# DESIGN AND SYNTHESIS OF MULTITASKING FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS

Ph.D. Thesis

By SHAGUFI NAZ ANSARI



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2020

# DESIGN AND SYNTHESIS OF MULTITASKING FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS

# A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> *by* SHAGUFI NAZ ANSARI



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2020



# **INDIAN INSTITUTE OF TECHNOLOGY INDORE**

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **DESIGN AND SYNTHESIS OF MULTITASKING FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** 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 September 2020 under the supervision of Dr. Shaikh M. Mobin, Associate Professor, Discipline of Chemistry, Indian Institute of Technology 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.

4/09/20

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

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#### ABSTRACT

The Investigations embodied in thesis entitled "DESIGN AND SYNTHESIS OF MULTITASKING FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS" was initiated in July 2015 in the Discipline of Chemistry, Indian Institute of Technology Indore.

The objectives of this thesis are to investigate the perspectives of developing new Functionalized Metal-Organic Frameworks (FMOFs) based on specific functional groups for the achievement of desired properties and significant results. The focal points of thesis work are as follow-

- Synthesis of a Lactam-functionalized porous MOF and exploring its catalytic activity for the chemical fixation of CO<sub>2</sub> to cyclic carbonates in an economically viable way.
- Utilization of the prepared Cu-MOF with graphene oxide nanosheets as an efficient adsorbent for the removal of MB dye in aqueous systems and a selective electrochemical sensor.
- Synthesis of a novel amino-functionalized MOF having layered porous channels and exploration of its energy storage applications by preparing the hybrid through the incorporation of CNTs.
- Exploration of solid-state structural reactivity with the phenomenon of Single-Crystal-to-Single-Crystal transformations in new Triazole-functionalized MOFs, obtaining novel topology.
- Preparation of a new imidazole derivative based ligand as a fluorescent receptor for sensing of metal ions and bio-imaging.

This thesis contains seven chapters and it begins with a general introduction emphasizing on the designing of MOFs constituted of various organic functional groups for the achievement of best possible performances (**Chapter 1**), followed by synthesis, structural description and applications of various functionalized metal-organic frameworks,

along with the synthesis a new imidazole based fluorescent chemosensor for the sensing of metal ions and presenting biologically active properties in subsequent chapters. Finally, the thesis concludes with views on the prospects of optimizing materials for sustainable and cost-effective potential applications of the synthesized materials.

#### **Thesis Chapters Contribution**

**Chapter 1** (General Introduction) of this thesis, gives an overview of Metal-Organic Frameworks (MOFs), their synthesis, structures, and properties which incite interest for their applications in various fields. This is followed by a brief discussion on, employment of unique design strategies of MOFs to impart functionalities to selected materials for the advancement of performance along with well-targeted applications. A brief literature on the synergistic point of view of hybrid materials derived from MOFs by post synthetic approach has been offered, presenting enhanced properties with a wide range of applications.

In Chapter 2, we have discussed about a porous, Cu(II)-metal organic framework, (Cu-MOF), constituted by a rigid lactam functionalized ditopic ligand  $(H_2L)$  $\{H_2L=(5-(1-0x0-2,3-dihydro-1H-inden-2$ yl)isophthalic acid)}. Cu-MOF is synthesized at room temperature under slow evaporation condition. Single crystal X-ray studies revealed the formation of a 3D framework of Cu-MOF with one dimensional (1D) channels decorated with lactam groups and exposed metal centers in the crystallographic c-axis. Interestingly, Cu(II) coordinated DMF molecules were eliminated from the Cu(II) metal center on activation of Cu-MOF at a temperature of 150°C under a high vacuum to generate a solvent-free framework with pores lined with unsaturated Lewis acidic Cu(II) ions i.e. Cu-MOF'. The lactam functionalized channels are inclined towards the CO<sub>2</sub>, which interacts with the Cu(II) metal sites lined in the channels of **Cu-MOF'** and exhibits fascinating solvent-free heterogeneous catalytic conversion of  $CO_2$  to cyclic carbonates at atmospheric pressure of  $CO_2$ , under mild conditions. Furthermore, the **Cu-MOF'** catalyst was easily recycled and reused for several cycles without significant loss in catalytic activity.

In **Chapter 3**, a new composite material (Cu-MOF/GO) was prepared utilizing Lactam-functionalized MOF and graphene oxide nanosheets, through the simple ultra-sonication method. The as-synthesized material was characterized by PXRD, and Scanning Electron Microscopy (SEM) techniques. The Cu-MOF/GO composite was studied for the rapid adsorption of Methylene Blue dye (50 PPM) from aqueous solution, showing quick adsorption of 99.5 % within 60 minutes. Adsorption capacity at equilibrium was obtained to be 99.6 mg/g for a contact time of 60 min. Further, the Cu-MOF/GO composite was also employed for electrochemical sensing of cholesterol with limit of detection as 0.09mM. To the best of our knowledge this is the first report on MOF/GO based composition employed as an electrochemical sensor for cholesterol.

**Chapter 4**, describes the synthesis of a new functionalized layered Cu(II)coordinated metal-organic framework, named **IITI-1** by employing newly design linker H<sub>2</sub>L and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in a mixed solvent system of N,Ndimethyl formamide (DMF) and H<sub>2</sub>O. Further, to explore the energy storage application of **IITI-1**, we have prepared the **IITI-1/CNT** hybrid by a simple ultra-sonication technique. Incorporation of CNT in the layers of **IITI-1** gives rise to enhanced electrolyte accessibility along with the improved electrochemical storage capacity. The electrochemical investigations reveal a high specific capacitance (380 F g<sup>-1</sup> at 1.6 A g<sup>-1</sup>) with a good rate performance of **IITI-1/CNT** hybrid. The **IITI-1** MOF and **IITI-1/CNT** hybrid were characterized by PXRD, BET, SEM, and TEM techniques. Moreover, **IITI-1** MOF was also authenticated by single-crystal X-ray diffraction studies. In Chapter 5, we have discussed the facile in-situ synthesis of a new sodium coordinated metal-organic framework (MOF), Na-MOF1 having rare parallel polycatenated (6,3-c) *kgd* nets. Na-MOF1 undergoes high-pressure vacuum mediated SCSC transformations resulting in a newly structured MOF Na-MOF2 comprising of novel 3-periodic 3,3,12-c net topology (named *smm*1). Further, the SCSC transformation of Na-MOF1 to Na-MOF2 reveals activation of N-N-atoms in 1,2,3-triazole unit. Na-MOF1 and Na-MOF2 were authenticated by single-crystal X-ray diffraction analysis and the bulk was confirmed by BET studies and powder X-ray diffraction analysis.

Chapter 6, describes the synthesis of a new fluorescent receptor HL by an easy condensation reaction of ortho-Vanillin and 1-(3-aminopropyl) imidazole. The probe HL was found to be highly selective and sensitive towards  $Zn^{2+}/Cu^{2+}$  ions in the presence of a wide range of metal cations. The interaction of **HL** with  $Zn^{2+}$  ions presented a distinct fluorescence enhancement (turn-on) at 470 nm. Moreover, after the subsequent addition of  $Cu^{2+}$  ion into the same solution fluorescence 'turn-off' phenomenon was observed. The sensing ability of chemodosimeter HL, towards Zn<sup>2+</sup> was confirmed by Fluorescence, UV-Vis, and <sup>1</sup>H NMR titration experiment. The binding mode of **HL** towards  $Zn^{2+}$  and  $Cu^{2+}$  was authenticated by single-crystal X-ray analysis, which divulges the formation of dinuclear complexes 1 and 2. Furthermore, we performed NOESY and COSY study of complexes 1 and 2 to detect the shape and interlocking units. Moreover, cytotoxicity of HL and 1 was observed towards Hela cancer cells and found to be non-cytotoxic which prompted us to explore intracellular fluorescence turn-on sensing with  $Zn^{2+}$  ions. The intracellular sensing behavior of HL towards Zn<sup>2+</sup> was confirmed towards two cancer cell lines viz., Hela, and DU-145 cell lines. The limit of detection (LOD) with  $Zn^{2+}$  and  $Cu^{2+}$  was found to be 31.044 nM and 11.64 nM respectively.

**Chapter 7** outlines the future perspective of this work.

#### LIST OF PUBLICATIONS

- Ansari S. N., Verma S. K., Garin A., Mobin S. M. (2018), Vacuum mediated Single-Crystal-to-Single-Crystal (SCSC) transformation in Na-MOFs: Rare to novel topology and activation of nitrogen in triazole moieties, *Cryst. Growth Des.* 18, 1287–1292 (DOI:10.1021/acs.cgd.7b01753) Published. Impact factor 4.089
- Ansari S. N., Saini A. K., Kumari P., Mobin S. M. (2019), An imidazole derivative-based chemodosimeter for Zn<sup>2+</sup> and Cu<sup>2+</sup> ions through "On-Off-On" switching with intracellular Zn<sup>2+</sup> detection, *Inorg. Chem. Front.*, 6, 736-745 (DOI:10.1039/C8QI01127C) Published. Impact factor 5.934
- 3. Ansari S. N., Saraf M., Gupta A. K., Mobin S. M. (2019), Functionalized Cu-MOF@CNT hybrid: Synthesis, crystal structure and applicability in supercapacitors, *Chem. Asian J.* 14, 1-7 (DOI:10.1002/asia.201900629) Published. Impact factor 4.056
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- Ansari S. N., Kumar P., Ahmad K., Kumar R., Mobin S. M. (2020), Construction of Multifunctional Cu-MOF/GO composite for Efficient Adsorption of Methylene Blue and Sensing of Cholesterol, *Manuscript in process*.

#### **Other Publications**

 Rajak R., Kumar R, Ansari S. N., Saraf M., Mobin S. M. (2020), Recent highlights and future prospects on mixed-metal MOFs as emerging contestants for supercapacitors, *Dalton Trans.*, 49,11792-11818 (DOI: https://doi.org/10.1039/D0DT01676D). Impact factor 4.174

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- Ahmad K., Ansari S. N., Natarajan K. Mobin S. M. (2018), Design and synthesis of 1D-polymeric chain based [(CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>Bi<sub>2</sub>Cl<sub>9</sub>]n perovskite: A new light absorber material for lead-free perovskite solar cells, ACS Appl. Energy Mater. 1, 2405-2409 (DOI:10.1021/acsaem.8b00437) Published. Impact factor 4.473
- 11. Verma S. K., Kumari P., Ansari S. N., Ansari M. O., Deori, D., Mobin S. M. (2018), A novel mesoionic carbene based highly fluorescent Pd(ii) complex as an endoplasmic reticulum tracker in live cells, *Dalton Trans.* 47, 15646-15650 (DOI:10.1039/c8dt02778a) Published. Impact factor 4.174
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- 16. Singh A., Torubaev Y., Ansari S. N., Singh S. K., Mathur P., Mobin S. M. (2020), The borderline: exploring the structural landscape of triptycene in cocrystallization with ferrocene *CrystEnggCommun.* 22, 1314-1320 (DOI:10.1039/C9CE01734H) Published. Impact factor 3.117
- 17. Khan M. A., Ghosh S., Bera S., Hoque A., Sk S., Ansari S. N., Mobin S. M. (2020), Alam, M. A., Crystallographic Elucidation of Stimuli-Controlled for a Reversible Molecular Rotation Sol–Gel Transformation. J. 85. 6. Org. Chem. 4019-4025 (DOI:10.1021/acs.joc.9b02944) Published. Impact factor 4.

#### **Conferences/Workshop/Oral/Poster Presentations**

#### **Oral presentation**

 "43<sup>rd</sup> International Conference on Coordination Chemistry (ICCC 2018)" organized by Tohoku University, Sendai, Japan, July 30 – August 4, 2018. (Oral Presentation).

#### Poster presentation

- "2nd International Conference on Crystal Engineering: From Molecule to Crystal-2020 (CEFMC-2020)" organized by Department of Chemistry, Indian Institute of Technology Patna, 19
   - 20 June, 2020. (Best Poster Presentation Prize).
- "Chem 2019, In-house Chemistry Symposium" organized by Discipline of Chemistry, IIT Indore, February 28, 2019. (Best Poster Presentation Prize).
- 4. "Inter-Disciplinary Exploration in Chemistry (I-DEC 2018)" organized by IISER Bhopal, 06 08 Dec, 2018 (Poster Presentation).
- 5. "Inorganic Chemistry of Imaging: Magnetic Resonance and Optical Imaging with Coordination Complexes" a Global Initiative on Academic Networks (GIAN) Course Organized by Discipline of Chemistry, Indian Institute of Technology Indore, an initiatives from MHRD, New Delhi, from January 8–12, 2018.
- "21st CRSI National Symposium in Chemistry (NSC-21)" organized by IICT Hyderabad, 13 - 16 July, 2017 (Poster Presentation).
- 7. *"Catalysis by Metal Complexes"* a Global Initiative on Academic Networks (GIAN) Course Organized by Discipline of Chemistry,

Indian Institute of Technology Indore, an initiatives from MHRD, New Delhi, from November 21–26, 2016.

 "Rigaku Oxford Diffraction SMX User Meeting" organized by Rigaku Oxford Diffraction and supported by I. R. Technology Service PVC and Department of Chemistry, IIT Bombay, India. On Oct, 18<sup>th</sup> –19<sup>th</sup>, 2016.

## LIST OF ABBREVIATIONS

MOF	Metal-organic frameworks
SBUs	Secondary building units
SCSC	Single-Crystal-to-Single-Crystal
СР	Coordination polymer
GCE	Glassy Carbon Electrode
GO	Graphene oxide
MB	Methylene Blue
CNT	Carbon nanotubes
EDLC	Electrical double layer capacitance
GCD	Galvanostatic charge-discharge
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
SCSC	Single-Crystal-to-Single-Crystal
ESI-MS	Electrospray ionization mass spectrometry
HRMS	High Resolution Mass Spectrometry
TGA	Thermogravimetric analysis
SCXRD	Single crystal X-ray diffractometer
UV light	Ultraviolet light
NMR	Nuclear magnetic resonance spectroscopy

ICT	Internal charge transfer
PET	Photo-induced electron transfer
THF	Tetrahydrofuran
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Zinc nitrate hexahydrate
$Cu(NO_3)_2 \cdot 3H_2O$	Copper(II) nitrate trihydrate
МеОН	Methanol
EtOH	Ethanol
KBr	Potassium bromide
Et <sub>3</sub> N	Triethylamine
ACN	Acetonitrile
DMSO	Dimethyl sulfoxide
CDCl <sub>3</sub>	Deuterated chloroform
DMSO-d <sub>6</sub>	Deuterated dimethyl sulfoxide
$D_2O$	Deuterium oxide (Heavy water)
DMF	Dimethylformamide
EtOAc	Ethylacetate
LOD	Limit of detection
RT	Room temperature
EDTA	Ethylenediaminetetraacetic acid
HEPES	(4-(2-hydroxyethyl)-1-piperazineethanesulfonic

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aciu
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MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-
	diphenyltetrazolium bromide
DU145	Human prostate cancer cell line
HeLa	Cervical cancer cell line
TLC	Thin-layer chromatography
HPLC	High-performance liquid chromatography
PBS	Phosphate-buffered saline
ppm	Parts per million
MHz	Megahertz
GCE	Glassy carbon electrode
FESEM	Field-Emission Scanning Electron Microscope CV Cyclic voltammetry
Т	Temperature
С	Celsius
0	Degree
К	kelvin
рН	Potential of hydrogen
PXRD	Powder X-ray diffraction
IR	Infrared spectroscopy
Å	Angstrom

nm	nanometer
μm	micrometer
g	gram
mg	milligram
mL	milliliter L Liter

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#### **Chapter 1**

#### **1.1. Introduction**

The ambition of designing new materials to accomplish precise applications has grown to be a mission for scientists pursuing the critical demands of the real-world. Significant actions have been taken to meet this target by developing innovative routes towards designing and synthesis of materials with required features and properties. Therefore, superior functionality materials came in existence built by a combination of multiple components. Metal-organic frameworks (MOFs) are the most passionately researched class of porous functional materials, especially in the fields of chemistry and material science due to their unique and innovative structures with constructive properties.[1,2] The term "metalorganic framework" was coined by Omar M. Yaghi and coworkers in 1995.



Figure 1.1. Different MOFs structures synthesized by various research groups.[3]

More than 20,000 MOFs structures have been reported and studied since its discovery (Figure 1.1).[3] MOFs are very attractive owing to their modular structure proposing vast structural diversity with the prospects of designing materials having tailored properties such as tunable pore sizes, flexible assemblies, highly ordered and crystalline framework, countless compositions, and easy functionalization.[4,5,6] One of the main features of MOFs is its reproducibility in synthesis and the possibility of postsynthetic treatment after synthesis. These constructive features make MOFs a worthy candidate for use in gas adsorption, separation, and purification, catalysis and ion exchange reactions, drug delivery systems, semiconductors, photoactive and magnetic materials, wastewater treatment, development of optical and luminescent materials and so on.[7-16] The high crystallinity in MOFs confirms uniform shape and pore size along with providing a technique of their study and characterization. A variation in the size of MOFs crystals is observed from the nanometer to millimeter regime analyzed by X-ray crystallography making them easier to study than zeolites, activated carbons, and porous silica.[17]

#### **1.2.** Structural features of metal-organic frameworks

Metal-organic frameworks are also known as porous coordination polymers, which can be prepared through coordinating the organic linkers with metal ions or metal clusters as organic and inorganic molecular building blocks. Di- or polytopic protonated organic linkers coordinate to the metal-containing secondary building units (SBUs) to form networks of two- or three-dimensional units. Several metal SBUs have diverse geometries and coordination numbers such as linear, Tetrahedral, T- or Yshaped, Square-planar, Octahedral, Square-pyramidal, Trigonal-prismatic, and Trigonal-bipyramidal, etc. The linkers can be cationic/anionic/neutral generally range from two to six in connectivity, particularly employed as pillars in constructing assemblies of 3D networks (**Figure 1.2**).[18,19]
Carboxylates are broadly employed as anionic linkers due to their fast association with metal ions to form stable frameworks.[20,21] However, cationic organic linkers are occasionally used due to minor affinity for metal ions.[22,23] Rigid linkers are favored due to their stability to withstand the open-pore structure after solvents removal at high temperatures. Infinite MOFs structures with different features can be synthesized by altering metal ions and building different arrangements with various organic linkers having various lengths, geometries, and functionalities.



Figure 1.2. Illustration of the construction of various MOFs from SBUs and linkers.[19]

MOFs can have well-regulated pore sizes (2 nm-50 nm) by varying the length of the carbon chain of the linker, whereas additional selectivity and unique chemical properties can be regulated by the introduction of various functional groups and different substituents into the linker.[23,25,26]

# 1.3. Methods for the synthesis of MOFs

MOFs can be synthesized through various methods, such as solvothermal (hydrothermal), microwave-assisted, electrochemical, sonochemical mechanochemical, and slow evaporation synthesis techniques as described below (**Figure 1.3**):

- Hydrothermal/Solvothermal synthesis: This is the most preferred technique of MOFs synthesis occur at very high temperature and pressure in a solvothermal or hydrothermal medium in an autoclave system. The quality and morphology of the crystals depend on the solvent polarity, reactants solubility, reaction time and temperature, stirring rate, and the molar ratio of starting materials. ZIF-8 prepared in DMF solvent had a huge surface area (BET: 1630 m<sup>2</sup>/g) with stability up to 550 °C temperature.[27,28] However it as a time-consuming method in comparison to other techniques.
- Microwave-assisted synthesis: It is an energy-efficient and time-saving heating method. High temperatures in the microwave zone encourage fast nucleation for the MOFs synthesis with large annealing causing fast crystallization in a few minutes. Choi and coworkers examined MOF-5 structural properties by variation in the irradiation time, temperature, power level, and substrate composition. Uniform cubic crystals of MOF-5 (20-25 µm size) in 30 minutes were obtained with 3008 m<sup>2</sup>/g surface area.[29]
- Mechanochemical synthesis: This solvent free technique has a great potential for the energy-efficient and clean production of MOFs. This approach is based on breaking down the intramolecular bonds, driven by mechanical forces in a mechanical ball milling system which allows the chemical

transformation at RT. Klimakow and coworkers used this method for HKUST-1 preparation in 25 min taking copper acetate and trimesic acid as precursors and further removing the gaseous by-product obtaining the high surface area of 1713  $m^2/g.[30]$ 



**Figure 1.3.** Synthetic procedures of MOF by a) hydrothermal/solvothermal, b) microwave-assisted method, c) sonochemical/Ultrasound synthesis, d) mechanochemical synthesis, e) and electrochemical methods.[27]

Sonochemical/Ultrasonic assisted synthesis: It is a facile costeffective method for the easy production of nano-sized MOFs using high energy ultrasound (20 kHz-15 MHz) as an environment friendly synthesis tool. This technique provides homogeneous nucleation with a high rate of heating and cooling achieved in short periods. The high-intensity ultrasound waves enhance the reactivity of metals, extensively reducing the crystallization time as compared with conventional oven heating. The high yield of microporous HKUST-1 was obtained using trimesic acid and cupric acetate in short reaction times (5-60 min) under ultrasonic irradiation in DMF/EtOH/H<sub>2</sub>O solution at ambient temperature and pressure.[31]

- Electrochemical synthesis: MOFs are prepared by this method on an industrial scale with the benefit of faster synthesis at lower temperatures utilizing metal ions instead of metal salts. Initially, HKUST-1 (CuBTC) was synthesized in a reaction occurring at a short time duration at low temperatures (50°C) by the electrochemical method.[32]
- Slow evaporation method: This energy-saving conventional method operates by the slow evaporation or diffusion of solvents/solution in the reaction system. It occurs at room temperature in the absence of external energy sources by dissolving metal salts and organic ligands in solvent systems. A facile contra-diffusion method was developed by Yao *et al.* to prepare films of ZIF-8 MOF over the nylon substrate, by crystallizing it on the surfaces of the membrane employing a solution contra-diffusion.[33]

To use the MOFs for various applications, it is mandatory to remove the guest solvent molecules trapped within the pores carefully without collapsing the structure, which is termed as *activation* of MOFs. The conventional activation method (heat and vacuum treatment) and solvent-exchange method are the most general approaches of MOFs activation depending on its chemical and thermal stability.[34,35]

# **1.4. Applications of MOFs**

Rational designing can incorporate an entire array of electrical, catalytic, structural, optical, and magnetic properties into the metal-organic frameworks. Owing to such unique characteristics, MOFs have great potential for applications in diverse areas (**Figure 1.4**). In recent years, a lot of research has been done in developing MOFs as adsorbents for  $CO_2$  capture.  $CO_2$  is the major greenhouse gas and is recognized for being a major contributor to global warming.



Figure 1.4. Representation of widespread potential applications are shown by MOFs.[17]

The most effective approach to regulate and monitor the emission of  $CO_2$  is the selective capturing and storing of  $CO_2$  at its production point in power generation plants.  $H_2$  and  $CH_4$  being alternate sources of energy face difficulty in their storage and transportation. MOFs are a potential candidate to overcome the limitation of selective gas adsorption due to their orderly defined porous framework and thermal stability as compared to other porous materials.[36] Yaghi and coworkers have synthesized a series of highly porous MOFs among which MOF-210 composed of Zn<sub>4</sub>O SBU coordinated with two types of organic linkers has BET and Langmuir

surface areas of 6240 and 10,400  $m^2g^{-1}$ , respectively, revealing an ultrahigh storage capacity of CO<sub>2</sub> as 2870 milligrams per gram (**Figure 1.5**).[37]

Farha *et al.* reported a benchmark MOF material based on copper paddlewheel (NU-100) having a surface area of 6143 m<sup>2</sup> g<sup>-1</sup> exhibiting the highest storage capacity for H<sub>2</sub> gas as 164 mg g<sup>-1</sup> at 77 K and 56 bar.[38]



**Figure 1.5.** Representation of (a,b) Crystal structure of MOF-210, (c,d) High-pressure H<sub>2</sub> isotherms and CO<sub>2</sub> isotherms of the MOFs measured at 77K and 298 K respectively.[37]

Unsaturated metal nodes of MOFs and the high surface area plays a role of active catalytic centers showing Lewis acid characteristics in catalysis reactions. Jiang *et al.* synthesized a USTC-253 MOF by adding TFA (trifluoroacetic acid) during synthesis which created defects in the structure and exposed metal centers. The catalytic activity of USTC-253-TFA MOF was analyzed in CO<sub>2</sub> cycloaddition to propylene oxide conversion at RT and 1 bar pressure revealing a high conversion (81.3%) correlating with its ideal CO<sub>2</sub> adsorption capability (**Figure 1.6**).[39]



**Figure 1.6.** Synthetic scheme of USTC-253 and defect-engineered USTC-253-TFA showing open metal sites, (b)  $CO_2$  cycloaddition for epoxide conversion into cyclic carbonate over USTC-253-TFA.[39]

MOFs have been evolved as powerful energy storage devices due to its superior cyclic stability and higher charge-discharge ability.[40-42]. Yang *et al.* reported a Ni-coordinated MOF to fabricate electrodes for supercapacitors for the first time. A high value of specific capacitance was achieved as 1127 F g<sup>-1</sup> showing a long and stable cycle-life at the current density of 0.5 A g<sup>-1</sup>.[43] In 2014, Yaghi and co-workers synthesized a series of MOFs with various pore sizes and shapes employing multiple metal ions and organic functionalities resulting in large and small nanocrystals such as MOF-5, nHKUST-1, nNi-MOF-74, nUiO-66, nMOF-177, and nMOF-867. Areal capacitances were highest in the case of zirconium MOF (nMOF-867) displaying 0.64 and 5.09 mF cm<sup>-2</sup> retaining performance after 10000 charge/discharge cycles i.e. equals to 6 times presented by an activated carbon material available commercially (**Figure 1.7**).[45]

Recently MOFs also emerged as a potential aspirant for the removal of heavy metal ions and organic contaminants from wastewater due to their tailor structural surfaces towards specific targets.[46] MOF-235 [Fe<sub>3</sub>O(BDC)<sub>3</sub>(DMF)<sub>3</sub>]·FeCl<sub>4</sub>, was reported to remove organic dyes (methylene orange and methyl blue) and UiO-67 performed for the

removal of organophosphates.[47,48] Inorganic heavy metal pollutants are more toxic as they are non-degradable which requires their direct capture by the adsorbent materials. The arsenic uptake reported by Wang *et al.* was the highest adsorption capacity of 303 mg/g reported to date exceeding that for commercial adsorbents such as activated carbon, powdered zeolite, and activated alumina.[49]



**Figure 1.7.** Schematic presentation of nMOF-867 formation and its superior supercapacitance performance in comparison to commercial materials.[45]

# **1.5.** MOFs Design: Effect of functionalization on the structural properties and applications

The ability of MOFs to be decorated with various types of functional groups including organic bridging ligands, metal ions/clusters, and empty voids inside the cavities is one of the most significant features of MOFs (**Figure 1.8**).[50] Organic functional groups are plentifully employed to synthesize FMOFs (functionalized metal-organic-frameworks). The efficiency of MOFs can be efficiently improved by adjusting their functionalization and host-guest chemistry through organic functional groups and can be applied for diverse applications. Additionally, the

physical properties of MOFs can also be influenced by the functionalization such as stability, crystallinity, flexibility, porosity, and topology. Therefore, FMOFs can be successfully pre-designed for specific applications with anticipated properties by functionalization consuming ideal organic functional groups.



Figure 1.8. Pictorial illustration of Functionalizable parts of MOFs.[50]

Organic functional groups generally employed for constructing FMOFs can be classified based on their structural and chemical features as: (i) Carbonyl-based functional groups, (ii) Nitrogen-based functional groups, (iii) Oxygen and Sulfur-based functional groups. These functional groups can further function as coordinating sites or sites for guest-interaction influencing the applicability of metal-organic frameworks and the materials derived from them in various areas (**Figure 1.9**).



**Figure 1.9.** Functionalities categorized on the basis of their structural properties and chemical characteristics.[50]

### **1.5.1.** Carbonyl-based functions

Structural frameworks of MOFs are synthesized in a significant numbers employing functionalities of carbonyl-containing groups such as amide, squaramide, oxalamide, imide, carboxyl, ketone, etc.[51,52,53] Amide group introduction in FMOFs can augment the host-guest chemistry due to strong polarizing power and electrical field. The presence of (–CO–) as acceptor site and (–NH) as donor site contributes to hydrogen bonding

interactions, and electron-rich oxygen provides Lewis basicity. Amide functionalized MOFs can perceive enhanced CO<sub>2</sub>-framework interactions escalating the adsorption capacity and selectivity for CO<sub>2</sub> molecules and does not show desirability for CH<sub>4</sub> and N<sub>2</sub> (non-polar) molecules. (Figure. **1.10 a, b).** Forgan *et al.* synthesized a Zn coordinated MOF [Zn<sub>2</sub>(L1)<sub>2</sub>(P1)] showing topology features of *pcu* net (Figure 1.10 c-e) and replaced non-functionalized ligands with ligands of amide functionality [Zn(L2)(P1)] in the synthesis (where  $H_2L2 = 4-(4$ forming carboxybezamido)benzoic acid, P1 = 4,4'-bipyridine and P2 = N-(pyridin-4-yl)-isonicotinamide).[50,54] Some dissimilarities were observed in the orientation of the SBUs of resulting structure when compared to previous one, however the overall structure and topology were retained. It is observed that heavy metal ions such as Cr<sup>3+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup> show greater affinity to amides due to its basic nature achieving the selective removal with higher efficiency.[55]



**Figure 1.10.** Probable interactions between (a) Amide-CO<sub>2</sub> interactions, (b) Amide-C<sub>2</sub>H<sub>2</sub> interactions, (c-e) Retaining of topology after amide functionalization.[50]

Squaramide functionality has higher structural rigidity, Brønsted acidity, and dual molecular recognition characters for cations and anions. squaramide is a considerable hydrogen bond accepter because of its (– CO–) functions, and strong donor of hydrogen bond due to the presence of two (–NH–) spots and can be implemented in asymmetric organocatalysis as a strong bifunctional hydrogen bonding catalyst.[56-58] The first squaramide functionalized MOF was reported by Hupp and coworkers taking a porous UiO-67 MOF derivative and incorporating the amide moiety leading to an enhancement in its catalytic activity from 38% yield to 78% yield. An extraordinary acceleration in the Friedel-Crafts reaction was observed between indole and  $\beta$ -nitrostyrene in biorelevant aspect.[59]

Carbonyl groups are strongly polarized Lewis base having a rigid structure due to the existence of dipole moment and oxygen atomcontaining high density of electrons. The introduction of carbonyl functional group enhances the rigidity of the framework due to the availability of polar sp<sup>2</sup> (-CO-) group of methylene moiety in place of sp<sup>3</sup> methylene moiety.[60] MOFs having carbonyl functionalized are generally practical for sensing of organic molecules showing colorimetric detection approach as they can efficiently interact with electron-deficient Lewis acids. Drache *et al.* reported a carbonyl decorated MOF as DUT-122, [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(fdc)<sub>6</sub>)·0.1BA·7.6H<sub>2</sub>O] containing fluorenone motif where H<sub>2</sub>fdc = 9-fluorenone-2,7-dicarboxylic acid, exhibiting fluorescent properties with colorimetric guest-response in presence of various polar and non-polar, protic, aprotic, aliphatic, and aromatic solvent vapors (**Figure 1.11 a and b**).[50,61]



**Figure 1.11.** Representation of (a) crystal structure of DUT-122, (b) showing colorimetric sensing of various polar and non-polar, protic, aprotic, aliphatic, and aromatic solvent vapors.[50]

So far, Imide function (–CO–NR–CO–) is well known to employ phenyl, naphthalene, and perylene cores to form aromatic functionalized molecules (**Figure 1.12a**). Naphthalene-diimide is conjugated planar moiety having a chemically robust, and thermally stable organization with a high melting point. Its high electron deficiency results in  $\pi$ -ion interactions,  $\pi$ -halogen interactions, and  $\pi$ - $\pi$  stacking, whereas the existence of high charge and electron transfer mobility makes it highly conductive, and electronically active site.[62] Zeng *et al.* synthesized a coordination polymer, Zn-PDI, containing PDI functionalization which revealed visible light driven selective oxidation of alcohols to carbonyls and amines to imines. Zn-PDI also efficiently reduced the aryl halides driven by visible light through the formation of C–C bonds and C–H bonds. (**Figure 1.12b**).[50,63]



**Figure 1.12.** (a) Illustration of aromatic imide functionalized cores. (b) Organized PDI arrangements in Zn-PDI for efficient photocatalyst development with the oxidation of alcohol and reduction of aryl halides in the presence of visible light.[50]

In another example, Mallick *et al.* prepared a naphthalenediimide functionalized porous MOF, Mg-NDI utilizing H<sub>4</sub>BINDI as a linker (N,N'bis(5-isophthalic acid)naphthalenediimide) displaying a color-changing response in presence of benzene substitutes and organic amines (**Figure. 1.13**).[50,64] Moreover, small size organic amines can be effectively detected by the MOF showing effective quenching in its fluorescence intensity alongside screening a change in color response. The sensing behavior is justified due to the formation of charge-transfer complex between NDI moieties within the framework and electron-rich organic amines. Molecules showing color change response. (**a**) Mg-NDI showing Solvatochromic behavior, (**b**) Color changing image of Mg-NDI by adding different aromatic-substitutes.[64]



Figure 1.13. Application of imide functionalized Mg-NDI to detect guest.[50]

#### 1.5.2. Nitrogen-based functions

Numerous FMOFs are constructed by consuming nitrogen-containing functional groups which can be categorized as: i) heterocyclic azine, heterocyclic-azole, (iii) ionic, and (iv) noncyclic moieties considering the chemical properties and functional configuration:

Heterocyclic azine N-based functions involve pyridine, diazines, tetrazine (1,2,4,5-tetrazine), triazine, etc. Heterocyclic azines containing a low number of nitrogen atoms perform as coordinating sites whereas high nitrogen azine members generally act as guest-interactive sites due to high electron deficiency in the ring for example triazine and tetrazine (**Figure 1.14**).[50,65]



Figure 1.14. Heterocyclic azine N-based functions are compared based on their basicity.[50]

Pyridine functionalized MOFs act as Lewis base for applications in  $CO_2$  and  $C_2H_2$  molecules storage and selective capturing of  $CO_2$  and  $C_2H_2$ gases showing less affinity for N<sub>2</sub> and CH<sub>4</sub> molecules. Binding energy and electron density on nitrogen atoms are proportional to each other which decides the  $CO_2(C)$ ...(N) heterocyclic interactions. [66] Functionalized MOFs with triazine moiety have been conveniently utilized to adsorb and separate light hydrocarbons in the mixture of benzene/cyclohexane molecules. Huang et al. synthesized triazine decorated porous FJU-C1 MOF which displayed great adsorption behavior towards polar solvent vapors like water, ethanol, and methanol while presenting low affinity for nonpolar molecules. Benzene was efficiently adsorbed and separated selectively employing FJU-C1 MOF from cyclohexane due to the presence of  $\pi$  deficient- $\pi$  rich interactions among the s-triazine rings of MOF and benzene molecules.[67] On the other hand, nitrogen-rich tetrazine functionalized MOFs are  $\pi$ -rich frameworks that have a good affinity for non-polar gases such as CH<sub>4</sub> and H<sub>2</sub> gases showing their effective adsorption.

N-based functions having non-cyclic structures contain imine, amine, azide, azine, and functions.[68,69] azo Amine functionalized MOFs are well known for applications in diverse areas like gas storage and separation, sensing, removal of contaminants, catalysis and photocatalysis, drug delivery, and electrochemistry. Amine functionalization in MOFs makes it beneficial due to its polar nature with the ability to form hydrogen bond interactions and behaving as Lewis basic or Brønsted acid through N atom. Amine based FMOFs are reported to form structures providing high affinity for CO<sub>2</sub> through interactions between  $CO_2(O)\cdots(H)$  amine and  $CO_2(C)\cdots(N)$  amine.

Electrochemical properties of the porous electrode materials are reported to be well augmented through the incorporation of polar amine groups by inducing the hydrophilicity in the system which in result improves the interaction of electrode with the electrolyte. An innovative supercapattery device was reported by Li *et al.* prepared from an aminefunctionalized MOF taking activated carbon (AC/NF) and NH<sub>2</sub>-Co-MOF-NS/NF as the negative electrode and positive electrode respectively. A great value of energy density and power density was attained as 0.351 mW h cm<sup>-2</sup> and 1.70 mW cm<sup>-2</sup> respectively by the system showing a maximum value of 6.7 C cm<sup>-2</sup> (1861  $\mu$ A h cm<sup>-2</sup>) as areal specific capacitance. Outstanding stability of cycles was achieved retaining capacitance of 91.8% after uninterrupted 5000 cycles of charge-discharge process (**Figure 1.15**).[71]



**Figure 1.15.** (a) Representation of supercapattery device prepared from aminefunctionalized MOF, (b) Comparison of supercapacitance performance of Co-MOF-MP/NF and, NH<sub>2</sub>-Co-MOF-NS/NF.[71]

In another example DeMello *et al.* have reported that functionalization of MOF UiO-66 by  $-NH_2$  group can induce its sensing ability for NO<sub>2</sub>, CO<sub>2</sub>, and SO<sub>2</sub>. The electronic properties of MOFs can be revised by the interactions between  $-NH_2$  groups of linker and gas molecules such as a charge transfer complex can be formed between high grade acidic SO<sub>2</sub> gas and  $-NH_2$  functionality (**Figure 1.16**).[70]



**Figure 1.16.** Presenting the variation in the organic linker of UiO-66 MOF for sensing of acidic gases via a change in chemical properties.[70]

Similarly, azo functionalized MOF, PCN-123 reported by Park *et al.* exhibited instant trapping and discharging of CO<sub>2</sub> gas driven by light

(Figure 1.17).[72] CO<sub>2</sub> capacity was observed to be decreased immediately by 26.6% after exposure to light radiation, however, decrement in capacity is 53.9% when exposed to UV light for 5 h continuously which can be recovered fully after the sample is heated at for 20 h 60 °C. The change in the capacity of adsorption is due to the presence of azobenzene groups located inside the framework chain undergoing *trans–cis* photo-isomerization.



**Figure 1.17.** Schematic illustration of of UV rays triggered isomerization of the azobenzene groups from trans-to-cis form and heat-induced cis-to-trans isomerization. Representation of change in adsorption of  $CO_2$  molecules in the framework of MOF-5, structure of PC.[50]

#### **1.5.3.** Oxygen and Sulfur-based functions

Functional groups confined within this group involves hydroxy, ether, azoxy, enoxide, oxopyridine functions etc. They are significant due to the presence of oxygen atoms having electron-rich nature and high polarity. MOF cavities decorated with an uncoordinated hydroxyl group (–OH) can enhance its affinity unexpectedly toward CO<sub>2</sub> analogous to amine (–NH<sub>2</sub>) function. Yang *et al.* reported a hydroxyl-containing framework, NOTT-300 ([Al<sub>2</sub>(OH)<sub>2</sub>(L1)](H<sub>2</sub>O)<sub>6</sub>) for the efficient removal of harmful SO<sub>2</sub> and CO<sub>2</sub> gases [73]. PCN-222 MOF prepared by Zhao *et al.* was employed for

waste-water treatment by efficient elimination of chloramphenicol drug from wastewater. The structure of PCN-222 with special pore design form electrostatic interactions and hydrogen bond with the drug displaying its large uptake of  $370 \text{ mg.g}^{-1}$  in 58 s.[74]

MOFs having Ether functionality in the main or side chain are significantly flexible and prepares a platform for breathing MOFs. The C-O-C motif confirms the free rotation which enhances the flexibility of the framework. Breathing MOFs structure can reversibly undergo structural transformations providing adsorption and desorption of guest molecules upon a change in temperature or pressure.  $CO_2$  gas can enter easily through the molecular gate whereas due to the polar nature of the ether chains.

MOFs functionalized with Sulfonate ( $-SO_3^-$ )/sulfonic acid ( $-SO_3H$ ) is reported to have a platform for proton conductivity due to its strong Brønsted acid character and show catalytic activity in acidcatalyzed reactions.[75] Phang *et al.* reported a highly conductive sulfonate functionalized UiO-66 framework with a cooperative hydrophilic and acidic character displaying the maximum value for conductivity as  $0.34 \times 10^{-2}$  S.cm<sup>-1</sup> at 97% room humidity and 303 K temperature. E<sub>a</sub> value was found to be 0.27 eV.[76] Phang *et al.* reported an example where the framework MIL-101-SO<sub>3</sub>H worked as photocatalyst for the catalysis of esterification reaction (**Figure 1.18**).[50,78] Possibility of variations in coordination modes of sulfonate permit polymorphism leading to poor quality crystallinity in sulfonate functions.



**Figure 1.18.** MIL-101-SO<sub>3</sub>H is employed for light-enhanced acid-catalytic reaction assisting the protons releasing action through the transfer of electrons from –SO<sub>3</sub> clusters to Cr-oxo groups.[50]

#### 1.5.4. Post-synthetic modification of MOFs:

The post-synthetic modification approach of MOF functionalization is particularly practiced to form targeted MOF units, which cannot be produced by direct synthesis methods. The typical post-synthetic modification can be achieved by incorporating the new metal ions, polymers, or carbon nanomaterials into the pores of MOFs by Insitu approach or by physical mixing with MOFs under hydrothermal technique or microwave-induced synthesis (**Figure 1.19**).[79]



**Figure 1.19.** Schematic representation of GO-incorporated MOFs formation through solvothermal method reported by Wang *et al.*[79]

This can enhance the complexity of the MOFs framework by inducing the redox-active sites further tuning the physical and chemical properties of MOFs for the targeted applications. Analysis of such MOFs hybrid system is done by transmission electron microscopy (TEM). In 2012 Zhu and coworkers modified Fe<sub>3</sub>O<sub>4</sub> microspheres by thioglycolic acid and further submerged it into a copper acetate and benzene- 1,3,5tricarboxylic acid (H<sub>3</sub>BTC) solution at 25 °C under solvothermal conditions. Core-shell structured microspheres were obtained with significantly increased pore volume which was further used for targeted drug delivery application (**Figure 1.20**).[80] In another example, Li *et al.* reported HKUST-1 MOF synthesis in a setup containing palladium nanoparticles in the solution. The prepared composite displayed a huge hydrogen gas absorption as 74% greater in comparison to bare palladium nanoparticles.[81]



**Figure 1.20.** (a) Synthesis of Fe<sub>3</sub>O<sub>4</sub> microspheres surrounded by the Porous MOF shell, (b)TEM image of core shell microspheres [Fe@[Cu<sub>3</sub>(btc)<sub>2</sub>].[80]

Conducting polymers (CPs) like polyethylene dioxythiophene (PEDOT), polyaniline (PANI), and polypyrrole (Ppy) intercalation with

MOFs are reported to enhance the electrochemical properties of pristine MOFs.[82,83] Hybridizing existing parent MOFs with some external constituents gives rise to new combinations having characteristics analogous to both the accompanying parent materials. An approach proposed by Wang *et al.* involves the interweaving of the MOF crystals by conductive chains of PANI to increase the electrochemical properties of MOF.[84] The attained hybrid was further deposited on carbon cloth fibers and utilized for the fabrication of electrodes to develop a solid-state flexible supercapacitor device. A terrifically high value of areal capacitance was offered by the designed setup as 2146 mF cm<sup>-2</sup> at a scan rate of 10 mV/s. The initial capacitance was retained upto 80% of the initial value after 2000 cycles (**Figure 1.21**).



**Figure 1.21.** (a) Representation of flexible solid-state device prepared from PANI-ZIF-67-CC. (b–d) Normal, bent, and twisted state presentation of the fabricated device. (e) Three SCs connected in series to power red light-emitting-diode (LED).[84]

Bhattacharjee *et al.* reported porous and stable MOFs showing phosphorescence property were constructed from dicarboxylate ligands and  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(carboxylate)_{12}$  as secondary building units. Functionalization of the framework with platinum nanoparticles through K<sub>2</sub>PtCl<sub>4</sub> photooxidation were further used as a photocatalyst system displaying five times more efficient than their analogous systems and high recyclability.[85]

## **1.6. Scope of Present Work**

The aforementioned work discusses the design and synthesis of various functionalized MOFs at ambient conditions further exploring their structural features and applications in catalysis, sensing, energy storage, and solid-state structural reactivity. Moreover, an imidazole functionalized ligand has also been synthesized as a fluorescent chemosensor for metal ions sensing and bio-imaging. The motivation is to investigate the perspectives of developing new MOFs based on various functional groups for the achievement of desired properties and significant results. The focal points of thesis work are as follow-

- 1. Synthesis of a Lactam-functionalized porous MOF and exploring its catalytic activity for the chemical fixation of CO<sub>2</sub> to cyclic carbonates in an economically viable way.
- 2. Utilization of the prepared Cu-MOF with graphene oxide nanosheets as an efficient adsorbent for the removal of MB dye in aqueous systems and a selective electrochemical sensor.
- 3. Synthesis of a novel amino-functionalized MOF having layered porous channels and exploration of its energy storage applications by preparing the hybrid through the incorporation of CNTs.
- 4. Exploration of solid-state structural reactivity with the phenomenon of Single-Crystal-to-Single-Crystal transformations in new Triazole-functionalized MOFs, obtaining novel topology.
- 5. Preparation of a new imidazole derivative based ligand as a fluorescent receptor for sensing of metal ions and bio-imaging.

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# Chapter 2

# Catalytic CO<sub>2</sub> Fixation over a Robust Lactam-Functionalized Cu(II) Metal-Organic Framework

## **2.1. Introduction**

The excessive use of fossil fuels as a primary source of energy releases huge quantities of carbon dioxide (CO<sub>2</sub>) *i.e.* leading greenhouse gases.[1] Thus, capturing and conversion of CO<sub>2</sub> into some non-toxic, abundant, renewable, and economically viable valuable chemical products is the need for an hour.[2-6] In this regard, the catalytic conversion of CO<sub>2</sub> into the synthesis of five-membered cyclic carbonates is considered to be an alternative and potential CO<sub>2</sub> utilization process.[7-9] These cyclic carbonates may be used as (i) solvents, (ii) well-known intermediates in the synthesis of ethylene glycol and acyclic carbonates, (iii) precursors for pharmaceutical products, (iv) electrolyte in batteries, and (v) as a raw material for cosmetics.[9-14] The synthesis of five-membered cyclic carbonates through CO<sub>2</sub> fixation with epoxides have been extensively effective with several homo- and heterogeneous catalysts.[15-18] However, in the case of homogeneous catalysts, product separation is generally tedious and catalyst recycling is expensive, is the real concern. Considerably, these concerns have been deal to a greater extent by utilizing the heterogeneous catalysts such as coordination complexes, zeolites, metal oxides, and functional polymers, which demonstrates lower activity in vast circumstances or leaching.[19-23] Such lower activity has been overcome by utilizing a new and innovative class of porous materials *i.e.* Metal-organic frameworks (MOFs), which might be ultimate catalysts in a heterogeneous system.[23-27]

MOFs are an architect of nanoporous organic-inorganic hybrid materials with organic linkers are connected to metal ions/clusters.[28] The framework when design and tuned appropriately shows the following properties (i) Chemical and thermal stability, (ii) functional pore with high surface area, and (iii) permanent porosity which leads to various potential applications such as energy storage, heterogeneous catalysis, fluorescence sensing, ferroelectricity, drug delivery, gas storage and separation etc.[29-34] In particular, MOFs advocate the unique opportunity as heterogeneous catalysts based on following rationales: (i) presence of functionalized pores for the substrates selectivity, (ii) presence of clear and uniformly distributed metal centers as active catalytic sites, and (iii) recovery and reusability due to its heterogeneous nature.[24,35,26] MOFs with large pore volume, nitrogen base functionalized channels, thermal stability, and exposed unsaturated metal centers (UMCs) is a good choice for chemical fixation of CO<sub>2</sub> to value-added chemicals such as cyclic carbonates, urea derivatives, and formic acid.[37-39]

Currently, various MOFs exhibited excellent CO<sub>2</sub> catalytic conversion under high temperatures and some MOFs demonstrated moderate CO<sub>2</sub> catalytic conversion at room temperature throughout 48 h.[24,40-42] In terms of industrial scale-up of CO<sub>2</sub> conversion into cyclic carbonates, which is a ubiquitous intermediate in pharmaceutical and electrochemical industries produced by extremely toxic phosgene gas hydrolysis, an unconventional atom economic and environmentally benign route is anticipated.[43-47] In this regards, recently, various MOFs have been efficiently employed as reusable heterogeneous catalysts for the conversion of CO<sub>2</sub> into cyclic carbonates.[40,48,49] The development of efficient and facile synthesized MOF as a catalyst will be an ideal choice for easy and economically viable workup procedures.[50,51] Pioneering experimental results proved that a Lewis acid–base sites consisting binary catalytic system with a leaving halide anion synergistically supports the  $CO_2$  cycloaddition to epoxide.[26] Moreover, the MOF functionalized with nitrogen bases and other polar functional groups improve the selectivity as well as the affinity of  $CO_2$  molecule towards the catalysts.[25,52].

Keeping all these features in mind we have facilely synthesized the lactam functionalized, porous 3D **Cu-MOF** which displays an excellent thermal and chemical stability. Further, activation of **Cu-MOF** to **Cu-MOF'** reveals the presence of both accessible lactam group and exposed Cu sites which makes **Cu-MOF'** a potential candidate for  $CO_2$  fixation under milder conditions. This work not only offers an excellent heterogeneous catalytic activity for  $CO_2$  fixation but also provides a structural–catalytic relationship which is an ingenious strategy for building functionalized MOFs.

#### 2.2. Results and discussion

The **Cu-MOF** is synthesized in a facile manner by employing rigid lactam functionalized ditopic ligand (H<sub>2</sub>L) and Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O at room temperature under slow evaporation condition {H<sub>2</sub>L=(5-(1-oxo-2,3dihydro-1H-inden-2-yl)isophthalic acid)} (**Scheme 2.1**). The earlier report shows its synthesis through the solvothermal condition and reports only its structural description.[55] Compared to that, here a cost-effective synthetic protocol has been applied. The synthesized **Cu-MOF** has been characterized by SCXRD, PXRD, FT-IR and SEM techniques. The stability of **Cu-MOF** in common organic solvents and air was further authenticated by recording unit cell parameters by employing singlecrystal X-ray diffraction studies and no changes were observed which was also validated by elemental analysis.



Scheme 2.1. Schematic synthesis of Cu-MOF.

#### 2.2.1. Structural aspects of Cu-MOF

The single-crystal X-ray diffraction study shows that **Cu-MOF** is crystallized in the trigonal crystal system with R-3 space group (Table A1). One unit each of H<sub>2</sub>L, Cu(II) ion, and coordinated DMF molecule (Figure 2.1a) are present in the asymmetric unit of Cu-MOF where distorted square pyramidal geometry is exhibited by the Cu(II) ion with four different carboxylate linkers provide four O atoms [Cu···O: 1.922(4)Å – 2.110(7)Å] and the fifth O atom originates from the DMF molecule [Cu···O: 1.922(4)Å]. The extension of this asymmetric unit results in the formation of a framework consisting of  $\{ [Cu_2(CO_2)_4] \cdot 2DMF \}$  secondary building units (SBUs) of paddle-wheel shape (Figures 2.1b). Further, a  $\pi - \pi$  stacking interaction is observed between the two adjacent linkers and act as tetra-carboxylate moieties *i.e.* pseudo-tetracarboxylate linkers. A closer view shows the connection of three isophthalate units of the pseudotetra-carboxylate linker by three SBUs with the creation of a triangular-shaped window. Three pseudo-tetracarboxylic linkers are further connected to two such windows in a staggered fashion leading to a Cu<sub>6</sub>(CO<sub>2</sub>)<sub>12</sub> polyhedra based secondary building blocks (SBBs) (Figure 2.1c). This polyhedral is present with spherical cages having an internal diameter of approximately 12.061(1) Å<sup>2</sup> (distance denotes Cu-to-Cu linking, and discounting the DMF coordinated), that can be accessed through its square and triangular faces (Figure 2.1d). Six SBBs are interconnected in the packing structures of **Cu-MOF** along the crystallographic *c*-axis. This results in the formation of a supramolecular 3D framework (Figure 2.2a). This complete framework possesses uniform one-dimensional channels of 10.956(0) Å, in

diameter (**Figure 2.2b**), which is occupied by disordered solvent molecules. These lattices as well as coordinated solvent molecules were treated by SQUEEZE refinement of PLATON<sup>54</sup> to check the effective solvent-accessible void volume, which was found to be ~40% (Å<sup>3</sup>) per unit cell. In **Cu-MOF'**, the lactam decorated and metal exposed channels may offer supplementary pathways for CO<sub>2</sub> insertion, and suitable for heterogeneous catalytic CO<sub>2</sub> fixation.



**Figure 2.1.** Representation of (a) asymmetric unit of **Cu-MOF**, (b) pseudotetracarboxylate linker based SBUs containing Cu(II) ion; hydrogen atoms are omitted for clarity, (c) supramolecular building block (SBB), (d) internal spherical cage in the SBB.



**Figure 2.2.** (a) View showing the lactam decorated cages, and (b) Space-filled view of the 1D channels in the framework.

#### 2.2.2. Characterization of the bulk Cu-MOF

Figure 2.3 shows the SEM images of the Cu-MOF at different magnification (100  $\mu$ m, 30  $\mu$ m, and 20  $\mu$ m) and confirming its block-shaped morphology.



Figure 2.3. SEM images of the Cu-MOF at different magnifications.

The intense peaks of the as-synthesized sample obtained in the powder Xray diffraction (PXRD) method well matches with the simulated pattern obtained from single-crystal X-ray diffraction, confirming the phase purity for the bulk sample of **Cu-MOF** (**Figure 2.4a**). Also, the PXRD patterns of the as-synthesized, acetone exchanged, and activated samples are wellmatched, confirming the framework of integrity towards the process of solvent exchange and activation (**Figure 2.4b**). Further, the thermal stability of the as-synthesized **Cu-MOF** and acetone exchanged samples are verified by variable temperature powder X-ray diffraction (VTPXRD) measurements (**Figure 2.5**).



**Figure 2.4.** Powder X-ray diffraction patterns (a) of simulated (Black) and as-synthesized (Red) of MOF1, (b) after solvent exchange and activation of **Cu-MOF**.



**Figure 2.5.** Variable temperature powder X-ray diffraction (VTPXRD) measurements of (a) as-synthesized **Cu-MOF** and (b) acetone exchanged samples.

#### 2.2.3. Gas adsorption and Catalytic CO<sub>2</sub> Fixation

First, we activated the acetone-exchanged **Cu-MOF** followed by heating at 150 °C under a high vacuum for 8 h to yield the fully activated Cu-MOF'. The porosity of Cu-MOF' has been established at 1 bar pressure and 77 K temperature by nitrogen adsorption (Figure 2.6a). The  $N_2$ adsorption isotherm exhibited maximum  $N_2$  uptake of 65.37 cm<sup>3</sup> g<sup>-1</sup>. We have further checked the adsorption studies for the CO<sub>2</sub> at 1 bar pressure and 195 K as well as 298 K. As shown in, the CO<sub>2</sub> adsorption isotherms exhibited its maximum uptake 34.14 cm<sup>3</sup> g<sup>-1</sup> at 298 K and 108.22 cm<sup>3</sup> g<sup>-1</sup> at 195 K. The adsorption studies of  $CO_2$  and  $N_2$  at 298 K were also compared and it was observed that CO<sub>2</sub> adsorption isotherm presented type 1 behavior illuminating its microporous assembly with saturation adsorption of 34.14 cm<sup>3</sup> g<sup>-1</sup> (6.71 wt %) whereas  $N_2$  adsorption isotherm displays its maximum uptake of 4.64 cm<sup>3</sup> g<sup>-1</sup> (0.29 wt %) (Figure 2.6b). The above results confirm the good selectivity of CO<sub>2</sub> over the N<sub>2</sub> adsorption for Cu-MOF'. Further, the pore size distribution analysis demonstrates (Figure 2.7) that pores are of an average diameter of 11.32 Å, are in good accordance with the measured pore size.



**Figure 2.6.** (a) Gas adsorption isotherm of **Cu-MOF'**: CO<sub>2</sub> at 195 K and 298 K temperature, N<sub>2</sub> at 77 K temperature, and 1 atm pressure. (b) Selectivity graph of **Cu-MOF'**: CO<sub>2</sub> and N<sub>2</sub> at 298 K and 1 atm pressure.



Figure 2.7. Pore-size distribution calculated from the isotherms.

The selective CO<sub>2</sub> adsorption, large pore volume with lactam functionalized channels, good thermal stability, and the exposed Cu(II) sites in the activated framework encouraged us to examine its catalytic activity for chemical fixation of CO<sub>2</sub> to cyclic carbonates. The present study is concerned with the cycloaddition reaction of CO<sub>2</sub> with epoxides (20 mmol) by using activated **Cu-MOF'** (5 wt%) as a catalyst along with tetra butyl ammonium bromide (TBAB) (1 mmol) as a co-catalyst at 30 °C and 70 °C (based on the boiling point of the epoxides) for 10h (**Scheme 2.2**).



Scheme 2.2. Cycloaddition reaction of CO<sub>2</sub> with epoxides catalyzed by Cu-MOF'.

The cycloaddition reaction of  $CO_2$  with styrene oxide (E1) as a model substrate was examined in presence of **Cu-MOF'** and TBAB at 70 °C for 10h, afforded the 92% product conversion (**Table 1**, entry 1), as confirmed by the <sup>1</sup>H NMR (**Section 2.6, Figure 2.19**). Further, we optimized the reaction condition on the influence of reaction time, catalysts, and cocatalysts amount. First, we carried out the reaction at the above condition for 15h and found that maximum conversion was achieved after 10h. Once we got the reaction time, we examined several reactions at different catalyst and co-catalyst loading, found that the optimum conversion was obtained at 5 wt% of catalyst and 1 mmol of co-catalyst (**Figure 2.8**) (**Section 2.6, Figure 2.20-2.22**). Also, to study the effect of other halides, we performed the optimized reaction with Tetrabutylammonium chloride (TBAC) (1 mmol) and Tetrabutylammonium iodide (TBAI) (1 mmol) (Table 1, entry) and found that TBAB exhibited good conversion relative to others (**section 2.6, Figure 2.23**).



**Figure 2.8.** Showing the optimized (a) reaction time in h, (b) catalyst loading in wt %, and (c), TBAB loading in mmol.

To extend the synthetic scope of the CO<sub>2</sub> fixation for cyclic carbonates syntheses, a variety of epoxides (**Figure 2.9**) viz. glycidyl phenyl ether (**E2**), benzyl glycidyl ether (**E3**), 1,2-butylene oxide (**E4**), and 1,2-epoxy hexane (**E5**) were used under the same reaction conditions as for model reaction, except a slight change in temperatures from 30 °C for **E3** and **E4** and 70 °C for **E2** and **E5**. The evaluation of corresponding products conversion was achieved from the <sup>1</sup>H NMR spectra by the integration of epoxide versus cyclic carbonate peaks (**section 2.7, Figures Figure 2.24–2.27**) and found that 79%, 86%, >99%, and >99% conversion was observed for **E2**, **E3**, **E4**, and **E5**, respectively (**Table 2.1**, entries 4, 7, 10 and 13). Interestingly, as the molecular sizes of epoxide substrates increases, a steady decrease in the conversion of cyclic carbonates was

observed, possibly due to the lower diffusion into the  $Cu_6(CO_2)_{12}$  polyhedral cages of **Cu-MOF'**.[59,60]



Figure 2.9. Various epoxides are used in the CO<sub>2</sub> cycloaddition reaction.

Furthermore, in absence of catalyst, no conversion was observed in model reaction (**Table 2.1**, entry 16), while utilization of **Cu-MOF'** catalyst and TBAB co-catalyst independently resulted in a 23% and 8% conversion (**Table 2.1**, entries 2 and 3), respectively (**section 2.6, Figure 2.28**). Further, this controlled experiments were performed with other epoxy compounds (**Table 2.1**, entries 5, 6, 8, 9, 11, 12, 14 and 15) suggested that the presence of both the **Cu-MOF'** catalyst and TBAB co-catalyst are essentially required for the conversion of epoxide to cyclic carbonate, where TBAB is acting as a nucleophile and facilitates the epoxides ring opening.<sup>61, 62</sup> Conversion of epoxides into corresponding cyclic carbonate in each case were evaluated by <sup>1</sup>H NMR (**section 2.6, Figures 2.29–2.32**).

S. No.	Epoxide	Catalyst	Temp (°C)	Time (h)	Conversion (%) <sup>b</sup>
1		Cu-MOF'+TBAB			92
2	<b>E</b> 1	Cu-MOF'	70	10	23
3		TBAB			8
4		Cu-MOF'+TBAB			79
5	E2	Cu-MOF'	70	10	15

Table 2.1. Cycloaddition of CO<sub>2</sub> and Various Epoxides

6		TBAB			6
7		Cu-MOF'+TBAB			86
8	E3	Cu-MOF'	30	10	21
9		TBAB			7
10		Cu-MOF'+TBAB			>99
11	E4	Cu-MOF'	30	10	36
12		TBAB			13
13		Cu-MOF'+TBAB			>99
14	E5	Cu-MOF'	70	10	26
15		TBAB			15
16	E1		70	10	0
17	E1	TBAI	70	10	35
18	E1	TBAC	70	10	55

(**reaction conditions:** epoxide (20 mmol), catalyst (5 wt%), TBAB (1 mmol). <sup>b</sup>Conversion was evaluated from the <sup>1</sup>H NMR spectra by the integration of epoxide versus cyclic carbonate peaks.)

To check the recyclability of the **Cu-MOF'** catalyst, the model reaction mixture was filtered after the completion of the reaction, to isolate the catalyst which was further washed with chloroform and acetone (3 mL and five times by each) and dried at 150 °C under high vacuum to regain the active catalyst. Further, the recyclability experiments were checked by utilizing the regenerated catalyst in the subsequent run and found that the catalytic activity is similar for each run until four consecutive cycles (**Figure 2.10a**). The PXRD patterns of the catalyst after each catalytic

cycle is shown in **Figure 2.10b**, which displayed that the framework integrity is maintained after four catalytic cycles. Furthermore, the heterogeneous nature of the **Cu-MOF'** was examined by the hot filtration experiment, where the model reaction mixture was filtered after 2h to separate out the catalyst. Subsequently, only a slight increment in the conversion of styrene oxide was observed, suggested that the true heterogeneous nature (**Figure 2.11**). Also, ICP-MS analysis (**Table 2.2**) of the filtrate after the fourth cycle (0.45 ppm) ruled out the possibility of leaching of Cu(II) ions from **Cu-MOF'** into solution, further confirming the heterogeneous nature of **Cu-MOF**.



**Figure 2.10.** Recycling test of **Cu-MOF'** (a) for successive cycles of cycloaddition of  $CO_2$  with styrene oxide, and (b) PXRD of **Cu-MOF** after each cycle.



**Figure 2.11.** Showing the hot-filtration experiment, confirming the heterogeneous nature of **Cu-MOF**.

Table 2.2. ICP-MS	data for Cu-N	<b>IOF</b> catalyst after 4	4 catalytic cycles
		2	2 2

Catalyst	ICP-MS (ppm)
Cu-MOF	0.45

Finally, a circumstantial table has been introduced to compare the catalytic CO<sub>2</sub> fixation of **Cu-MOF'** with various MOFs (**Table 2.3**) exhibiting the excellent or comparable catalytic activity of **Cu-MOF'**. Here, we are comparing the catalytic conversion of the styrene oxide (E1) and butylene oxide (E4) as well as the reaction conditions and time. The percent conversion value is higher or comparable to these MOFs, such as MOF-Zn-1 (E1; 54%),[25] (E1; 51.3%),[26] Cu-MOF (E1; 69%),[40] Ba-MOF (E1; 19.8%),[41] WM-MOF (E1; 99%),[48] VPI-100-Ni (E4; 50%),[49] [Co(tp)(bpy)] (E1; 95.02%),[63] MOF1 (E1; 80.8%),[64] InDCPN-Cl (E1; 86%)[65] and TMOF-1 (E1; >99%) measured at different temperature and pressures. The excellent catalytic activity of **Cu-MOF'** towards CO<sub>2</sub>

cycloaddition with epoxides, elucidates its believability as a promising candidate for  $CO_2$  fixation under mild conditions.

# 2.2.4. Proposed mechanism for cycloaddition of CO<sub>2</sub> with epoxide catalyzed by Cu-MOF

Based on the earlier reports, we found that a binary catalytic system *i.e.* Lewis acid catalyst and a nucleophilic cocatalyst (TBAB) is usually engaged in effective cycloaddition reaction of CO<sub>2</sub> with epoxides.[62] Here, the **Cu-MOF'** with unsaturated Lewis acidic Cu(II) centers and TBAB act as a binary catalytic system. The proposed catalytic mechanism of CO<sub>2</sub> cycloaddition with epoxides is shown in **scheme 2.3**, where the epoxide oxygen is coordinated with unsaturated Lewis acidic Cu(II) center. Further, the Br<sup>-</sup> anion of TBAB attack as a nucleophile which leads to the epoxide ring opening to form metal coordinated Bromo-alkoxide, which is a rate-determining step considerably.[41,67] Subsequently, CO<sub>2</sub> insertion takes place between metal alkoxide and forming a metal carbonate species which further leads to cyclic carbonate undergoing an intramolecular ring closure. The metal center eliminates the cyclic carbonate which regenerates the active catalyst and makes the catalytic cycle reversible.

S. No.	MOF (M)	Linker	Epoxi de	Temp (°C) / Pressure (bar)	Time (h)	Conversion (%) / Yield (%)	Ref.
1	[L <sub>Cu</sub> ] (Cu)	2'-amino-1,1':4',1"- terphenyl-3,3",5,5"- tetracarbox-ylic acid	E1	120 / 20	12	50 /	24
2	[MOF- Zn-1] (Zn)	2,5- thiophenedicarboxyli c acid	E1	80 / 3	3	/ 54	25
3	[1] (Zn)	Tricarboxytriphenyl amine + 1,3-	E1	80 / 1	4	51.3 /	26

**Table 2.3.** Comparison of catalytic performance with MOFs as heterogeneous catalytic materials towards cycloaddition of  $CO_2$  with epoxides.

		bis(imidazol-1- ylmethyl)benzene					
4	[Cu- MOF] (Cu)	H4DAIA	E1	100 / 1	4	69 /	40
5	[Ba- MOF] (Ba)	N,N'-bis(isophthalic acid)-oxalamide	E1	30 / 48	48	19.8 /	41
6	[WM- MOF] (Zr)	nickel-tetrakis(4- carboxyphenyl)- porphyrin	E1	60 / 30	30	99 /	48
7	[VPI-100- Cu] (Zr)	6,13-Dicarboxy- 1,4,8,11- tetraazacyclotetradec ane)- copper(II) Perchlorate	E4	90 / 10	6	60 /	49
8	[VPI-100- Ni] (Zr)	6,13-Dicarboxy- 1,4,8,11- tetraazacyclotetradec ane)- nickel(II) Perchlorate	E4	60 / 10	6	50 /	49
9	[Co(tp)(b py)] (Co)	Terephthalic acid + 4, 4'-bipyridine	E1	100 / 1(MPa)	7	95.02 / 93.12	63
10	[MOF1] (Co)	1,2,4,5-Tetrakis(4- carboxyphenyl)benze ne)	E1	80 / 0.1 (MPa)	9	80.8 /	64
11	[InDCPN- Cl] (In)	5-(3',5'- dicarboxylphenyl)nic otinic	E1	80 / 1	24	86 /	65
12	[TMOF- 1] (Cu)	Disodium 1,2- ethanedisulfonate + 4,4'-bipyridine	E4	RT / 1		/ >99	66
13	[Cu- MOF] (Cu)	5-(1-oxo-2,3- dihydro-1H-inden-2- yl)isophthalic acid	E1	70 / 1	10	92 /	This work
14	[ <b>Cu-</b> MOF] (Cu)	5-(1-oxo-2,3- dihydro-1H-inden-2- yl)isophthalic acid	E4	70 / 1	10	>99 /	This work



Scheme 2.3. The proposed reaction mechanism for the cycloaddition of  $CO_2$  with epoxides catalyzed by **Cu-MOF'**.

### **2.3.** Conclusions

In summary, we report the facile synthesis of a lactam functionalized Cu(II) ion based porous 3D metal-organic frameworks, **Cu-MOF**. The framework possesses 1D lactam decorated channels along with exposed Cu (II) metal centers after activation of **Cu-MOF**. The synergistic effect of lactam decorated pores with open metal sites was studied towards the cycloaddition reaction of  $CO_2$  with epoxides. Further, the activated **Cu-MOF'** exhibits fascinating solvent-free heterogeneous catalytic conversion of  $CO_2$  to cyclic carbonates in at atmospheric pressure of  $CO_2$ , under mild conditions with good recyclability and reusability. This work demonstrates the new possibilities for designing of Lewis acids/bases incorporating MOFs for efficient conversion of  $CO_2$  into cyclic carbonates in a more economically viable way.

#### **2.4.** Experimental Section

**2.4.1. Materials:** All the reagents employed were commercially available and used as provided without further purification. Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (98%), 5-Aminoisophthalic acid, and 2-(bromomethyl)benzonitrile were obtained from Sigma Aldrich and used as received. Other chemicals *i.e.* HCl, KOH, K<sub>2</sub>CO<sub>3</sub>, SOCl<sub>2</sub>, and solvents were procured from Loba Chemie and S. D. fine Chemicals (India). All solvents were dried and purified before the use of standard methods.

2.4.2. Synthesis of diethyl 5-((2-cyanobenzyl)amino)isophthalate : In an N<sub>2</sub> atmosphere, 5-Aminoisophthalic acid diethyl ester (2 g, 8.4 mmol) was taken in a round-bottom flask and added dry acetonitrile (100 mL) and dry K<sub>2</sub>CO<sub>3</sub> (1.7 g, 12.6 mmol) were mixed in a round-bottom flask under an inert atmosphere, and the mixture was stirred for 30 min at 80 °C. The mixture was treated with 2-(bromomethyl)benzonitrile (1.65 g, 8.4 mmol), and the resulting solution was refluxed for 24 h. At the end of this period, it was allowed to cool to room temperature and poured in ice-cold water (75 mL) to obtain a white solid that was collected by filtration and dried in air. Yield: 2.7g (91%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C, Me<sub>4</sub>Si):  $\delta =$ 8.8003(s, 2H, Ar-H), 8.4001 (s, 1H, N-H), 7.6911 (d, 1H, J = 6.88 Hz, Ar-H), 7.5380 - 7.4605 (m, 4H, Ar-H), 4.9692 (s, 2H), 4.4153 (q, 4H, J = 7.18 Hz, -CH<sub>2</sub>-), 1.4148 (t, 6H, J = 7.16 Hz, -CH<sub>3</sub>) ppm;  ${}^{13}$ C NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C, Me<sub>4</sub>Si): δ =165.97, 150.92, 145.77, 138.05, 131.81, 131.32, 128.28, 124.71, 124.43, 122.95, 121.73, 101.83, 61.58, 53.46, 14.44 ppm; ESI-MS: m/z [M+H]<sup>+</sup> 353.15 (100%) (Figure 2.12-2.14).

**2.4.3.** Synthesis of 5-(1-oxoisoindolin-2-yl)isophthalic acid (H<sub>2</sub>L): Compound obtained as above (2 g, 5.17 mmol) was hydrolyzed by refluxing it with 6(N) NaOH solution (20 mL) for 24 h. After cooling to 5 °C, the resulting solution was acidified with 6(N) HCl solution to obtain a white precipitate. It was collected by filtration, washed thoroughly with water, and dried in air. Yield: 1.35 g (80%). It has been characterized by <sup>1</sup>H, <sup>13</sup>C NMR, mass Spectrometry, elemental analysis. <sup>1</sup>H NMR (DMSO*d*<sub>6</sub>, 400 MHz, 25 °C, Me<sub>4</sub>Si):  $\delta = 8.6766$  (s, 2H, Ar-H), 8.2290 (s, 1H, -NH), 7.7869 – 7.7679 (d, 1H, J = 7.60Hz, Ar-H), 7.6720 – 7.6572 (m, 2H, Ar-H), 7.5433 – 7.5037 (m, 1H, Ar-H), 5.1083 (s, 2H, -CH<sub>2</sub>-) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz, 25 °C, Me<sub>4</sub>Si):  $\delta = 167.64$ , 167.05, 141.68, 140.66, 133.01, 132.66, 132.50, 128.83, 125.60, 124.04, 123.94, 123.69, 50.97 ppm; ESI-MS: m/z [M]<sup>+</sup> 298.07 (100) ((**Figure 2.15-2.17**).).

**2.4.4.** Synthesis of Cu-MOF: The Cu-MOF was synthesized at room temperature under a slow evaporation condition. H<sub>2</sub>L (30 mg, 0.1 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (40 mg, 0.16 mmol) were dissolved in 4 mL of DMF and 1.5 mL of H<sub>2</sub>O respectively in two different conical flasks. These solutions were heated on the hot plate till the appearance of a clear solution followed by their mixing in hot conditions. Then three drops of 1M HCl were added in the reaction mixture which was then stirred and mixed well. The final mixture was placed carefully for slow evaporation at ambient conditions. After four days, block-shaped and sky blue colored crystals appeared on the walls and the base of the flask which was further filtered, washed with DMF and H<sub>2</sub>O, and collected. Yield = 20 mg, 84%. (based on H<sub>2</sub>L linker). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>CuN<sub>2</sub>O<sub>7.5</sub> (458.9091): C 49.73, H 4.17, N 6.10%. Found: C 50.12, H 4.11, N 5.78%. FT-IR (KBr, cm<sup>-1</sup>): 3417 (br), 2978 (m), 1665 (m), 1631 (s), 1568 (s), 1412 (s), 1371 (m), 1300 (m), 1078 (m), 775 (m), 728 (m), 650 (m). (Figure 2.18).

**2.4.5.** Activation of Cu-MOF: Before starting the catalytic  $CO_2$  fixation, the framework must be activated to create the solvent-free sample containing Lewis acidic Cu(II) centers with unsaturated coordinations.<sup>35</sup> To generate the activated framework, first, the solvent exchange experiment was carried out by keeping the as-synthesized sample in acetone for 7 days and changing the acetone twice a day. The second step

begins with the heating of acetone exchanged sample at 150 °C, under ultra-high vacuum pressure for 8 h which results in the generation of a complete solvent-free framework. Upon activation the **Cu-MOF'** sample changes its color from blue to black signifying the loss of metal bound DMF molecules, resulting in the generation of coordinatively unsaturated *i.e.* 4-coordinated, Lewis acidic Cu(II) ions. PXRD pattern of bulk samples of **Cu-MOF** confirms the purity and integrity of the framework of the activated sample, which well-matched with the as-synthesized **Cu-MOF**.

**2.4.6. General procedure for catalytic cycloaddition reaction of CO**<sub>2</sub>: The catalytic CO<sub>2</sub> fixation was carried out by cycloaddition with epoxides. The reaction was performed in a 20 mL shrink tube furnished with a magnetic stirrer. Reagents *viz*. Epoxide (20 mmol), catalyst **Cu-MOF'** (5 wt%), and co-catalyst Bu<sub>4</sub>NBr (1 mmol) were taken in a schlenk tube and stirred at room temperature at 70 °C (based on the boiling point of epoxides) under CO<sub>2</sub> (99.999%) bubbling at atmospheric pressure. After completion of the reaction, 5 mL CHCl<sub>3</sub> was added followed by the filtration of the reaction mixture for separation of the catalyst from it. The solvent was evaporated at room temperature to get the cyclic carbonates and the analysis of the conversion was completed through <sup>1</sup>H NMR spectroscopy.

#### (%) conversion calculation:

The conversion was calculated from 1H NMR according to equation (1). NMR results showed that there is no formation of side products. The sole product is only the cyclic carbonate.

Conversion = *I*Hb / (*I*Ha+*I*Hb)



Ha and Hb belongs to the starting material and the product respectively

2.4.7. Characterization and Instrumentation: Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer FTIR spectrophotometer with KBr pellets from 500 to 4000 cm<sup>-1</sup> region. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL-ECX 400 FT (400 MHz and 100 MHz respectively) instrument in DMSO-d<sub>6</sub> and CDCl<sub>3</sub> with Me<sub>4</sub>Si as the internal. ESI-mass spectra were obtained by the WATERS Q-TOF Premier mass spectrometer. Microanalysis (carbon, hydrogen, and nitrogen) of the samples were performed using a Flash 2000 Elemental Analyzer (Thermo Fischer). Single-crystal X-ray structural studies were conducted on a Rigaku-Oxford Supernova CCD diffractometer. The Powder X-ray diffraction (PXRD) data were recorded on a Rigaku SmartLab X-ray diffractometer using monochromatic Cu-Ka radiation (1.54 Å), the tube voltage and current were 40 kV and 40 mA, respectively. The Scanning electron microscopy (SEM) images of the samples were obtained by the Supra55 Zeiss field-emission scanning electron microscope. The gas adsorption studies were accomplished by the Quantachrome Quadrasorb automatic volumetric instrument.

**2.4.8.** X–ray Crystallography: A suitable single crystal of Cu-MOF has been collected on a RigakuOxford Supernova CCD Diffractometer (graphite monochromated Mo K $\alpha$  radiation,  $\lambda \alpha = 0.71073$  Å) at 100 K. The data collections were evaluated using the CrysAlisPro CCD software and collected by the standard  $\varphi$ – $\omega$  scan techniques. Also, data were scaled and reduced by CrysAlisPro RED software. The direct method was used for solving crystal structure, followed by full-matrix least-squares refinements against  $F^2$  (all data HKLF 4 format) using the SHELXL 2014/7<sup>53</sup> and difference Fourier synthesis and least-squares refinement revealed the positions of the non-hydrogen atoms. The crystal system, orientation matrix, and cell dimensions were determined according to the established procedures, as well as Lorentz polarization and multi-scan absorption correction was applied. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were placed geometrically at calculated positions and refined isotropically. The lattice solvent molecules of Cu-MOF are highly disordered and cannot be modeled as discrete atomic sites, therefore, the PLATON-SQUEEZE<sup>54</sup> refinement program was used to calculate the solvent contributions. The solvent composition was estimated based on a combined study of TGA and squeezed electron counts which are included in the molecular formula. The lattice parameter, the data collection and refinement parameter are summarized in Table A1, while selected bond distances and bond angles are given in **Table A2**.

2.5. NMR, mass and FT-IR spectra of diethyl 5-(2 cyanobenzyloxy)isophthalate, H<sub>2</sub>L and Cu-MOF



Figure 2.12. The <sup>1</sup>H NMR spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.



Figure 2.13. The <sup>13</sup>C NMR spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.



Figure 2.14. ESI-MS spectrum of diethyl 5-(2-cyanobenzyloxy)isophthalate.



**Figure 2.15.** The <sup>1</sup>H NMR spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (H<sub>2</sub>L).



**Figure 2.16.** The <sup>13</sup>C NMR spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (H<sub>2</sub>L).



Figure 2.17. ESI-MS spectrum of 5-(2-carboxybenzyloxy)isophthalic acid (H<sub>2</sub>L).



Figure 2.18. FT-IR spectrum of Cu-MOF.

2.6. <sup>1</sup>H NMR spectra and data to evaluate conversion of epoxides



**Figure 2.19.** <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one: (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.4519 – 7.3378 (m, 5H, Ar–H), 5.6616 (t, J = 8.04 Hz, 1H, -CH), 4.7847 (t, J = 8.48 Hz, 1H, -CH<sub>2</sub>), 4.3309 (t, J = 8.2 Hz, 1H, -CH<sub>2</sub>) ppm.



Figure 2.20. <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one at different time.



Figure 2.21. <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one at different catalyst loading.



Figure 2.22. <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one at different co-catalyst loading.



**Figure 2.23.** <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one after utilizing the different tetrabutyl ammonium halide.



**Figure 2.24.** <sup>1</sup>H NMR of 4-(phenoxymethyl)-1,3-dioxolan-2-one: (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.2947 - 7.2469$  (m, 2H, Ar–H), 7.0042 – 6.8840 (m, 3H, Ar–H), 5.0019 – 4.9568 (m, 1H, -CH), 4.5665 (t, J = 8.52 Hz, 1H, -CH<sub>2</sub>), 4.5113 – 4.4749 (m, 1H, -CH<sub>2</sub>), 4.2267 – 4.2095 (m, 1H, , -CH<sub>2</sub>) ppm.



**Figure 2.25.** <sup>1</sup>H NMR of 4-((benzyloxy)methyl)-1,3-dioxolan-2-one: (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.3441 - 7.2911$  (m, 5H, Ar-H), 4.8158 - 4.7609 (m, 1H, -CH), 4.6170 - 4.5396 (m, 2H, -CH<sub>2</sub>), 4.4505 (t, J = 8.32 Hz, 1H, -CH<sub>2</sub>), 4.3751 - 4.3389 (m, 1H, -CH<sub>2</sub>) 3.7086 - 3.6718 (m, 1H, -CH<sub>2</sub>), 3.6126 - 3.5759 (m, 1H, -CH<sub>2</sub>) ppm.



**Figure 2.26.** <sup>1</sup>H NMR of 4-ethyl-1,3-dioxolan-2-one: (400 MHz, CDCl<sub>3</sub>): δ = 4.6557 – 4.6223 (m, 1H, -CH), 4.4997 (t, J = 8.32 Hz, 1H, -CH<sub>2</sub>), 4.0748 – 4.0363 (m, 1H, -CH<sub>2</sub>), 1.8260 – 1.6852 (m, 2H, -CH<sub>2</sub>), 0.9951 (t, J = 7.40 Hz, 3H, -CH<sub>3</sub>) ppm.



**Figure 2.27.** <sup>1</sup>H NMR of 4-butyl-1,3-dioxolan-2-one: (400 MHz, CDCl<sub>3</sub>):  $\delta = 4.7003 - 4.6304$  (m, 1H, -CH), 4.4888 (t, J = 8.32 Hz, 1H, -CH<sub>2</sub>), 4.0420 - 4.0030 (m, 1H, -CH<sub>2</sub>), 1.7609 - 1.6108 (m, 2H, -CH<sub>2</sub>), 1.4019 - 1.2922 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>), 0.8704 (t, J = 6.72 Hz, 3H, -CH<sub>3</sub>) ppm.



Figure 2.28. <sup>1</sup>H NMR of 4-phenyl-1,3-dioxolan-2-one for the control experiments.



**Figure 2.29.** <sup>1</sup>H NMR of 4-(phenoxymethyl)-1,3-dioxolan-2-one for the control experiments.



**Figure 2.30.** <sup>1</sup>H NMR of 4-((benzyloxy)methyl)-1,3-dioxolan-2-one for the control experiments.



Figure 2.31. <sup>1</sup>H NMR of 4-ethyl-1,3-dioxolan-2-one for the control experiments.



Figure 2.32. <sup>1</sup>H NMR of 4-butyl-1,3-dioxolan-2-one for the control experiments.

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## Chapter 3

# Construction of Multifunctional Cu-MOF/GO composite for Efficient Adsorption of Methylene Blue and Sensing of Cholesterol

## **3.1. Introduction**

As a result of rapid industrialization, a large quantity of hazardous wastes and toxic gases are released in addition to the desired products. These hazardous wastewaters generated from industrial effluents are when released in the environment without any treatment result in water pollution.[1] Wastewater pollution is at an alarming level in many developing countries due to the immense growth of textile and dyeing industries. Various surface water sources have been found contaminated by several pollutants such as pharmaceutical and personal care products (PPCPs), herbicides/pesticides, dyes, spilled oil, and aromatics/organics [2-6]. Dyes are the most common water pollutant which is highly toxic and carcinogenic. About 100,000 commercially available dyes are produced annually with a rate of  $7 \times 10^5$  tons and generally, two percent of the products are discharged as waste into water systems.[7] Most of them are non-biodegradable and have mutagenic effects on living systems, which outcomes to be a huge threat to the ecosystem and human life. Methylene Blue (MB) is among the most common coloring elements found in discarded waters of printing, textile, paper, and other industries. A remarkable threat has been imposed in the environment due to its carcinogenic and toxic nature with transmuted effects. So far, numerous techniques and methods have been implemented to remove/treat dyes however, these pollutants are quite stable in oxidizing agents, heat, or light. Among all techniques of dyes removal, the adsorption process is found to be one of the simplest and most effective methods for this purpose.[8-10] Considerable attention has been given to the adsorbent materials such as activated carbons, zeolites, clay, red mud, nanoparticles, etc. along with some agriculturally produced biomasses to eliminate dyes from the polluted water.[11-20] These adsorbents are either expensive due to their high operating costs, regeneration of the used adsorbent, or consuming a huge time in adsorption which limits their practice on a larger scale.

Porous materials are considered to be excellent adsorbents as they play a vital role in adsorptive separation and purifications. Metal-organic frameworks (MOFs) are crystalline porous materials containing rich metal centers coordinated to multiple organic linkers forming robust structures. [21- 25] These structures comprise of large surface area, tunable pores, and high thermal and mechanical stability prominence for many potential applications such as sensors, catalysis, separations, drug delivery, and photocatalysis, super capacitance.[26-31] A lot of research has been reported on MOFs and MOF based composites concerning environmental decontamination including dye degradation and adsorption.[32, 33] In many cases, MOF derived materials are more effective in applications due to the synergistic effects of participating parent components, enhancing the properties of the resulted material.[33-36]

Cholesterol is one of the most essential lipids produced in the liver for a few of the key processes in the human body such as skeleton maintenance of cellular membranes, acting as starting materials for several steroids, bile acids, and hormones, etc.[37] Unbalanced concentration of cholesterol causes adverse effects on the human body resulting in heart diseases, atherosclerosis, cancer, hypertension, depression.[38] Hence a precise measurement of cholesterol's concentration in human blood plays a crucial role in monitoring the diagnosis process. Various methods were examined for the purpose but major disadvantage related to them was pretreatments of the sample, time-consuming process, low sensitivity, and selectivity. Out of which electrochemical sensing possesses advantages over different methods such as fluorometric, high-performance liquid chromatography (HPLC) colorimetric, electrophoresis, etc.[40-42] The electrochemical method is more practical due to its simplicity, fast sample preparation process, high selectivity over other methods. There are certain reports on electrochemical sensing of cholesterol by nanoparticles, but MOF derived composites were not entertained till now as electrochemical sensors of cholesterol. Wu *et al.* used a Fe3O4 coated MOF (Fe3O4@MIL-100(Fe)) for the cholesterol sensing, however they had utilized the colorimetric technique.[43] Although the electrochemical method has various advantages over the colorimetric technique as mentioned above, there are no such reports from MOF based compositions used as an electrochemical sensor for cholesterol sensing.

Motivated by the above-mentioned facts, herein we have implemented a fast and simple ultrasonic technique to synthesize a new hybrid material fabricating graphene oxide (GO) layers within the Lactamfunctionalize porous copper coordinated MOF. The composite **Cu-MOF/GO** exhibited a significant performance for selective adsorption towards MB dye. The effects of adsorbent dosage and time on the adsorption of MB were measured along with the recycling studies of **Cu-MOF/GO**. From these experimental data, the adsorption efficiency of Cu-MOF/GO and its adsorption capacity at equilibrium were calculated. Further, we have also examined **Cu-MOF/GO** as an electrochemical sensor for cholesterol which further verifies its application potential.

## 3.2. Results and discussion

#### 3.2.1 Synthesis and characterization

**Cu-MOF/GO** has been prepared by blending Cu-MOF and GO through the simple ultrasonication assisted technique. Equimolar concentrations of GO and Cu-MOF (by weight) were suspended in ethanol. This mixture then undergoes an ultrasonication process for 1 h followed by rotary evaporation. A sensible schematic representation for the formation of this hybrid is shown in **Scheme 3.1**. **Cu-MOF/GO** was characterized by PXRD, SEM analysis.



Scheme 3.1. Plausible scheme for the synthesis of Cu-MOF/GO.

**Figure 3.1** represents the observed PXRD analysis of as-prepared GO, Cu-MOF, and **Cu-MOF/GO** samples. The peaks pattern of **Cu-MOF/GO** is almost similar to that of Cu-MOF, signifying the crystalline structure of Cu-MOF remains unaffected after the incorporation of GO nano-sheets. The signal at  $2\theta = 10.35^{\circ}$  and an emerging hump in the region of  $25^{\circ}$  to  $35^{\circ}$  is indicating the successful incorporation of GO in Cu-MOF representing the oxygen-containing functional groups present on the

carbon sheets. Peaks pattern and their intensity reveal that the material is crystalline and contains characteristics of both contributing materials without devastating the properties of parent components. The structural morphology of the as-prepared Cu-MOF and **Cu-MOF/GO** samples are characterized by SEM. The block-shaped morphology is observed for Cu-MOF crystals which are following our previous report in chapter 2 (**Figure 3.2a, b**).[19] Uniform and well enveloped Cu-MOF crystals in GO sheets are witnessed in the case of **Cu-MOF/GO** (**Figure 3.2c, d**) confirming the successful formation of the composite.



Figure 3.1. PXRD pattern of as-prepared (a) GO, (b) Cu-MOF, and Cu-MOF/GO.



Figure 3.2. SEM images of (a) as-prepared Cu-MOF, (b) Cu-MOF/GO.

#### **3.2.2.** Dye adsorption study on Cu-MOF/GO.

Herein we included Methylene Blue (MB) as a model dye in water (50 PPM) to employ the dye adsorption experiment on Cu-MOF and **Cu-MOF/GO** as adsorbents (0.5mg/ml) at RT. Samples were collected at different time intervals followed by their centrifugation and were monitored using UV-vis spectroscopy to measure their adsorption abilities towards MB dye. The UV graphs of adsorption of MB dye on Cu-MOF and **Cu-MOF/GO** are displayed in **Figure 3.3**. It is observed that **Cu-MOF/GO** is proficiently adsorbing the MB dye, up to 97 % within 10 min, indicated by a notable decrement in the peak of MB dye at 582 nm. The adsorption reached more than 99 % in just 30 minutes and the color of the solution changed from dark blue to colorless. Though Cu-MOF is showing minor adsorption after 120 min, slow adsorption (44 %) was observed when it was left for 12 h dispersed in the same dye solution. A comparison of the adsorption efficiency of Cu-MOF and **Cu-MOF/GO** 

has been displayed in **Figure 3.4**. After observing an incredible adsorption efficiency of **Cu-MOF/GO**, the study has been further extended to investigate the effect of adsorbent dosage and varying time on the adsorption behavior of MB on **Cu-MOF/GO** along with the recycle studies of the adsorbent.



Figure 3.3. Adsorption behavior of MB on a) Cu-MOF/GO, b) Cu-MOF.



**Figure 3.4**. Percentage adsorption of MB (Methylene Blue) on Cu-MOF and **Cu-MOF/GO** after 12 hr. period. (Concentration of MB: 10 ppm).

The real quantity of adsorbent needed for complete adsorption of the pollutant is determined by the effect of adsorbent dosage which is a very crucial characteristic to expect the cost of the experiment. The optimization of the minimum quantity of adsorbent required for the complete adsorption of the dye with maximum efficiency is presented in **Figure 3.5**. This study has been carried out by taking three different concentrations of **Cu-MOF/GO** (0.25, 0.35, 0.5 mg/ml) in a 50 ml solution of MB (50 mg/L; 50 PPM). It was observed that the minimum loading of adsorbent required for adsorption of dye is 0.5 mg/ml, revealing 99.5 % efficiency. More active sites were available on increasing the amount of adsorbent which increases the efficiency of the adsorbent.



Figure 3.5. Effect of adsorbent dosage on MB adsorption

Further, the adsorbent (**Cu-MOF/GO**) was examined for its exposure time to MB dye using 50 mg/L of dye solution and 0.5 mg/ml of adsorbent dispersed in 50 ml of dye solution. The analysis was conducted at pH 7 in ambient conditions. Percent adsorption of MB dye on **Cu-MOF/GO** composite with time is demonstrated in **Figure 3.6**. Results revealed that adsorption reached up to 97 % within 10 min. and nearly 99 % in 20 min. showing an incredibly fast and superior adsorption process. Adsorption reaches more than 99.5 % in 60 minutes and attained equilibrium. The adsorption capacity at equilibrium is found to be 99.6 mg g<sup>-1</sup> for the contact time of 60 min.



**Figure 3.6.** Effect of time on adsorption of MB on **Cu-MOF/GO**. (Concentration of MB: 50 PPM; Concentration of **Cu-MOF/GO**: 0.5mg/ml)

The practical implications of adsorbent are based on the stability and recyclability criteria. The recycling experiments were performed in which the used adsorbent was recovered via centrifugation followed by repeated washing and drying. Further, the adsorption experiments were performed on recycled **Cu-MOF/GO** under identical conditions. It is observed that there is a negligible decrease in adsorption efficiency after each run, though it decreased to 88 % till the 5<sup>th</sup> cycle (**Figure 3.7**). This decent recyclability supports the feasibility of the composite in practical applications.



Figure 3.7. Recyclability test for the adsorption of MB on Cu-MOF/GO.

#### 3.2.3. Probable mechanism of adsorption

From SEM images and PXRD analysis of **Cu-MOF/GO** after dye adsorption, it was observed that MB dye was adsorbed on the surface of **Cu-MOF/GO**. Small rectangular crystals of MB dye ( $\mu$ m size) on composite material can be seen in **Figure 3.8**. This observation is further proved by PXRD analysis where the peaks pattern of the composite is conserved but decreased in intensity indicating the adsorption of MB dye on it **Figure 3.9**.



Figure 3.8. (a,b) SEM images of MB dye adsorbed on the surface of Cu-MOF/GO.



Figure 3.9. PXRD pattern of MB dye adsorbed on the surface of Cu-MOF/GO.

The prompt adsorption behavior of MB is mainly due to available higher active sites in the composite as it acquires more negative charge due to the presence of epoxy, hydroxyl, and carboxyl groups of GO in addition to the carboxyl functional groups of Cu-MOF. These negative charges are favorable for the adsorption of the cationic MB dye through electrostatic force of attraction. Moreover, the  $\pi$ - $\pi$  interactions and hydrogen bonds are the weak interactions present between isophthalic acid in Cu-MOF and the MB dye molecules might also complement the adsorption efficiency. Also, the incorporation of GO into the MOF leads to an increase in the overall surface area which helped in the adsorption of dye effectively. Thus it can be concluded that **Cu-MOF/GO** has advantages over Cu-MOF to be used as an adsorbent and sensor in terms of efficiency and reusability. The synergistic effects of Cu-MOF and GO enhance the effectiveness of the prepared material incorporating the properties of both parent materials resulting in the augmentation of the properties.

#### 3.2.4. Electrochemical sensing of Cholesterol by Cu-MOF/GO

The cyclic voltammetry (CV) was used to check the performance of the modified electrode (**Cu-MOF/GO/GCE**) in the absence and presence of cholesterol in PBS of 0.1M at pH=7.0 at applied scan rate=100mV/s. The recorded CV curves of the **Cu-MOF/GO/GCE** in the presence and absence of 1mM cholesterol (red) and absence of cholesterol (black) in 0.1M PBS at scan rate=100mV/s have shown in **Figure 3.10a**. The observations revealed that **Cu-MOF/GO/GCE** exhibits poor current response in absence of an analyte without appearing of any redox peak. However, in the presence of cholesterol, it shows improved electrochemical performance. The **Cu-MOF/GO/GCE** in the presence of 1mM cholesterol displayed the oxidation-reduction peaks corresponding to the oxidation and reduction reactions taking place at the electrode surface for the sensing of cholesterol. Furthermore, the effect of concentrations was also investigated using the CV method. The recorded CV curves of the **Cu-MOF/GO/GCE** in the presence of different

concentrations (0.1mM to 1mM) of cholesterol have been shown in **Figure 3.10b**. The obtained results revealed that current responses are enhanced with an increase in the concentration of the cholesterol.



**Figure 3.10.** CV of **Cu-MOF/GO/GCE** (a) in the presence of 1mM cholesterol (red) and absence of cholesterol (black) in 0.1M PBS at scan rate=100mV/s, (b) in presence of different concentrations (0.1mM to 1mM) of cholesterol in 0.1M PBS in pH 7.0 at scan rate=100mV/s.

The increased current response was found to be linear concerning the concentrations of the cholesterol. The linear calibration plot of the redox peak currents versus concentrations of the cholesterol has been presented in **Figure 3.11**. The Figure confirmed the above statements of the linear current response. The oxidation peak is denoted as O1 and the reduction peak is denoted as R1 for a better understanding of the redox reactions. Furthermore, the detection limit was calculated using the below equation. The equation used to calculate the limit of detection

 $(LOD) = 3.3(\sigma/S)[54-56],$ 

where  $\sigma$  is the standard error and S is the slope of the calibration curve and sensitivity was calculated using the equation, Sensitivity = Slope/Area of the working electrode.

The detection limit was found to be 0.09 mM for cholesterol sensing along with the linear range of 01.mM to 1mM. The obtained detection limit is remarkably good and suggested the potential of novel composite **Cu-MOF/GO/GCE** in electrochemical applications.



Figure 3.11. Calibration plot of the current peak versus concentrations of the cholesterol.

The interference study of any sensor is an important tool. Thus we have recorded the CV curves of the **Cu-MOF/GO/GCE** in presence of different electroactive/interference species. The recorded CV graphs have been presented in **Figure 3.12**. In the first step, the CV curve of the **Cu-MOF/GO-GCE** was recorded in the presence of 1mM cholesterol. In the second step, CV curves of the **Cu-MOF/GO/GCE** were recorded in presence of different interference species (2mM of glucose, urea, fructose, uric acid, dopamine, ascorbic acid) in 1mM cholesterol (**Figure 3.12a**). The observations showed that the addition of the interfering species does not alter the performance of the **Cu-MOF/GO/GCE**. This suggested the selective nature of the **Cu-MOF/GO/GCE** towards the sensing of cholesterol. The stability of the prepared electrode is also an important task. Hence, we have recorded the CV 20 cycles of the **Cu-MOF/GO/GCE** in 0.1mM cholesterol and the obtained data has been

shown in **Figure 3.12b**. The obtained results showed the good stability of the prepared **Cu-MOF/GO/GCE**.



**Figure 3.12.** (a) CV curves of the **Cu-MOF/GO/GCE** in presence of different interference species (2mM of glucose, urea, fructose, uric acid, dopamine, ascorbic acid) in 1mM cholesterol in 0.1M PBS of pH 7.0 at scan rate=100mV/s. (b) 20 CV cycles of the Cu-MOF/GO/GCE in presence of 0.1mM cholesterol in .1M PBS of pH=7.0 at scan rate= 100mV/s.

## **3.3.** Conclusions

In summary, we have reported a new prepared Cu-MOF/GO composite as an adsorbent for the removal of the MB dye from the aqueous system and an effective electrochemical sensor for sensing of cholesterol. The incorporation of GO in the Cu-coordinated metal-organic framework has improved the properties of Cu-MOF for water purification process by rapid adsorption of MB dye (more than 97 % in 10 min.). Nano-sheets of GO and Cu-MOF containing functional groups provide more active sites to the composite material which results in the  $\pi$ - $\pi$  interactions and hydrogen bonding interactions with the MB dye. Detailed studies of the impact of adsorbent dosage and varying time on MB adsorption have been conducted. Incredible adsorption efficiency even after five cycles supports their use in practical applications and industries. To the best of our knowledge, no such report is there on hybrid material prepared from metal-organic frameworks and graphene oxide for electrochemical sensing of cholesterol. The obtained results were found to be satisfactory and the good detection limit was obtained for the sensing of cholesterol which may be due to the synergistic effects and surface structural interactions between GO and Cu-MOF. We believe this kind of hybrid composites could be used for other electrochemical applications too such as water splitting and supercapacitors.

#### **3.4. Experimental Section**

**Cautions:** Methyl blue (MB), is highly toxic. The handling of these compounds should be done carefully. The number of such compounds should be low or recommended by the suppliers. For more details on the use of this compound, the MSDS data sheet should be taken into consideration.

**3.4.1. Materials:** All the reagents employed were commercially available and used as provided without further purification. Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (98%), 5-Aminoisophthalic acid, and 2-(bromomethyl)benzonitrile, Methyl Blue was obtained from Sigma Aldrich and used as received. Graphene Oxide was prepared by Hummer's method.[33] All solvents were dried and purified before use the following standard methods. Dyes used for the study were purchased from Merck/Sigma.

**3.4.2.** Synthesis of Lactam functionalized Cu-MOF: Cu-MOF was synthesized at ambient conditions through slow evaporation using our procedure given in chapter number 2 of this thesis.[19].

**3.4.3.** Synthesis of GO (Graphene Oxide): graphite flakes(1.0 g) and NaNO<sub>3</sub> (0.5 g) were stirred in concentrated H<sub>2</sub>SO<sub>4</sub> (23.0 mL) at RT continuously for 60 min. Then KMnO<sub>4</sub> (3.0 g) was added slowly into the reaction mixture maintaining the temperature below 20 °C in an ice bath avoiding the extreme exotherm. The reaction was stirred continuously overnight at 35 °C. Afterward, 60 mL of D.I. water was added into the reaction mixture followed by the gradual addition of 1.5 g of KMnO<sub>4</sub> continuous stirring at 35 °C for 14 h. The mixture cooled to RT followed by the addition of 500 mL of D.I. with 30% of H<sub>2</sub>O<sub>2</sub> (7.0 mL). The D.I. water was used to wash the obtained suspension to separate the solid product and unreacted materials. Further, the product was repeatedly washed with 1 M HCl solution. The final product was again washed with

excess D.I. water and dried under vacuum at 50 C for 6 h to get the desired product.[33]

**3.4.4.** Synthesis of Cu-MOF/GO composite: Cu-MOF/GO composite was prepared by blending Cu-MOF and GO through ultra-sonication assisted technique. Equimolar concentrations of GO and Cu-MOF (by weight) were suspended in ethanol. This mixture then undergoes an ultrasonication process for 1 h followed by evaporation of the solvent by rotary evaporation process and drying.

**3.4.5. Dye adsorption experiments:** Adsorption experiments were conducted at 25 °C under neutral conditions. A 0.5 mg/ml sample of the Co-MOF/GO composite was suspended in 50 mL of MB solution (50 PPM). The suspension was stirred at 25 °C. At regular time intervals, 4 ml of the solution was removed, centrifuged, and analyzed. The MB dye concentration of the solutions was determined by UV–visible spectroscopy (Varian Cary 100 Bio UV-Visible Spectrophotometer) at the wavelength of 582 nm. The dye removal percentage from aqueous solution was calculated from the following equation [11]:

Efficiency (%) = 
$$\frac{(C_0 - C_t)}{C_0} \times 100\%$$
(1)

Where  $C_0$  = initial concentration of dye (mg L<sup>-1</sup>) and Ct = dye concentration (mg L<sup>-1</sup>) at time t.

The adsorption capacity of the adsorbent at equilibrium was calculated from the following equation [11]:

$$Q_{\rm e} = \frac{(C_{\rm i} - C_{\rm e}) V}{W}$$
(2)

Where  $Q_e$  is the amount of dye adsorbed by the adsorbent (mg/g), *C*i is the initial dye concentration (mg/L) and C<sub>e</sub> is the final concentration after the adsorption process (mg/L), *V* is the volume of the dye solution (L) and *W* is the amount of adsorbent use (g).

**3.4.6. Characterization and Instrumentation:** The phase and purity of the synthesized sample were determined by Powder X-ray diffraction (PXRD). Powder X-ray diffraction data were recorded on a Rigaku SmartLab X-ray diffractometer using monochromatic Cu-K $\alpha$  radiation (1.54 Å). UV- visible analysis was conducted using Varian Cary 100 Bio UV-Visible Spectrophotometer. The morphologies were characterized by the Supra 55 Zeiss field-emission scanning electron microscope (FESEM). All electrochemical measurements were performed on Metrohm Autolab PGSTAT 302N using NOVA software version 1.10. Glassy carbon (3 mm in diameter) as a working electrode, a platinum wire as a counter electrode, and Ag/AgCl as a reference electrode were used for all electrochemical measurements.

#### **3.4.7. Electrochemical Measurements and Fabrication of electrodes:**

The glassy carbon electrode (GCE) was cleaned and washed with alumina slurry and DI water. Further  $5.5\mu$ L of **Cu-MOF/GO** dispersion (0.2mg/2mL) was deposited and dried in air for 8h. The electrochemical cyclic voltammetry was used for the sensing of cholesterol using a three-electrode assembly consists of a working electrode, reference electrode, and counter electrode.

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## **Chapter 4**

# Functionalized Cu-MOF@CNT Hybrid: Synthesis, Crystal Structure and Applicability in Supercapacitors

### 4.1. Introduction

Owing to an increase in the engineering of commercial compact electronic devices, the demand for high energy storage in miniature form has increased enormously.[1-7] In this regard, the electrochemical storage device such as supercapacitors is the most prominent candidate for highly efficient energy storage applications compared to fuel cell and lithium-ion batteries, because of its high Coulombic efficiency, quick chargedischarge process, outstanding environment friendliness, excellent cycling stability and reversibility, which can fulfill the demand for energy consumption and makes them superior to batteries having ordinary power density and cycle life span.[8,9] To store the energy, supercapacitors exhibits electrical double layer capacitance (EDLC) and pseudocapacitance-based charge storage mechanisms.[10] Electrode materials for supercapacitors plays important role in the overall performance. Generally, this electrode materials include carbonaceous materials, metal oxides/hydroxides, and conductive polymers, but have some limitations such as large-scale production, low capacitance in the case of carbonaceous materials, poor cycle stability in the case of metal oxides/hydroxides, and structural instability as well as fast capacitance deterioration in case of conductive polymers, which restrict their practical applications.[11-16] Thus, the construction of electrode materials with durability and low cost remains a great challenge and has attracted significant research efforts for the development of high-performance

supercapacitors, that possesses the ability to enhance diffusion kinetics and provide a high accessible surface area.

To overcome these limitations, the introduction of robust metalorganic frameworks (MOFs) and their composite have shown remarkable performances as electrode material for electrochemical energy storage applications.[17-20] MOFs have witnessed tremendous growth in various potential applications such as electrochemical energy storage/generation, sensors, catalysis, gas storage/separation owing to their high porosity, robust structure, high specific surface area, conductivity, versatile functionalities, and good thermal stability.[21-26] Furthermore, the direct use of bare MOFs as electrode materials can offer a porous skeleton, but they usually exhibit low energy storage performance. For example, Cobased MOFs presented a lower capacitance of around 200 F g<sup>-1</sup> in LiOH solution, because of low electrical conductivity along with the presence of steric interference to ion insertion.[27] In this regard, the assembly of MOFs with graphene, CNTs, carbon black, and so on has emerged as an exceptional strategy for improving energy storage efficiency.[28] Wen et al. fabricated Ni-MOF/CNT composites, which exhibited a brilliant supercapacitor performance due to the synergism between the specific structure of Ni-MOF and the high conductivity of CNTs.[28] In this work, CNTs surfaces facilitate the uniform growth of the Ni-MOF, which helped in shortening the pathway of electron transport throughout the chargedischarge process. Additionally, electronic transportation from active materials towards the current collector was improved by the high electronic conductivity of CNTs. Hence, introducing conducting additives such as CNTs in the porous MOF structures can be a viable strategy for advanced energy storage platforms.

Keeping all these features in mind we have developed a facile method to synthesize a novel amino-functionalized, copper coordinated
metal-organic framework having layered porous channels at RT which displayed high porosity and chemical stability. Further, the MOF was employed to prepare a hybrid with CNT (Carbon Nanotubes) delivering high supercapacitor performance. This work highlights the importance of MOF/carbonaceous materials hybrid as a promising high energy storage systems in a cost-effective approach.

### 4.2. Results and discussion

We have synthesized a newly designed linker ( $H_2L$ ) through a cross-coupling Suzuki reaction of 2,6-dibromo-4-(trifluoromethyl)aniline and 4-(ethoxycarbonyl)phenylboronic acid, further proceeded by the hydrolysis of diester and its acidification in presence of HCl (**Scheme 4.1**).



Scheme 4.1. Synthetic scheme for the ligand, H<sub>2</sub>L.

Further, a reaction between the H<sub>2</sub>L and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in a mixed solvent system of N,N-dimethyl formamide (DMF), and H<sub>2</sub>O at room temperature, imparted block shape and green colored crystals of metal-organic frameworks *via* slow evaporation method in ambient conditions. The construction of MOF named **IITI-1** (*IITI: Indian Institute of Technology Indore*) is well illustrated in a schematic representation (Scheme 4.2). Further, **IITI-1** was characterized by Single-crystal x-ray diffraction (SCXRD), PXRD, BET, SEM, and TEM analysis. Structural analyses show the robustness of the framework.



Scheme 4.2. Schematic representation for the synthesis of IITI-1.

Furthermore, a new composite was prepared as **IITI-1/CNT** by blending **IITI-1** and CNT via a simple ultra-sonication method. A reasonable schematic diagram presenting the formation of this composite is displayed in **Scheme 4.3**. **IITI-1/CNT** was characterized by PXRD, BET, SEM, and TEM analysis techniques.



Scheme 4.3. A reasonable systematic diagram of the formation of IITI-1/CNT hybrid.

#### 4.2.1. Structural aspects of IITI-1

**IITI-1** is a well-defined metal-organic framework constructed of 2-D layers. Single-crystal X-ray diffraction analysis indicated that IITI-1 crystallizes in the monoclinic C2/c space group (Table A3). Its asymmetric unit contains one copper(II) ion, one DMF molecule, and one deprotonated H<sub>2</sub>L linker. Each Cu ion is coordinated by four carboxylate oxygen atoms from H<sub>2</sub>L ligands at basal positions and at the apical position, it is coordinated to one copper atom and one oxygen atom from the DMF molecule showing distorted octahedral geometry. The supramolecular framework is constructed of 4-connected paddle-wheel dinuclear Cu<sub>2</sub>(COO)<sub>4</sub> secondary building units (SBUs) with a Cu---Cu distance of 2.634(2) Å (Figure 4.1a). Each H<sub>2</sub>L ligand coordinates to four Cu(II) atoms through two carboxylate groups claiming  $\mu_2$ - $\eta^1$ : $\eta^1$  and  $\mu_2$ - $\eta^1$ : $\eta^1$  coordination modes, respectively. The spanning range of calculated Cu···O bond measurements ranges from 1.957(4) to 2.199(7) (Å) to form a 2-D layered framework (Figure 4.1b). All measured bond distances were comparable to literature values (Table A4).[29]



**Figure 4.1.** Ball & stick model showing (a) the coordination environment around Cu(II) ion in **IITI-1**, (b) the 2-D sheet between ab axis; Color code: Cu: green; O: red; N: blue; and C: olive (hydrogen atoms are omitted for clarity).

The 2-D layers of **IITI-1** oriented along the *b*-axis are stacked in a slipped fashion driven by CH··· $\pi$  interactions and hydrogen bonding (C-H···O

interaction) leading to a unique  $2D + 2D \rightarrow 3D$  array (**Figure 4.2a**). The array contains 1-D pores representing the porosity in the supramolecular layered framework (**Figure 4.2b**). The arrangement of carboxylate linkers forms one more type of channel decorated CF<sub>3</sub> groups having dimensions of 19.901 Å × 14.022 Å (**Figure 4.2c**), through which the permeation of electrolytes could be easily allowed. CH<sup>...</sup> $\pi$  interactions are present in the framework with the distance of C17–H<sup>...</sup> $\pi$ =2.873 Å and ∠C14–H14<sup>...</sup> $\pi$ =109.08°.



**Figure 4.2.** (a) Space fill model displaying the layered stacking in **IITI-1**, (b) Ball & stick model showing NH<sub>2</sub> decorated pores in the supramolecular 3D framework along the *c*-axis, (c) CF<sub>3</sub> decorated channels having dimensions of 19.901 Å × 14.022 Å. Color code: Cu: green; O: red; N: blue; and C: olive (hydrogen atoms are omitted for clarity).

### 4.2.2. Characterization of the bulk samples of IITI-1 and IITI-1/CNT

The phase purity of the bulk material of **IITI-1** was confirmed by powder X-ray diffraction experiment, which displays that bulk samples are in good agreement with those of the corresponding simulated one obtained

from SC-XRD data, indicating the presence of crystalline phase (**Figure 4.3a**). PXRD spectrum of **IITI-1** represents its crystalline structure and the diffraction pattern of CNT is reliable with the literature. In contrast, PXRD of **IITI-1/CNT** reveals that the material is crystalline and contains characteristics of both participating materials without debilitating their properties (**Figure 4.3b**).



**Figure 4.3.** (a) PXRD image for **IITI-1** (observed and simulated). (b) Comparing **IITI-1**, CNT and **IITI-1/CNT** hybrid.

The BET surface area for **IITI-1**, **CNT** and **IITI-1/CNT** hybrid and their porosity information were recorded by measuring and analyzing the sorption isotherms at 77 K using N<sub>2</sub> gas. The results display type IV adsorption isotherm profile for **IITI-1** and type III adsorption isotherm profile for **CNT** and **IITI-1/CNT**. The evaluated BET surface areas of **IITI-1**, **CNT**, and **IITI-1/CNT** are 986.764 m<sup>2</sup> g<sup>-1</sup>, 421.491 m<sup>2</sup> g<sup>-1</sup>, and 185.008 m<sup>2</sup> g<sup>-1</sup>, respectively. The respective plots for BJH pore size distribution are presented in the insets of (**Figure 4.4-Figure 4.6**).



**Figure 4.4.** N<sub>2</sub> isotherm and corresponding BJH desorption pore size distribution profile of **IITI-1**.



**Figure 4.5.** N<sub>2</sub> isotherm and corresponding BJH desorption pore size distribution profile of CNT.



**Figure 4.6.** N<sub>2</sub> isotherm and corresponding BJH desorption pore size distribution profile of **IITI-1/CNT**.

The morphology and structure of prepared samples were perceived by

SEM and TEM techniques. SEM images of **IITI-1** display irregular blockshaped structure of size varying between 1-10  $\mu$ m (**Figure 4.7a,b**), whereas both blocks shaped crystals, as well as typical nanotubes of carbon, are present in the **IITI-1/CNT** (**Figure 4.7c,d**). These observations were further confirmed in TEM results, where block-shaped particles were observed for **IITI-1** (**Figure 4.8a,b**), distinct nanotubes were observed for CNT (**Figure 4.8c,d**), and a uniform enwrapping of CNTs by **IITI-1** was found in **IITI-1/CNT** (**Figure 4.8e,f**). The SEM and TEM results verify the hybrid formation as both types of structures were present in the material.



Figure 4.7. FESEM images of (a,b) IITI-1 and (c,d) IITI-1/CNT, at different magnifications.



Figure 4.8. TEM images of (a,b) IITI-1, (c,d) CNT, and (e,f) IITI-1/CNT.

### 4.2.3. Supercapacitor properties of IITI-1, CNT and IITI-1/CNT

The electrochemical investigations of **IITI-1/CNT** composite were carried out using a three-electrode cell in 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte in the absence of any commercial binders. This approach of binderless preparation of the working electrode can be cost-effective for real-world device applications. The drop-cast electrodes of **IITI-1**, CNT and **IITI-1/CNT** were denoted as **IITI-1**/GCE, CNT/GCE, and **IITI-1/CNT**/GCE, respectively, and their supercapacitor properties were compared systematically by cyclic voltammetry (CV) and galvanostatic chargedischarge (GCD) techniques.

In the initially conducted experiments, CV profiles of all three electrodes were compared at 100 mV s<sup>-1</sup>, which shows a remarkably

enhanced charge propagation and the integrated area under the curve for **IITI-1/CNT/GCE** compared to other electrodes (**Figure 4.9a**). This observation suggests a high specific capacitance of composite over individual materials.



**Figure 4.9.** (a) Comparison of CV profiles of **IITI-1**/GCE, CNT/GCE and **IITI-1**/CNT/GCE at 100 mV s<sup>-1</sup>, (b) CV profiles of **IITI-1**/CNT/GCE at different scan rates (10-500 mV s<sup>-1</sup>), (c) comparison of GCD profiles of **IITI-1**/GCE, CNT/GCE, and **IITI-1**/CNT/GCE at 1.6 A g<sup>-1</sup>, and (d) GCD profiles of **IITI-1**/CNT/GCE at different current densities (1.6-16 A g<sup>-1</sup>). (Electrolyte: 1M Na<sub>2</sub>SO<sub>4</sub>).

The CV profiles of **IITI-1**/GCE exhibits a lethargic charge transfer process with a very less induced current (**Figure 4.10a**). Moreover, CV profiles at different scan rates (10-500 mV s<sup>-1</sup>) do not present any ideal rectangular CV curves, which suggest the absence of a double-layer capacitive process and the appearance of peaks recommends the possibility of a pseudocapacitive process. In contrast, CNT/GCE, being a

carbon material, presents nearly rectangular CV profiles at different scan rates (**Figure 4.10b**) with good charge propagation compared to **IITI-1**/GCE, however, it is still insufficient to generate very high specific capacitance. The enhanced current response of CNT/GCE over **IITI-1**/GCE can be assessed by comparing the y-axes of **Figure 4.10a and b**.



**Figure 4.10.** (a,b) CV profiles of **IITI-1**/GCE and CNT/GCE at different scan rates (10– 500 mV s<sup>-1</sup>), and (c,d) GCD profiles of **IITI-1**/GCE and CNT/GCE at different current densities (1.6–16 A g<sup>-1</sup>) (Electrolyte: 1M Na<sub>2</sub>SO<sub>4</sub>).

Looking into CV profiles, it is observed that in comparison with **IITI-**1/GCE and CNT/GCE, **IITI-1/CNT**/GCE exhibits massively promoted charge propagation and storage capacity, signifying the benefit of elaborated MOF architecture with the support of CNTs (**Figure 4.9b**). Moreover, CV profiles of **IITI-1/CNT**/GCE attain quasi-rectangular behavior, which shows a good synergy of CNT with MOF. The continuously enhanced CV integrated area under the curves for IITI-1/CNT/GCE along with the amplified current response without any noticeable signal loss at higher scan rates reveal its good charge storage characteristics and high rate ability. This escalated charge storage and related properties is the outcome of the positive synergistic properties between 2-D Cu-MOF and highly conducting CNT.[2,7] In conclusion, the promoted charge storage characteristics in IITI-1/CNT/GCE can be assigned as a synergistic alliance of pseudocapacitive IITI-1/GCE and double-layer capacitive CNT/GCE. The observed synergy between MOF and CNT was further observed in galvanostatic charge-discharge (GCD) observations. The comparison of GCD profiles of all three electrodes is presented in Figure 4.9c, which shows the greatest discharge time in the case of **IITI-**1/CNT/GCE. This observation suggests the highest specific capacitance of IITI-1/CNT/GCE over other electrodes. IITI-1/GCE displays a non-ideal triangular shape of GCD curves owing to possible dominance of the redox process, which is a characteristic of pseudocapacitance (Figure 4.10c). Furthermore, the sluggish chargingdischarging process was accompanied by IR drop (potential drop) due to internal resistance. This IR drop keeps on growing with increasing current densities, which may be assigned due to electronic hindrance associated with electroactive materials and ionic resistance correlated to the conductivity of electrolyte and mobility of ions and results in low charge storing efficiency.[2,12,16] Similar observations were noticed for CNT/GCE, where the value of IR drop was comparably larger than **IITI**-1/GCE at each current densities (Figure 4.10d). However, this potential drop remains disappeared in **IITI-1/CNT/GCE** at each current densities indicating the minimized internal resistance (Figure 4.9d), which shows its good conductivity and excellent charge storage efficiency. Furthermore, the GCD profiles of IITI-1/CNT/GCE were somewhat triangular due to a healthy alliance between MOF and CNT. The GCD curve profiles at each

current density display the highest discharge time for IITI-1/CNT/GCE over other electrodes (Figure 4.9d), which is the confirmation of the largest specific capacitance of hybrid over IITI-1 and CNT. These results are in line with those obtained through the CV. The calculated specific capacitances for IITI-1/CNT/GCE at current densities of 1.6, 2, 2.4, 2.8, 3.2, 3.6, 4, 8 and 16 are 380, 330, 312, 285, 276, 273, 264, 261, 260 and 240 F g<sup>-1</sup>, respectively. The calculated areal capacitance at 0.282 mA cm<sup>-2</sup> was 0.067 F cm<sup>-2</sup> and at a high current density of 2.8 mA cm<sup>-2</sup> was 0.044 F cm<sup>-2</sup>. Due to insufficient utilization of active ionic species, the energy storage capability reduces at higher current densities as shown by the plotted graph of applied current densities and the obtained specific capacitance (Figure 4.11a).[2,16] A good rate performance was observed for IITI-1/CNT/GCE, which can retain 63.15% of its initial capacitance up to 16 A g<sup>-1</sup>.[14] The specific capacitance and other performance parameters are not given for IITI-1/GCE and CNT/GCE, as they are considerably lower than IITI-1/CNT/GCE, indicated in both CV and GCD results. The high performance of IITI-1/CNT/GCE or IITI-1/CNT can be assigned to the following factors: (i) the precisely defined porous structure of **IITI-1** stimulates the electrolyte access to the electrolyte, (b) the IITI-1 structure wrapped by the CNT can function as a current collector along with a long-route charge carrier throughout the process of charge-discharge mode, and (c) the electron transportation can be improved by the high electronic conductivity of CNT via decreasing equivalent series resistance. As one of the essential requirements and important features of supercapacitors, the cycling stability test was also performed for IITI-1/CNT/GCE at 16 A g<sup>-1</sup> (Figure 4.11b). A long life cycle is obtained with 63.63% retention of initial capacitance up to 4000 cycles, validating its superior long-lasting efficiency. The inset of Figure 4.11b presents the first 25 GCD cycles, which show excellent reversibility. Such good cyclic efficiency of hybrid is the outcome of stable and robust composite formation due to a proper association between **IITI-1** and CNT, which alleviate the requirement of any commercial expensive binders.



**Figure 4.11.** (a) Plot of calculated specific capacitance against current densities, (b) cycling stability analysis test for **IITI-1/CNT/GCE** up to 4000 cycles, where inset shows the first 25 cycles (Electrolyte: 1M Na<sub>2</sub>SO<sub>4</sub>).

The comparison of supercapacitor performance of **IITI-1**/CNT with some advanced MOF structures and hybrids have been displayed in **Table 4.1**. Several considerations have been taken into account to conclude that **IITI-1**/CNT, a hybrid structure of **IITI-1** and CNT, is an emerging aspirant for next-generation supercapacitors.

**Table 4.1.** A comparison of the supercapacitor performance of **IITI-1/CNT** with theprevious state-of-the-art MOFs and related composite materials.

MOFs	Material	Specific Capacitance (F g <sup>-1</sup> )	Rate (mV s <sup>-1</sup> /A g <sup>-1</sup> )	Electrolyte	Retention of specific capacitance	Ref.
Fe-MIL-88B- NH <sub>2</sub>	Fe₃O₄/carbon	139	-/2	1 М КОН	83.3% after 4000 cycles	7
HKUST-1	rGO/HKUST-1	385	-/10	$0.5\mathrm{M}~\mathrm{Na_2SO_4}$	98.5 % after 4000 cycles	8
MOX-Fe	Fe <sub>3</sub> O <sub>4</sub> /Fe/C	600	-/1	6 M KOH	>80% after 5000 cycles	9
FA-MOF-5	NPC	258	-/0.25	$1\mathrm{M}\mathrm{H_2SO_4}$	NA	10
Ni-ZIF-8	C/NiO nanosheet	414	-/5	1 M LiPF <sub>6</sub>	92.2 % after 3000 cycles	11

Zn-NDC	C-Zn-NDC	114	-/1	$1 \mathrm{MH}_2 \mathrm{SO}_4$	80 % cycles NA	12
Zn-PAA	C-Zn-PAA	110	-/1	$1 \mathrm{MH}_2 \mathrm{SO}_4$	74 % cycles NA	12
Zn-ADA	C-Zn-ADA	95	-/1	$1~\mathrm{M}~\mathrm{H_2SO_4}$	63 % cycles NA	12
Zn-BTC	C-Zn-BTC	134	-/1	1 M H <sub>2</sub> SO <sub>4</sub>	84	12
Mn-MOF	CNTs@Mn-MOF	203.1	-/1	1 M Na <sub>2</sub> SO <sub>4</sub>	88 % after 3000 cycles	13
Carbonized Zn-MOF	MOF/PANI	477	-/1	$1~\mathrm{M}~\mathrm{H_2SO_4}$	>90% after 100 cycles	14
MOF-5	FA/MOF-5 NPC	204	5/	1 M H <sub>2</sub> SO <sub>4</sub>	>78% cycles NA	15
MOF-5	FA/MOF-5 NPC	100	5/	1 M H <sub>2</sub> SO <sub>4</sub>	NA	16
MOF-5	МС-А	208	2/-	6 M KOH	80 %	17
MOF-5	MAC	104	2/-	6 M KOH	41 %	17
MOF-5	MAC-A	271	2/-	6 M KOH	65 %	17
ZIF-8	ZIF-8/FA	~200	-/0.25	$1\mathrm{MH_2SO_4}$	15 % after 1000 cycles	18
MOF-5	MOF-5/AC	193	2/-	1М КОН	91.5 % after 1000 cycles	19
ZIF-8	CNT@NiO//PCPs	245	-/1	1М КОН	93% after 10000 cycles	20
Zn-MOF	Carbon nanosheets	278	10/-	6М КОН	98.8 % after 5000 cycles	21
Co-Mn MOF	MOF	106.7	10/-	2М КОН	95 % after 1500 cycles	22
Co-ZnMof	ZnCo <sub>2</sub> O <sub>4</sub> nanoparticles	451	5/-	6М КОН	97.9 % after 1500 cycles	23
Co@carbon nanocomposites	(Co-MOF)	109	-/0.25	6М КОН	99 % after 1000 cycles	24
Co <sub>3</sub> O <sub>4</sub> @carbon nanocomposites	(Co-MOF)	261	-/1	6M KOH	99 % after 1000 cycles	24
PPF-3	CoSNC	360.1	-/1.5	2M KOH	56.8 % CYCLES na	25
Co-MOF	Co-MOF/PEG	206.76	-/0.6	LiOH	98.5 % after 1000 cycles	26
ZIF-69	C-ZIF-69	168	5/	$0.5~\mathrm{M~H_2SO_4}$	NA	27
ПТІ-1	IITI-1/CNT	380	-/1.6	$1 \mathrm{M} \mathrm{Na}_2 \mathrm{SO}_4$	63.63 % after 4000 cycles (Binder free electrode)	This Work

Electrochemical Impedance Spectroscopy (EIS) experiments were used to further examine the charge transfer characteristics of **IITI-1**/GCE and **IITI-1/CNT**/GCE electrodes. A single semicircle was largely observed in the Nyquist plots from the EIS spectrum, corresponding to one impedance element. This was correspondingly mapped to a simple RC series circuit with a series resistance with the capacitance replaced by a Constant Phase Element (CPE) due to the non-ideal behavior of the plot, assumed to be due to the double-layer phenomena.[30] The mapped values according to the circuit in the inset are shown in (**Table 4.2, Figure 4.12**). attributed to the participation of CNT in the redox process, leading to higher capacitance values in the capacitance tests.[31] It is observed that  $R_{ct}$ value increases with the addition of CNT, but this is The value of  $\phi$  is 0.7, which is leaning towards capacitance characteristics for the Nyquist impedance. After cycling, there is a significant rise in the charge transfer resistance  $R_{ct}$ , which is attributed to structural degradation.[32]

	IITI-1	IITI-1	<i>IITI-1</i> /CNT	<i>IITI-1</i> /CNT
		(after cycling)		(after cycling)
Rser	1.8352e-012	2.3535e-012	0.0679e001	2.9167e001
CPE <sub>dl</sub>	7.09729e-002	6.71905e-002	4.15779e-004	6.48658e-004
Phi	0.7	0.7	0.7	0.7
R <sub>ct</sub>	9.80319e003	1.84833e004	Rct = 2.7659e004	1.66301e016

**Table 4.2.** A6 Nyquist parameters generated after fitting the circuit

Rser : Resistance (series);

CPE<sub>dl</sub>: Constant Phase element (double layer);

R<sub>ct</sub>: Resistance (Charge Transfer).



Figure 4.12. EIS of IITI-1 and IITI-1/CNT.

# **4.3.** Conclusions

In summary, a novel amino-functionalized layered metal-organic framework (**IITI-1**) has been synthesized at room temperature in ambient conditions. Simple ultrasonication technique has been employed for the preparation of **IITI-1/CNT** hybrid. Incorporation of CNT in the layered **IITI-1** gives rise to synergistically improved electrochemical energy storage efficiency, which is evident in noteworthy high specific capacitance and good rate performance of **IITI-1/CNT**. From the results, it can be presumed that the precisely defined porous structure of **IITI-1** decorated with amino-functions stimulates the electrolyte access to the active sites by enhancing the hydrophilicity in the system which improves the interaction of electrode with the electrolyte. The high electronic conductivity of CNTs can accelerate electronic transportation, which contributes immensely in delivering high electrochemical performance. The present work highlights the importance of MOF/carbonaceous materials to be promising supercapacitor electrode materials.

# **4.4. Experimental Section**

**4.4.1. Materials:** The common reagents and solvents were purchased from Merck and S. D. Fine Chem. Ltd. Solvents were distilled following the standard literature methods before their use. Reagent grade chemicals 4- (trifluoromethyl)aniline, 1-bromo- 3,5-dimethylbenzene,  $Pd(OAc)_2$  (98%), and  $Cu(NO_3)_2$ ·3H<sub>2</sub>O were obtained from Sigma-Aldrich and used as received.

**4.4.2.** Synthesis of 2,6-dibromo-4-(trifluoromethyl)aniline: This compound was synthesized according to previous literature <sup>[6]</sup> where a mixture of 4-(trifluoromethyl)aniline (2.52 mL, 20 mmol) and water (12 mL) was stirred under dark condition. Further, a mixture of 30% aq. H<sub>2</sub>O<sub>2</sub> (4.28 mL, 42 mmol) and 48% aq. HBr (5.7 mL, 50 mmol) was added dropwise at room temperature. After completion of the reaction, 120 mL of hexane: ethyl acetate (10: 1, v/v) was added in the reaction mixture followed by the addition of the NaHSO<sub>3</sub> to reduce the unreacted Br<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. Finally, passed through Na<sub>2</sub>SO<sub>4</sub> and dried. <sup>1</sup>H NMR (400 MHz, CDCl3, 25 °C)  $\delta$  = 7.66 (s, 2 H, Ar–H), 4.92 (br s, 2H, NH2) ppm; <sup>13</sup>C{1H} NMR (100 MHz, CDCl3, 25 °C)  $\delta$  = 107.70 (Ar–C), 120.66–121.67 (q, CF3), 124.37 (Ar–C), 129.00 (Ar–C), 144.85 (Ar–C) ppm. (**Figure 4.13-Figure 4.14**)

**4.4.3.** Synthesis of diester: In a round bottom flask, 2,6-dibromo-4-(trifluoromethyl)aniline (330 mg, 1 mmol) and (4- (ethoxycarbonyl) phenyl)boronic acid (777 mg, 2 mmol), were dissolved in DMF (18 mL) followed by the addition of aqueous  $K_2CO_3$  (690 mg, 5 mmol) and palladium acetate (25 mg). The reaction mixture was stirred under nitrogen at 80 °C for 12 h. After cooling the reaction to room temperature, it was extracted with Ethyl Acetate three to four times followed by its washing with water. The anhydrous Na<sub>2</sub>SO<sub>4</sub> was passed through the organic phase and the crude product was obtained by evaporating the solvent in a rotary evaporator. The pure product (diester) was obtained by silica gel column chromatography eluting with 15% ethyl acetate in hexane as a cream yellow solid (854 mg, 77 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta = 8.15$  (d, 4H, Ar–H), 7.36 (s, 2H, Ar–H), 4.40 (q, J = 7.2 Hz, 4H, –COOCH<sub>2</sub>–), 4.11 (s, 2H, –NH<sub>2</sub>), 1.41 (t, J = 7.2 Hz, 6H, –CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta = 14.42$  (–CH<sub>3</sub>), 61.26 (–CH<sub>2</sub>–), 120.41 (Ar–C), 126.58 (–CF<sub>3</sub>), 126.63 (Ar–C), 127.04 (Ar–C), 129.25 (Ar–C), 130.20 (Ar–C), 130.49 (Ar–C), 142.83 (Ar–C), 143.64 (Ar–C), 166.25 (–CO–) ppm; ESI-MS: (m/z): 458.1570 (100%). (**Figure 4.15-Figure 4.17**)

**4.4.4. Synthesis of H<sub>2</sub>L:** A mixture of diester (457 mg, 1 mmol), aq. KOH (4 N, 15 mL), and ethanol (30 mL) was taken in a flask and refluxed for 24 h to hydrolyze the ester followed by the removal of most of the solvents by a rotary evaporator. The resulting aqueous solution was subjected to filtration and the obtained filtrate was further cooled in an ice bath followed by its acidification with concentrated HCl to pH ~ 5. A light yellow precipitate appeared which was collected by filtration method. Further this precipitate was washed with cold water and dehydrated under vacuum. Light yellow powder was obtained as the final product. (yield : 305 mg, 66%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 25 °C)  $\delta$  = 8.02 (s, 4H, Ar–H), 7.59 (s, 4H, Ar–H), 7.30 (s, 2H, Ar–H), 5.01 (s, 2H, –NH<sub>2</sub>) ppm; <sup>13</sup>C {1H} NMR (125 MHz DMSO-*d*<sub>6</sub>, 25 °C)  $\delta$  = 117.73 (Ar–C), 124.05 (Ar–C), 126.45 (–CF3), 127.15(Ar–C), 129.79 (Ar–C), 130.59 (Ar–C), 142.93 (Ar–C), 145.75 (Ar–C), 167.64 (Ar–C), 170.00 (–COOH) ppm; ESI-MS: m/z 400.0758 (100%). (**Figure 4.18-Figure 4.20**)

**4.4.5.** Characterization and Instrumentation: <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) instrument by using CDCl<sub>3</sub> and DMSO- $d_6$  solvents. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent

residual peak (DMSO- $d_6$ , 2.50 ppm) and <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (DMSO- $d_6$ , 39.7 ppm). The HRMS spectrum was recorded on a Bruker-Daltonics, micrOTOF-QII mass spectrometer. Infrared spectra were recorded on a PerkinElmer Model 1320 spectrometer (KBr disk, 400–4000 cm<sup>-1</sup>). The surface area measurements were obtained using Autosorb Iq apparatus, version 1.11 (Quantachrome Instruments), and calculated from BET plots of the N<sub>2</sub> isotherms. FE-SEM was done using Supra55 Zeiss Field-Emission Scanning Electron Microscope. Transmission Electron Microscopy was carried on FEI Tecnai G2 12 Twin TEM. Electrochemical impedance spectroscopy (EIS) was performed with a frequency range of 1 Hz to 100 000 Hz using the same electrochemical cell as previously described. The electrochemical workstation used was an AUTOLAB PGSTAT 204N.

4.4.6. X-ray Crystallography: Single-crystal X-ray diffraction data were collected using an Oxford Diffraction (Rigaku Oxford Diffraction) SuperNova diffractometer fitted with an Oxford Cryosystems Cryostream 700 Plus open-flow nitrogen cooling device.[33] All crystals were coated in perfluoropolyether oil and mounted on a MiTeGen loop. Crystal Clear and CrysAlisPro[34] was used for data collection and reduction. Data at 100 K were collected at Diamond Light Source (beamline I19) ( $\lambda = 0.6889$ A°) fitted with an Oxford Cryosystems HeliX open-flow helium cryostat, and Rigaku Saturn 724+ CCD detector.[35] The structures were solved by direct methods using SHELXS-2014.[36] The positions of all the atoms were obtained by direct methods. All nonhydrogen atoms were refined anisotropically and the remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally  $1.2 \times \text{Ueq}$  of their parent atoms. All the H-bonding, C- $H^{...}\pi$  interactions, and molecular structure drawings were prepared using the program Mercury (ver 3.1) and Diamond (ver 3.1d). The crystallographic refinement data are placed in **Table A3** and selected bond distances and bond angles are shown in **Table A4**.

**4.4.7. Electrochemical Measurements and Fabrication of electrodes:** An Autolab PGSTAT 204N electrochemical set-up was utilized for the supercapacitor experiments, which uses NOVA software, version 1.10. A standard three-electrode assembly, consisting of a reference electrode (Ag/AgCl), the counter electrode (platinum plate), and the working electrode (glassy carbon electrode, 3 mm in diameter), was used. All observations were recorded at room temperature in 1 M Na<sub>2</sub>SO<sub>4</sub>. The glassy carbon electrodes (GCEs) were modified according to our previous works. Briefly, GCEs were cleaned and 5  $\mu$ L of suspensions (sample powder in ethanol) were deposited on the electrodes and dried (Mass Loading: 12.5  $\mu$ g). The prepared electrodes of **IITI-1**, CNT and **IITI-1/CNT**/GCE, respectively.

4.5. NMR and mass spectra of 2,6-dibromo-4-(trifluoromethyl)aniline, diester, and H<sub>2</sub>L



Figure 4.13. The <sup>1</sup>H NMR spectrum of 2,6-dibromo-4-(trifluoromethyl)aniline.



Figure 4.14. The <sup>13</sup>C{1H} NMR spectrum of 2,6-dibromo-4-(trifluoromethyl)aniline.



Figure 4.15. The <sup>1</sup>H NMR spectrum of diester.



Figure 4.16. The  ${}^{13}C{1H}$  NMR spectrum of diester.



Figure 4.17. ESI-MS of diester.



**Figure 4.18.** The <sup>1</sup>H NMR spectrum of  $H_2L$ .



Figure 4.19. The  ${}^{13}$ C NMR spectrum of H<sub>2</sub>L.



Figure 4.20. The ESI-MS of H<sub>2</sub>L.

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# **Chapter 5**

Vacuum Mediated Single-Crystal-to-Single-Crystal (SCSC) Transformation in Na-MOFs: Rare to Novel Topology and Activation of Nitrogen in Triazole Moieties

# **5.1. Introduction**

Owing to the structural flexibility, high porosity and its stability against any external forces such as heat, light, and vapor, metal-organic frameworks (MOFs) have gained tremendous attention in the field of gas adsorption, drug delivery, energy storage, catalysis, and fluorescent sensors.[1-6] Apart from these applications the studies to simplify the complicated frameworks with simple topology have also been evolved as a fascinating tool. MOFs with several network topologies can be designed and synthesized using a simple node-and-linker approach.[7] Highconnected nets with mixed connectivity such as (3,6)-, (4,6)-, (4,8)-, (3,7)-, (3,8)-, (3,10)-, and (3,12) connected frameworks are sporadically documented because of coordination number and geometric limitation.[8] Moreover, frameworks consisting of parallel polycatenated **kgd**-layers with (3,6)-connectivity are very rare.[9-10]

The construction of MOFs varies depending on the reaction conditions such as hydro/solvothermal methods, solvent, concentration, temperature, and the ratio of reactants and pH.[11] Although, the transition and lanthanides metals based MOFs have been explored extensively with excellent properties but alkali metal-based MOFs remain unexplored. In specific, sodium-based MOFs are very rare and involves a challenging task since sodium prefers to coordinate large ratios of solvents instead of organic linkers which results in unstable frameworks. Only recently, Yaghi

MOFs; et al reported two stable sodium the MOF-705,  $[Na_4(BDA)(CH_3OH)(H_2O)]$ and the extended version MOF-706,  $[Na_4(BPDA)(H_2O)_2],$ BDA= (2S,2'S)-2,2'-(terephthaloylbis(azanediyl))disuccinate.[12]

The nitrogen-rich 1,2,3-triazole containing derivatives synthesized *via* CLICK chemistry by a triple Huisgen 1,3-dipolar cycloaddition have gained considerable interest in the various field *viz* biological activities, material science, organic and coordination chemistry.[13a] Due to high aromaticity, they possess high stability under basic and acidic as well as reductive and oxidative conditions.[13b]

The formation of newer materials with fascinating properties by Single-Crystal-to-Single–Crystal (SCSC) transformation employing techniques have gained wider popularity in the last decade due to their potential applications in sensor technology, magnetic materials, catalysis, and gas storage materials.[14] The SCSC transformation by external stimuli such as heat, light, and vapor is commonly employed and able to maintain the desired crystallinity after transformation at a discrete and polymeric level.[15,16] However, less explored is the high-vacuum pressure mediated SCSC transformation where the transformed product results in the collapse of a structure due to bond breaking and bond formation in the lattice which in turn results in loss of crystallinity. Thus, vacuum mediated SCSC transformation in which crystallinity is retained has been recognized as a challenging process.[17,18] To explore the effect of the introduction of nitrogen-rich moiety along with flexible functionality on the sorption as well as the topology of MOFs, we report the facile *in-situ* synthesis of **Na-MOF1**, as the first example of Na based parallel polycatenated framework.

# 5.2. Results and discussion

A reaction of 1,3,5-triethynylbenzene and azidoglycine ethylester, using the standard "Click" conditions yielded {4-[3,5-Bis-(1-carbonylmethyl-1H-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}triacetate  $L(Et)_3$  with three flexible arms (**Scheme 5.1**).  $L(Et)_3$  has been characterized by <sup>1</sup>H and <sup>13</sup>C NMR and authenticated by single-crystal x-ray studies.



Scheme 5.1. Schematic representation for the synthesis of ligand L(Et)3.

Further, colorless cube-shaped tiny-crystals of a new metal-organic framework **Na-MOF1** were obtained by *in-situ* reaction of  $L(Et)_3$  with the aqueous solution of NaOH in methanol at RT followed by a simple slow evaporation method (Scheme 5.2). To the best of our knowledge so far only one report is available which discussed the binding modes of tritopic linker ( $L^{3-}$ )( $L^{3-}$ : deprotonated LH<sub>3</sub>) with La metal ion, which was prepared in two steps (i) isolation of {4-[3,5-Bis-(1-carbonylmethyl-1H-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}acetic acid (LH<sub>3</sub>) from ester L(Et)<sub>3</sub> by using THF as solvent and then (ii) solvothermally reacting with La(NO<sub>3</sub>).6H<sub>2</sub>O salt at 100 °C.[19] However, we have reported a facile *in-situ* alteration of L(Et)<sub>3</sub> and a synthesis of Na-MOF1 at room temperature. Na-MOF1 is soluble in water, methanol, and ethanol and can be recrystallized easily in its original form from these solvents.



Scheme 5.2. Schematic representation for the synthesis of Na-MOF1.

#### 5.2.1. Structural aspects of L(Et)<sub>3</sub> and Na-MOF1

**L(Et)**<sub>3</sub> crystallizes in an orthorhombic crystal system with  $Pca2_1$  space group, lying in a three-fold axis (**Figure 5.1** and **Table A5**). However, **Na-MOF1** crystallizes in a *trigonal* crystal system with space group *R*-3*c* (**Table A6**). Its asymmetric unit contains one Na ion coordinated by two  $\mu_2$  bridging water molecules, one oxygen atom O(3) of the free water molecule, and one carboxylate (-COO<sup>-</sup>) oxygen atom from a **L**<sup>3-</sup> (**Figure 5.2a**). Four oxygen atoms from  $\mu_2$  bridging water molecules and one oxygen atom from terminal water molecule are at the equatorial position of Na(I) site, and rest two oxygen atoms from two -COO<sup>-</sup> of **L**<sup>3-</sup> ligands are in the axial position giving 7 coordination number to each Na atom (**Figure 5.2b**). The bridging water molecules between the Na ions form a Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> closed ring cluster.


Figure 5.1. Structure of ligand, L(ET)<sub>3</sub>.



Figure 5.2. (a) Asymmetric unit of Na-MOF1. (b) Distorted pentagonal bipyramidal geometry of each Na ion in Na-MOF1.

The Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> cluster shows Na-Na(adjacent) separation of 3.976(0) Å and Na-Na(opposite) distance of 7.724(0) Å, which are coordinated to the neighboring clusters *via*  $6L^{3-}$  ligands leading to the formation of a 3-dimensional framework (**Figure 5.3a-c**). The whole framework is further stabilized by intra/inter-molecular hydrogen bondings (**Table A7**) and  $\pi \cdots \pi$  interactions (**Figure 5.3d**).



**Figure 5.3.** Ball-stick model of **Na-MOF1** showing the (a) Coordination environment around the Na ion centre and Na-Na distance, (b) Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> clusters linked to the neighboring clusters via  $6L^{3-}$  ligand, (c) 3D network along c-axis (d)  $\pi^{\bullet\bullet\bullet}\pi$  interactions between phenyl rings of **Na-MOF1**; distance 3.4215(9) Å, where (D represents the centroid of benzene ring).

The Na–O bond distances including bridging and coordinated H<sub>2</sub>O molecules to Na-atoms are found to be in the range of 2.3249–2.7102 Å (**Table A8**). Furthermore, the asymmetric unit contains one highly disordered methanol molecule with partial occupancy in a special position, which cannot be resolved. Thus, SQUEEZE was applied to remove this disordered methanol molecule.  $L^{3-}$  in Na-MOF1 shows unique features compared to the reported La-MOF with  $L^{3-}$ .[19] In Na-MOF1 all the three arms of  $L^{3-}$  are in *syn*-position bonded alternatively to each neighboring Na ions forming a *molecular-drone* shape (Figure 5.4).



**Figure 5.4.** Ball-stick model of **Na-MOF1** showing the (a) syn-arrangement of three arms of  $L^{3-}$  ligand, forming (d) molecular-drone shape. Hydrogen atoms are removed for clarity, D represents the centre core of the metal cluster ring.

This highly hydrated cyclized **Na-MOF1** that can easily yield good quality crystals prompted us to explore the solid-state structural reactivity of dehydrated product by introducing Single-Crystal-to-Single-Crystal (SCSC) transformation technique by applying external stimuli. Exposure of **Na-MOF1** crystal to high-pressure vacuum (10<sup>-3</sup> Torr) for 1.5 h resulted in the transformation of the framework as **Na-MOF2** to our surprise by retaining the crystallinity as observed by good X-ray diffraction pattern (**Scheme 5.3**).



Scheme 5.3. Single-Crystal-to-Single Crystal transformation of Na-MOF1 to Na-MOF2.

# 5.2.2. Structural aspects of Na-MOF2

The single-crystal X-ray analysis of post vacuum treated MOF crystals shows a similar trigonal, R-3c space group with about 25% shrinkage of

overall cell volume, which established the formation of dehydrated Na-MOF2 (Table A6). In Na-MOF2, each Na(I) site exists with coordination number 5, involving four coordinated O-atoms from three COO<sup>-</sup> unit and one N-atom from the 1,2,3-triazole ring of  $L^{3-}$  (Figure 5.5a). The measured bond distances between two adjacent and oppositely located Na ions in metal cluster core were found to be contracted to 3.704(4) Å and 6.882(1) Å, respectively as compared to Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> cluster in Na-MOF1 (Figure 5.5b). This dehydrated Na<sub>6</sub> cluster is further coordinated to form a condensed 3D-network (Figure 5.5c). The Na–O bond distances are in the ranges of 2.420(5)–2.867(9) Å and Na(1)–N(3) bond distance is 2.486(6) Å. (Table A7 and Table A8).



**Figure 5.5.** Ball-stick model of **Na-MOF2** showing: (a) 3D-network along c-axis (b) Coordination environment around Na ion (c) Na-Na bond distances. D represents the centre core of the metal cluster ring.

The SCSC transformation from **Na-MOF1** to **Na-MOF2**, results in the: (i) contraction of metal cluster cavity size from 7.728(0) Å to 6.882(1) Å, due to the removal of both bridging and coordinated water molecules and (ii)

activation of the N-N atoms of the 1,2,3-triazole ring. In Na-MOF1 the angle between the plane of central benzene ring and 1,2,3-triazole ring of  $L^{3-}$  is found to be 6.57° with the nearest Na…N non-bonding distances as Na(1)-N(2) 4.988 Å and Na(1)-N(3) 5.612 Å, whereas after transformation to the dehydrated Na-MOF2 the corresponding angle shows a deviation to 14.54° with the formation of Na…N coordinate bond. Furthermore, the Centroid-Centroid distance increases from 3.421 Å to 3.575 Å in the case of Na-MOF2 (Table A9).

Though proposing actual mechanisms in the case of MOFs is a challenging task. However, the SCSC transformation of **Na-MOF1** to **Na-MOF2** may be explained by the probable mechanistic pathways as shown in **Scheme 5.4**. To better understand the mechanism we have taken a slice of the highly hydrated Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> cluster of **Na-MOF1**. In the first step, the highly hydrated Na<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub> undergoes removal of both bridging and coordinated H<sub>2</sub>O molecules followed by rearrangement of  $-COO^{-}$  from bidentate in **Na-MOF1** to  $\mu_2$ -bridged in **Na-MOF2** retaining the Na<sub>6</sub> clusters with shrinkage in cavity size. This rearrangement leads to move the overall 1,2,3-triazole unit closer to each other (from 3.623 Å to 3.334 Å) leading to the formation of **Na-MOF2** with new Na-N bonds.



**Scheme 5.4.** Proposed mechanistic pathways of **Na-MOF1** to **Na-MOF2** via (i) Removal of water molecules (ii) Rearrangement of carboxylate group and (iii) Activation of nitrogen atoms (coming closer from 3.623 Å to 3.334 Å).

# 5.2.3. Topological analysis of Na-MOF and Na-MOF2

We have compared the topologies of the **Na-MOF1** and **Na-MOF2** and found to be unique and interesting. In **Na-MOF1**, organic ligands are considered as linkers, Na-based clusters can be identified as six-connected nodes. Thus, the topology of the structure can be simplified as a binodal 2periodic (6,3-c) **kgd** network with the point symbol  $(4^3)_2(4^6.6^6.8^3).[20]$ This **kgd-layers** are oriented perpendicular to (0,0,1) and catenated to two adjacent layers, resulting in Doc=2 and Is=1.[10a] So, these catenated layers form a 3D parallel polycatenated array (**Figure 5.6**).



**Figure 5.6.** The schematic view of (a) Underlying 6,3-c kgd net. (b)  $2D+2D\rightarrow 3D$  parallel polycatenation of kgd nets.

In Na-MOF2, the new bonding due to the coordination between Na ion and the nitrogen atom (the elongated Na-N bond was ignored while assigning topology of Na-MOF2) leads to unprecedented 3,3,12-c topology with point symbol:  $(4.6^2)_6(4^6.6^{24}.8^{24}.10^{12})(6^3)_2$  (Figure 5.7). We can see this new single 3D net as derived from the catenation of kgdlayers connected by an additional edge that corresponds to a new bonding interaction between the Na and the nitrogen of the 1,2,3-triazole.(Figure 5.8a) This new topology shows also the feature of self-catenation of 8membered rings (Figure 5.8b).[10a,21a] These relations could be illustrated by the procedure of network decomposition, which is realized in the ToposPro program package.[21b] The procedure consists of sequentially breaking of equivalent edges until the subnet of the net is no longer self-catenated (Figure 5.9 and Figure 5.10).[21c] We collected this net in the ToposPro database as a new entry smm1 (Shaikh M. Mobin1).



Figure 5.7. Underlying 3,3,12-c net as new topology *smm*1.



**Figure 5.8.** (a) A fragment of initial structure merged with simplified 8-rings (3,3,12-c Topology), (b) Catenation of two strong 8-rings (feature shown by 3,3,12-c Topology).



**Figure 5.9.** Procedure of (a) decomposition of the 3,3,12-c net smm1. Dashed lines correspond to deleted edges. In result, we obtain the set of parallel polycatenated 3,6-c kgd layers with extra 2-c nodes, (b) decomposition of the 3,3,12-c net (Environment of the 6-c node). Dashed lines correspond to deleted edges.



**Figure 5.10.** Relations between 3,6-c kgd (yellow dashed lines) layers and 2,3,6-c (blue and brownish-red continuous lines) layers. **kgd** topology is obtained from 3,2,6-c topology by removing 2-c bridging nodes.

# 5.2.4. Characterization of the bulk samples of Na-MOF1 and Na-MOF2

The Powder X-ray Diffraction patterns of Na-MOF1 and Na-MOF2 are in agreement with the simulation (Figure 5.11), demonstrating the material's bulk purity. The thermal studies (TGA) show that both Na-MOF1 and Na-MOF2 are stable up to  $300^{\circ}$ C (Figure 5.12). N<sub>2</sub> adsorption isotherms were performed at 77K. The observed adsorption isotherm is typical of type-I behavior. The BET (Brunauer–Emmett–Teller) surface area of Na-MOF1 was determined to be 34.624  $m^2/g$  which increases up to 103.182  $m^2/g$  in Na-MOF2 as shown in Figure 5.13 and Figure 5.14).



Figure 5.11. Powder XRD spectra of Na-MOF1 and Na-MOF2.



Figure 5.12. TGA graph of Na-MOF1 and Na-MOF2.



Figure 5.13. (a) Adsorption-Desorption isotherm of  $N_2$  @77 K of Na-MOF1. (b) pore size distribution (in nm).



**Figure 5.14.** (a) Adsorption-Desorption isotherm of  $N_2$  @77 K of **Na-MOF2**, (b) pore size distribution (in nm).

# **5.3.** Conclusions

In summary, a facile *in-situ* access to sodium metal coordinated metalorganic framework **Na-MOF1**, as the first example of Na based parallel polycatenated framework. Single-Crystal-to-Single-Crystal transformation of **Na-MOF1** to a new framework **Na-MOF2** was explored successfully despite being a challenging task to retain crystallinity after exposure to vacuum pressure. The SCSC transformation of **Na-MOF1** to **Na-MOF2** reveals the activation of N-N atoms of the 1,2,3-triazole unit. Moreover, the topology features of the MOFs were found to be from rare parallel polycatenated *kgd* nets to novel 3-periodic 3,3,12-c net topology which is assigned as *smm*1. Furthermore, this complex SCSC transformation of **Na-MOF1** to **Na-MOF2** was elucidated by the mechanistic pathways. Owing to facile synthesis, stability, and solubility, **Na-MOF1** and **Na-MOF2** can be employed for applications in various fields. The unique topological analysis could be utilized for designing of new MOFs.

# **5.4. Experimental Section**

**5.4.1. Materials:** Commercially available starting materials and reagent grade solvents were used as received. The common reagents and solvents were procured from Merck and S. D. Fine Chem. Ltd. The solvents were dried and distilled following the standard literature procedures before their use. 1,3,5-Triethynyl Benzene was purchased from Sigma Aldrich Chemical Co., USA, and used as received without further purifications.

5.4.2. Synthesis of L(Et)<sub>3</sub>: {4-[3,5-Bis-(1-ethoxycarbonylmethyl-1H-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}acetic acid ethyl ester}: Ligand  $L(Et)_3$  was synthesized according to previous literature with slight modifications<sup>2</sup>. Ethyl azidoacetate solution  $\sim 25\%$  in toluene (NMR) (387) mg, 3 mmol, 3 Eq., M=129.11) and 1,3,5-Triethynylbenzene 97%, (366 mg, 1mmol, M = 150.17) were suspended in a 1:1 mixture of water and tert-butyl alcohol (20 mL). Further sodium ascorbate (5.0 mol %) was added, followed by copper (II) sulfate pentahydrate (1.0 mol %). The heterogeneous mixture was stirred for 3-4 h, the progress of the reaction was continuously monitored by TLC which indicates complete consumption of the reactants giving transparent yellow color solution. The reaction mixture was diluted with water (10 mL), cooled in ice, and the yellow precipitate was collected by filtration. The precipitate was washed with cold water (2  $\times$  10 mL) and dried under vacuum. The resulting washed product was filtrated over a pad of silica, elution with EtOAc(Rf=0.5) gave the title product in pure form as an off white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.10 (s, 3H), 8.07 (s, 3H), 5.22 (s, 6H), 4.27 (q, 6H), 1.29 (t, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 166.24, 147.14, 131.18, 122.57, 122.11, 62.47, 51.09, 14.03.

### 5.4.3. Synthesis of Na-MOF1

The above-synthesized triester  $L(Et)_3$  (214mg, 0.4 mmol, M = 537.32) was dissolved in 30 mL of methanol, to this an aqueous solution (3mL of water) of sodium hydroxide (48 mg, 1.2 mmol, 3 equiv.) was added. After 12 h of stirring at RT, the resulting aqueous solution was kept for slow evaporation. The colorless cube-like crystals appeared within 24-48 h in good yield (yield ~96%, 247.07 mg, 0.38 mmol).

### 5.4.4. SCSC transformation of Na-MOF1 to Na-MOF2

Crystals of **Na-MOF1** obtained from the slow evaporation process were treated under a high vacuum process (10<sup>-3</sup> Torr or 0.133 Pascal) for 1.5 h, results in SCSC transformation of **Na-MOF1** to **Na-MOF2** with the removal of bridging and coordinated water molecules.

5.4.5. Characterization and Instrumentation: Single-crystal X-ray structural studies were conducted on a Rigaku-Oxford Supernova CCD diffractometer equipped with a low-temperature attachment. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku Smart Lab X-ray diffractometer using monochromated Cu-K $\alpha$  radiation (0.154 nm). <sup>1</sup>H NMR (400 MHz), and <sup>13</sup>C NMR (400 MHz) spectra were collected on the Bruker Advance (III) instrument by using CDCl<sub>3</sub>. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) concerning the solvent residual peak (CDCl<sub>3</sub>, 7.25 ppm). Chemical shifts of <sup>13</sup>C NMR are presented solvent residual peak (CDCl<sub>3</sub>, relative to the 77.00 ppm. Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO (TGA/DSC 1) system by using STAR<sup>e</sup> software system up to 800 °C under N<sub>2</sub> flow with a heating rate of 10 °C min<sup>-1</sup>. The N<sub>2</sub> isotherm was measured on a Quantachrome Instrument (Autosorb iQ, version 1.11). Na-MOF1 and Na-MOF2 were degassed at 100 °C and N<sub>2</sub> adsorption isotherms were performed at 77K for Na-MOF1 and Na-MOF2.

5.4.6. X-ray Crystallography: The single crystal of L(ET)3, Na-MOF1, and NaMOF2 were mounted on a Rigaku-Oxford Supernova CCD Diffractometer and the data were collected at 150 K using graphitemonochromated Cu-K $\alpha$  ( $\lambda \alpha = 1.54814$  Å). The data collections were evaluated using the CrysAlisPro CCD software. The data were collected by the standard  $\phi - \omega$  scan techniques and scaled as well as reduced by CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97, refining on F<sup>2</sup>.[22] All non-H atoms were refined anisotropically and all the H atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally  $1.2 \times \text{Ueq}$  of their parent atoms. The hydrogen-bonding interactions, molecular drawings and mean-plane analysis were obtained using the Diamond (ver. 3.1d).[23] In Na-MOF1, the asymmetric unit contains one highly disordered methanol molecule with partial occupancy in a special position, which cannot be resolved. Thus, SQUEEZE was applied to remove this disordered methanol molecule. Furthermore, O5 has been assigned a 1/3 occupancy. Similarly, in Na-MOF2 there exists one highly disordered lattice water molecule occupying a special position with high thermal parameters. Despite several attempts and collecting a large number of data-set for Na-MOF2, we were unable to get better quality data. However, we have found a reasonably good structure solution for Na-MOF2 after data was cut off upto approx. 54%. This is due to the fact crystal undergoes vacuum treatment, which restricts good crystallinity. The crystal and refinement data are summarized in Table A5 and Table A6, hydrogen bondings are shown in Table A7 and selected bond distances and bond angles are shown in Table A8 and Table A9.

# 5.5. NMR spectra of L(Et)<sub>3</sub>, diester and H<sub>2</sub>L



Figure 5.15. The <sup>1</sup>H NMR spectrum of ligand L(Et)<sub>3</sub>.



Figure 5.16. The <sup>13</sup>C NMR spectrum of ligand L(Et)<sub>3</sub>.

# **5.6. References**

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# **Chapter 6**

# An imidazole derivative-based chemodosimeter for $Zn^{2+}$ and $Cu^{2+}$ ions through "ON–OFF–ON" switching with intracellular $Zn^{2+}$ detection

# **6.1. Introduction**

The development of new fluorescent chemodosimeter for the quantitative and qualitative detection of metal ions have gained interest in supramolecular and analytical chemistry due to several advantages like cost-effectiveness, design simplicity, high selectivity, sensitivity, and low detection limit.[1-8] Fluorescent chemosensors have emerged as an important method to sense in-vivo and in-vitro biologically important species such as metal cations, anions, and biomolecules.[9-12] Ideally, fluorescent chemosensors have a receptor-linked fluorophore which translates the underlying event as a fluorescence signal.[13] Thus, the ideal fluorescent chemosensors are characterized by two fundamental tenets: (i) strong affinity of the receptor unit with the binding-selectivity and (ii) non-interference of the fluorescence signal with environmental factors such as concentration, the environment around the sensor molecule (pH, polarity, temperature, etc.), stability under illumination and photobleaching.[14] Therefore, to develop selective and sensitive fluorescent chemosensors is a challenging task.

The  $Zn^{2+}$  ion is the second biggest heavy and crucial element in the human body after iron.[15] The majority of  $Zn^{2+}$  ions are strongly bound to proteins and play a critical catalytic role.[16] A smaller amount of weakly bound, charitable, or mobile zinc ions are available in high concentrations in numerous tissues, especially in the prostate, pancreas, and brain tissues.[17-19] It plays a prominent role in various biological

processes, such as regulation of gene transcription and expression, immune function, natural signal transmitters or modulators, neurotransmission, cellular metabolism, mammalian reproduction, and apoptosis.[20-25] Various genetic irregularities or environmental factors that cause irregularities in intracellular  $Zn^{2+}$  concentration to lead to various diseases such as Parkinson's disease, amyotrophic lateral sclerosis (ALS), and epilepsy cerebral ischemia.[26] Fluorescence-based sensing of  $Zn^{2+}$  ion is a powerful tool for bio-imaging because even very low concentration can be detected due to rapid response and high sensitivity.[27-30]

The major disadvantage of many reported Zn<sup>2+</sup> sensors is interference from other transition metal ions, especially Cd<sup>2+</sup> and followed by a tedious multistep synthesis process.[31] Therefore, synthesis of the  $Zn^{2+}$  sensing probe with high sensitivity and selectivity for detecting trace amounts of Zn<sup>2+</sup> in particular intracellular has shown tremendous potential in biomedical device applications.[32] Furthermore,  $Cu^{2+}$  is the third most abundant metal ions in the human body after iron and zinc. Imbalance of Cu<sup>2+</sup> ion in the human body leads to serious threads including Menkes syndrome, Wilson's disease, etc.[33] Generally, Cu<sup>2+</sup> ion which is a paramagnetic center shows a fluorescence turn-off phenomenon due to the fast electron/energy transfer.[33-37] Zn<sup>2+</sup> and Cu<sup>2+</sup> incorporated Schiff complexes have potential applications viz., base antibacterial, antimicrobial, photosensitizers, diabetics, insulin, and anticancer agents.[38] Fruitful host-guest interaction leads perturb the to fluorophore's optical property which results in fluorescence enhancements/quenching/shifts in the original fluorescence signal due to mechanisms such as photo-induced electron transfer (PET), internal charge transfer (ICT), C=N isomerization, and fluorescence resonance energy transfer (FRET), etc.[39]

Herein, we report the highly selective and sensitive fluorescence turn-on/off type sensing probe **HL** for  $Zn^{2+}$  and  $Cu^{2+}$ . **HL** shows a fluorescence turn-on signal in the presence of  $Zn^{2+}$  ions, which gets turned off in the presence of  $Cu^{2+}$  ions. The sensing nature of HL towards  $Zn^{2+/}Cu^{2+}$  was primarily investigated by UV-vis spectroscopy and further confirmed by fluorescence techniques that show the fluorescence turn-on/ turn-off behaviors. **HL** exhibit intracellular sensing of  $Zn^{2+}$  ions towards Hela and DU-145 cancer cells.

# 6.2. Results and discussion

A new ligand 2-[(3-imidazol-1-yl-propylimino)-methyl]-6-methoxyphenol (**HL**) was obtained by the condensation reaction of 3-imidazol-1yl-propylamine with 2-hydroxy-3-methoxy-benzaldehyde (1:1) in methanol under reflux conditions for 6 h (**Scheme 6.1**). **HL** has been characterized by NMR, HRMS, and IR spectroscopic techniques. Moreover, the molecular structure of **HL** was authenticated by singlecrystal X-ray diffraction analysis.



Scheme 6.1. Synthesis of HL.

# 6.2.1. Structural aspects of HL

**HL** crystallizes in the monoclinic  $P2_12_12_1$  space group (**Figure 6.1 and Table A10**).[40] In the X-ray structure of **HL**, the imidazole unit was found to be perpendicular to the phenyl unit and C(8)-N(1) bond length was found to be 1.268 Å, confirming the C=N double bond between them.



Figure 6.1. Perspective view of HL.

The packing feature of **HL** shows the presence of C–H···O and C–H···N types intermolecular H-bonding interactions. C–H···O interactions involve between hydrogen atom of a methylene group (H13) and donor oxygen atoms of phenyl unit (O1) and methoxy group (O2): C(13)–H(13)···O(1), 2.642(0.002) Å and C(13)–H(13)···O(2), 2.622(0.002) Å respectively, which leads to the formation of a 1-D polymeric chain which is further linked with another chain *via* C(8) – H(8)···N(3), 2.523(0.003) Å and C(11)–H(11B)···O(1), 2.664(0.002) Å respectively leads to the formation of the supramolecular 2-D network (**Figure 6.2 and Table A11**).



**Figure 6.2.** Packing diagram of **HL**, showing C-H···O and C-H···N, H-bonding interaction forming 1D and 2D network.

## 6.2.2. Photophysical Behaviour of HL

The absorption spectra of **HL** in an ACN–H<sub>2</sub>O mixture (7:3 v/v in 10  $\mu$ M HEPES buffer at pH = 7.2) displays two prominent absorption bands at 260 nm and 330 nm wavelengths due to  $\pi - \pi^*$  and  $n - \pi^*$  electronic transitions respectively. Furthermore, different monovalent, divalent and trivalent metal ions such as, Ag<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Mg<sup>2+</sup>,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^2$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$ ,  $Cr^{3+}$ , and  $Al^{3+}$  at similar concentrations were introduced to the HL solution and the absorption spectra were recorded. Interestingly, in the case of  $Zn^{2+}$  and  $Cu^{2+}$  ions, bathochromic shifts of 50 and 45 nm wavelengths were observed (Figure 6.3a). Furthermore, we performed the absorption titration of HL against  $Zn^{2+}$  ions and  $Cu^{2+}$  ions of variable concentrations. The subsequent addition of  $Zn^{2+}$  ions into the solution of **HL** results in a gradual decrease of the absorption peak at 330 nm and an increase at 380 nm wavelength with the formation of four distinct isosbestic points at 250 nm, 270 nm, 307 nm, and 342 nm wavelength, respectively (Figure 6.3b), while in case of Cu<sup>2+</sup> four isosbestic points were observed at 252 nm, 267 nm, 320 nm, and 345 nm wavelengths (Figure 6.3c). However, the absorption titration of HL with other metal ions (except  $Zn^{2+}$  and  $Cu^{2+}$ ) results in no significant changes in the absorption spectra. Moreover, the addition of different metal ions into the solution of **HL** (1: 5, L: M ratio) subjected to under UV light results in blue fluorescence in the case of  $Zn^{2+}$  ions, which clearly shows the colorimetric sensing behavior of **HL** towards  $Zn^{2+}$  ions (**Figure 6.4**).



**Figure 6.3.** (a) UV-visible titration spectra of **HL** with different metal cations (nitrates, chlorides etc.), (b) absorption titration spectra of HL with  $Zn^{2+}$  metal ions, (c) absorption titration spectra of HL with  $Cu^{2+}$  ions (concentration of HL other metal ions,  $c = 1.0 \times 10^{-5}$  M and  $c = 1.0 \times 10^{-4}$  M respectively).



**Figure 6.4.** Colorimetric detection of  $Zn^{2+}$  using **HL** (10 equivalent of each metal ions with respect to HL).

In the case of emission, HL shows very weak fluorescence at 450 nm wavelength which is characteristic of the excited state intramolecular proton transfer (ESIPT) from -OH group to the Schiff base nitrogen at 370 nm wavelength excitation, and isomerization of the imine bond (-HC=N).[15] Furthermore, we recorded the fluorescence spectra of HL with different metal ions (Figure 6.5a). To our surprise, the fluorescence intensity was found to be maximum in the case of  $Zn^{2+}$  ions. Although, in the case of Cd<sup>2+</sup> the fluorescence intensity was found to be weak compare to  $Zn^{2+}$  ions. Moreover, we performed fluorescence titration of **HL** against  $Zn^{2+}$  ions. In the fluorescence titration experiment, subsequent addition of  $Zn^{2+}$  ions into the solution of HL results in a continuous fluorescence enhancement at 470 nm which may be due to the formation of the Zinc complex. The fluorescence turn-on was observed to be ~39 fold and a very high stokes shift of 50 nm was observed (Figure 6.5b). HL show fluorescence predominantly in the blue region (emission maxima 450 nm), while the emission of HL-Zn<sup>2+</sup> extends to higher wavelength with emission maxima at 520 nm with an FWHM value of 143 nm (wavelength window 440-583 nm) which reflects the resultant fluorescence in the bluegreen region (Figure 6.5a) The limit of detection (LOD) of HL with  $Zn^{2+}$ was found to be 31.044 nM. Moreover, the fluorescence turn-on phenomenon was not observed with other metal ions.



**Figure 6.5.** (a) Fluorescence spectra of **HL** with different metal ions. (b) Fluorescence titration of **HL** towards  $Zn^{2+}$  ions. Conditions, **HL** (c =  $1.0 \times 10^{-5}$  M) in aq. ACN (ACN/H<sub>2</sub>O = 7:3 v/v, 10  $\mu$ M HEPES buffer, pH = 7.2), concentration of different metal ions including  $Zn^{2+} = 1.0 \times 10^{-4}$  M. Inset: Inset: relative fluorescence intensity changes with respect to  $Zn^{2+}$ .

The possible reason for fluorescence turn-on towards  $Zn^{2+}$  may be the following: (i) an imine -CH=N- group is coordinated by  $Zn^{2+}$  which restricts the isomerization of the imine group and (ii) a new band or bathochromic shift appears in the absorption spectrum. The limit of detection (LOD) is calculated using the equation LOD =  $3.3(\sigma/S)$ , where  $\sigma$  is the standard error and S is the slope of calibration. The LOD with  $Zn^{2+}$  was determined to be 31.044 nM.[41]

# 6.2.3. Selectivity of HL and dual sensing of Cu<sup>2+</sup> ions

The selectivity test is executed using a different monovalent, divalent, and trivalent metal ion which exhibits that only  $Zn^{2+}$  ion exhibit fluorescence 'turn-on' phenomenon. Furthermore, a competitive selectivity test was also performed with different metal ions in the presence of  $Zn^{2+}$  ions in 1:5 ratios. We observed only a slight decay in the fluorescence intensity except for the addition of Cu<sup>2+</sup> ions (**Figure 6.6**).



**Figure 6.6.** (a) Relative fluorescence response (Histogram) of various metal ions (c = 1.0  $\times 10^{-4}$  M) with **HL** (c =  $1.0 \times 10^{-5}$  M) in aq. CH<sub>3</sub>CN (ACN/H<sub>2</sub>O = 7:3 v/v, 10  $\mu$ M HEPES buffer, pH = 7.2). (b) The effect of the influence of different metal ions in the presence of Zn<sup>2+</sup> ions and HL (A = **HL** + Zn<sup>2+</sup>, Data: Mean  $\pm$  SD).

To our surprise fluorescence intensity of the HL-Zn(II) system was found to be quenched after adding  $Cu^{2+}$  ions. Furthermore, we have performed a fluorescence titration of HL-Zn(II) system with  $Cu^{2+}$  ions. After the subsequent addition of  $Cu^{2+}$  ions into the HL-Zn(II) system, the fluorescence intensity was found to be quenched after every addition indicating the fluorescence 'turn-off' behavior of the system (**Figure 6.7**). The limit of detection (LOD) of HL with  $Cu^{2+}$  was found to be 11.64 nM.

The fluorescence turn-off phenomenon was not observed (except  $Cu^{2+}$ ) with other metal ions confirmed the selective sensing nature of the HL-Zn(II) system towards  $Cu^{2+}$  ions. The quantity of Zn<sup>2+</sup> and Cu<sup>2+</sup> ions was equal in turn-on as well as in turn-off fluorescence experiments. Hence, the results obtained from UV-vis as well as from fluorescence studies indicate highly selective and sensitive detection of Zn<sup>2+</sup> and Cu<sup>2+</sup> metal ions by employing **HL**.



**Figure 6.7.** Fluorescence quenching spectra of HL-Zn(II) in presence of Cu<sup>2+</sup> ions. Conditions, **HL** (c =  $1.0 \times 10^{-5}$  M) in aq. ACN (ACN/H<sub>2</sub>O = 7:3 v/v, 10 µM HEPES buffer, pH = 7.2), concentration of Cu<sup>2+</sup> =  $1.0 \times 10^{-4}$  M. Inset: Inset: relative fluorescence intensity changes with respect to Cu<sup>2+</sup>.

# 6.2.4. Mode of binding of HL towards Zn<sup>2+</sup>/Cu<sup>2+</sup> metal ions

To better understand the mode of interaction between **HL** and  $Zn^{2+}$ , we performed a <sup>1</sup>HNMR titration experiment in DMSO-*d*<sub>6</sub> (**HL**) and D<sub>2</sub>O (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) solvent system. In this experiment, the hydroxyl –OH peaks were found to disappear slowly after the subsequent addition of  $Zn^{2+}$  ions into **HL** solution in the NMR tube. After the addition of 0.5 Equiv. of  $Zn^{2+}$  ions, the –OH peaks were found to be complete disappear at 13.6 ppm (**Figure 6.8**).[41] Hence, NMR titration results clearly showed that there might be a strong interaction between –OH groups of the **HL** with  $Zn^{2+}$  ions.



**Figure 6.8.** <sup>1</sup>H NMR spectra of **HL** in **DMSO-***d*<sub>6</sub> at 25°C and the analogous changes after the continuous addition of different equivalents of  $Zn(NO_3)_2$ •6H<sub>2</sub>O in D<sub>2</sub>O from (a) HL, (b) **HL** + 0.1 equiv.  $Zn^{2+}$ , (c) **HL** + 0.2 equiv.  $Zn^{2+}$ , (d) **HL** + 0.3 equiv.  $Zn^{2+}$ , (e) **HL** + 0.4 equiv.  $Zn^{2+}$  and (f) **HL** + 0.5 equiv.  $Zn^{2+}$ 

To understand the complex formation of **HL** towards  $Zn^{2+}$  and  $Cu^{2+}$  ions, we have performed reactions of **HL** with  $Zn(NO_3)_2 \cdot 6H_2O$  and  $Cu(NO_3)_2 \cdot 3H_2O$  in MeOH at room temperature which results in single crystals of dimeric  $Zn^{2+}$  (1) and  $Cu^{2+}$  (2) complexes within 7 days (Scheme 6.2).



Scheme 6.2. Preparation of compounds 1 and 2.

# 6.2.5. Structural aspects of 1 and 2

**1** and **2** crystallize in the Monoclinic I2/a space group with a crystallographically imposed reversal center (**Table A10**). Molecular structure of **1** and **2** confirm the dimeric nature in which each  $Zn^{2+}$  and  $Cu^{2+}$  ions are in an N<sub>3</sub>O<sub>2</sub> Penta-coordinated environment from two **HL** ligands forming a distorted trigonal bipyramidal (TBP) geometry (**Figure 6.9** and **6.10**). Structures of **1** and **2** were found to be iso-structural.



**Figure 6.9.** (a) Molecular structure of **1**. (b) Penta-coordinated environment (distorted trigonal bipyramidal geometry) in **1**. (Hydrogen atoms have been removed for clarity).



**Figure 6.10.** (a) Molecular structure of **2**. (b) Penta-coordinated environment (distorted trigonal bipyramidal geometry) in **2**. (Hydrogen atoms have been removed for clarity).

The distances between two adjacent  $Zn^{2+}$  and  $Cu^{2+}$  centers are 8.263 Å and 8.465 Å respectively. In **1** and **2**, a 16 membered metallacycle was observed with a cavity size of  $5.053 \times 5.053$  Å and  $4.991 \times 4.991$  Å respectively (**Figure 6.11**). Moreover, all the Zn-N, Zn-O, Cu-N, and Cu-O bond distance are comparable with other related systems.[43] The molecular structure of **1** is in good understanding with Job's plot The maxima in the job's plot at the mole fraction of 0.67 confirms 1:2 (Metal to Ligand) stoichiometry between **HL** and Zn<sup>2+</sup> ions (**Figure 6.12**).[44]



Figure 6.11. 16-membered metallacycle in (a) 1 and (b) 2 with representation of cavity size.



Figure 6.12. Job's plot showing  $Zn^{2+}$ :HL(1:2) complex recorded in CH<sub>3</sub>CN-H<sub>2</sub>O solution.

The packing feature of **1** and **2** confirms the presence of intermolecular C–H<sup>...</sup> $\pi$  and C–H<sup>...</sup>O hydrogen bonding interactions. Intermolecular C–H<sup>...</sup>O, hydrogen bonding involves the donor oxygen atom (O3) of the phenyl moiety and a hydrogen atom (H20) of the phenyl unit of another molecule with the bond length of C(20)–H(20)···O(3), 2.638(0.003) Å and C(20)–H(20)···O(3), 2.642(0.008) Å respectively. Another intermolecular C–H<sup>...</sup> $\pi$  interactions in **1** and **2** is present between a hydrogen atom (H18) of phenyl unit and  $\pi$  e- a cloud of imidazole ring forming a linear 1-D chain structure (**Figure 6.13 and Figure 6.15**), which are further connected leading to the formation of a 2D-network (**Fig. 6.14, Figure 6.16, Table A11-A13**).



**Figure 6.13**. Packing diagram of intermolecular Hydrogen Bonding and  $C-H\cdots \pi$  interactions forming 1D layer in **1**, where D is the dummy atom.



**Figure 6.14.** Intermolecular C-H<sup> $\dots$ </sup> $\pi$  and H-bonding interactions in **1** (D represent the dummy atom).



**Figure 6.15.** Intermolecular. Packing diagram of intermolecular Hydrogen Bonding and C–H··· $\pi$  interactions forming 1D layer in **2**, where D is the dummy atom.


**Figure 6.16.** Intermolecular. Packing diagram of intermolecular hydrogen bonding and C-H<sup>...</sup> $\pi$  interactions in **2**. (Where D is the dummy atom).

Moreover, **1** and **2** were characterized by HRMS, FT-IR, NOESY, and COSY spectroscopic techniques. The average lifetime and fluorescence quantum yield of **1** was found to be  $\langle \tau \rangle = 7.50$  ns and  $\Phi = 0.520$  respectively (**Table 6.1, Table 6.2, and Figure 6.17**).



**Figure 6.17.** (a) Average lifetime measurement of **1** in ACN. (b) Fluorescence spectra of **1** in ACN.

 Table 6.1. Average Life time measurement of 1.

τ1	τ2	α1	<b>a</b> 2	$\chi^2$	<7>
0.10 ns	9.73 ns	0.23	0.77	1.09	7.50 ns

Compound <sup>a</sup>	$\lambda(_{S0\rightarrow S1})$ (nm)	$\epsilon (M^{-1} cm^{-1})$	$\lambda_{em}^{b}$ (nm)	$\Phi^{c}$
HL	265	$6.1 \times 10^{4}$	-	-
	330	$1.3 \times 10^{4}$	-	-
1	275	$4.3  imes 10^4$	-	-
	380	$1.2 \times 10^4$	470	0.520
2	276	$7.1  imes 10^4$	-	-
	377	$1.7  imes 10^4$	-	-

Table 6.2. Photophysical properties of HL, and 1 and 2.

<sup>a</sup>Recorded in Acetonitrile. <sup>b</sup>Excited at  $\lambda_{S0 \rightarrow S1.}$  <sup>c</sup>Determined by using quinine sulfate as standard( $\Phi_{st}$ =0.54, 0.1 M H<sub>2</sub>SO<sub>4</sub>).

#### 6.2.6. Reversibility of sensor

To understand the reversibility of **HL** towards  $Zn^{2+}$ , we performed a fluorescence titration of **HL** with  $Zn^{2+}$  ions and ethylenediaminetetraacetic acid (EDTA). The interaction of **HL** towards  $Zn^{2+}$  ions increases in fluorescence intensity, which on the addition of EDTA in a stoichiometric ratio was found to be quenched. Further addition of  $Zn^{2+}$  ion in the same cuvette results in the increase in the fluorescence intensity showing the reversible nature of the chemodosimeter **HL** (**Scheme 6.3, Figure 6.18a, and Figure 6.19**). Moreover, on the addition of  $Cu^{2+}$  ions into the solution of the HL- $Zn^{2+}$  system, fluorescence intensity was found to be diminished. Further, on the addition of EDTA into the same cuvette containing both  $Zn^{2+}$  and  $Cu^{2+}$  ions (HL +  $Zn^{2+}$  +  $Cu^{2+}$ ) results in recovery of the fluorescence intensity of **HL** showing '*On-Off-On*' type behavior of chemosensor (**Figure 6.18b**).[41]



Scheme 6.3. Schematic representation showing the reversible nature of HL.



Figure 6.18. Reversible nature and 'On-Off-On' behavior of chemodosimeter HL.



Figure 6.19. Schematic representation of fluorescence quenching.

Furthermore, the fluorescence stability of **1** was observed under UV illumination up to 100 minutes and varied pH (4-13), which exhibits the high photo-stability of **1** (**Figure 6.20a,b**).



Figure 6.20. Stability of fluorescence intensity of 1 at (a) varied pH, (b) varied UV illumination.

#### 6.2.7. Cytotoxicity studies

After displaying excellent sensing response of **HL** towards  $Zn^{2+}$  ions, to understand the practicability of chemodosimeter **HL**, we performed a cytotoxicity test of **HL** and **1** towards HeLa cancer cell lines. High cellular viability is essential for intracellular sensing of metal ions as well as bio-imaging. Thus, MTT cell viability assay was performed that measures the amount of reduction of tetrazolium salts by mitochondrial dehydrogenases.[45] The amount of purple formazan produce is directly proportional to the number of surviving cells. The result revealed that ligand **HL** and **1** are found to be highly biocompatible for cellular proliferation without any deleterious side-effects within the concentration range 10–150  $\mu$ M (**Figure 6.21**).



Figure 6.21. Cell viability assay of HL and 1 by the colorimetric assay after 16 h incubation at  $37^{\circ}$ C against HeLa cells and the results shown in mean  $\pm$  SD of three separate measurements.

### 6.2.8. Intracellular sensing of Zn<sup>2+</sup> ions

Low cytotoxicity of **HL** and **1** indicated us to examine intracellular sensing of  $Zn^{2+}$  ions by **HL**.  $Zn^{2+}$  ions play a crucial role in various physiological developments in the living system.[14] Thus, HeLa and DU145 cancer cells were incubated with **HL** (25 µM for 2 h) and later on subsequently 25 µM Zinc pyrithione (ZnPT) added in media without disturbing cells position. Cells uptake Zinc pyrithione slowly and fluorescence signal intensity increases with time, as **HL** coordinates with zinc ions (**Figure 6.22 and Figure 6.23**). Fluorescence signals were distributed throughout the cells, indicating that **HL** can easily penetrate and detect  $Zn^{2+}$  ion in living cells (**Figure 6.22a and Figure 6.23a**). Fluorescence intensity reaches a maximum after 50 min and remains almost constant. This may be due to all **HL** molecules inside the cells get coordinated with  $Zn^{2+}$  ions (**Figure 6.22b and Figure 6.23b**). Thus, we can conclude that **HL** behaves as a chemodosimeter for  $Zn^{2+}$  ion during intracellular activity.



**Figure 6.22.** (a) HeLa cells pre-incubated with **HL** (25  $\mu$ M; 2 h), after washing with PBS, image was taken (0 min image) then treated with Zinc pyrithione (ZnPT) without disturbing cells position. Images were captured after different time intervals. (**HL**  $\lambda_{ex} = 405$ ,  $\lambda_{em} = 420-470$ ). (b) Quantification of the change in fluorescence signal intensity of HL after the addition of ZnPT on HeLa cells.



**Figure 6.23.** (a) DU145 cells pre-incubated with **HL** (25  $\mu$ M; 2 h), after washing with PBS, image was taken (0 min image) then treated with Zinc pyrithione (ZnPT) without disturbing cells position. Images were captured after a different time interval. (HL  $\lambda_{ex} = 405$ ,  $\lambda_{em} = 420-470$ ). (b) Quantification of the change in fluorescence signal intensity of HL after the addition of ZnPT on DU145 cells.

## **6.3.** Conclusions

In summary, a simple new molecular probe **HL** has been synthesized and employed for metal ion sensing both *in-vivo* and *in-vitro* systems. The probe **HL** was found to be selective, sensitive, and reversible towards  $Zn^{2+}$  metal ions among different types of metal ions. **HL** exhibits fluorescence turn-on behavior with  $Zn^{2+}$  ions. Moreover, the increased fluorescence intensity of the HL-Zn(II) system was found to be quenched after the successive addition of  $Cu^{2+}$  ions into the system showing dualsensing behavior of *via* fluorescence turn-off phenomenon. The binding of **HL** towards  $Zn^{2+}/Cu^{2+}$  was confirmed by a single-crystal X-ray diffraction study which reveals the formation of dinuclear  $Zn^{2+}/Cu^{2+}$  complexes. Furthermore, **HL** was found to be non-toxic which enables the intracellular sensing response of **HL** towards  $Zn^{2+}$  ions on HeLa and DU-145 cancer cell lines.

## **6.4. Experimental Section**

**6.4.1. Materials:** The common reagents and solvents were purchased from Merck and S. D. Fine Chem. Ltd. Solvents were distilled following the standard literature methods before their use. O-Vanillin, MTT, and 1-(3-Aminopropyl)Imidazole were procured from Sigma Aldrich Chemical Co., USA. Dulbecco's modified eagle medium (DMEM) were procured from Gibco. DU145 (prostate cancer) and HeLa cells (cervical cancer cell line) cell lines were obtained from the National Centre for Cell Science, Pune. India

**6.4.2. Physical measurements**: The common reagents and solvents were purchased from Merck and S. D. Fine Chem. Ltd. Solvents were distilled following the standard literature methods before their use. O-Vanillin, MTT, and 1-(3-Aminopropyl)Imidazole were procured from Sigma Aldrich Chemical Co., USA. Dulbecco's modified eagle medium (DMEM) were procured from Gibco. DU145 (prostate cancer) and HeLa cells (cervical cancer cell line) cell lines were obtained from the National Centre for Cell Science, Pune. India

**6.4.3. X-ray Crystallography:** Single-crystal X-ray data were collected at 293 K using graphite-monochromated Mo K $\alpha$  ( $\lambda \alpha = 0.71073$  Å) source. The approach for the data collection of **HL**, **1**, and **2** was appraised by using CrysAlisPro CCD software. The data were collected by using the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-2014.[40] The positions of all the atoms were obtained by direct methods. All nonhydrogen atoms were refined anisotropically and the remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 × Ueq of their parent atoms. Despite several attempts, we were unable to generate better quality crystals for **2**. All the H-bonding, C–H<sup>...</sup> $\pi$ 

interactions, and molecular structure drawings were prepared using the program Mercury (ver 3.1) and Diamond (ver 3.1d).[48] The crystallographic refinement data are placed in **Table A10** and selected bond distances and bond angles are shown in **Table A11-Table A13**.

6.4.4. Synthesis of C14H17N3O2 (HL): 1-(3-Aminopropyl)Imidazol (250 mg, 2 mmol) dissolved in dry methanol (10 ml) was added to a solution of O-Vanillin (304 mg, 2 mmol) in methanol (20 mL). The content of the reaction mixture was heated under reflux condition for 6 h using dean stark apparatus. The solvent was evaporated using rotary evaporator under high vacuum and washed two times with diethyl ether. The square shaped light yellow crystals were obtained in chloroform: ether system (layering method) within three days. <sup>1</sup>H NMR (DMSO-*d*6, δH ppm):13.6006(s, 1H), 8.5411(s, 1H, CH=N), 7.6693(s, 1H, CH=N), 7.2323(s, 1H), 7.0712(m, J=6.56 Hz, 1H), 7.0548(m, J=6.24 Hz, 1H), 6.9368(s, 1H), 6.8370(t, J=7.88 Hz, 1H), 4.0756(t, J=7 Hz, 2H), 3.8108(s, 3H), 3.5609(t, J=6.72 Hz, 2H), 2.1252(p, J=6.84 Hz, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δH ppm): 167.03, 151.92, 148.49, 137.73, 129.02, 123.65, 119.73, 118.87, 118.26, 115.24, 56.23, 55.50, 44.28, 32.08. ESI-MS (m/z): 261.1 [M+1], Yield = 97%. IR (KBr, cm<sup>-1</sup>): 3424 (br), 2935 (s), 1632 (vs), 1599 (s), 1511 (s), 1468 (s), 1254 (vs), 1214 (vs), 1082 (s), 739 (s). UV–Vis (ACN,  $\lambda_{max}$  (nm  $(\varepsilon M^{-1} cm^{-1})$ : 260 (61000), 330 (13000).

**6.4.5.** Synthesis of C<sub>56</sub>H<sub>64</sub>N<sub>12</sub>O<sub>8</sub>Zn<sub>2</sub> (1): An aqueous solution (15 mL) of  $Zn(NO_3)_2$ · 6H<sub>2</sub>O (0.297 g, 1 mmol) was added dropwise to a deprotonated solution of HL (0.518 g, 2 mmol) in methanol (15 mL). The reaction mixture was stirred for 10 h. The solid yellow colored product was precipitated, collected by filtration and washed with hexane. Light yellow color brick shaped single crystals were achieved by recrystallization within 4 days in ethanol:hexane solvent systems. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ H ppm): 8.3244(s, 4H, CH=N), 8.0166(s, 4H), 7.3701(s, 4H), 7.0089(s, 4H),

6.8487(d, J=7.50 Hz, 4H), 6.8124(d, J= 7.37 Hz, 4H), 6.4142(t, J=7.65 Hz, 4H), 3.9832(s, 8H), 3.6750(s, 12H), 3.4987(s, 8H), 1.7870(s, 8H). HRMS (m/z = m/2) 581.18, Yield = 72%. IR (KBr, cm<sup>-1</sup>): 3441 (br), 2922 (s), 1621 (vs), 1472 (s), 1451 (s), 1215 (vs), 1093 (s), 1032 (br), 801 (s), 744 (s). UV–Vis (ACN,  $\lambda_{max}$  (nm ( $\epsilon$  M<sup>-1</sup>cm<sup>-1</sup>): 275 (43000), 380 (12000).

**6.4.6.** Synthesis of C<sub>56</sub>H<sub>64</sub>N<sub>12</sub>O<sub>8</sub>Cu<sub>2</sub> (2): Compound 2 was prepared in a similar manner applied for compound 1, using Cu(NO<sub>3</sub>)<sub>2</sub>· 3H<sub>2</sub>O (0.241 g, 1 mmol) instead of Zn(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O. Dark green color brick shaped single crystals were obtained by recrystallization within 4 days in ethanol:hexane solvent systems. <sup>1</sup>H NMR (DMSO-*d*6,  $\delta$ H ppm): 8.4953(s, 4H, CH=N), 8.0078(s, 4H), 7.3972(s, 4H), 7.0436(m, 4H), 7.0079(m, 4H), 6.9905(m, 4H), 6.7971(s, 4H), 4.1107(s, 8H), 3.7549(s, 12H), 3.5469(m, 8H), 2.1178(s, 8H). HRMS (*m*/*z* = m/2) 580.18, Yield = 69%. IR (KBr, cm<sup>-1</sup>): 3440 (br), 2924 (s), 1619 (vs), 1471 (s), 1451 (s), 1384 (vs), 1243(s), 1223 (s), 1094 (br), 744 (s).UV-Vis (ACN,  $\lambda_{max}$  (nm ( $\epsilon$  M<sup>-1</sup>cm<sup>-1</sup>): 275 (71000), 377 (17200).

NMR, ESI-MS, and FT-IR spectra of HL, 1 and 2 are depicted in Figure 6.24–6.33

#### 6.4.7. Cell viability assay

To determine the cell viability MTT assay was performed. The reduction of MTT (3-(4,5-dimethylthiazolyl-2-)-2,5-diphenyltetrazolium bromide) by mitochondrial dehydrogenases of metabolically active cells into purple formazan. The number of surviving cells is directly proportional to the amount of formazan measured by the spectroscope. For this purpose, 8000 cells were seeded in 96 well plates in complete media (DMEM) and incubated for 24 h 37°C in 5% CO<sub>2</sub> atmosphere for cell adhesion. Cells were treated with **HL** for 24 h, final concentration ranging from (10–150 $\mu$ M), and incubated at 37°C followed by washing with PBS.

MTT (1mg/mL) was added and further incubated for 4 h. The supernatant removed and intracellular formazan crystal was solubilized in 100  $\mu$ L DMSO and shanked for 10 min. Absorbance at 570 nm was quantified by using the Synergy H1 Biotek microplate reader. The % cell viability was calculated as % cell viability = [Mean O.D. of the drug-treated cell/Mean O.D. of the control well] × 100. This is used to represent the % viability of cells.

**6.4.8. Imaging Zn<sup>2+</sup> in Live HeLa Cells:** To investigate the sensing of Zn<sup>2+</sup> ions in live HeLa by ligand **HL**, cells in confocal dishes were incubated with **HL** (25  $\mu$ M) for 2 h at 37°C in 5% CO<sub>2</sub> atmosphere. Then cells washed thrice with PBS and 1 mL media (DMEM) added. Acquisition of the initial image by confocal laser scanning microscope, without disturbing cells position 25  $\mu$ M Zinc pyrithione added in DMEM media to increase intracellular zinc levels. Cells were allowed to equilibrate zinc level for 20 min; images were acquired after 20 min, 40 min, 50 min, 70 min, 90 min, and 100 min.

**6.4.9. Quantum yield calculations:** The quantum yield ( $\Phi$ F) of compound 1 was calculated using eqn. (1)[47]

$$\Phi_{\rm F} = \Phi_{\rm st} \times \mathbf{S}_{\rm u} / \mathbf{S}_{\rm st} \times \mathbf{A}_{\rm st} / \mathbf{A}_{\rm u} \times \mathbf{n}^2_{\rm Du} / \mathbf{n}^2_{\rm Dst} \tag{1}$$

where  $A_{st}$  and  $A_u$  represent the absorbance of the standard and the sample at the excitation wavelength,  $\Phi_F$  is the fluorescence quantum yield of the sample,  $\Phi_{st}$  is the fluorescence quantum yield of the standard, while  $S_{st}$  and  $S_u$  are the integrated emission band areas of the standard and the sample, respectively, and  $n_{Dst}$  and  $n_{Du}$  are the solvent refractive index of the standard and the sample, and u and st refer to the unknown and the standard, sample respectively.

**6.4.10**. **Average lifetime measurement:** The amplitude weighted lifetime was calculated using the following equation:

$$<\tau> = \alpha_1 \tau_1 + \alpha_2 \tau_2 \tag{2}$$

Where  $\langle \tau \rangle$  is the average fluorescence lifetime of **1**.  $\tau_1$  and  $\tau_2$  are the average lifetimes of various fluorescent forms of compound **1** and  $\alpha_1$  and  $\alpha_2$  are the normalized pre-exponential factors. To obtain the best fitting in all the cases the  $\chi^2$  was kept near to unity.





Figure 6.24. <sup>1</sup>H NMR spectra of HL.



Figure 6.25. <sup>13</sup>C NMR spectra of HL.



Figure 6.26. HR-MS mass spectra of HL.



Figure 6.27. IR Spectrum of HL.



Figure 6.28. <sup>1</sup>H NMR spectrum of Complex 1.



Figure 6.29. IR Spectrum of complex 1.



Figure 6.30. HRMS spectrum of complex 1.



Figure 6.31. <sup>1</sup>H NMR spectrum of Complex 2.



Figure 6.32. HRMS spectrum of complex 2.



Figure 6.33. IR Spectrum of complex 2.



Figure 6.34. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1.



Figure 6.35. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1 (Aromatic region).



Figure 6.36. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1 (Aliphatic region).



Figure 6.37. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2.



Figure 6.38. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2 (Aromatic region).



Figure 6.39. COSY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2 (Aliphatic region).



Figure 6.40. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1.



Figure 6.41. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1 (Aromatic region).



Figure 6.42. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 1 (Aliphatic region).



Figure 6.43. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2.



Figure 6.44. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2 (Aromatic region).



Figure 6.45. NOESY (DMSO-*d*<sub>6</sub>, 500MHz) of Complex 2 (Aliphatic region).

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# Chapter 7

## **Conclusions and Future Outlook**

This thesis focus on the perspectives of developing new functionalized metal-organic frameworks synthesized at ambient conditions further achieving significant results in various applications. The structural features are well explained and have been related to the chemical properties of the synthesized MOFs. Firstly, a Cu-coordinated 3D MOF was synthesized at room temperature constituted of lactam functionalized porous channels, which exhibited fascinating solvent-free heterogeneous catalytic conversion of  $CO_2$  to cyclic carbonates at atmospheric pressure of  $CO_2$ . This work demonstrates the new possibilities for designing of Lewis acids/bases incorporating MOFs for efficient conversion of  $CO_2$  into cyclic carbonates in a more economically viable way.

Further, the above synthesized MOF was combined with graphene oxide for efficient and rapid adsorption of Methylene Blue dye in aqueous systems along with the electrochemical sensing of Cholesterol displaying the enhanced properties of hybrid materials.

Additionally, the energy storage applications of a new aminofunctionalized layered Cu(II)-coordinated MOF was explored by combining it with CNTs. This hybrid allows enhanced electrolyte accessibility along with the improved electrochemical storage capacity through its synergistic effects. The promising results offer capable possibilities for their further exploration in practical applicability as sustainable energy sources. Also, the free amino-group can be modified by post-synthetic treatment of MOF and can be further utilized for various targeted applications. Moreover, a novel alkali metal-coordinated MOF was synthesized by in-situ method and was explored for the phenomenon of SCSCtransformations by exposing it to a high-pressure vacuum. The process was explained by the mechanistic pathways with detailed discussion on topologies. The simplified net topology proposes better visualization into the structural features of the complicated MOF structures and could be exploited in designing of new frameworks and study their interactions.

Finally, an imidazole and imine functionalized ligand was synthesized as a chemosensor for the sensing of metal ions in the aqueous system along with intracellular zinc ion detection. The above-synthesized ligand could be explored as a linker of MOFs for various applications.

The work described in the thesis presents several opportunities for researchers working in the fields of catalysis, gas adsorption, sensing, crystal engineering, wastewater treatment, and energy storage and can be further explored for new possibilities in the augmentation of targeted applications by insertion of new functionalities. This work also gives an idea to explore MOFs from monometallic to heterometallic frameworks known to have better redox chemistry which is essential for enhanced electrochemical applications.

# **ANNEXURE 1**

Table A1-A13

# Chapter 2

Parameters	{[Cu(L)(DMF)]·1.5(H <sub>2</sub> O)} <sub>n</sub> (Cu-MOF)			
Empirical formula	$C_{19}H_{19}CuN_2O_{7.5}$			
Formula wt.	458.91			
Crystal system	Trigonal			
Space group	<i>R</i> -3			
a, Å	21.8786(3)			
b, Å	21.8786(3)			
<i>c</i> , Å	21.3088(3)			
$\alpha$ (deg)	90			
$\beta$ (deg)	90			
γ (deg)	120			
$V, Å^3$	8833.4(3)			
Ζ	18			
$\rho_{\rm calc}  {\rm g/cm^3}$	1.461			
$\mu$ , mm <sup>-1</sup>	1.150			
Temperature (K)	100(2)			
$\theta$ max	29.118			
F(000)	3978			
Refl. collected	33671			
Independent refl.	4978			
GOOF	1.088			
Final R indices $(R_1^a, WR_2^b)$ [I>2 $\sigma$ (I)]	$R_1 = 0.0479, wR_2 = 0.0479$			
R indices $(R_1^a, wR_2^b)$ (all data)	$R_1 = 0.1249, wR_2 = 0.1366$			
CCDC	1904186			

Table A1. Crystal structure and refinement parameters for Cu-MOF

<sup>a</sup> $R_1 = \sum (|Fo| - |Fc|) / \sum |Fo|$ . <sup>b</sup> $R_2 = [\sum \{w(Fo^2 - Fc^2)^2\} / \sum \{w(Fo^2)^2\}]^{1/2}$ .

{[Cu(L)(DMF)]·1.5(H <sub>2</sub> O)} <sub>n</sub> (Cu-MOF)						
Bond Distances (Å)						
Cu01—Cu01	2.6116(6)	Cu01—O002	1.993(2)	Cu01—O003	1.966(2)	
Cu01—O004	1.978(2)	Cu01—O005	1.954(2)	Cu01—O007	2.150(2)	
O006—C00I	1.220(4)	N008-C00I	1.382(4)			
Bond Angles (°)						
O002-Cu01-Cu01	83.41(6)	O002-Cu01-O007	91.13(10)	O003-Cu01-Cu01	82.84(6)	
O003-Cu01-O002	91.01(9)	O003-Cu01-O004	90.06(10)	O003-Cu01-O007	100.94(10)	
O004-Cu01-Cu01	85.59(6)	O004-Cu01-O002	168.73(9)	O004-Cu01-O007	99.69(10)	
O005-Cu01-Cu01	85.99(6)	O005-Cu01-O002	88.42(10)	O005-Cu01-O003	168.81(9)	
O005-Cu01-O004	88.36(10)	O005-Cu01-O007	90.25(10)	O007-Cu01-Cu01	173.44(8)	
C00Q-O007-Cu01	119.4(3)	O006-C00I-N008	126.2(3)	C00G-N008-C00L	120.4(3)	
C00I-N008-C00G	127.0(3)	N00P-C00Q-O007	145.9(8)			

## Table A2. Selected bond distances (Å) and bond angles (°) in Cu-MOF
## Chapter 3

Parameters	{[Cu(L)(DMF)]·(Solvent) <sub>x</sub> } <sub>n</sub>	
	( <i>IITI-1</i> )	
Empirical formula	$C_{24}H_{19}CuF_3N_2O_5$	
Formula wt.	535.95	
Crystal system	Monoclinic	
Space group	<i>C</i> 2/ <i>c</i>	
<i>a</i> , Å	18.6779(13)	
<i>b</i> , Å	23.8970(9)	
<i>c</i> , Å	18.2463(7)	
a (deg)	90	
$\beta$ (deg)	96.960(5)	
γ (deg)	90	
$V, Å^3$	8084.1(7)	
Ζ	8	
$\rho_{\rm calc}  {\rm g/cm^3}$	0.881	
$\mu$ , mm <sup>-1</sup>	0.532	
Temperature (K)	100	
$\theta$ max	25.000	
F(000)	2184	
Refl. collected	50175	
Independent refl.	7802	
GOOF	1.089	
Final R indices $(R_1^a, wR_2^b)$	$\mathbf{R}_1 = 0.0708 \ w \mathbf{R}_2 = 0.2530$	
[I>2σ(I)]	$\mathbf{K}_1 = 0.0790, W\mathbf{K}_2 = 0.2559$	
R indices $(R_1^a, wR_2^b)$	$R_1 = 0.0977 \ wR_2 = 0.2740$	
(all data)	$\mathbf{x}_1 = 0.0777, \mathbf{x}_2 = 0.2740$	
CCDC	1915096	

Table A3. Crystal structure and refinement parameters for IITI-1

<sup>a</sup> $R_1 = \sum (|Fo| - |Fc|) / \sum |Fo|$ . <sup>b</sup> $R_2 = [\sum \{w(Fo^2 - Fc^2)^2\} / \sum \{w(Fo^2)^2\}]^{1/2}$ .

{[Cu(L)(DMF)]-(Solvent) <sub>x</sub> } <sub>n</sub> ( <i>HTI-1</i> )					
Bond Distances (	Å)				
Cu—Cu	2.6336(10)	Cu—O1	1.962(3)	Cu—O2	1.964(3)
Cu—O3	1.961(3)	Cu—O4	1.955(3)	Cu—O5	2.202(5)
Bond Angles (°)					
O1–Cu–Cu	85.20(10)	O2–Cu–Cu	83.23(10)	O3–Cu–Cu	82.95(10)
O4–Cu–Cu	85.12(9)	O5–Cu–Cu	172.64(11)	01–Cu–O2	168.40(13)
01–Cu–O5	99.83(14)	02–Cu–O5	91.62(14)	O3-Cu-O1	88.29(12)
03–Cu–O2	89.49(13)	O3–Cu–O5	91.78(14)	04-Cu-O1	89.25(12)
04–Cu–O2	90.55(13)	O4CuO3	167.98(13)	O4CuO5	100.24(14)
C1–O1–Cu	121.5(2)	C1–O2–Cu	124.1(3)	C21–O3–Cu	124.3(3)
C21–O4–Cu	122.4(3)	C22–O5–Cu	115.5(8)		

Table A4. Selected bond distances (Å) and bond angles (°) in *IITI-1*.

## Chapter 4

Compound Name	L(Et)3	
Empirical formula	$C_{24} H_{27} N_9 O_6$	
Formula weight	537.54	
Temperature/K	293(2) K	
Wavelength	0.71073 A	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
<i>a</i> (Å)	25.637(4)	
<i>b</i> (Å)	4.8405(8)	
<i>c</i> (Å)	20.895(4)	
a (degree)	90	
β (degree)	90	
γ (degree)	90	
Volume (A <sup>3</sup> )	2592.9(7)	
Z	4	
Density (calculated)	1.377 Mg/m <sup>3</sup>	
Absorption coefficient	0.102 mm <sup>-1</sup>	
F(000)	1128	
Crystal size	0.230 x 0.200 x 0.160 mm	
Theta range for data collection	3.325 to 24.984°	
	-27<=h<=30,	
Index ranges	-5<=k<=5,	
	-24<=1<=24	
Reflections collected	17992	
Unique reflections	4528 [R(int) = 0.1712]	
Radiation	$CuK\alpha (\lambda = 1.54184)$	
Completeness to theta = $67.684$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Max. and min. transmission	1.00000 and 0.55187	
Data/restraints/parameters	4528 / 1 / 352	
Goodness-of-fit on F <sup>2</sup>	1.011	

Table A5. Crystal data and structure refinement for Ligand  $L(Et)_3$ 

Absolute structure parameter	7.1(10)
Final R indices [I>= $2\sigma$ (I)]	R1 = 0.0895, wR2 = 0.1843
R indices [all data]	R1 = 0.2032, wR2 = 0.2516
Largest diff. peak and hole	0.201 and -0.276 e.A <sup>-3</sup>
CCDC number	1576279

### Table A6. Data and structure refinement for Na-MOF1 and Na-MOF2

Compound Name	Na-MOF1	Na-MOF2	Na-MOF2 ( with CutOff data)
Empirical formula	C18 H24 N9 Na3 O13	C36 H24 N18 Na6 O13	C36 H24 N18 Na6 O13
Formula weight	643.43	1054.67	1054.67
Temperature/K	150(2) K	150(2) K	150(2) K
Wavelength	1.54184 A	1.54184 A	1.54184 A
Crystal system	Trigonal	Trigonal	Trigonal
Space group	R-3c	R-3c	R-3c
a (Å)	16.6879(5)	14.270(4)	14.270(4)
<i>b</i> (Å)	16.6879(5)	14.270(4)	14.270(4)
<i>c</i> (Å)	35.6864(12)	35.247(6)	35.247(6)
a (degree)	90	90	90
β (degree)	90	90	90
γ (degree)	120	120	120
Volume (A <sup>3</sup> )	8606.7(6)	6216(4)	6216(4)
Z	12	6	6
Density (calculated)	1.490 Mg/m <sup>3</sup>	1.691 Mg/m <sup>3</sup>	1.691 Mg/m <sup>3</sup>
Absorption coefficient	1.473 mm^-1	1.656 mm <sup>-1</sup>	1.656 mm <sup>-1</sup>
F(000)	3984.0	3216.0	3216.0
Crystal size	0.230 x 0.180 x 0.120 mm	0.230 x 0.160 x 0.120 mm	0.230 x 0.160 x 0.120 mm
Theta range for data collection	3.936 to 71.459°.	4.370 to 71.147°	9.584 to 70.949°.
	-14<=h<=20,	-15<=h<=17,	-13<=h<=8,
Index ranges	-20<=k<=16,	-17<=k<=12,	-5<=k<=11,
	-38<=1<=43	-38<=1<=42	-42<=1<=38
Reflections collected	18733	12295	1444
Unique reflections	1870 [R(int) = 0.0696]	1352 [R(int) = 0.0732]	717 [R(int) = 0.0394]
Radiation	$CuK\alpha$ ( $\lambda = 1.54184$ )	$CuK\alpha (\lambda = 1.54184)$	$CuK\alpha (\lambda = 1.54184)$
Completeness to theta = 67.684	100.0 %	100.0 %	54.6%
Absorption	Semi-empirical from	Semi-empirical from	Semi-empirical from
correction	equivalents	equivalents	equivalents

Refinement method	Full-matrix least-squares	Semi-empirical from	Full-matrix least-squares	
Refinement method	on F <sup>2</sup>	equivalents	on F <sup>2</sup>	
Max. and min.	1 00000 and 0 58255	1 00000 and 0 75650	1 00000 and 0 75650	
transmission	1.00000 and 0.38555	1.00000 and 0.75659	1.00000 and 0.75059	
Data/restraints/param	1870 / 2 / 138	1352 / 102 / 112	717 / 109 / 111	
eters	10/07 27 150	15527 1027 112	/1//10//111	
Goodness-of-fit on F <sup>2</sup>	1.045	1.380	1.076	
Final R indices	R1 = 0.0472, wR2 =	R1 = 0.1580, wR2 =	R1 = 0.0892, wR2 =	
[I>=2σ (I)]	0.1386	0.4661	0.2250	
D indiana [all data]	R1 = 0.0508, wR2 =	R1 = 0.1672, wR2 =	R1 = 0.1172, wR2 =	
K malces [an data]	0.1438	0.4882	0.2648	
Extinction coefficient	n/a	n/a	n/a	
Largest diff. peak				
and hole	0.309 and -0.378 e.A <sup>-3</sup>	0.757 and -0.665 e.A <sup>-3</sup>	0.388 and -0.518 e.A <sup>-3</sup>	
CCDC number	1557220	1575808	Na-MOF2 ( with CutOff	
CEDC humber	1557257	15/5090	data)	

 Table A7. Hydrogen bonding of Na-MOF1 [Å and (°)].

	D-H····A	d(D-H)	d(H····A)	d(D····A)	<(DHA)
1	O(3)-H(101)····N2 (#1)	0.85	2.13	2.98	172
2	O(4)-H(103)····N2 (#1)	0.81	2.80	3.51	146
3	O(4)-H(103)····N3 (#1)	0.81	2.15	2.15	170
4	O(3)-H(102)····O2 (#2)	0.85	1.94	2.79	169
5	O(4)-H(104)····O1 (#3)	0.93	1.89	2.76	152
6	O(4)-H(104)····N2 (#3)	0.93	2.82	3.42	122

#1: x-1/3,+x-y+1/3,+z-1/6 #2: -x+y+2/3,+y+1/3,+z-1/6 #3: x-y+1/3,+x-1/3,-z+2/3

### Table A8. Bond lengths for Na-MOF1 and Na-MOF2

Atoms	Bond length (Na-MOF1)	Bond length (Na-MOF2)
Na(1)-O(1)	2.3701 (15)	2.417(5)
Na(1)-O(2)#1	2.3700 (15)	2.892(9)
Na(1)-Na(1)#2	3.9757(9)	3.705(4)
Na(1)-Na(1)#1	3.9757(9)	3.705(4)
O(1)-C(6)	1.240(2)	1.227(9)
O(2)-C(6)#2	1.235(10)	1.235(10)
O(2)-Na(1)#2	2.3700 (15)	2.891(9)
N(1)-C(1)	1.344(2)	1.318(9)
N(1)-N(2)	1.335(2)	1.318(7)
N(1)-C(5)	1.454(2)	1.455(8)
N(2)-N(3)	1.314(2)	1.300(9)
N(3)-C(2)	1.363(2)	1.362(9)
C(1)-C(2)	1.377(2)	1.381(10)
C(2)-C(3)	1.469(2)	1.483(9)
C(3)-C(4)#3	1.393(2)	1.385(10)
C(3)-C(4)	1.396(2)	1.416(10)
C(4)-C(3)#4	1.393(2)	1.385(10)
C(5)-C(6)	1.5333(2)	1.530(9)
Na(1)-N(2)	-	2.943(7)
Na(1)-N(3)	-	2.486(6)
Na(1)-O(3)	2.3252(18)	
Na(1)-O(4)	2.438(2)	
Na(1)-O(5)	2.504(5)	
Na(1)-O(5)#2	2.577(5)	
Na(1)-O(4)#1	2.7104(19)	
O(4)-Na(1)#2	2.7103(19)	

Bond Angles	Na-MOF1	Na-MOF2
O(2)#1-Na(1)-O(1)	154.54(7)	89.6(3)
O(2)#1-Na(1)-Na(1)#1	68.75(4)	37.12(15)
C(6)-O(1)-Na(1)	138.48(12)	104.2(5)
Na(1)#2-Na(1)-Na(1)#1	112.784(19)	102.98
O(2)-Na(1)-O(1)#1	-	101.8(3)
O(2)-Na(1)-O(1)	-	89.6(3)
O(1)#1-Na(1)-O(1)	-	124.3(3)
O(2)-Na(1)-N(3)	-	128.1(3)
O(1)#1-Na(1)-N(3)	-	103.6(3)
O(1)-Na(1)-N(3)	-	111.1(2)
O(2)-Na(1)-O(2)#1	-	103.0(5)
O(2)#1-Na(1)-Na(1)#2	118.39(5)	71.39(19)
O(3)-Na(1)-O(5)	157.93(13)	-
O(2)#1-Na(1)-O(5)	74.60(12)	-
O(1)-Na(1)-O(5)	83.24(11)	-
O(4)-Na(1)-O(5)	113.27(12)	-
O(3)-Na(1)-O(5)#2	160.51(12)	-
O(2)#1-Na(1)-O(5)#2	90.79(11)	-
O(1)-Na(1)-O(5)#2	79.82(11)	-
O(4)-Na(1)-O(5)#2	73.25(11)	-
O(5)-Na(1)-O(5)#2	40.12(15)	-
O(3)-Na(1)-O(4)#1	94.23(6)	-
O(2)#1-Na(1)-O(4)#1	94.89(6)	-
O(1)-Na(1)-O(4)#1	65.30(5)	-
O(4)-Na(1)-O(4)#1	155.11(4)	-
O(5)-Na(1)-O(4)#1	69.96(12)	
O(5)#2-Na(1)-O(4)#1	104.70(11)	-
O(3)-Na(1)-Na(1)#2	126.05(5)	-
O(3)-Na(1)-O(2)#1	92.17(6)	-

#### Table A9. Bond Angles for Na-MOF1 and Na-MOF2.

O(3)-Na(1)-O(1)	104.58(6)	-
O(4)-Na(1)-Na(1)#2	42.01(4)	-
O(5)-Na(1)-Na(1)#2	76.02(11)	-
O(5)#2-Na(1)-Na(1)#2	37.85(10)	-
O(4)#1-Na(1)-Na(1)#2	123.05(5)	-
O(3)-Na(1)-Na(1)#1	119.73(5)	-
O(2)#1-Na(1)-O(4)	109.86(6)	-
O(3)-Na(1)-O(4)	87.64(6)	-
O(4)-Na(1)-Na(1)#1	152.42(5)	-
O(5)-Na(1)-Na(1)#1	39.15(11)	-
O(5)#2-Na(1)-Na(1)#1	79.20(10)	-
O(4)#1-Na(1)-Na(1)#1	37.02(4)	-
O(1)-Na(1)-O(4)	90.18(6)	-
C(6)-O(2)-Na(1)#2	134.26(12)	-
Na(1)-O(3)-H(101)	109.6	-
Na(1)-O(3)-H(102)	109.5	-
Na(1)-O(4)-Na(1)#2	100.97(6)	-
Na(1)-O(4)-H(104)	126.3	-
Na(1)#2-O(4)-H(104)	69.4	-
Na(1)-O(4)-H(103)	121.8	-
Na(1)#2-O(4)-H(103)	127.1	-
O(5)#2-O(5)-Na(1)	72.2(3)	-
O(5)#1-O(5)-Na(1)	155.5(4)	-
O(5)#2-O(5)-Na(1)#1	172.8(3)	-
O(5)#1-O(5)-Na(1)#1	67.7(3)	-
Na(1)-O(5)-Na(1)#1	102.99(15)	-

#1 y+1/3,-x+y+2/3,-z+2/3 #2 x-y+1/3,x-1/3,-z+2/3 #3 -y+1,x-y+1,z #4 -x+y,-x+1

# Chapter 5

Compound	HL	1	2
Empirical formula	$C_{14}H_{17}N_3O_2$	C <sub>28</sub> H <sub>32</sub> N <sub>6</sub> O <sub>4</sub> Zn	$C_{28}H_{32}N_6O_4Cu$
Formula weight	458.33	581.96	580.12
Temperature/K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 A	0.71073 A	0.71073 A
Crystal system, Space group	Orthorhombic , $P2_12_12_1$	Monoclinic, <i>I</i> 2/a	Monoclinic, <i>I</i> 2/a
<i>a</i> (Å)	7.6721(2)	22.8871(14)	22.941(5)
<i>b</i> (Å)	11.4426(2)	7.6537(5)	7.6098(12)
<i>c</i> (Å)	15.8174(4)	34.918(2)	34.505(7)
α/°	90	90	90
β/°	90	105.510(7)	105.03(2)
γ/°	90	90	90
Volume (Å <sup>3</sup> )	1388.59(6)	5893.8(7)	5818(2)
Z, Density (calculated)	4, 1.240 Mg/m <sup>3</sup>	8, 1.312 Mg/m <sup>3</sup>	4, 1.325
Absorption coefficient	0.085 mm <sup>-1</sup>	0.875 mm <sup>-1</sup>	0.793
F(000)	552	2432	2424
Theta range for data collection	2.951 to 24.997°	2.967 to 24.998°	3.176 to 24.997°
	-8<=h<=9,	-27<=h<=22,	-27<=h<=27,
Index ranges	-13<=k<=13,	-9<=k<=9,	-9<=k<=9,
	-18<=l<=18	-39<=l<=41	-41<=l<=38
Reflections collected, Unique	10420, 2439 [R(int) = 0.0289]	19824, 5149 [R(int) = 0.0666]	29351 / 5105 [R(int) = 0.2812]

Table A10. Crystallographic parameters of HL, 1 and 2

Data/restraints/p arameters	2439 / 0 / 174	5149 / 1 / 354	5105 / 0 / 354
Goodness-of-fit on F <sup>2</sup>	1.164	1.073	0.940
Final R indices [I>=2σ (I)]	R1 = 0.0403, wR2 = 0.1086	R1 = 0.0513, w $R2 = 0.1289$	R1 = 0.0865, wR2 = 0.1855
R indices [all data]	R1 = 0.0432, wR2 = 0.1110	R1 = 0.0771, wR2 = 0.1693	R1 = 0.2606, wR2 = 0.2688
CCDC number	1848465	1848466	1854143

Table A11. Hydrogen Bonding in HL, 1 and 2 [Å and (°)].

	D HA	d(D H)	d(H··· A)		<(DHA)
	D-II A	u(D-11)	u(II A)	10 10	(DIIA)
				d(D <sup></sup> A)	
		HL			
1	C(13)-H(13)N···O(1)#(2)	0.930(.000)	2.642	3.537	161.72( 0.04)
2	C(13)-H(13)N···O(2)#(2)	0.930(.000)	2.622	3.375	138.44( 0.02)
Equivalent positions: x-1/2,-y+1/2,-z+1					
	r	1	-	1	
3	C(20)H(20)N···O(3)#(2)	0.930(.004)	2.638(0.003	3.515(0.0	157.39(0.37)
			)	05)	
Equivalent positions: -x+1,+y-1/2,-z+1/2+1 2					
4	C(20)-H(20)N···O(3)#(2)	0.930(.013)	2.642(0.008	3.496(0.0	153.01(0.85)
			)	15)	
Equivalent positions: -x+1,+y+1/2,-z+1/2					

Bond Distances	1	2
Zn(1)-O(2)	2.011(3)	-
Zn(1)-O(3)	2.015(3)	-
Zn(1)-N(2)	2.096(3)	-
Zn(1)-N(1)	2.112(3)	-
Zn(1)-N(4)	2.087(3)	-
Cu(1)-O(2)	-	1.916(6)
Cu(1)-O(3)	-	1.906(6)
Cu(1)-N(2)	-	2.272(7)
Cu(1)-N(1)	-	2.030(7)
Cu(1)-N(4)	-	2.029(7)
Cu(1)-O(2)	_	1.916(6)

Table A12. Selected bond distances  $(\dot{A})$  of 1 and 2

 Table A13. Selected bond angles(•) of 1 and 2.

Bond angles	1	
O(2)-Zn(1)-O(3)	175.76(11)	-
O(2)-Zn(1)-N(4)	92.20(13)	-
O(3)-Zn(1)-N(4)	88.90(12)	-
O(2)-Zn(1)-N(2)	94.06(13)	-
O(3)-Zn(1)-N(2)	89.19(12)	-
N(4)-Zn(1)-N(2)	114.81(13)	-
O(2)-Zn(1)-N(1)	87.37(12)	-
O(3)-Zn(1)-N(1)	89.04(12)	-
N(4)-Zn(1)-N(1)	137.04(13)	-
O(3)-Cu(1)-O(2)	-	176.2(3)
O(3)-Cu(1)-N(1)	-	88.0(4)
O(2)-Cu(1)-N(1)	-	90.2(3)
O(3)-Cu(1)-N(4)	-	90.8(3)

O(2)-Cu(1)-N(4)	-	91.5(3)
N(1)-Cu(1)-N(4)	-	147.3(3)
O(3)-Cu(1)-N(2)#1	-	87.4(3)
O(2)-Cu(1)-N(2)#1	-	89.8(3)
N(1)-Cu(1)-N(2)#1	-	104.1(3)
N(4)-Cu(1)-N(2)#1	-	108.5(3)

Table A14. Permissions for re-producing the materials

Figure 1.1	Illustration of the construction of various MOFs from SBUs and linkers Illustration of the construction of	Reproduced from Ref. [3], with permission from Royal Society of Chemistry Reproduced from Ref. [19],
1.2	various MOFs from SBUs and linkers.	with permission from the Royal Society of Chemistry
Figure 1.3	Synthetic procedures of MOF by a) hydrothermal/solvothermal, b) microwave-assisted method, c) sonochemical/Ultrasound synthesis, d) mechanochemical synthesis, e) and electrochemical methods.	Reproduced from Ref. [27], with permission from the Royal Society of Chemistry
Figure 1.4	Representation of widespread potential applications shown by MOFs	Reproduced from Ref. [17], with permission from the Royal Society of Chemistry
Figure 1.5	Representation of (a,b) Crystal structure of MOF-210, (c,d) High- pressure H2 isotherms and CO2 isotherms of the MOFs measured at 77K and 298 K respectively	Reproduced from Ref. [37], with permission from the Science Publishing Group
Figure 1.6	Synthetic scheme of USTC-253 and defect-engineered USTC-253- TFA showing open metal sites, (b) CO2 cycloaddition for epoxide conversion into cyclic carbonate over USTC-253-TFA	Reproduced from Ref. [39], with permission from the Wiley
Figure	Schematic presentation of nMOF- 867 formation and its superior	Reproduced from Ref. [45],

1.7	supercapacitance performance in comparison to commercial materials	with permission from American Chemical Society
Figure 1.8	Pictorial illustration of Functionalizable parts of MOFs	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.9	Functionalities based on groups categorized on the basis of their structural properties chemical and characteristics	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.10	Probable interactions between (a) Amide-CO2 interactions, (b) Amide-C2H2 interactions, (c-e) Retaining of topology after amide functionalization	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.11	Representation of (a) crystal structure of DUT-122, (b) showing colorimetric sensing of various polar and non-polar, protic, aprotic, aliphatic, and aromatic solvent vapors	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.12	(a) Illustration of aromatic imide functionalized cores. (b) Organized PDI arrangements in Zn-PDI for efficient photocatalyst development with the oxidation of alcohol and reduction of aryl halides in the presence of visible light	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.13	Application of imide functionalized Mg-NDI to detect guest	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.14	Heterocyclic azine N-based functions are compared based on their basicity	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.15	<ul> <li>(a) Representation of supercapattery device prepared from amine-functionalized MOF,</li> <li>(b) Comparison of supercapacitance performance of Co-MOF-MP/NF and, NH2-Co- MOF-NS/NF</li> </ul>	Reproduced from Ref. [71], with permission from Elsevier
Figure 1.16	Presenting the variation in the organic linker of UiO-66 MOF for sensing of acidic gases via a	Reproduced from Ref. [70], with permission from Elsevier

	change in chemical properties	
Figure 1.17	Schematic illustration of of UV rays triggered isomerization of the azobenzene groups from trans-to- cis form and heat-induced cis-to- trans isomerization. Representation of change in adsorption of CO2 molecules in the framework of MOF-5, structure of PC	Reproduced from Ref. [50], with permission from Elsevier
Figure 1.18	MIL-101-SO <sub>3</sub> H is employed for light-enhanced acid-catalytic reaction assisting the protons releasing action through the transfer of electrons from –SO <sub>3</sub> clusters to Cr-oxo groups	Reproduced from Ref. [71], with permission from the Royal Society of Chemistry
Figure 1.19	Schematic representation of GO- incorporated MOFs formation through solvothermal method reported by Wang et al	Reproduced from Ref. [79], with permission from the Royal Society of Chemistry
Figure 1.20	(a) Synthesis of Fe <sub>3</sub> O <sub>4</sub> microspheres surrounded by the Porous MOF shell, (b)TEM image of core shell microspheres [Fe@[Cu <sub>3</sub> (btc) <sub>2</sub> ].	Reproduced from Ref. [80], with permission from the Royal Society of Chemistry
Figure 1.21	(a) Representation of flexible solid-state device prepared from PANI-ZIF-67-CC. (b–d) Normal, bent, and twisted state presentation of the fabricated device. (e) Three SCs connected in series to power red light-emitting-diode (LED	Reproduced from Ref. [84], with permission from Elsevier