Synthesis of Nano MOFs and Their Characterization

M.Sc. Thesis

By

Aditya Kumar Bharti

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE 2017

Synthesis of Nano MOFs and Their Characterization

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree
of
Master of Science

by
Aditya Kumar Bharti

DISCIPLINE OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE
JUNE 2017

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis of Nano MOFs and Their Characterization** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2015 to June 2017 under the supervision of Dr. Anjan Chakraborty, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Aditya Kumar Bharti

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Dr. Anjan Chakraborty

Aditya Kumar Bharti has successfully given his M.Sc. Oral Examination held on **12 July 2017**.

Signature(s) of Supervisor(s) of MSc thesis
Date:

Convener, DPGC
Date:

Signature of PSPC Member#1
Date:

Signature of PSPC Member #2
Date:

ACKNOWLEDGEMENT

First I would like to thank my supervisor, Dr. Anjan Chakraborty for his guidance during this research work. I thank him not only for providing lab facility but also for emotional support and constructive criticism.

I will also like to thank PSPC members Dr. Satya S. Bulusu and Dr. Tridib K. Sarma for valuable suggestions and support in various aspects.

I am pleased to thank Mr. Soumya Kanti De and Ms. Nishu Kanwa, who helped me in MOF synthesis and characterization. I am also grateful to Mr. Mirajuddin Ahamed for help in drawing scheme and reading literature.

Further I extend my thanks to my classmates for their selfless co-operation.

Finally I would like to thank Sophisticated Instrumentation Center (SIC), IIT Indore and IIT Indore for providing infrastructure and all others who helped and supported me directly and indirectly.

Aditya Kumar Bharti

Abstract

Metal-organic frameworks (MOFs) are a unique class of hybrid porous solids based on metals and organic linkers. Compared to traditional porous materials, they possess predominance of large surface areas, tunable pore size and shape, adjustable composition and functionalized pore surface, which enable them unique advantages and promises for applications in adsorption and release of therapeutic agents.

In the domain of health, one important challenge is the efficient delivery of drugs in the body using non-toxic nanocarriers. The nanosize also allows for access into the cell and various cellular compartments including the nucleus. Most of the existing carrier materials (MOFs) were in micrometer range and/or show poor drug loading (usually less than 5 wt% of the transported drug versus the carrier material) and/or rapid release of the proportion of the drug that is simply adsorbed (or anchored) at the external surface of the nanocarrier.

In this context, biocompatible, non-toxic, porous hybrid solids, with the ability to tune their structures and porosities for better drug interactions and high loadings, are studied to serve as nanocarriers for drug delivery.

TABLE OF CONTENTS

LIST OF FIGURES

ACRONYMS

MOF	Metal Organic Framework
SEM	Scanning Electron Microscope
PXRD	Powder X-ray Diffraction
TGA	Thermogravimetric Analysis
BSA	Bovine serum albumin
PBS	Phosphate buffered solution
MIL	Materials of Institut Lavoisier
IR	Isoreticular
DMF	Dimrthyl formamide
DCM	Dichloro methane
TEA	Triethyl amine

NOMENCLATURE

nm	Nanometer
M	Molar concentration
°C	Degree centrigrade
g	Gram

CHAPTER ONE

1.1 Introduction

Metal-Organic frameworks are porous materials constructed from metal containing nodes and organic linkers. Due to their structural and functional tenability, the area of MOFs has become one of the fastest growing fields in chemistry.

The properties of MOFs to capture and store molecular species has led to their application in CO_2 sequestration, storage of hydrogen and other gases, and drug delivery, heterogeneous catalysis and electronic devices.[1,2] The MOF structures are highly tunable by variation of the metal or the organic ligands (with different length, geometry, number of functionalities, etc.) over a wide range, which makes it possible to obtain a tailor-made MOF material with the required structures and functionalities for specific applications. The term of Metal-Organic Framework (MOF) was first introduced by Yaghi in 1995 for the newly synthesized copper-4,4'-bipyridyl complex that exhibited extended metal-organic interactions.[3]

1.2 Building Units of MOF

The building units of MOF are mainly metal cations and organic ligands and also known as primary building units.

1.2.1 Metal Cations

Commonly Fe^{3+}, Zn^{2+}, Cr^{3+} etc. (first row transition metals) metal cations are versatile connectors in the construction of MOFs. [4-6] Alkali metal ions, [7-8] alkaline earth metal ions [9-11] and rare earth metal ions [12-16] have also been used as metal ions for formation of MOFs.

Different metal cations varies in its size and its oxidation state and hence coordination number varies for different metal cations. That give rise to various geometries which play an important role in different structure and different pore size of MOFs.

1.2.2 Organic Ligands

The other important units for MOF formation are organic ligands. Some of them are given in figure with single unit of structure.

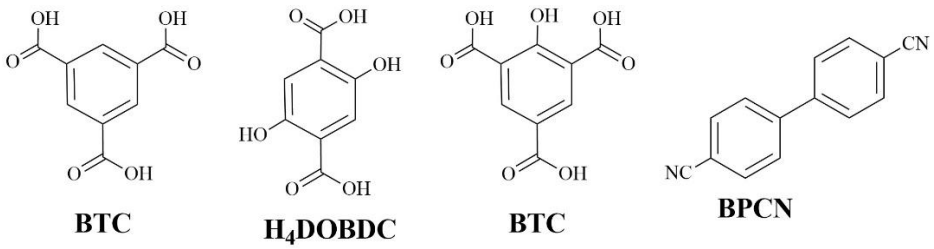

Figure 1.2.2: Molecular structure of organic ligand used for MOF construction.

CHAPTER 2

2.1 Applications of MOFs

MOFs have been studied wildly and found application in many fields. In this chapter, some extensively studied applications of MOF materials are introduced briefly.

2.1.1 MOFs as abosorbents for molecule separation

Other than the property of MOFs of high porosity, another feature of MOF materials is their high structure tenability with tuneable pore size, channel topology and inner surface properties, which makes them suitable materials as adsorbents for selective gas/solvent separation.[17] The pore sizes within the MOF is crucial to induce highly efficient separation of guest molecules by the size/shape exclusion effect in which large molecules are prevented from entering the pores while small molecules are allowed to pass through.[18-19]

2.1.2 MOFs as host materials

Property of high porosity of MOF materials, accounts MOFs could serve as host materials with an exceptional guest molecule loading capacity. All kinds of gas molecules, liquid adsorbates, and nano particles have been encapsulated into MOFs.

MOFs show some of the highest porosities known with pore sizes between 0.4 and ~3 nm, which is ideal for gas storage applications and MOFs have been highlighted many times recently for their excellent gas storage properties. [20]

Morris et al. study on storage and delivery of H_2S showed Nitrogen adsorption data measured volumetrically at 77K gives a Langmuir and BET surface area of 1545.32 m^2 g^{-1} and 1193.18 m^2 g^{-1} respectively for Ni-CPO after
dehydration at 150 °C. [21] The study of loading Liquid adsorbates (or dissolved in liquid), such as ferrocene has been successfully done by Fisher et al. by using highly porous metalorganic framework compound [Al(OH)(bdc)]x (MIL-53; bdc = 1,4-benzenedicarboxylate). [22]

2.1.3 MOFs as catalysts

Heterogeneous catalysis was one of the earliest demonstrated applications for MOF materials. In 1994, the first example was reported by Fujita and co-workers on the cyanosilylation of aldehydes under the catalysis of a two-dimensional MOF ($[Cd(4,4\text{-}BPY)_2(NO_3)_2]$), with active Cd(II) sites.[23]

It was revealed that on the outer surfaces of MOF particles, exposed terminal metal sites and terminal ligand sites respectively play a role as Lewis acids and Lewis bases, which may function well as active sites for catalysis.[24, 25]

2.1.4 Other applications of MOFs

Other than the above applications, MOFs have also been explored for their interesting properties, including optical, luminescent and magnetic properties etc.
Very recently, the most attractive applications of MOFs in biomedical applications have attracted attention strongly. Since this research aims at the study of possible biological applications of MOFs.

2.2 Biological applications of MOFs

Among numerous MOF studies, the biological application of MOFs is still a very new field. Until now, only few studies concerning MOFs as biomaterials have been reported. Several properties, such as biocompatibility, degradability, efficacy, and imaging properties of MOFs remain to be investigated. And extended biological applications of MOFs need to be explored.

2.2.1 MOFs as biomaterials for drug delivery

MOFs applied as potential drug carriers for biomedical and pharmaceutical applications aiming at targeted drug delivery to specific sites with controlled rate and avoiding the "burst effect" (a large drug volume is quickly released within the first minutes) has attracted more interest recently.[26,27]

2.2.2 Toxicity of MOFs

Fast growing studies concerning MOFs as biomaterials show positive scope in biological or therapeutic applications besides this it has some issues with the toxic nature of MOFs. Toxicity of novel purely organic (fullerenes, carbon nanotubes) or inorganic nanoparticles (quantum dots, silica, iron oxides) is not fully understood. [28] Therefore, prior to any practical use of nano MOFs, particularly for biological applications, it is of a high societal relevance to investigate their possible toxic effects. As inorganic nanoparticles are often not biodegradable, toxicity of these hybrid nano MOFs could be suspected.[29] Until now, most toxicity information has concerned the metal salts precursors or the linkers alone (i.e. material safety data sheets or MSDS of constitutive compounds) or some scarce cytotoxicity data of nano MOFs.

2.2.3 Biodegradable nature of MOFs

The main reason to use MOFs as for drug carrier in biomedical applications of biodegradable nature under physiological conditions (such as phosphate buffered solution, PBS, pH=7.4, at 37°C, or bovine serum albumin, BSA) as a result of relatively labile metal-ligand bonds. However, for biomedical applications, an amount of instability of MOFs is desirable characteristic to skip endogeneous accumulation.

Some MOFs have higher rate to get degraded often within hours or minutes. The study of Lin *et al.* demonstrated that material has a life of 3.5 h in water at 37 °C and a dramatically reduced half-life of 18 min under physiological conditions.[30] The more smaller size of MOFs may also contribute to the higher rate of degradation. Lin and coworkers studied that the degradation of nanosized MIL-101 (Fe) under physiological conditions occurs with a half-life of 1.2 h.[31]

2.2.4 Requirement of size of MOFs for biological applications

The size of MOF particles in range of micrometers to millimeters is not appropriate for many biomedical applications. Mirkin et al. published a review in year 2009, on Infinite coordination polymers (ICPs) comparing their porosity surface area and size with MOFs. Crystalline MOFs in the majority of cases are not dynamic structures, and once made cannot be re-transformed into different macroscopic structures. This constitutes a major difference between MOFs and the vast majority of organic polymers, which easily reorganize upon changes to external conditions (solvent, pH, temperature, pressure, etc.). Therefore, in some respects, many ICP particles resemble classical polymers more than MOFs, but in contrast with organic polymers, one can use the coordination sites of ICP particles as a powerful way of

controlling their 3D structures, and chemical and physical properties, even after particle formation. And hence less controlled size makes MOFs unsuitable for many biological applications. [32]
Consequently, lowering the size of MOFs to the nanometer dominion will lead to more possibilities of MOFs for biological applications.

2.3 Methods of synthesis for Small-sized MOFs

2.3.1 Microemulsion method

Water-in-oil, or reverse, microemulsion method is a method for the preparation of nanoparticles and has been utilized for nano-family MOF synthesis. Water-in-oil microemulsions are the systems those consist of nanometer-sized water droplets by adding a surfactant to stabilize the system. The micelles in the microemulsion essentially act as "nanoreactors" that assist in controlling the kinetics of particle nucleation and growth. The size and number of micelles within the microemulsion can be tuned by varying the water to surfactant ratio.
Using the water-in-oil, or reverse, microemulsion methods, Lin *et al.* has done work on synthesis of nanoscale MOFs.[33-35]
Although dimensions of the nanoscale materials can be controlled by the microemulsion and reverse-phase microemulsion methods, using the surfactants in these systems make less useful MOFs in applications of biomedical.

2.3.2 Hydrothermal method

The most commonly method used to synthesize MOFs is conventional hydro/solvothermal method, which usually requires a long reaction time (days to weeks) and result in well-crystallized solids on the micrometer to millimeters scale. Generally, not of nano regime

MOFs are not produced by this method, but to synthesize of nano regime MOFs well-designed conditions and finely-controlled procedures are needed. [36]

2.3.3 Microwave assisted method

It is recently reported that microwave-assisted method to be a good route to synthesize MOFs with high rate of formation within minutes. This method not even gives the high efficiency, although it is to be beneficial for synthesis of small-sized MOFs with better phase purity, macroscopic morphology and yield. [37]

In 2006, Masel *et al.* synthesized small IRMOF-1, -2 and -3 crystals in the submicrometer range by the use of a microwave-assisted method. [38] Similarly, Ahn *et al.* revealed that microwave heating facilitates the fast crystallization of IRMOF-1 with downsized regime compared with the conventional solvothermal method. [39]

2.4 Objectives of the work

This work involved the synthesis and characterization of MOF materials.

The main objectives of the work are:

- Lowering the size of MOF crystals to a nano scale or small micrometer by developing effective synthesis methods.

- Studying the effect of the synthesis conditions on the properties of products (e.g. variation in temperature, solvent and time etc.).

  Studying the anticancer drugs release property of these materials in different pH values solution with the help of Fluorescence spectrophotometer.

CHAPTER 3

3.1 Synthesis of Zn-Carnosine MOF

5.26mL of $Zn(NO_3)_2 \cdot 6H_2O$(0.525g) aqueous solution(0.336M), 2mL of carnosine aqueous solution(0.442 M), 2mL water and 20mL DMF were loaded in a 40mL vial. The vial was heated at 100°C for 12h with a ramping rate of 1°C/min and was cooled down to room temperature at 1°C/min. After this time needle shaped crystal covered the wall and bottom of vial. The product was collected with filtration and washed with methane. [36]

3.2 Synthesis of Zn-Carnosine MOF by emulsion method

3.2.1 Route 1

Two separate solutions of $Zn(NO_3)_2 \cdot 6H_2O$(0.999g, 0.224M) and carnosine(0.499g, 0.1473M) were prepared in 15mL of DMF solvent and the obtained solutions were sonicated separately for 15 minutes. After sonication 50mL of cyclohexane was added in carnosine solution and this solution was sonicated for again 15 minutes. In this solution, metal solution was introduced and an emulsion formed. A total amount of 18.5mL of DCM (emulsifier) was added to stabilize the emulsion, with ultrasonication after each one mL addition of DCM. The mixture was kept for 12 hours in oil bath at 90°C with constant stirring. To remove the cyclohexane, the product formed was heated at 120°C. And formed product was washed with ethanol.

3.2.2 Route 2

Two separate solutions of $Zn(NO_3)_2 \cdot 6H_2O$(0.999g, 0.M) and carnosine(0.499g, 0.M) were prepared in 20mL and 15mL in water respectively and the obtained solutions were sonicated separately for 15 minutes. Carnosine solution was added to 30mL of vegetable oil and formed emulsion was ultrasonicated for 10 minutes and put the emulsion in oil bath with reflux at 100°C. Metal solution was added to the emulsion through the walls of round bottom flask and reaction

was kept for 24h with constant stirring. Formed crystals were washed with water many times.

3.3 Synthesis of IRMOF-0

Acetylenedicarboxylic acid (2.01 g, 17.6 mmol) was dissolved in DMF (50 mL) and $Zn(OAc)_2 \cdot 2H_2O$ (8.00 g, 36.4 mmol) was dissolved in DMF (60 mL). The two solutions were combined with stirring. TEA (5 mL) was added to the stirring mixture and the reaction was allowed to run overnight.

3.4 Synthesis of MgMOF-74

3.4.1 Route 1

A solid mixture of $Mg(NO_3) \cdot 6H_2O$ (1.33 g, Sigma-Aldrich) and H_4dhtp (0.310 g) was dissolved in 140 mL of a solvent mixture of DMF, ethanol, and de-ionized water (15 : 1 : 1, v/v/v) with stirring. The substrate mixture was introduced to an autoclave of 200 mL volume and kept autoclave for 24 h at 125 °C in an oven.

After the synthesis, the obtained dark yellow Mg-MOF-74 crystals were washed with water and ethanol. And finally a light yellow material was formed after drying under vacuum.

3.4.2 Route 2

A solid mixture of $Mg(NO_3)$ •$6H_2O$ (0.190 g) and H_4dhtp (0.04428 g) was dissolved in 20 mL of a solvent mixture of DMF, ethanol, and de-ionized water. The substrate was sonicated with Pump Probe Sonicator for 2 h on the gap of 15 minutes. The substrate was introduced to hydrothermal reaction for 24 h at 150 °C. After the synthesis, crystals were washed with water many times and dried under vacuum.

CHAPTER 4

CHARACTERIZATION

4.1 ZnCar.DMF

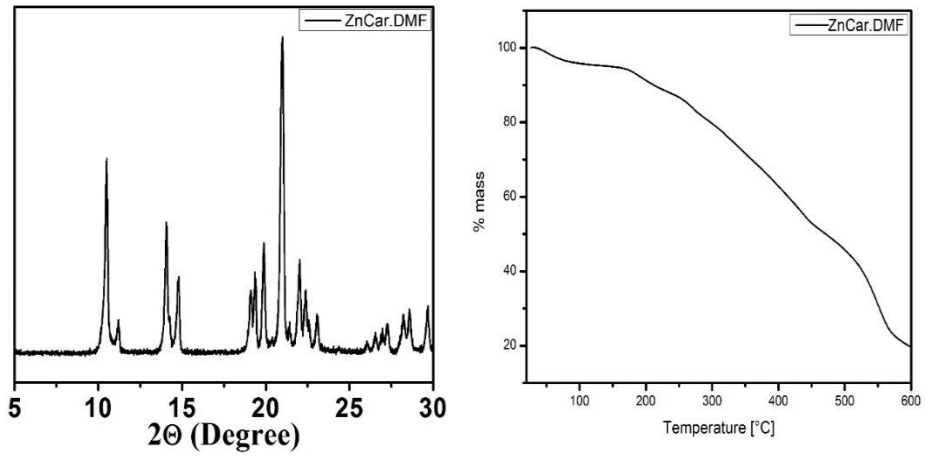

Figure 4.1(a): PXRD and TGA pattern for ZnCar.DMF

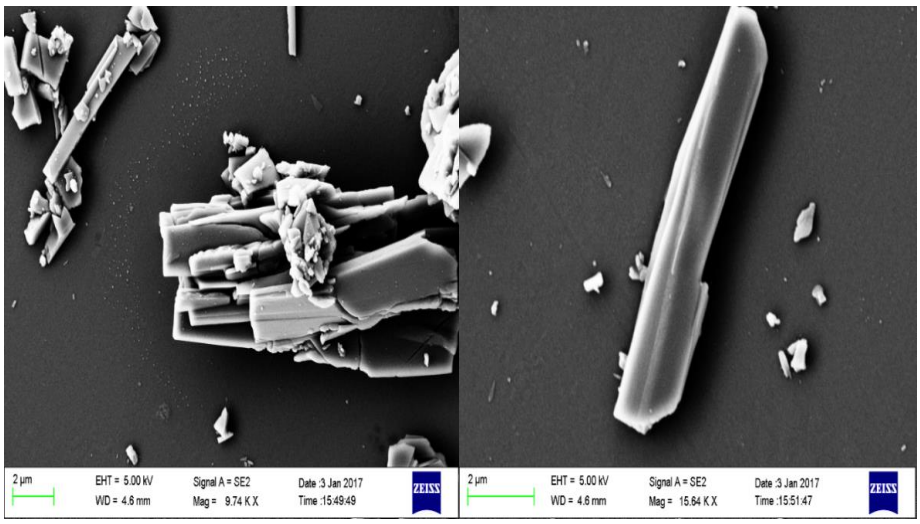

Figure 4.1(b): SEM images for ZnCar.DMF

Brunauer-Emmett-Teller (BET) data of ZnCar.DMF MOF

Property	Value
Surface Area	3.831m^2/g
Pore Volume	0.010cc/g
Pore Diameter	39.202 Å

Synthesized MOF is mesoporous material having 3.9202 nm pore diameter.

4.2 ZnCar MOF By Emulsion method

Route 1

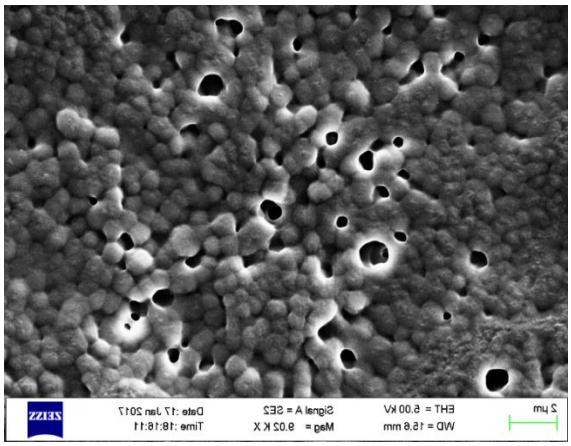

Figure 4.2 (a): SEM images of ZnCar MOF obtained by Route1

Route 2

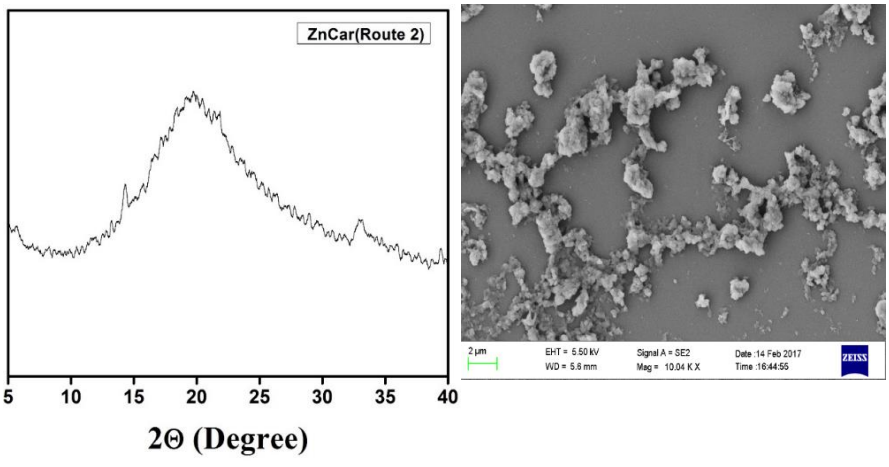

Figure 4.2(b): PXRD pattern and SEM images for ZnCar

4.3 IRMOF-0

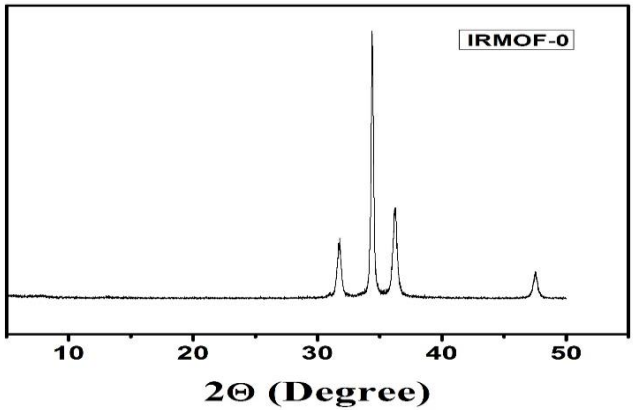

Figure 4.3 (a): PXRD pattern of IRMOF-0

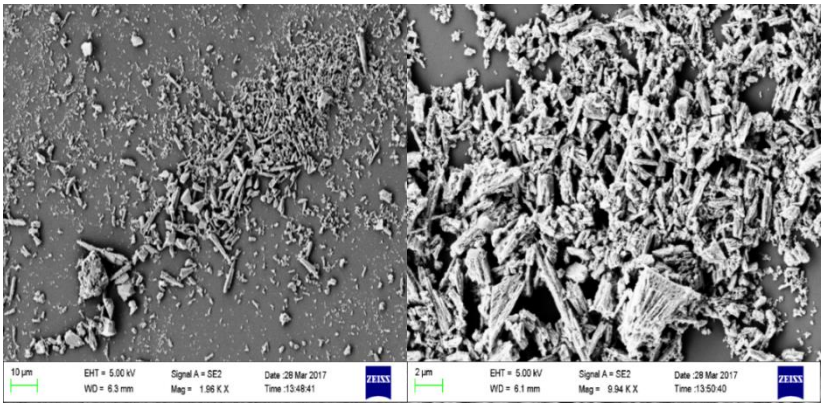

Figure 4.3 (b): SEM images of IRMOF-0

4.4 Mg-MOF-74

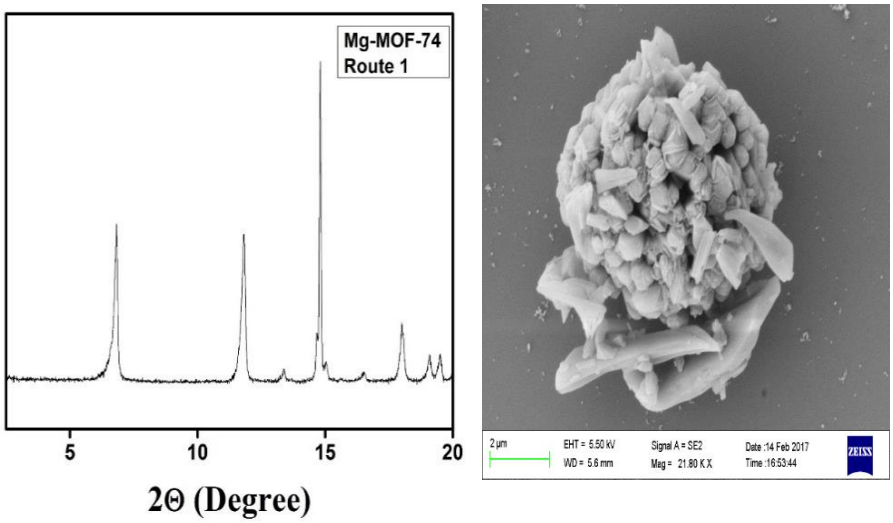

Figure 4.4 (a): PXRD pattern and SEM images for Mg-MOF-74 synthesized by route 1

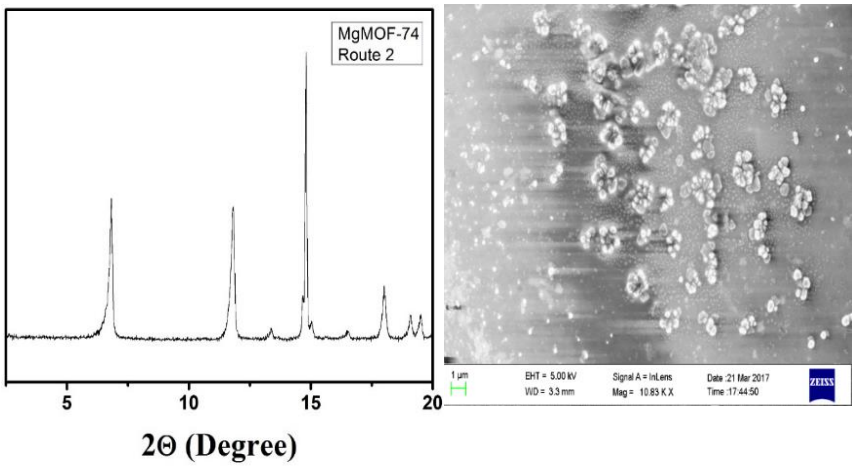

Figure 4.4 (b): PXRD pattern and SEM images for Mg-MOF-74 synthesized by route 2

CHAPTER 5

Application

Anticancer drug doxorubicin (DOX) was loaded in ZnCar.DMF MOF and done the drug release study using pH as a external stimuli.

Procedure for Drug Encapsulation: To incorporate DOX inside MOFs, post synthesis loading procedure was followed for the MOFs. Briefly, 2 mL of 0.5 mM drug solution was added to the 100 mg of MOFs and was stirred for 48 h. Then the drug-loaded MOFs were separated by centrifugation, washed several times by methanol, and dried before doing further experiments.

Encapsulation Efficiency = (Amount of loaded drug/ the initial amount of drug) X 100

Encapsulation Efficiency = (92.8926 µg / 106.7392 µg) X 100

= 87.0276 %

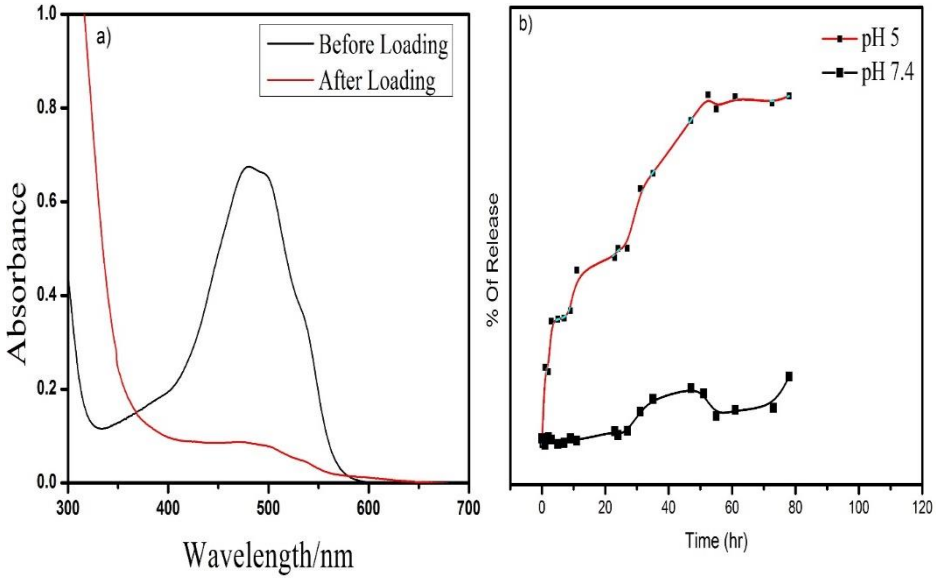

Figure 5: a) UV data of DOX before and after loading in ZnCar.DMF MOF. b) Release study of ZnCar.DMF at pH 5 and pH 7.4

Drug Release under pH Stimuli from MOF: We start our discussion with the release of drug from MOF using pH stimuli. We monitored the drug release at pH 7.4 and 5 respectively. This range of pH will be able to unravel how the drug release is affected while going from physiological pH to little acidic pH. The cancer cells are little bit acidic (pH varies from 4 to 6); thus an ideal DDS should release drug molecule at this pH range. It is reported that the MOF is normally stable at neutral pH while the framework gets dissociated in acidic pH. The reason behind this dissociation is detachment of the coordination between metal ion and ligands in this range of pH. We monitored the fluorescence emission intensity of DOX at 590 nm. A 50 mg of drug loaded sample was taken in a 50 ml pirex bottle and kept in the release medium(pH 7.4 and 5), from which a 2 ml of sample was replaced by fresh release medium at regular intervals to monitor the amount of released drug.

CHAPTER 6

CONCLUSION

Remarkable development has been made in adapting MOFs and NMOFs for drug delivery. With these inorganic-organic hybrid systems, an extensive number of metal centers and organic building blocks can be pieced together and specifically tailored to form new materials with desirable characteristics as drug carriers. Since NMOFs represent most suitable tuning properties of pore size for loading drugs into them,a foreseeable future is becoming visible in MOFs and NMOFS as drug carrier. The ability to carry both imaging and therapeutic agents in NMOFs should greatly facilitate the efficacy studies of this promising class of nanotherapeutics. The future for MOFs and NMOFs in drug delivery is bright, although many more improvements are needed before they can be considered for clinical applications.

REFERENCES

[1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.

[2] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.

[3] H. K. Chae, D. Y. Siberio-perez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523.

[4] H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* **2009**, *131*, 4995.

[5] D. Zacher, O. Shekhah, C. Woll, R. A. Fischer, *Chem. Soc. Rev.* **2009**, *38*, 1418.

[6] Loredana Valenzano, B. Civalleri, W. F. Perger, *Mater. Res. Soc. Symp. Proc.* **2011**, 1366.

[7] T. A. Maark, S. Pal, *Int. J. Hydrogen Energy* **2010**, *35*, 12846.

[8] Y.-K. Lv, C.-H. Zhan, Y.-L. Feng, *CrystEngComm* **2010**, *12*, 3052.

[9] L.-M. Yang, P.Vajeeston, P. Ravindram, H. Fjellvag, M. Tilset, *Phys. Chem. Chem. Phys.* **2011,** 13, 10191.

[10] A. E. Platero-Prats, M. Iglesias, N. Snejko, A. Monge E. Gutierrez-Puebla, *Cryst. Growth Des.* **2011**, *11*, 1750.

[11] A. E. Platero Prats, V. A. de la Peña-O'Shea, M. Iglesias, N. Snejko, Á. Monge, E.Gutiérrez-Puebla, *ChemCatChem* **2010**, *2*, 147.

[12] C. Serre, G. Ferey, *J. Mater. Chem.* **2002**, *12*, 3053.

[13] C. Serre, F. Millange, J. Marrot, G. Ferey, *Chem. Mater.* **2002**, *14*, 2409.

[14] T. M. Reineke, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **1999**, *38*, 2590.

[15] F. Serpaggi, G. Ferey, *J. Mater. Chem.* **1998**, *8*, 2737.

[16] F. Serpaggi, G. Ferey, *Microporous Mesoporous Mater.* **1999**, *32*, 311.

[17] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477.

[18] D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 32.

[19] M. Dinca, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376.

[20] N. J. Hinks, A. C. McKinlay, B. Xiao, P. S. Wheatley, R. E. Morris, *Microporous Mesoporous Mater.* **2010**, *129*, 330.

[21] B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 1203.

[22] M. Meilikhov, K. Yusenko, R. A. Fischer, *Dalton Trans.* **2009**, 600.

[23] M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151.

[24] F. X. Llabres i Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, *250*, 294.

[25] U. Ravon, M. E. Domine, C. Gaudillere, A. Desmartin-Chomel, D. Farrusseng, New. J. Chem. **2008**, *32*, 937.

[26] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayetter, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur, R. Gref, *Nat Mater* **2010**, *9*, 172.

[27] A. C. McKinlay, R. E. Morris, P. Horcajada, G. Férey, R. Gref, P. Couvreur, C. Serre, *Angew. Chem. Int. Ed.* **2006**, *45*, 5974.

[28] M. Sajid, *Environ Sci Pollut Res* **2016**, *23*, 14805–14807.

[29] T. Baati, L. Njim, F. Neffati, A. Kerkeni, M. Bouttemi, R. Gref, M. F. Najjar, A. Zakhama, P. Couvreur, C. Serre and P. Horcajada, *Chem. Sci*., **2013**, *4*, 1597.

[30] K. M. L. Taylor, W. J. Rieter, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 14358.

[31] K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, W. Lin, *J. Am. Chem. Soc.* **2009,** *131*, 14261.

[32] A. M. Spokoyny, D. Kim, A. Sumrein, C. A. Mirkin, *Chem. Soc. Rev*. **2009**, *38*, 1218.

[33] W. J. Rieter, K. M. L. Taylor, H. An, W. Lin, W. Lin, *J. Am. Chem. Soc.* **2006**, *128*,9024.

[34] K. M. L. Taylor, A. Jin, W. Lin, *Angew. Chem. Int. Ed.* **2008**, *47*, 7722.

[35] K. M. L. Taylor, W. J. Rieter, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 14358.

[36] A. P. Katsoulidis, K. S. Park, D. Antypov, C. M.-Gastaldo, G. J. Miller, J. E. Warren, C. M. Robertson, F. Blanc, G. R. Darling, N.G. Berry, J. A. Purton, D. J. Adams, and M. J. Rosseinsky, *Angew. Chem. Int. Ed.* **2014**, *53*, 193 –198.

[37] Y.-K. Seo, G. Hundal, I. T. Jang, Y. K. Hwang, C.-H. Jun, J.-S. Chang, *Microporous Mesoporous Mater.* **2009**, *119*, 331.

[38] Z. Ni, R. I. Masel, *J. Am. Chem. Soc.* **2006**, *128*, 12394.

[39] J.-S. Choi, W.-J. Son, J. Kim, W.-S. Ahn, *Microporous Mesoporous Mater.* **2008**, *116*, 727.