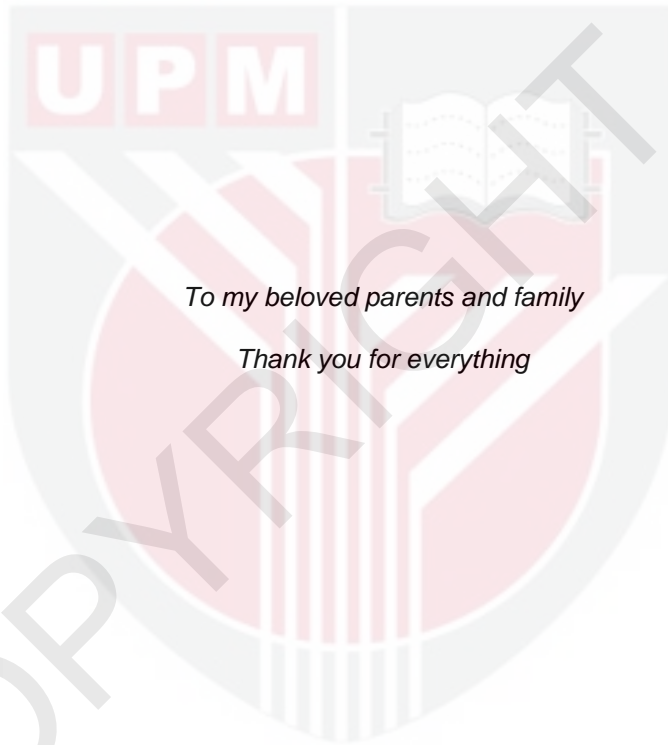
**November 2019**

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## DEDICATION



*To my beloved parents and family*

*Thank you for everything*

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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**November 2019**

**Chairman : Thahira Begum, PhD**  
**Faculty : Science**

Metal organic frameworks (MOFs) represent a new class of porous crystalline materials which contains of organic linkers and inorganic joints. In particular, the synthesis of MOFs with nitrogen-rich ligands are extremely versatile materials. Nitrobenzene (NB) is a carcinogenic organic compound that is widely used in the manufacturing and chemical industries. The spill of industrial waste contain high level of NB can be harmful to human health. Hence, the development of MOFs as electrochemical sensors for determination of NB are essential. Three novel mixed ligand Cd(II) MOFs, namely MOF-717 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with 4,4'-oxybis(benzoic acid) ( $\text{H}_2\text{oba}$ ) and 3,5-diamino-1,2,4-triazole ( $\text{Hdatrz}$ )), MOF-718 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with  $\text{H}_2\text{oba}$  and 3-amino-1,2,4-triazole ( $\text{Hatrz}$ ) and MOF-719 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with 2,6-naphthalenedicarboxylic acid ( $\text{H}_2\text{ndc}$ ) and  $\text{Hdatrz}$ ) were successfully synthesised using solvothermal with 1 : 2 : 2 molar ratio of Cd :  $\text{L}_1$  :  $\text{L}_2$  condition ( $\text{L}_1 = \text{H}_2\text{oba}/\text{H}_2\text{ndc}$  and  $\text{L}_2 = \text{Hdatrz}/\text{Hatrz}$ ) at 120 °C. The compounds were characterised via Powder X-ray Diffraction (PXRD) analysis, Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectroscopies, thermogravimetric analysis (TGA), Scanning Emission Microscopy (SEM),  $\text{N}_2$  physisorption analysis and the structural determination of MOFs was performed by Single-crystal X-ray Diffraction analysis (SXRD). The peaks at low angles in the PXRD pattern indicated the formation of large lattice unit cell of the frameworks. FTIR analysis shows reduction of C=O peaks intensity and this indicated the successful bonding of  $\text{H}_2\text{oba}/\text{H}_2\text{ndc}$  with Cd ions. NMR analysis confirmed the presence of both ligands in the frameworks. Thermal analysis indicated the MOFs had high thermal stability MOF 717 up to 450 °C, MOF-718 up to 467 °C and MOF-719 up to 480 °C. MOF-717 and MOF-718 crystallised in a monoclinic system with  $\text{C}2/m$  space group showing three dimensional (3D) structure with fluorite (flu) topology. MOF-719 crystallised in a triclinic system

with  $P\bar{1}$  space group showing a two dimensional (2D) underlayer structure and new topology. All the MOFs were modified with glassy carbon (GC) electrodes for electrochemical studies of nitrobenzene (NB) reduction using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. MOF-717/GC electrode showed the highest electrocatalytic activity with a low detection limit (LOD) of  $2.9 \times 10^{-8}$  M and high sensitivity of  $3.36 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ . This is due the present of active group of nitrogen and oxygen donor ligands from MOF-717 structures. This preliminary work indicated that these materials could be effective electrocatalysts in the electrochemical detection of the environmental pollutant NB.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS DAN KAJIAN STRUKTUR RANGKA ORGANIK LOGAM  
BERASASKAN KADMIUM MENGANDUNGI AZOL UNTUK PENGESANAN  
ELEKTROKIMIA NITROBENZENA**

Oleh

**NURUL NABIHAH BINTI MOHAMAD ISHAK**

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Rangka organik logam (MOFs) merupakan bahan liang berkristal kelas baharu yang terdiri daripada penyambung organik dan blok tak organik. Sintesis MOFs khususnya dengan ligan yang mengandungi lambakan atom nitrogen adalah sangat versatil. Nitrobenzena (NB) merupakan bahan organik karsinogen yang digunakan dalam industri pembuatan dan kimia. Tumpahan sisa industri yang mengandungi NB yang tinggi boleh membahayakan kesihatan manusia. Oleh itu, pembinaan MOFs sebagai alat pengesan elektrokimia adalah sangat penting. Tiga novel campuran ligan Cd(II) MOFs, dinamakan MOF-717 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  dengan 4,4'-oxibis(asid benzoik) ( $\text{H}_2\text{oba}$ ) dan 3,5-diamino-1,2,4-triazol (Hdatrz)), MOF-718 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  dengan  $\text{H}_2\text{oba}$  dan 3-amino-1,2,4-triazol (Hatrz) dan MOF-719 ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  dengan asid 2,6-naptalenadikarbosilik ( $\text{H}_2\text{ndc}$ ) dan Hdatrz) telah berjaya disintesis melalui kaedah solvoterma dengan nisbah mol 1 : 2 : 2 mewakili Cd :  $\text{L}_1$  :  $\text{L}_2$  ( $\text{L}_1 = \text{H}_2\text{oba}/\text{H}_2\text{ndc}$  and  $\text{L}_2 = \text{Hdatrz}/\text{Hatrz}$ ) pada suhu 120 °C. Semua sebatian telah dicirikan melalui Analisis Belauan Sinar-X (PXRD), Spektroskopi Transformasi Fourier Inframerah (FTIR), Resonans Magnetik Nuklear (NMR), Analisis Termogravimetri (TGA), Mikroskopi Pancaran Imbasan (SEM), Analisis penyerapan fizikal  $\text{N}_2$  dan struktur MOFs telah ditentukan melalui Analisis Belauan Sinar-X Hablur Tunggal (SXRD). Puncak pada sudut rendah dalam corak PXRD menunjukkan formasi unit kekisi besar pada rangka. Analisis FTIR menunjukkan berlaku penurunan intensiti puncak C=O menunjukkan ikatan antara  $\text{H}_2\text{oba}/\text{H}_2\text{ndc}$  dengan ion Cd telah berjaya. Analisis NMR mengesahkan kehadiran kedua-dua ligan di dalam rangka. Analisis terma mendapati MOFs mempunyai kestabilan terma yang tinggi dengan MOF-717 setinggi 450 °C, MOF-718 setinggi 467 °C dan MOF-719 setinggi 480 °C. MOF-717 dan MOF-718 telah dihablurkan dalam sistem monoklinik dengan kumpulan ruang  $\text{C2/m}$  yang menunjukkan struktur tiga dimensi (3D) serta topologi flourit (**flu**).

Manakala, MOF-719 telah dihablurkan dalam sistem triklinik dengan kumpulan ruang *Pt* menunjukkan struktur lapisan dua dimensi (2D) serta topologi yang baru. Kesemua MOFs telah diubah suai dengan elektrod karbon belemin (GC) bagi kajian elektrokimia terhadap pengurangan nitrobenzena (NB) dengan menggunakan teknik Voltametri Berkitar (CV) dan Voltametri Denyut Pembezaan (DPV). MOF-717/GC elektrod telah menunjukkan aktiviti eletrokatalitik yang tinggi dengan  $2.9 \times 10^{-8}$  M had pengesanan (LOD) dan  $3.36 \mu\text{A } \mu\text{M cm}^{-2}$  sensitiviti. Ini kerana kehadiran kumpulan aktif ligan penderma nitrogen dan oksigen dari struktur MOF-717. Kajian awal ini membuktikan bahan ini boleh menjadi efektif sebagai elektrokatalis untuk pengesanan elektrokimia bahan pencemar NB pada alam sekitar.





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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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## LIST OF ABBREVIATIONS

AuNPs-Zn-MOF	Gold nanoparticles incorporated with MOF-5 biphenyldicarboxylic acid
BPDC	4,4'-biphenyldicarboxylic acid
BTC	1,3,5-benzenetricarboxylic acid
CCDC	Cambridge Crystallographic Data Centre
Co-MOF-MPC	MOF made from cobalt chloride, 5-(4-pyridyl)tetrazole(4-H-ptz) and 1,3-bi(4-pyridyl)propane (bpp)
Cr-MIL-101	MOF made from chromium nitrate and benzenedicarboxylic acid
Cu(INA)	MOF made from copper acetate and isonicotic acid
Hatzr	3-amino-1,2,4- triazole
Hdatrz	3,5-diamino-1,2,4- triazole
H <sub>2</sub> ndc	2,6- naphthalene dicarboxylic acid
H <sub>2</sub> oba	4,4'-oxybis (benzoic acid)
HINA	Isonicotinic acid
HKUST-1	Hong Kong University of Science and Technology, HKUST; MOF made from copper nitrates and 1,3,5-benzenetricarboxylic acid
IRMOF-16	MOF made from zinc nitrate and terphenyl-2,2'-dicarboxylate (TPDC)
IR-MOF-9/10	Isorecticular MOF made from of zinc nitrate and 4,4'-biphenyldicarboxylic acid
IRMOFs	Isorecticular MOFs
ITQMOF-1 /-2	Instituto de Tecnologia Quimica Metal Organic Framework, ITQMOF; MOF made from lanthanide salts and 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid)
IUPAC	International Union of Pure and Applied Chemist
LOD	Limit of detection
MAF	Metal azolate frameworks
MAF-4	MAF consist of 2-methylimidazolate (Hmim) and Zn metal ions
MgMOF-1	MOF made from magnesium and pyridine-3,5-dicarboxylic acid
MgMOF-2	MOF made from magnesium and pyridine-2,6-dicarboxylic acid
MIL-53	MOF made from chromium nitrate and benzenedicarboxylic acid
MIL-68	MOF made from ferum nitrate and benzenedicarboxylic acid
MIL-88	MOF made from iron(III) nitrate and benzenedicarboxylic acid
MOF-5	MOF made from zinc nitrate and benzenedicarboxylic acid
MOF-717	MOF made from cadmium nitrate with 4,4'-oxybis (benzoic acid) (H <sub>2</sub> oba) and 3,5-diamino-1,2,4- triazole (Hdatrz) ligand

MOF-718	MOF made from cadmium nitrate with 4,4'-oxybis (benzoic acid) (H <sub>2</sub> oba) and 3-amino-1,2,4- triazole (Hatrz) ligand
MOF-719	MOF made from cadmium nitrate with 2,6- naphthalene dicarboxylic acid (H <sub>2</sub> ndc) and 3,5-diamino-1,2,4- triazole (Hdatrz) ligand
MOF-74	MOF made from magnesium nitrate and 2,5- dihydroxyterephthalic
MTBS	Methyl tributyl ammonium methyl sulfate
NHCPs-750	Nitrogen doped hollow carbon nanospheres
NU-1000	Northwestern University, NU; MOF made from zirconium chloride and tetratopic linker, 1,3,6,8-(p- benzoate)pyrene
PCN-6	Porous coordination network, PCN; MOF made from copper nitrate and 4,4',4"-s-triazine-2,4,6-triyl- tribenzoic acid
SBU	Secondary Building Units
TMPP/N-OMC	Tetra (4-methoxyphenyl)porphyrin functionalised N- doped mesoporous carbon
TPDC	Terphenyl-2,2'-dicarboxylate
UiO-66	Universitetet i Oslo, UiO (University of Oslo); MOF made from zirconium dichloride and benzene dicarboxylic acid
ZIF-8	Zeolitic Imidazolate Frameworks-8 ; MOF made from zinc nitrate and imidazole

# CHAPTER 1

## INTRODUCTION

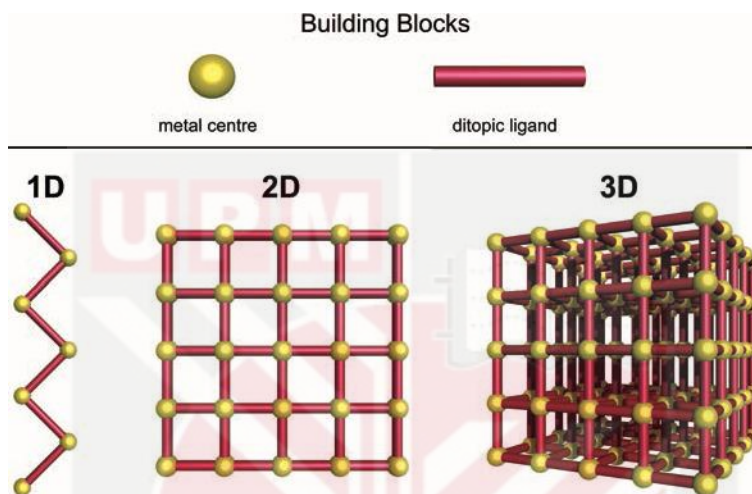
### 1.1 Background of research

Porous materials are a class of materials with low density, large specific surface area, and interesting physical, mechanical, thermal and electrical properties (Nishiyabu, 2012). According to International Union of Pure and Applied Chemistry (IUPAC), these materials can be classified based on their pore diameters, which are microporous (< 2 nm), mesoporous (2-0 nm) and macroporous (> 50 nm) (Xuan *et al.*, 2012). Porous materials such as zeolites, mesoporous silica, activated carbon and microporous polymer have been intensively investigated as ideal platforms for various applications especially in gas storage, chemical sensing, energy conversion and catalysis (Benzigar *et al.*, 2018).

Since the early 1990s, research into materials with polymeric and porous structures based on organic/inorganic hybrid materials has been on the rise. In relation to this, metal-organic frameworks (MOFs) are a rapidly emerging unique type of crystalline porous materials. MOFs are self-assembled from inorganic metal clusters and organic bridging ligands via strong covalent bonds. Via a self-assembly mechanism, the extended 1 dimensional (1D), 2 dimensional (2D) and 3 dimensional (3D) structures are built where the metal centres (known as the connector) are linked by ditopic or multitopic organic ligands, known as linkers (Figure 1.1) (Kitagawa *et al.*, 2004). An important feature of MOFs is that their framework structure, pore environment, functionality can be fine controlled by the choice of metal and organic building unit. Therefore, the topology of the network is determined by the intrinsic structural features of the choice of metal ions with different oxidation states and organic linkers (Lu *et al.*, 2014).

In the synthesis of such inorganic-organic hybrid materials, transition metal or lanthanide salts are reacted with rigid, often aromatic, organic donor ligands, which feature two or more Lewis-basic functional groups, usually neutral nitrogen donors (e.g., pyridyl, cyanide groups) or neutral/anionic oxygen donors (e.g., carbonyl, alkoxy, carboxylate groups) (Robson, 2008). The synthesis of MOFs are normally conducted under mild conditions. A few methods to synthesise MOFs have been reported including conventional synthesis which used electrical heating and non-conventional synthesis at room temperature. Other alternative synthetic routes including microwave-assisted, electrochemical, mechanochemical and sonochemical methods have also been used in the synthesis of MOFs. These methods can produce MOFs with varying particle sizes and size distributions as well as the morphologies that

can influence the material properties. In fact, the pore size, the pore shape, the network topology and surface functionality are more important to develop the unique structure of MOFs (Furukawa *et al.*, 2013). The structure of MOFs can also be influenced by a lot of other factors, such as the coordination environment of metal ions, the metal-to-ligand molar ratio, the ligand structure, the presence of solvent molecules, counter ions, reaction temperature, pH value of the solution and many other factors (Wang *et al.*, 2010).



**Figure 1.1: Extended structures of Metal-organic frameworks (MOFs) based on metal centre and linear ditopic ligands featuring different structural dimensionalities (Kitagawa *et al.*, 2004)**

MOFs have numerous advantages compared to conventional porous materials like zeolites or activated carbon, in terms of their ability to fine-tune the structures by rational design and incorporate functionalities into the molecular material. MOFs possess a highly crystalline nature, extraordinarily low densities (1.0 to 0.2 g/cm<sup>3</sup>), large pore sizes (up to 29 Å), large free volume, high surface area (500-4500 m<sup>2</sup>/g), and fascinating topologies (Li *et al.*, 2009). The choice of the initial metal cluster and organic linkers makes it possible to vary some parameters, such as the pore size as well as the specific surface area which leads to new ways to produce materials with tailored physicochemical properties.

Recently, the design on isostructural MOFs have been widely studied by using derivatives of aromatic rings contains substituents as a linker. Isostructural MOFs are MOFs that have same crystal morphology with different substituents on the organic linkers (for example; NO<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub> and Cl). These isostructural MOFs are promising as they have good active sites for specific applications such as gas adsorption, catalysis and chemical sensing. However, the presence of substituents in organic structure results in the



decrease of pore volumes and sizes (Morris *et al.*, 2011). Instead of having of one linker, the use of two different linkers were then introduced which offered advantageous in their properties with interesting crystal structures.

Many studies have reported the use of polycarboxylates and polypyridyls linkers due to their good ligating ability to metal ions and adjustable length and geometry. The approach of mixing carboxylate and pyridyl-types linkers was found to be very effective due to the versatility of oxygen donors to bind with metal ions of carboxylates and simple coordination nodes from pyridyls (Zhang *et al.*, 2012). However, pyridyl-type linkers have weak coordination ability and charge neutrality making them disadvantageous in controlling the compositions (such as metal /ligand ratio) during the synthesis (Gu *et al.*, 2010). Apart from that, azolate linkers are known as five-membered aromatic nitrogen heterocycle ligands that have strong and directional coordination bridging with metal ions (Zhang *et al.*, 2012). Hence, the strategies of designing mixed linkers consisting of polycarboxylate and azolate compounds were desirable to synthesise a wide range of coordination networks.

Many well-designed MOFs with mixed-ligands have showed fascinating physiochemical properties (Du *et al.*, 2013). Owing to their flexibility, high stability and porous structures, the diffusion of guest molecules to form permanent and highly ordered frameworks was easy. In addition, the presence of active sites in the frameworks promote host-guest interactions. (Morozan & Jaouen, 2012). These properties made MOFs promising candidates in gas separation, gas storage, and catalysis. The optical, electrical, and magnetic properties of MOFs extend their applications to chemical sensing and bioimaging. Among them, electrochemical sensing applications has received huge attention by electrodes modification with MOFs. It has been shown that the use of functional molecules and immobilization of metal nanoparticles with MOFs have improved the electrochemical sensing performance (Liu *et al.*, 2018).

Recently, MOF and MOF based composite modified electrodes have been reported have great performance as sensors in the detection of glutathione, L-cysteine, ascorbic acid, hydrogen peroxide and NADH (Arul & John, 2018). (NB) is known as an important raw material that is widely used in manufacturing industries. The huge waste disposal containing NB may lead to NB pollution which is considered harmful and can affect blood and nervous system leading to liver cancer (Emmanuel *et al.*, 2014). Therefore, development of selective and sensitive sensors for NB using electrodes modified with simple procedures is essential. Since there are limited studies on the use of MOF materials for the detection of NB, this study aimed to synthesise novel mixed-linkers MOFs using dicarboxylate and azolate derivatives as linkers. These materials were then modified with glassy carbon electrode and evaluated their electrochemical sensor properties in the detection of nitrobenzene by using cyclic voltammetry (CV) and dispersive pulse voltammetry (DPV) techniques. It is hoped that, the presence of

functional group in the organic ligands could enhance the performance of MOF modified electrodes in the nitrobenzene reduction.

## 1.2 Problem statement

Nitrobenzene (NB) is an important raw material in the chemical industry, which widely used as an intermediate in the synthesis of resins, pesticides, dyes and pharmaceutical (Arul & John, 2018). Generally, NB is stable in aqueous medium due to the presence of strong electron withdrawing groups in the nitro aromatic ring. There are several possible sources for NB pollution which include oil spills from industrial and domestic wastes. NB is harmful when its concentration level exceeds 0.11 mg/L and it affects mainly the blood and nervous systems in human which can lead to liver cancer (Emmanuel *et al.*, 2014). According to clear water act of USA, the permissible limit of NB in drinking water is 17 µg/L (OPPT, 1995).

Various techniques have been employed for the determination of NB in environmental samples such as High Performance Liquid Chromatography (HPLC) (Wang & Chen, 2002), Gas Chromatography (GC) (Ebrahimzadeh *et al.*, 2009), spectrophotometry (Cui *et al.*, 2010), spectrofluorimetry (Li *et al.*, 2014), and electrochemical techniques (Liu *et al.*, 2018; Velmurugan *et al.*, 2017). Among of these methods, electrochemical techniques are the most advantageous since they are low cost, highly selective, sensitive and have less time consumption (Zhang *et al.*, 2015).

Basically, the determination of NB by electrochemical techniques is by using electrodes. By fabricating the electrode with active materials containing NH<sub>2</sub>, NO<sub>2</sub> and OH group, the sensitivity and selectivity towards NB detection can be enhanced. This is due to the molecular interactions of the functional groups to reduce nitrobenzene to aminobenzene. Previously, many fabricated electrodes such as SiO<sub>2</sub>-AuNPs, Bi-film, Ni-tetraphenyl porphyrin nanocomposite, tetra(4-methoxyphenyl)porphyrin functionalised N-doped mesoporous carbon (TMPP/N-OMC), β-cyclodextrin graphene oxide (β-CD/GO, γ alumina polished (γ-Al<sub>2</sub>O<sub>3</sub>) and nitrogen doped hollow carbon nanospheres (NHCPs-750) modified GC electrode have been reported (Arul & John, 2018). MOF modified electrodes such as AuNPs-Zn-MOF and Co-MOF-MPC also have been reported for their good stability and permanent porosity (Yadav *et al.*, 2016; Zhang *et al.*, 2015). However, these electrodes required complicated fabrication procedure, high cost, less sensitivity and selectivity and tedious synthetic procedures.

Therefore, the designing of novel MOFs with more active site and development of selective and sensitive modified electrode sensors for the determination of NB is very important. MOFs containing of two mixed linkers with electron donor group such as oxygen and nitrogen are believed to enhance the sensing properties. Thus, the present work aims to fabricate novel mixed linkers MOFs

on GC electrodes by a simple method for the selective and sensitive determination of NB.

### 1.3 Research objectives

The general objectives of this study are to synthesise and structurally characterise new Metal-organic frameworks (MOFs) derived from triazole and dicarboxylate linkers. The specific objectives of this research include:

1. To synthesise and characterise new MOFs derived from triazole and dicarboxylate linkers via physicochemical and spectroscopic techniques including Powder X-ray Diffraction (PXRD) analysis, Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectroscopies, thermogravimetric analysis (TGA), Scanning Emission Microscopy (SEM) and N<sub>2</sub> physisorption analysis.
2. To elucidate the structure of the novel synthesised MOFs by Single Crystal X-ray diffraction (SXRD) analysis.
3. To investigate the electrocatalytic properties of the novel MOFs in nitrobenzene reduction

### 1.4 Scope of research

The scope of this study can be divided into three parts. The first part is synthesising new MOFs by using dicarboxylate and azolate derivatives. Different parameters were investigated in order to determine optimum synthesis condition and to grow high quality crystal. These parameters included the molar ratio of metal and ligand, temperature, time, type of solvents, volume of solvents and the use of modulator (acid or base). The compounds were then characterised with Powder X-ray Diffraction (PXRD) to determine crystal lattice of the MOFs. Fourier Transform Infrared Spectroscopy was used to determine presence of functional groups of the linkers. In order to determine the thermal stability and element composition of the MOFs, Thermogravimetric (TGA) and Elemental analysis (EA) were conducted. Nuclear Magnetic Resonance (NMR) spectroscopy analysis was used to determine the presence of both ligands in the frameworks. Scanning Emission Microscopy was done to observe the morphology of the crystals. Lastly, Nitrogen physisorption analysis was carried to determine the surface area and pore volume of the MOFs.

The second part is the elucidation and structural study of the new MOFs. Single crystal X-ray Diffraction analysis was performed as to determine the crystal structures of the new MOFs with two ligands bonded to the metal ions. The crystal data collected were then solved using OLEX2 software. The solvent disorder in voids was subtracted from the reflection data by the SQUEEZE procedure as implemented in the PLATON software package. The topological study was performed using *TOPOS 4.0* Professional software. This study was conducted to determine the bridging nodes between ligands and metals.

Lastly, the potential sensing applications of the novel synthesised MOFs in the detection of nitrobenzene were investigated. Electrochemical studies were conducted using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques on the modified MOFs with glassy carbon (GC) electrodes.



## REFERENCES

- Abrahams, B. F., Hoskins, B. F., Michail, D. M., & Robson, R. (1994). Assembly of porphyrin building blocks into network structures with large channels. *Nature*, 369(6483), 727-729.
- Al Haydar, M., Abid, H. R., Sunderland, B., & Wang, S. (2017). Metal organic frameworks as a drug delivery system for flurbiprofen. *Drug design, development and therapy*, 11, 2685-2695.
- Ameloot, R., Stappers, L., Franssaer, J., Alaerts, L., Sels, B. F., & De Vos, D. E. (2009). Patterned Growth of Metal-Organic Framework Coatings by Electrochemical Synthesis. *Chemistry of Materials*, 21(13), 2580-2582.
- An, J., Farha, O. K., Hupp, J. T., Pohl, E., Yeh, J. I., & Rosi, N. L. (2012). Metal-adeninate vertices for the construction of an exceptionally porous metal-organic framework. *Nature Communications*, 3, 604.
- Arul, P., & John, S. A. (2018). Size controlled synthesis of Ni-MOF using polyvinylpyrrolidone: New electrode material for the trace level determination of nitrobenzene. *Journal of Electroanalytical Chemistry*, 829, 168-176.
- Ayoub, G., Islamoglu, T., Goswami, S., Friscic, T., & Farha, O. K. (2019). Torsion Angle Effect on the Activation of UiO Metal-Organic Frameworks. *ACS Applied Materials & Interfaces*, 11(17), 15788-15794.
- Azhar, M. R., Periasamy, V., O. Tadé, M., Sun, H., & Wang, S. (2017). Submicron sized water-stable metal organic framework (bio-MOF-11) for catalytic degradation of pharmaceuticals and personal care products. *Chemosphere*, 196, 105-114.
- Batten, S. R., Hoskins, B. F., Moubaraki, B., Murray, K. S., & Robson, R. (1999). Crystal structures and magnetic properties of the interpenetrating rutile-related compounds  $M(\text{tcm})_2$  [ $M$  = octahedral, divalent metal;  $\text{tcm}^-$  = tricyanomethanide,  $\text{C}(\text{CN})_3^-$ ] and the sheet structures of  $[\text{M}(\text{tcm})_2(\text{EtOH})_2]$  ( $M$  = Co or Ni). *Journal of the Chemical Society, Dalton Transactions*(17), 2977-2986.
- Bauer, C. A., Timofeeva, T. V., Settersten, T. B., Patterson, B. D., Liu, V. H., Simmons, B. A., *et al.* (2007). Influence of connectivity and porosity on ligand-based luminescence in zinc metal-organic frameworks. *Journal of the American Chemical Society*, 129(22), 7136-7144.

- Bennett, T. D., Goodwin, A. L., Dove, M. T., Keen, D. A., Tucker, M. G., Barney, E. R., *et al.* (2010). Structure and Properties of an Amorphous Metal-Organic Framework. *Physical Review Letters*, *104*(11), 115503.
- Benzigar, M. R., Talapaneni, S. N., Joseph, S., Ramadass, K., Singh, G., Scaranto, J., *et al.* (2018). Recent advances in functionalized micro and mesoporous carbon materials: synthesis and applications. *Chemical Society Reviews*, *47*(8), 2680-2721.
- Bhattacharya, S., Goswami, A., Gole, B., Ganguly, S., Bala, S., Sengupta, S., *et al.* (2014). Construction of Bis-pyrazole Based Co(II) Metal-Organic Frameworks and Exploration of Their Chirality and Magnetic Properties. *Crystal Growth & Design*, *14*(6), 2853-2865.
- Biemmi, E., Christian, S., Stock, N., & Bein, T. (2009). High-throughput screening of synthesis parameters in the formation of the metal-organic frameworks MOF-5 and HKUST-1. *Microporous and Mesoporous Materials*, *117*(1), 111-117.
- Brunauer, S., & Emmett, P. H. (1937). The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Areas of Various Adsorbents. *Journal of the American Chemical Society*, *59*(12), 2682-2689.
- Bunck, D. N., & Dichtel, W. R. (2013). Mixed Linker Strategies for Organic Framework Functionalization. *Chemistry – A European Journal*, *19*(3), 818-827.
- Bureekaew, S., Shimomura, S., & Kitagawa, S. (2008). Chemistry and application of flexible porous coordination polymers. *Science and Technology of Advanced Materials*, *9*(1), 014108.
- Butova, V. V., Soldatov, M. A., Guda, A. A., Lomachenko, K. A., & Lamberti, C. (2016). Metal-organic frameworks: structure, properties, methods of synthesis and characterization. *Russian Chemical Reviews*, *85*(3), 280-307.
- Cavka, J. H., Jakobsen, S., Olsbye, U., Guillou, N., Lamberti, C., Bordiga, S., *et al.* (2008). A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *Journal of the American Chemical Society*, *130*(42), 13850-13851.
- Chae, H. K., Siberio-Pérez, D. Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A. J., *et al.* (2004). A route to high surface area, porosity and inclusion of large molecules in crystals. *Nature*, *427*(6974), 523-527.

- Chalati, T., Horcajada, P., Gref, R., Couvreur, P., & Serre, C. (2011). Optimisation of the synthesis of MOF nanoparticles made of flexible porous iron fumarate MIL-88A. *Journal of Materials Chemistry*, 21(7), 2220-2227.
- Chang, S.-S., Clair, B., Ruelle, J., Beauchêne, J., Di Renzo, F., Quignard, F., *et al.* (2009). Mesoporosity as a new parameter for understanding tension stress generation in trees. *Journal of Experimental Botany*, 60(11), 3023-3030.
- Chen, B., Yang, Y., Zapata, F., Lin, G., Qian, G., & Lobkovsky, E. B. (2007). Luminescent Open Metal Sites within a Metal–Organic Framework for Sensing Small Molecules. *Advanced Materials*, 19(13), 1693-1696.
- Chen, Y., Li, P., Modica, J. A., Drout, R. J., & Farha, O. K. (2018). Acid-Resistant Mesoporous Metal–Organic Framework toward Oral Insulin Delivery: Protein Encapsulation, Protection, and Release. *Journal of the American Chemical Society*, 140(17), 5678-5681.
- Chui, S. S. Y., Lo, S. M. F., Charmant, J. P. H., Orpen, A. G., & Williams, I. D. (1999). A Chemically Functionalizable Nanoporous Material. *Science*, 283(5405), 1148-1150.
- Chun, H., Dybtsev, D. N., Kim, H., & Kim, K. (2005). Synthesis, X-ray Crystal Structures, and Gas Sorption Properties of Pillared Square Grid Nets Based on Paddle-Wheel Motifs: Implications for Hydrogen Storage in Porous Materials. *Chemistry – A European Journal*, 11(12), 3521-3529.
- Cui, P., Ma, Y.-G., Li, H.-H., Zhao, B., Li, J.-R., Cheng, P., *et al.* (2012). Multipoint Interactions Enhanced CO<sub>2</sub> Uptake: A Zeolite-like Zinc–Tetrazole Framework with 24-Nuclear Zinc Cages. *Journal of the American Chemical Society*, 134(46), 18892-18895.
- Cui, S., Liu, X., Liu, Y., Shen, X., Lin, B., Han, G., *et al.* (2010). Adsorption properties of nitrobenzene in wastewater with silica aerogels. *Science China Technological Sciences*, 53(9), 2367-2371.
- Cui, Y., Chen, B., & Qian, G. (2014). Lanthanide metal-organic frameworks for luminescent sensing and light-emitting applications. *Coordination Chemistry Reviews*, 273-274, 76-86.
- Cui, Y., Li, B., He, H., Zhou, W., Chen, B., & Qian, G. (2016). Metal–Organic Frameworks as Platforms for Functional Materials. *Accounts of Chemical Research*, 49(3), 483-493.
- Deng, H., Grunder, S., Cordova, K. E., Valente, C., Furukawa, H., Hmadeh, M., *et al.* (2012). Large-Pore Apertures in a Series of Metal–Organic Frameworks. *Science*, 336(6084), 1018-1023.

- Díaz-García, M., & Sánchez-Sánchez, M. (2014). Synthesis and characterization of a new Cd-based metal-organic framework isostructural with MOF-74/CPO-27 materials. *Microporous and Mesoporous Materials*, *190*, 248-254.
- Dong, Y., Peng, P., Hu, B., Su, H., Li, S., & Pang, S. (2017). High-Density Energetic Metal-Organic Frameworks Based on the 5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole. *Molecules*, *22*(7), 1068.
- Du, M., Li, C. P., Liu, C. S., & Fang, S. M. (2013). Design and construction of coordination polymers with mixed-ligand synthetic strategy. *Coordination Chemistry Reviews*, *257*(7), 1282-1305.
- Ebrahimzadeh, H., Yamini, Y., & Kamarei, F. (2009). Optimization of dispersive liquid-liquid microextraction combined with gas chromatography for the analysis of nitroaromatic compounds in water. *Talanta*, *79*(5), 1472-1477.
- Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M., *et al.* (2001). Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Accounts of Chemical Research*, *34*(4), 319-330.
- Emmanuel, R., Karuppiyah, C., Chen, S.-M., Palanisamy, S., Padmavathy, S., & Prakash, P. (2014). Green synthesis of gold nanoparticles for trace level detection of a hazardous pollutant (nitrobenzene) causing Methemoglobinaemia. *Journal of Hazardous Materials*, *279*, 117-124.
- Farha, O. K., Eryazici, I., Jeong, N. C., Hauser, B. G., Wilmer, C. E., Sarjeant, A. A., *et al.* (2012). Metal-Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? *Journal of the American Chemical Society*, *134*(36), 15016-15021.
- Feng, Y., Liu, X., Duan, L., Yang, Q., Wei, Q., Xie, G., *et al.* (2015). In situ synthesized 3D heterometallic metal-organic framework (MOF) as a high-energy-density material shows high heat of detonation, good thermostability and insensitivity. *Dalton Transactions*, *44*(5), 2333-2339.
- Férey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surblé, S., *et al.* (2005). A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. *Science*, *309*(5743), 2040-2042.
- Forster, P. M., Stock, N., & Cheetham, A. K. (2005). A High-Throughput Investigation of the Role of pH, Temperature, Concentration, and Time on the Synthesis of Hybrid Inorganic-Organic Materials. *Angewandte Chemie International Edition*, *44*(46), 7608-7611.



- Fujiwara, Y.-i., Horike, S., Kongpatpanich, K., Sugiyama, T., Tabori, N., Nishihara, H., *et al.* (2015). Control of pore distribution of porous carbons derived from Mg<sup>2+</sup> porous coordination polymers. *Inorganic Chemistry Frontiers*, 2(5), 473-476.
- Furukawa, H., Cordova, K. E., O'Keeffe, M., & Yaghi, O. M. (2013). The chemistry and applications of metal-organic frameworks. *Science*, 341(6149), 1230444.
- Furukawa, H., Ko, N., Go, Y. B., Aratani, N., Choi, S. B., Choi, E., *et al.* (2010). Ultrahigh Porosity in Metal-Organic Frameworks. *Science*, 329(5990), 424-428.
- Gandara, F., & Bennett, T. D. (2014). Crystallography of metal-organic frameworks. *IUCrJ*, 1(6), 563-570.
- Gonzalez-Nelson, A., Coudert, F.-X., & van der Veen, A. M. (2019). Rotational Dynamics of Linkers in Metal–Organic Frameworks. *Nanomaterials*, 9(3), 330.
- Gowthaman, N. S. K., Sinduja, B., & John, S. A. (2016). Tuning the composition of gold–silver bimetallic nanoparticles for the electrochemical reduction of hydrogen peroxide and nitrobenzene. *RSC Advances*, 6(68), 63433-63444.
- Grünker, R., Senkovska, I., Biedermann, R., Klein, N., Lohe, M. R., Müller, P., *et al.* (2011). A highly porous flexible Metal–Organic Framework with corundum topology. *Chemical Communications*, 47(1), 490-492.
- Gu, X., Lu, Z.-H., & Xu, Q. (2010). High-connected mesoporous metal–organic framework. *Chemical Communications*, 46(39), 7400-7402.
- Guillou, N., Livage, C., Drillon, M., & Férey, G. (2003). The Chirality, Porosity, and Ferromagnetism of a 3D Nickel Glutarate with Intersecting 20-Membered Ring Channels. *Angewandte Chemie International Edition*, 42(43), 5314-5317.
- Han, D., Jiang, F.-L., Wu, M.-Y., Chen, L., Chen, Q.-H., & Hong, M.-C. (2011). A non-interpenetrated porous metal–organic framework with high gas-uptake capacity. *Chemical Communications*, 47(35), 9861-9863.
- Hao, J. M., Li, H. H., Li, G. Y., & Cui, G. H. (2013). Two dimensional cadmium (II) coordination polymer constructed from flexible bis(triazole) ligand: Synthesis, structure and fluorescence property. *Chinese Journal of Inorganic Chemistry*, 29(11), 2450-2454.

- Harbuzaru, B. V., Corma, A., Rey, F., Atienzar, P., Jordá, J. L., García, H., *et al.* (2008). Metal–Organic Nanoporous Structures with Anisotropic Photoluminescence and Magnetic Properties and Their Use as Sensors. *Angewandte Chemie International Edition*, 47(6), 1080-1083.
- He, Y.-P., Tan, Y.-X., & Zhang, J. (2012). Comparative Study of Activation Methods on Tuning Gas Sorption Properties of a Metal–Organic Framework with Nanosized Ligands. *Inorganic Chemistry*, 51(21), 11232-11234.
- Hoffmann, C. H., Debowski, M., Müller, P., Paasch, S., Senkovska, I., Kaskel, S., *et al.* (2012). Solid-State NMR Spectroscopy of Metal–Organic Framework Compounds (MOFs). *Materials*, 5(12), 2537-2572.
- Horike, S., Shimomura, S., & Kitagawa, S. (2009). Soft porous crystals. *Nature Chemistry*, 1, 695-704.
- Hoskins, B. F., & Robson, R. (1990). Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks  $[N(CH_3)_4][CuI ZnII(CN)_4]$  and  $CuI[4,4',4'',4''']$ -tetracyanotetraphenylmethane]BF<sub>4</sub>.x C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. *Journal of the American Chemical Society*, 112(4), 1546-1554.
- Hosseini, H., Ahmar, H., Dehghani, A., Bagheri, A., Tadjarodi, A., & Fakhari, A. R. (2013). A novel electrochemical sensor based on metal-organic framework for electro-catalytic oxidation of L-cysteine. *Biosensors and Bioelectronics*, 42, 426-429.
- Howarth, A. J., Peters, A. W., Vermeulen, N. A., Wang, T. C., Hupp, J. T., & Farha, O. K. (2017). Best Practices for the Synthesis, Activation, and Characterization of Metal–Organic Frameworks. *Chemistry of Materials*, 29(1), 26-39.
- Hu, Q., Yu, J., Liu, M., Liu, A., Dou, Z., & Yang, Y. (2014). A Low Cytotoxic Cationic Metal–Organic Framework Carrier for Controllable Drug Release. *Journal of Medicinal Chemistry*, 57(13), 5679-5685.
- Jamali, A., Tehrani, A. A., Shemirani, F., & Morsali, A. (2016). Lanthanide metal–organic frameworks as selective microporous materials for adsorption of heavy metal ions. *Dalton Transactions*, 45(22), 9193-9200.
- James, S. L. (2003). Metal-organic frameworks. *Chemical Society Reviews*, 32(5), 276-288.

- Janiak, C., & Vieth, J. K. (2010). MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs). *New Journal of Chemistry*, 34(11), 2366-2388.
- Jhung, S. H., Lee, J. H., Yoon, J. W., Serre, C., Férey, G., & Chang, J. S. (2007). Microwave Synthesis of Chromium Terephthalate MIL-101 and Its Benzene Sorption Ability. *Advanced Materials*, 19(1), 121-124.
- Jia, H.-P., Li, W., Ju, Z.-F., & Zhang, J. (2006). Synthesis, Structure and Magnetism of Metal-Organic Framework Materials with Doubly Pillared Layers. *European Journal of Inorganic Chemistry*, 2006(21), 4264-4270.
- Jung, K. T., & Bell, A. T. (2001). An in Situ Infrared Study of Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over Zirconia. *Journal of Catalysis*, 204(2), 339-347.
- Kalmutzki, M. J., Hanikel, N., & Yaghi, O. M. (2018). Secondary building units as the turning point in the development of the reticular chemistry of MOFs. *Science Advances*, 4(10), eaat9180.
- Karozis, S., Charalambopoulou, G., Steriotis, T., Stubos, A., & Kainourgiakis, M. (2017). Determining the specific surface area of Metal Organic Frameworks based on a computational approach. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 526, 14-19.
- Kepert, J. C., & Rosseinsky, J. M. (1999). Zeolite-like crystal structure of an empty microporous molecular framework. *Chemical Communications*(4), 375-376.
- Khan, N. A., Kang, I. J., Seok, H. Y., & Jhung, S. H. (2011). Facile synthesis of nano-sized metal-organic frameworks, chromium-benzenedicarboxylate, MIL-101. *Chemical Engineering Journal*, 166(3), 1152-1157.
- Kim, D., Liu, X., & Lah, M. S. (2015). Topology analysis of metal-organic frameworks based on metal-organic polyhedra as secondary or tertiary building units. *Inorganic Chemistry Frontiers*, 2(4), 336-360.
- Kim, J., Yang, S.-T., Choi, S. B., Sim, J., Kim, J., & Ahn, W.-S. (2011). Control of catenation in CuTATB-n metal-organic frameworks by sonochemical synthesis and its effect on CO<sub>2</sub> adsorption. *Journal of Materials Chemistry*, 21(9), 3070-3076.
- Kitagawa, S., Kitaura, R., & Noro, S.-i. (2004). Functional Porous Coordination Polymers. *Angewandte Chemie International Edition*, 43(18), 2334-2375.

- Kleist, W., Jutz, F., Maciejewski, M., & Baiker, A. (2009). Mixed-Linker Metal-Organic Frameworks as Catalysts for the Synthesis of Propylene Carbonate from Propylene Oxide and CO<sub>2</sub>. *European Journal of Inorganic Chemistry*, 2009(24), 3552-3561.
- Kleist, W., Maciejewski, M., & Baiker, A. (2010). MOF-5 based mixed-linker metal-organic frameworks: Synthesis, thermal stability and catalytic application. *Thermochimica Acta*, 499(1), 71-78.
- Koh, K., Van Oosterhout, J. D., Roy, S., Wong-Foy, A. G., & Matzger, A. J. (2012). Exceptional surface area from coordination copolymers derived from two linear linkers of differing lengths. *Chemical Science*, 3(8), 2429-2432.
- Koo, J., Hwang, I.-C., Yu, X., Saha, S., Kim, Y., & Kim, K. (2017). Hollowing out MOFs: hierarchical micro- and mesoporous MOFs with tailorable porosity via selective acid etching. *Chemical Science*, 8(10), 6799-6803.
- Kubendhiran, S., Sakthinathan, S., Chen, S.-M., Tamizhdurai, P., Shanthi, K., & Karuppiyah, C. (2017). Green reduction of reduced graphene oxide with nickel tetraphenyl porphyrin nanocomposite modified electrode for enhanced electrochemical determination of environmentally pollutant nitrobenzene. *Journal of Colloid and Interface Science*, 497, 207-216.
- Kumar, P., Deep, A., & Kim, K.-H. (2015). Metal organic frameworks for sensing applications. *TrAC Trends in Analytical Chemistry*, 73, 39-53.
- Kuppler, R. J., Timmons, D. J., Fang, Q.-R., Li, J.-R., Makal, T. A., Young, M. D., *et al.* (2009). Potential applications of metal-organic frameworks. *Coordination Chemistry Reviews*, 253(23), 3042-3066.
- Kurmoo, M. (2009). Magnetic metal-organic frameworks. *Chemical Society Reviews*, 38(5), 1353-1379.
- Lee, Y.-R., Kim, J., & Ahn, W.-S. (2013). Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical Engineering*, 30(9), 1667-1680.
- Lei, J., Qian, R., Ling, P., Cui, L., & Ju, H. (2014). Design and sensing applications of metal-organic framework composites. *TrAC Trends in Analytical Chemistry*, 58, 71-78.
- Li, H., Eddaoudi, M., O'Keeffe, M., & Yaghi, O. M. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, 402, 276.

- Li, J.-R., Kuppler, R. J., & Zhou, H.-C. (2009). Selective gas adsorption and separation in metal–organic frameworks. *Chemical Society Reviews*, 38(5), 1477-1504.
- Li, M., Li, D., O’Keeffe, M., & Yaghi, O. M. (2014). Topological Analysis of Metal–Organic Frameworks with Polytopic Linkers and/or Multiple Building Units and the Minimal Transitivity Principle. *Chemical Reviews*, 114(2), 1343-1370.
- Li, W.-J., Lü, J., Gao, S.-Y., Li, Q.-H., & Cao, R. (2014). Electrochemical preparation of metal–organic framework films for fast detection of nitro explosives. *Journal of Materials Chemistry A*, 2(45), 19473-19478.
- Lin, J.-D., Cheng, J.-W., & Du, S.-W. (2008). Five d10 3D Metal–Organic Frameworks Constructed From Aromatic Polycarboxylate Acids and Flexible Imidazole-Based Ligands. *Crystal Growth & Design*, 8(9), 3345-3353.
- Liu, L., Zhou, Y., Liu, S., & Xu, M. (2018). The Applications of Metal–Organic Frameworks in Electrochemical Sensors. *ChemElectroChem*, 5(1), 6-19.
- Liu, M., Zhang, T., Ren, H., Wang, L., Meng, T., Zhao, J., *et al.* (2018). Nitrogen-doped hollow carbon nanospheres for highly sensitive electrochemical sensing of nitrobenzene. *Materials Research Bulletin*, 104, 15-19.
- Liu, W., & Yin, X.-B. (2016). Metal–organic frameworks for electrochemical applications. *TrAC Trends in Analytical Chemistry*, 75, 86-96.
- Liu, Y., Xuan, W., & Cui, Y. (2010). Engineering Homochiral Metal–Organic Frameworks for Heterogeneous Asymmetric Catalysis and Enantioselective Separation. *Advanced Materials*, 22(37), 4112-4135.
- Lohe, M. R., Rose, M., & Kaskel, S. (2009). Metal–organic framework (MOF) aerogels with high micro- and macroporosity. *Chemical Communications*(40), 6056-6058.
- Lü, C.-N., Chen, M.-M., Zhang, W.-H., Li, D.-X., Dai, M., & Lang, J.-P. (2015). Construction of Zn(II) and Cd(II) metal–organic frameworks of diimidazole and dicarboxylate mixed ligands for the catalytic photodegradation of rhodamine B in water. *CrystEngComm*, 17(9), 1935-1943.
- Lu, C., Ben, T., Xu, S., & Qiu, S. (2014). Electrochemical Synthesis of a Microporous Conductive Polymer Based on a Metal–Organic Framework Thin Film. *Angewandte Chemie International Edition*, 53(25), 6454-6458.

- Lu, W., Wei, Z., Gu, Z.-Y., Liu, T.-F., Park, J., Park, J., *et al.* (2014). Tuning the structure and function of metal–organic frameworks via linker design. *Chemical Society Reviews*, 43(16), 5561-5593.
- Mallick, A., Saha, S., Pachfule, P., Roy, S., & Banerjee, R. (2010). Selective CO<sub>2</sub> and H<sub>2</sub> adsorption in a chiral magnesium-based metal organic framework (Mg-MOF) with open metal sites. *Journal of Materials Chemistry*, 20(41), 9073-9080.
- Marx, S., Kleist, W., Huang, J., Maciejewski, M., & Baiker, A. (2010). Tuning functional sites and thermal stability of mixed-linker MOFs based on MIL-53(Al). *Dalton Transactions*, 39(16), 3795-3798.
- Mondloch, J. E., Karagiari, O., Farha, O. K., & Hupp, J. T. (2013). Activation of metal–organic framework materials. *CrystEngComm*, 15, 9258-9264.
- Moroza, A., & Jaouen, F. (2012). Metal organic frameworks for electrochemical applications. *Energy & Environmental Science*, 5(11), 9269-9290.
- Morris, W., Taylor, R. E., Dybowski, C., Yaghi, O. M., & Garcia-Garibay, M. A. (2011). Framework mobility in the metal–organic framework crystal IRMOF-3: Evidence for aromatic ring and amine rotation. *Journal of Molecular Structure*, 1004(1), 94-101.
- Muhammad, H., Tahiri, I. A., Muhammad, M., Masood, Z., Versiani, M. A., Khaliq, O., *et al.* (2016). A comprehensive heterogeneous electron transfer rate constant evaluation of dissolved oxygen in DMSO at glassy carbon electrode measured by different electrochemical methods. *Journal of Electroanalytical Chemistry*, 775, 157-162.
- Nelson, A. P., Farha, O. K., Mulfort, K. L., & Hupp, J. T. (2009). Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal–Organic Framework Materials. *Journal of the American Chemical Society*, 131(2), 458-460.
- Nishiyabu, K. (2012). 15 - Powder space holder metal injection molding (PSH-MIM) of micro-porous metals. In D. F. Heaney (Ed.), *Handbook of Metal Injection Molding* (pp. 349-390): Woodhead Publishing.
- OPPT. (1995). *OPPT Chemical Fact Sheets-Nitrobenzene Fact Sheet: Support Document (CAS No. 98-95-3)*. EPA 749-F-95-015a.
- Perkins, W. D. (1986). Fourier transform-infrared spectroscopy: Part I. Instrumentation. *Journal of Chemical Education*, 63(1), A5.

- Perry, J. J. I., Perman, J. A., & Zaworotko, M. J. (2009). Design and synthesis of metal–organic frameworks using metal–organic polyhedra as supermolecular building blocks. *Chemical Society Reviews*, 38(5), 1400-1417.
- Pichon, A., & James, S. L. (2008). An array-based study of reactivity under solvent-free mechanochemical conditions—insights and trends. *CrystEngComm*, 10(12), 1839-1847.
- Pichon, A., Lazuen-Garay, A., & James, S. L. (2006). Solvent-free synthesis of a microporous metal–organic framework. *CrystEngComm*, 8(3), 211-214.
- Platero-Prats, A. E., de la Peña-O’Shea, V. A., Proserpio, D. M., Snejko, N., Gutiérrez-Puebla, E., & Monge, Á. (2012). Insight into the SBU Condensation in Mg Coordination and Supramolecular Frameworks: A Combined Experimental and Theoretical Study. *Journal of the American Chemical Society*, 134(10), 4762-4771.
- Prajapati, R., Mishra, L., Kimura, K., & Raghavaiah, P. (2009). Metal–organic frameworks (MOFs) constructed from ZnII/CdII-2,2'-bipyridines and polycarboxylic acids: Synthesis, characterization and microstructural studies. *Polyhedron*, 28(3), 600-608.
- Prasad, T. K., & Suh, M. P. (2012). Control of Interpenetration and Gas-Sorption Properties of Metal–Organic Frameworks by a Simple Change in Ligand Design. *Chemistry – A European Journal*, 18(28), 8673-8680.
- Qiu, L.-G., Li, Z.-Q., Wu, Y., Wang, W., Xu, T., & Jiang, X. (2008). Facile synthesis of nanocrystals of a microporous metal–organic framework by an ultrasonic method and selective sensing of organoamines. *Chemical Communications*(31), 3642-3644.
- Quinn, E. L. (1927). The Surface Tension of Liquid Carbon Dioxide. *Journal of the American Chemical Society*, 49(11), 2704-2711.
- Rigaku, O. D. (2017). A Rigaku Oxford Diffraction program for Absorption Corrections. ABSPACK SCALE
- Roales, J., Moscoso, G. F., Gámez, F., Lopes-Costa, T., Sousaraei, A., Casado, S., *et al.* (2017). Preparation of Luminescent Metal-Organic Framework Films by Soft-Imprinting for 2,4-Dinitrotoluene Sensing. *Materials*, 10(9), 992.
- Robson, R. (2008). Design and its limitations in the construction of bi- and poly-nuclear coordination complexes and coordination polymers (aka MOFs): a personal view. *Dalton Transactions*(38), 5113-5131.

- Serre, C., Millange, F., Thouvenot, C., Noguès, M., Marsolier, G., Louër, D., *et al.* (2002). Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or CrIII(OH)·{O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>}·{HO<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H}x·H<sub>2</sub>Oy. *Journal of the American Chemical Society*, 124(45), 13519-13526.
- Sheldrick, G. (2018). SHELXL2013, University of Göttingen, Germany, 2013.
- Sheng, T., Qi, Y.-J., Lin, X., Hu, P., Sun, S.-G., & Lin, W.-F. (2016). Insights into the mechanism of nitrobenzene reduction to aniline over Pt catalyst and the significance of the adsorption of phenyl group on kinetics. *Chemical Engineering Journal*, 293, 337-344.
- Shono, T., Mingos, D. M. P., Baghurst, D. R., & Lickiss, P. D. (2000). *Novel Energy Sources for Reactions*. (Vol. Chapter 4). The Press Syndicate of the University of Cambridge: Cambridge.
- Song, X., Kim, T. K., Kim, H., Kim, D., Jeong, S., Moon, H. R., *et al.* (2012). Post-Synthetic Modifications of Framework Metal Ions in Isostructural Metal–Organic Frameworks: Core–Shell Heterostructures via Selective Transmetalations. *Chemistry of Materials*, 24(15), 3065-3073.
- Spek, A. (2015). PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallographica Section C*, 71(1), 9-18.
- Stock, N., & Biswas, S. (2012). Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chemical Reviews*, 112(2), 933-969.
- Tan, Y.-X., Yang, X., Li, B.-B., & Yuan, D. (2016). Rational design of a flu-type heterometallic cluster-based Zr-MOF. *Chemical Communications*, 52(94), 13671-13674.
- Taylor-Pashow, K. M. L., Della Rocca, J., Xie, Z., Tran, S., & Lin, W. (2009). Postsynthetic Modifications of Iron-Carboxylate Nanoscale Metal–Organic Frameworks for Imaging and Drug Delivery. *Journal of the American Chemical Society*, 131(40), 14261-14263.
- Thommes, M., & Cychosz, K. A. (2014). Physical adsorption characterization of nanoporous materials: progress and challenges. *Adsorption*, 20(2), 233-250.
- Tsao, C.-S., Chen, C.-Y., Chung, T.-Y., Su, C.-J., Su, C.-H., Chen, H.-L., *et al.* (2010). Structural Analysis and Thermal Behavior of Pore Networks in High-Surface-Area Metal–Organic Framework. *The Journal of Physical Chemistry C*, 114(15), 7014-7020.



- Uma, K., Pan, G.-T., & Yang, T. C. K. (2017). The Preparation of Porous Sol-Gel Silica with Metal Organic Framework MIL-101(Cr) by Microwave-Assisted Hydrothermal Method for Adsorption Chillers. *Materials*, 10(6), 610.
- Umeyama, D., Horike, S., Inukai, M., Itakura, T., & Kitagawa, S. (2015). Reversible Solid-to-Liquid Phase Transition of Coordination Polymer Crystals. *Journal of the American Chemical Society*, 137(2), 864-870.
- Vasdev, A. S. R., Preston, D., Scottwell, Ø. S., Brooks, J. L. H., Crowley, D. J., & Schramm, P. M. (2016). Oxidatively Locked [Co<sub>2</sub>L<sub>3</sub>]<sup>6+</sup> Cylinders Derived from Bis(bidentate) 2-Pyridyl-1,2,3-triazole “Click” Ligands: Synthesis, Stability, and Antimicrobial Studies. *Molecules*, 21(11), 1548.
- Velmurugan, M., Karikalan, N., Chen, S.-M., & Dai, Z.-C. (2017). Studies on the influence of β-cyclodextrin on graphene oxide and its synergistic activity to the electrochemical detection of nitrobenzene. *Journal of Colloid and Interface Science*, 490, 365-371.
- Volkringer, C., Popov, D., Loiseau, T., Férey, G., Burghammer, M., Riekel, C., *et al.* (2009). Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100. *Chemistry of Materials*, 21(24), 5695-5697.
- Wang, H.-L., Yeh, H., Chen, Y.-C., Lai, Y.-C., Lin, C.-Y., Lu, K.-Y., *et al.* (2018). Thermal Stability of Metal–Organic Frameworks and Encapsulation of CuO Nanocrystals for Highly Active Catalysis. *ACS Applied Materials & Interfaces*, 10(11), 9332-9341.
- Wang, S.-P., & Chen, H.-J. (2002). Separation and determination of nitrobenzenes by micellar electrokinetic chromatography and high-performance liquid chromatography. *Journal of Chromatography A*, 979(1), 439-446.
- Wang, T. C., Vermeulen, N. A., Kim, I. S., Martinson, A. B. F., Stoddart, J. F., Hupp, J. T., *et al.* (2015). Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000. *Nature Protocols*, 11, 149-162.
- Wang, X.-L., Liu, D.-N., Luan, J., Lin, H.-Y., Le, M., & Liu, G.-C. (2015). Controllable assembly of three copper(II/I) metal–organic frameworks based on N,N'-bis(4-pyridinecarboxamide)-1,2-cyclohexane and 4,4'-oxydibenzoic acid: From three-dimensional interpenetrating framework to one-dimensional infinite chain. *Inorganica Chimica Acta*, 426, 39-44.

- Wang, Y., Wu, Y., Xie, J., Ge, H., & Hu, X. (2013). Multi-walled carbon nanotubes and metal–organic framework nanocomposites as novel hybrid electrode materials for the determination of nanomolar levels of lead in a lab-on-valve format. *Analyst*, 138(17), 5113-5120.
- Wang, Y. B., Liu, D. S., Pan, T. H., Liang, Q., Huang, X. H., Wu, S. T., et al. (2010). Structural variation from 1D to 3D: effect of metal centers on the construction of metal–organic coordination polymers with N-(1H-tetrazol-5-yl)benzamide ligand. *CrystEngComm*, 12(11), 3886-3893.
- Wu, H.-P., Janiak, C., Uehlin, L., Klüfers, P., & Mayer, P. (1998). 2,2'-Bi-1,6-naphthyridine metal complexes: a new ligand and a novel 2 × 2 inclined interpenetration of (4,4) nets or formation of helicoidal chains†. *Chemical Communications*(23), 2637-2638.
- Wu, H., Chua, Y. S., Krungleviciute, V., Tyagi, M., Chen, P., Yildirim, T., et al. (2013). Unusual and Highly Tunable Missing-Linker Defects in Zirconium Metal–Organic Framework UiO-66 and Their Important Effects on Gas Adsorption. *Journal of the American Chemical Society*, 135(28), 10525-10532.
- Wu, T.-T., Hsu, W., Yang, X.-K., He, H.-Y., & Chen, J.-D. (2015). Entanglement in Co(ii) coordination networks: polycatenation from single net to 2-fold and 3-fold interpenetrated nets. *CrystEngComm*, 17(4), 916-924.
- Xie, H., Fang, W.-J., & Yao, X.-Q. (2017). A cadmium(II) coordination polymer with both polyrotaxane and polycatenane features constructed by a V-shaped semi-rigid ligand: synthesis and fluorescence properties. *Acta Crystallographica Section C*, 73(7), 541-545.
- Xu, W., Li, G., Li, W., & Zhang, H. (2016). Facile room temperature synthesis of metal–organic frameworks from newly synthesized copper/zinc hydroxide and their application in adsorptive desulfurization. *RSC Advances*, 6(44), 37530-37534.
- Xuan, W., Zhu, C., Liu, Y., & Cui, Y. (2012). Mesoporous metal–organic framework materials. *Chemical Society Reviews*, 41(5), 1677-1695.
- Yadav, D. K., Ganesan, V., Sonkar, P. K., Gupta, R., & Rastogi, P. K. (2016). Electrochemical investigation of gold nanoparticles incorporated zinc based metal-organic framework for selective recognition of nitrite and nitrobenzene. *Electrochimica Acta*, 200, 276-282.

- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M., & Kim, J. (2003). Reticular synthesis and the design of new materials. *Nature*, 423(6941), 705-714.
- Yakovenko, A. A., Reibenspies, J. H., Bhuvanesh, N., & Zhou, H.-C. (2013). Generation and applications of structure envelopes for porous metal-organic frameworks. *Journal of Applied Crystallography*, 46(2), 346-353.
- Yang, E.-C., Liu, Z.-Y., Liu, T.-Y., Li, L.-L., & Zhao, X.-J. (2011). Co-ligand-directed structural and magnetic diversities in an anisotropic Coll-triazolate system. *Dalton Transactions*, 40(32), 8132-8139.
- Yang, E.-C., Zhao, H.-K., Ding, B., Wang, X.-G., & Zhao, X.-J. (2007). Four Novel Three-Dimensional Triazole-Based Zinc(II) Metal-Organic Frameworks Controlled by the Spacers of Dicarboxylate Ligands: Hydrothermal Synthesis, Crystal Structure, and Luminescence Properties. *Crystal Growth & Design*, 7(10), 2009-2015.
- Yang, Y., Du, P., Liu, Y.-Y., & Ma, J.-F. (2013). A Series of Coordination Polymers Constructed by Flexible 4-Substituted Bis(1,2,4-triazole) Ligands and Polycarboxylate Anions: Syntheses, Structures, and Photoluminescent Properties. *Crystal Growth & Design*, 13(11), 4781-4795.
- Yaws, C. L., & Richmond, P. C. (2009). Chapter 21 - Surface tension—Organic compounds. In C. L. Yaws (Ed.), *Thermophysical Properties of Chemicals and Hydrocarbons* (pp. 686-781). Norwich, NY: William Andrew Publishing.
- Yu, C., Ma, S., Pechan, M. J., & Zhou, H.-c. (2007). Magnetic properties of a noninterpenetrating chiral porous cobalt metal-organic framework. *Journal of Applied Physics*, 101(9), 09E108.
- Zhang, J.-P., Zhu, A.-X., Lin, R.-B., Qi, X.-L., & Chen, X.-M. (2011). Pore Surface Tailored SOD-Type Metal-Organic Zeolites. *Advanced Materials*, 23(10), 1268-1271.
- Zhang, J., & Shreeve, J. n. M. (2016). 3D Nitrogen-rich metal-organic frameworks: opportunities for safer energetics. *Dalton Transactions*, 45(6), 2363-2368.
- Zhang, J. P., Zhang, Y. B., Lin, J. B., & Chen, X. M. (2012). Metal azolate frameworks: from crystal engineering to functional materials. *Chem Rev*, 112(2), 1001-1033.

- Zhang, X., Zhang, X., Johnson, J. A., Chen, Y.-S., & Zhang, J. (2016). Highly Porous Zirconium Metal–Organic Frameworks with  $\beta$ -UH3-like Topology Based on Elongated Tetrahedral Linkers. *Journal of the American Chemical Society*, 138(27), 8380-8383.
- Zhang, Y., Bo, X., Nsabimana, A., Han, C., Li, M., & Guo, L. (2015). Electrocatalytically active cobalt-based metal–organic framework with incorporated macroporous carbon composite for electrochemical applications. *Journal of Materials Chemistry A*, 3(2), 732-738.
- Zhang, Z., Wojtas, L., Eddaoudi, M., & Zaworotko, M. J. (2013). Stepwise Transformation of the Molecular Building Blocks in a Porphyrin-Encapsulating Metal–Organic Material. *Journal of the American Chemical Society*, 135(16), 5982-5985.

## BIODATA OF STUDENT

Nurul Nabihah binti Mohamad Ishak was born in 23<sup>rd</sup> of January 1994 in Jerteh, Terengganu. She started her primary school at Sekolah Rendah Kebangsaan Taman Damai Jaya, Johor Bahru and completed her secondary school at MARA Junior Science College Batu Pahat, Johor. Later, she continued her eight months foundation level at Universiti Teknologi Malaysia, Skudai, Johor. In 2012, she pursued her tertiary education at Universiti Teknologi Malaysia pursuing BSc of Science (Chemistry). In February 2017, she furthered her study in the field of Inorganic Chemistry at the Faculty of Science, Universiti Putra Malaysia to obtain a Master degree.



## LIST OF PUBLICATIONS

**Ishak, N. N. M.**, Jamsari, J., Ismail, A. Z., Tahir, M. I. M., Tiekink, E. R. T., Veerakumarasivam, A., *et al.* (2019). Synthesis, characterisation and biological studies of mixed-ligand nickel (II) complexes containing imidazole derivatives and thiosemicarbazide Schiff bases. *Journal of Molecular Structure*, 1198, 126888.

Yusof, E. N. M., **Ishak, N. N. M.**, Latif, M. A. M., Tahir, M. I. M., Sakoff, J. A., Page, A. J., *et al.* (2020). Selective cytotoxicity of organotin(IV) compounds with 2,3-dihydroxybenzylidithiocarbamate Schiff bases. *Research on Chemical Intermediates*.

**Ishak, N. N. M.**, Gowthaman, N. S. K., Lim, H. N. M., Tahir, M. I. M., Gandara, F, Ravoof, T. B. S. A. Azole containing Metal-organic Frameworks (MOFs) for efficient electrocatalytic nitrobenzene reduction. *Advanced Functional Materials*. (In preparation)

**N. N. M. Ishak**, N. N. M. Khiruddin, N. Nasri, T. B. S. A. Ravoof, (2019). Chapter 5: Metal-Organic Frameworks (MOFs). *Contemporary Nanomaterials in Material Engineering Applications*. Science and Technology, Springer. (Edited)



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