# **Synthesis of Bimetallic Metal-Organic Frameworks and their Application**

M.Sc. Thesis

By GURPREET KAUR



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016

# **Synthesis of Bimetallic Metal-Organic Frameworks and their Application**

A THESIS

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

> *by* **GURPREET KAUR**



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016



# INDIAN INSTITUTE OF TECHNOLOGY INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Synthesis of Bimetallic Metal-Organic Frameworks and their Application" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2014 to June 2016 under the supervision of Dr. Sanjay K. Singh, Assistant Professor, 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.

#### **GURPREET KAUR**

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

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**GURPREET KAUR** has successfully given her M.Sc. Oral Examination held on July 4, 2016.

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To my best friends and family far away, thank you for your endless love. Making you happy is the biggest motivation in my life.

> Gurpreet Kaur Discipline of Chemistry IIT Indore

I dedicate this thesis to my parents

#### Abstract

A mixed metal Co-Zn based metal organic framework with ligand 2-methyl imidazole has been prepared with different doping percentages of Co (25~75% of  $Co^{2+}$ ) along with monometallic ZIFs at room temperature. The tuneability of pore size, pore volume and surface area of Co doped ZIF-8 has been extensively studied by Brunauer-Emmett-Teller (BET). The highest surface area (enhanced by ~40% compared to ZIF-8) and pore volume (enhanced by ~33% compared to ZIF-8) was observed with 75% doping of the Cobalt in ZIF-8 (Co75%-ZIF-8). The particle size of various doped Co-ZIF-8 particles by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that they were 150-300 nm in size. The crystal lattice structure of the doped ZIFs-8 framework is continuously maintained as parent ZIF-8, regardless of the doping percentage. The synthesized material was characterized by powder Xray diffraction (PXRD), thermo gravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDS), and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The prepared material showed a high CO<sub>2</sub> uptake capacity, recorded at room temperature up to 1 bar pressure. Noteworthy enhancement of  $\sim 30\%$  in the CO<sub>2</sub> uptake was displayed by Co75%-ZIF-8 frameworks as compared to Zn-ZIF-8 under analogous conditions.

#### LIST OF PUBLICATIONS

Room-temperature synthesis of bimetallic Co-Zn based Zeolitic Imidazolate Frameworks in water for enhanced CO<sub>2</sub> uptake Gurpreet Kaur, Rohit K. Rai, Deepika Tyagi, Yao Xin, Pei-Zhou Li, Xin-Chun Yang, Yanli Zhao, Qiang Xu, Sanjay K. Singh\* J. Mater. Chem. A (Manuscript submission No. TA-COM-05-2016-004342)

Synthesis and Characterisation of Mixed Metal Co-Zn in Zeolitic Imidazole Framework (Co-ZIF-8) Gurpreet Kaur, Rohit K. Rai, Yao Xin, Pei-Zhou Li, Xin-Chun Yang, Yanli Zhao, Qiang Xu, Sanjay K. Singh\* Poster presentation in "Frontiers in Inorganic and Organometallics

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# NOMENCLATURE

mol	mole
mmol	millimole
0	degree
С	celsius
mg	milligram
KV	kilovolt
K	kelvin
Å	armstrong
nm	nanometer
θ	theta
%	percentage
g	gram
cm	centimeter
m	meter
min	minute
mL	milliliter
MPa	megapascal
L	liter

# ACRONYMS

MOF s	Metal Organic Frameworks
MOCNs	Metal-Organic Coordination Networks
PCPs	Porous Coordination Polymers
SBU	Secondary Building Unit
AlO <sub>4</sub>	Alumina
$SiO_4$	Silica
pta	1,3,5-triaza-7-phospaadamantane
PSM	Post-Synthesis Modification
Μ	Metal
С	Carbon
0	Oxygen
Cr	Chromium
Н	Hydrogen
Fe	Iron
Mn	Manganese
Pd	Paladium
Au	Gold
Al	Aluminium
$CO_2$	Carbon Dioxide
$N_2$	dinitrogen
$CH_4$	Methane
Cr <sub>3</sub> O	Trichromium Oxide
POM	Polyoxometalate
CUS	Coordinatively Unsaturated Site
3D	Three Dimentonal
BTC	benzene-1,3,5-tricarboxylate
SOD	Sodalite
DMF	N,N-dimethyl formamide
Im	Imidazole
Me	Methyl
Zn	Zinc
Co	Cobalt
UiO-66	University of Oslo
HKUST-1	Hong Kong University of Science and Technology

MIL	Materials of The Institute Lavoisier	
ZIF	Zeolitic Imidazole Framework	
rpm	Rotation per minute	
rt	Room temperature	
BET	Brunauer-Emmett-Teller	
TGA	Thermo Gravimetric Analysis	
PXRD	Powder X-Ray Diffraction	
EDS	Energy Dispersive X-Ray Spectroscopy	
SEM	Scanning Electron Microscopy	
TEM	Transmission Electron Microscopy	
ICP-AES	Inductively Coupled Plasma Atomic Emission	
	Spectroscopy	

### **1. Introduction**

Porous materials are becoming increasingly trendy and important in numerous high impact sectors due to their wide range of features.[1,2] They can be classified into three sub category on the basis of the size of the material, a) microporous (less than 2 nm) such as zeolites, b) mesoporous (2-50 nm) such as molecular sieves, activated alimuna, silica gels and c) macroporous (more than 50 nm) such as activated carbon.

One such material widely accepted and discussed is "Metal Organic Frameworks (MOFs)", also known as metal-organic coordination networks (MOCNs) and porous coordination polymers (PCPs), is a new class of porous material which has emerged over the past 20 years, or so. They can be defined as "hybrid inorganicorganic framework material that spreads indefinitely into onedimensional, two- dimensional or three- dimensional". The molecular range offered by MOFs varies, depending on the type of the MOF, noticed to be as large as 29 Å. They are composed by linking metal containing nodes known as secondary building blocks (SBUs) with organic linkers via metal-ligand bonds (generally covalent bond). Therefore, MOFs which are born from Zeolites are an ideal material which possesses mixed characters of an organic species as well as an inorganic species. unlike Zeolites. Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO<sub>4</sub>) and silica (SiO<sub>4</sub>) which are purely inorganic in nature offering channel width ranging from 3-12 Å.

#### 1.1. Salient features of MOFs

MOFs possess properties such as large pore apertures, high surface area, self-assembly synthesis, high geometric regularity and high stability towards heat and chemicals. Few of the salient features are discussed below:-

#### 1.1.1. Exceptionally large pore aperture

MOFs offer large pores, even up to 2 nm in size, and this property of MOFs make them very superior as they can accommodate various species of appropriate size, inside the cavity generated in them (Figure 1). In most cases, these structures are sturdy in nature and allow the removal of the incorporated guest species resulting in permanent porosity. Additionally, the size of the pores is tuneable in nature which means that they can be altered according to the requirement. The easiest way to alter them is to make changes in the organic linker by using it of arbitrary length and many in numbers.



Figure 1. Different MOFs with their formula, pore size and surface area. Reproduced with permission (*J. Am. Chem. Soc.*, 2005, **127**, 17998-17999)

#### **1.1.2. High thermal and chemical stability**

MOFs can with stand as high as 500 °C of temperature and many of them remain unaffected under solvents like methanol water, benzene, etc.[1-5] One of the reasons for their high stability may be because they are formed of highly stable and strong cage having bonds like C-C, C-H, C-O, M-O etc. For example, ZIFs show exceptionally high chemical and thermal stability,[2] MIL-53 (Al) is stable and highly resistant to hydrolysis in neutral and acidic solutions, although in basic aqueous medium it undergoes structural transformations.[5]

#### **1.1.3.** Post synthetic modification (PSM)

Post synthetic modification simply means, the modifications made to the MOF after it has been synthesized. This provides an additional feature that MOFs can also be altered when they are already synthesized.[6-11] There are three ways for PSM (a) covalent PSM, (b) dative PSM and (c) postsynthetic deprotection, depicted beautifully in Figure 2.



Figure 2. Three postsynthetic methods (a) covalent PSM, (b) dative PSM and (c) postsynthetic deprotection. Reproduced with permission (*Chem. Rev.*, 2012, **112**, 970-1000)

#### 1.1.4. High surface area and pore volume

MOFs have large surface area and high pore volume which can be utilised for the storage and adsorption of gases like CO<sub>2</sub>, methane, hydrogen etc. For example, Cu-BTC MOF was investigated gas sensing applications because of high surface area property of MOFs.[12]

#### **1.2. Applications of MOFs**

As MOFs possess so many characteristics, they serve a wide range of applications which are mentioned below:-

#### 1.2.1. Catalysis

MOFs can serve as excellent catalysts in organic transformation reactions through various ways. They provide catalytic sites for the reaction which are present in the framework. Secondly the catalytic site can be provided by the encapsulation of certain species to the active site. Also there are reports on catalytic site produced by postsynthetic modification (as discussed in above). MOFs are used in both heterogeneous as well as homogeneous catalysis and it is proven to be excellent catalyst in terms of reusability. For example, the epoxidation of styrene using the Fe (Cr)-MIL-101,[13] aerobic oxidation of alcohols using gold supported MIL-101 as a heterogeneous catalyst,[14] hydrogenation of nitrobenzene to aniline using Ni supported MIL-53(Al), MIL-96(Al), and MIL-120(Al)[15] and generation of hydrogen from formic acid using Au-Pd NPs immobilized in MIL-101.[16]

#### 1.2.3. CO<sub>2</sub> capture

The increasing amount of  $CO_2$  in the atmosphere, a greenhouse gas along with other gases, has alarmed us to protect the environment from depleting further. Thus we require ways by which we can control the rising amount of  $CO_2$ . MOFs being porous in nature and having appropriate pore size shows its application for the capture of  $CO_2$ .[17-19] Although this requires high selectivity and capacity with minimal energetic input for the release of the captured  $CO_2$ . For example, Mg-MOF-74, is used in  $CO_2$  capture, with 8.9 weight % and it undergoes facile  $CO_2$  release at significantly lower temperature, 80 °C,[18] extraordinary capacity for storing  $CO_2$  is seen by ZIF-69 (1 L of ZIF-69 can hold ~83 L of  $CO_2$  at 273 K under ambient pressure).[19]

#### 1.2.3. Gas storage

MOFs are widely used for the storage of various gases such as methane, hydrogen for clean energy application. For example, hydrogen adsorption on MOF-177 at 298 K and 10 MPa showed adsorption capacity of ~0.62 weight %, which is among the highest hydrogen storage capacities reported in porous materials at ambient temperatures.[20] CO<sub>2</sub> storage using MOF-2, MOF-505, Cu<sub>3</sub>(BTC)<sub>2</sub>, MOF-74, IRMOFs-11, -3, -6, and -1, and MOF-177,[21] hydrogen storage by adsorption using MOF-5, up to 4.5 weight percent (17.2 hydrogen molecules per formula unit) at 78 K and 1.0 weight % at room temperature and pressure of 20 bar.[22]

#### 1.2.4. Sensors

MOFs can be used as sensors. For example detection of nitroaromatic explosives via a fluorescence quenching mechanism using Zn(II) metal–organic framework (MOF),[23] recognition and sensing of anions, exhibiting a high-sensitivity sensing function with respect to fluoride using a luminescent microporous metal–organic framework Tb(BTC)G, [24] fast and reversible detection of the vapors of the nitroaromatic explosive 2,4-dinitrotoluene and the plastic explosive taggant 2,3-dimethyl-2,3-dinitrobutane, through redox fluorescence quenching using highly luminescent microporous metal–organic framework,  $[Zn_2(bpdc)_2(bpee)]$  (bpdc=4,4'-biphenyldicarboxylate; bpee=1,2-bipyridylethene).[25]

#### 1.2.5. Drug delivery

Some MOF materials have high amount of drug loading ability because of their useful features such as high BET surface area, excellent biocompatibility and functional diversity. For example, loading biological molecules such as anticancer drugs into the pores of the MOFs,[26] remarkable capacity of Ibuprofen hosting and delivery by MIL-100 and MIL-101,[27] delivery of two antitumor drugs (mitroxantrone and [Ru(*p*-cymene)Cl<sub>2</sub>(pta)] (RAPTA-C) where pta = 1,3,5-triaza-7-phospaadamantane) using isoreticular zinc bis(pyrazolate) metal-organic framework nanoparticles.[28]



Figure 3. Generalized scheme for the use of MOFs as drug delivery vehicles. Reproduced with permission (*Ind. Eng. Chem. Res.*, 2011, **50**, 1799-1812)

#### **1.2.6.** Gas separation

MOFs can be used for the separation of gases, using its property of selectively adsorption of gases.[29-32] Selective adsorption can take place when different affinities for different substances on the surface of an adsorbent emerge at given conditions. If a two or more gases are separated successfully, it may also lead to purification of gases using MOFs. For example, removal of sulfur odorant components from natural gas using Cu-BTC-MOF,[30] in cryogenic air separated as narcotic medical gas and krypton as filler for lamp industry. Also, increased selectivity in CO<sub>2</sub>/CH<sub>4</sub> separations by orders of magnitude using amine functionalised MIL-53(Al) while maintaining a very high capacity for  $CO_2$  capture[31] (Figure 4), and exceptional selectivity for  $CO_2$  and  $N_2$  at 273 K (81:1) and 298 K (75:1), using bio-MOF-11.[32]



Figure 4. Representation of CO<sub>2</sub>/CH<sub>4</sub> separations using MIL-53(Al). Reproduced with permission (*J. Am. Chem. Soc.*, 2009, **131**, 6326-6327)

#### **1.3. Examples of MOFs**

Some examples of the well known MOFs along with their structural details.

#### 1.3.1. MIL-101 (Materials of the Institute

#### Lavoisier)

The MIL-n family of materials is a group of MOFs, originally developed by Serre *et al.* For example, MIL-101, MIL-53, MIL-100 and many more.



Figure 5. (a) Structural representation of Cr-MIL-101, (b) Schematic diagram of the pentagonal and hexagonal windows of MIL-101. Reproduced with permission (*RSC Adv.*, 2014, **4**, 52500-52525)

MIL-101 is assembled by corner-sharing supertetrahedra, which consist of Cr<sub>3</sub>O trimers and 1, 4-benzenedicarboxylic acids. The 4 vertices and 6 edges of the supertetrahedra are occupied by the trimers and organic linkers, respectively. MIL-101 has an augmented threedimensional zeotype structure with a very large cell volume (~702000  $Å^3$ ). Two types of mesoporous cages exist in MIL-101: a small cage of 20 supertetrahedra and a free diameter of 29 Å accessible through a pentagonal window with a 12 Å aperture, and a large cage of 28 supertetrahedra and a free diameter of 34 Å accessible through both hexagonal and pentagonal windows with a 14.7 x 16  $Å^2$  aperture (Figure 5). MIL-101 is highly porous with BET of about 4100  $m^2g^{-1}$ . Each octahedral Cr is bonded to 4 oxygen atoms from carboxylates, 1  $\mu_3$ -O oxygen atom, and 1 terminal site. The terminal site could be occupied by a fluorine atom or a terminal water molecule. As a consequence, there are 3 terminal sites in each Cr<sub>3</sub>O trimer and the ratio of fluorine to water is 1:2. The terminal water molecules can be removed after dehydration, thus providing exposed metallic Lewis acid sites in MIL-10.[33]

The material exhibits excellent stability against moisture and other chemicals, and the terminal water molecules in MIL-101 can be removed by heating in air or under vacuum at 423 K, which generates two coordinatively unsaturated open metal sites (CUS) per trimeric Cr(III) octahedral cluster which provides mild Lewis acid properties.[34] The acidic CUS sites allow for the post-synthesis modification of MIL-101 with amines that transform MIL-101 into a basic catalyst functional in a knoevenagel condensation. Due to its open-pore structure with large cavities, MIL- 101 can be functionalized by Pd or Au nanoparticles and polyoxometalate (POM) anions, making the resulting composite materials effective in hydrogenation reactions and as oxidation catalysts.[35]

# **1.3.2. HKUST-1 (Hong Kong University of Science and Technology)**

HKUST-1 is a copper-based MOF which is also known as Cu-BTC (copper benzene-1,3,5-tricarboxylate) or MOF-199. Singlecrystal data have shown that this material forms face centered-cubic crystals that contain an intersecting three dimensional (3D) system of large square-shaped pores (9 × 9 Å). Figure 6.a) and b) reports a pictorial representation of the tridimensional structure. In HKUST-1,  $Cu^{2+}$  ions form dimers, where each copper atom is coordinated by four oxygen, coming from the benzene-1,3,5-tricarboxilate linkers and by one water molecule.[36]



Figure 6. Schematic representation of the building blocks of HKUST-1. Two  $Cu^{2+}$  ions and four benzene-1,3,5 tricarboxylate linkers are bonded to give rise to the final 3D structure.  $Cu^{2+}$  is black; O is dark grey and C is light grey. Reproduced with permission (*Phys. Chem. Chem. Phys.*, 2007, **9**, 2676-2685)

HKUST-1 has three kinds of pores, the smallest one is around 4 Å in diameter and the two larger ones are around 10 Å in diameter. It is one of the most extensively studied MOFs due to its high surface area (normally in a range of 600-1600  $m^2g^{-1}$ , large pore volume (0.70  $cm^3g^{-1}$ ) and good thermal stability (thermally stable up to 350 °C).[37] Consequently, various applications of HKUST-1 in the fields of gas storage or catalysis have been reported. For example Cu-BTC exhibited high catalytic activity in knoevenagel condensation reactions, friedländer quinoline synthesis as well as in other C-C bond-forming reactions.[38] The presence of water molecules in the first coordination sphere of copper ions has suggested the possibility to obtain a coordinative vacancy on Cu<sup>2+</sup> species, by sample dehydration: a fact

that could result in potential interesting catalytic activities.[36] HKUST-1 is the bench mark material for methane storage, due to the small accessible pores and the open metal sites in the structure.[39,40]

#### **1.3.3.** ZIFs (Zeolitic Imidazolate Framework)

ZIFs (Zeolitic imidazole frameworks) are a subclass of MOFs which are formulated of tetrahedral metal ions such as zinc, cobalt, interlinked by imidazoles. Unique structural diversity, high porosity and surface area and enhanced thermal and chemical stability of zeolitic imidazole frameworks[2] have established these materials as potential candidate for wide application in catalysis,[41-45] separations and gas storage,[46-59] and chemical sensors.[60-66] They are present in different topologies like SOD (e.g. ZIF-7 (Zn(benzimidazole)<sub>2</sub>), ZIF-8 (Zn(2-methylimidazole)<sub>2</sub>), ZIF-9 (Co(benzimidazole)<sub>2</sub>), ZIF-90 (Zn(imidazolate-2-carboxaldehyde)<sub>2</sub>)), RHO (e.g. ZIF-71 (Zn(4,5-dichloroimidazole)<sub>2</sub>), POZ (e.g. ZIF-95 (Zn(5-chlorobenzimidazole)<sub>2</sub>))), GME (e.g. ZIF-78 (Zn(nbIm)(nIm) where nbIm: 5-nitrobenzimidazole; nIm: 2-nitroimidazole)) etc.[67,68,69] Amongst all these analogues, the sodalite (SOD or sod) net has the highest occurrence.



Figure 7. Examples of different topologies showed by ZIFs. Reproduced with permission (*RSC Adv.*, 2012, **2**, 6028-6035)

#### 1.3.3a. ZIF-8 (Zn(Me-Im)<sub>2</sub>)

ZIF-8 is obtained from the combination of zinc salt and 2methyl imidazole (H-Me-Im) which can be synthesized in various solvents like methanol, ethanol, N,N-dimethyl formamide (DMF) or water.[70] It is a prototypical structure with a sodalite topology that has been studied as a molecular sieve for the purification of hydrogen due to the narrow size of the 6-ring windows (~3.40 Å) that connect the large cavities (~11.6 Å of diameter).[71]



Figure 8. (a) Structural representation of ZIF-8 where blue colour represents zinc, sky blue represents nitrogen and grey colour represents carbon, (b) Single repeating unit of ZIF-8

ZIF-8 has high thermal stability (550 °C) and high surface area (BET surface are 1630 m<sup>2</sup>g<sup>-1</sup>).[2] Moreover, it is stable in solvents like water, ethanol, methanol etc. These properties have made ZIF-8 an impressive material. ZIF materials show high adsorption of gases that make them good candidates for gas storage and also gas phase catalysis. Also, because of the small window size, ZIF-8 is expected to separate hydrogen (2.89 Å kinetic diameter) from larger molecules including methane (3.80 Å) and nitrogen (3.60 Å). However, it has been observed experimentally that the molecules which are theoretically too large to pass through the windows of the framework such as methane and nitrogen are adsorbed in the material.[71]



Figure 9. (a,c) shows different orientation of the ZIF-8 by the rotation of the framework, whereas (b,d) are the corresponding magnified images which clearly shows the cubic and hexagonal windows present in the ZIF-8 frameworks

#### 1.3.3b. ZIF-67 (Co(Me-Im)<sub>2</sub>)

ZIF-67 is another example of ZIFs which is comprised of a combination of cobalt as the metal node and 2-methyl imidazole as the linker. Interestingly, ZIF-67 is isoreticular with ZIF-8 and possesses sodalite topology as shown in Figure 10.



Figure 10. (a) Structural representation of ZIF-67 where red colour represents cobalt, sky blue represents nitrogen and grey colour represents carbon, (b) Single repeating unit of ZIF-67

ZIF-67 is used in various fields, for example, copper doped ZIF-67 was used to tune the gas sorption and photocatalytic

properties.[72] ZIF-67 has also proven to be an efficient heterogeneous catalyst for the cyclization reaction of 2-aminobenzoketones and benzylamine derivatives to form quinazoline products.[73] ZIF-67 was investigated for the adsorption of malachite green in water due to its ultrahigh adsorption capacity.[74] Recently, ZIF-67 has been reported to be a new candidate for propylene/propane separation with the use of computational techniques.[75]

#### 1.4. Synthesis of MOFs and their modification

#### 1.4.1. Synthesis of MOFs

With the combination of various metals (called nodes) and organic linkers, we obtain number of MOFs. Figure 11 shows various linkers which are used in the formation of MOFs whereas formation of MOFs is shown in Figure 12.



Figure 11. Various linkers which are used in the formation of MOFs. Reproduced with permission (*Science*, 2013, **341**, 1230444-12)



Figure 12. Formation of MOFs using different nodes and linkers. Reproduced with permission (*Chem. Soc. Rev.*, 2014, **43**, 5561-5593)

#### 1.4.2. Modification

Modification of MOFs can be done with various ways. Amongst them, introducing different metal ions within the frameworks while keeping the overall framework intact is an interesting idea, to get the chemically distinct MOFs. This is also possible if we attempt to change the ligand or organic linkers[76] and by this we often end up into a new MOF whose features are much more superior to that of the well-established MOFs.

#### 1.4.2a. Mixed linker MOFs

Mixed linker MOFs can be obtained if we alter some percentage of the linker of a MOF with another suitable linker and keeping the node constant.[77-81] For example, Baiker and co-workers (2010)reported highly porous mixed-linker metal-organic frameworks, in which MOF-5 was used where 5% and 10% of the benzene-1,4-dicarboxylate linkers have been substituted by a functionalized linker, 2- aminobenzene-1,4-dicarboxylate and studied them for the oxidation of CO.[80] Further the same research group (2011), synthesized Cu-BTC structure in which the benzene-1,3,5tricarboxylate (BTC) linkers have been partially replaced by pyridine-3,5-dicarboxylate (PyDC) (Figure 13). They observed that 50% of the BTC linker can be replaced with that of PyDC without any significant change in the parent structure and the as-synthesized MOF showed activity toward the homogeneous catalytic reaction of direct hydroxylation of toluene, both in acetonitrile and in neat substrate.[81]



Figure 13. Illustration of replacing BTC with PyDC. Reproduced with permission (*Journal of Catalysis*, 2011, **281**, 76-87)

#### 1.4.2.b. Mixed Metal MOFs

This strategy includes incorporation of metal cluster within the robust MOF (ZIF-frameworks)[60], or systematically synthesis of bimetallic MOFs.[41,60,36,43,82-98] For example, incorporating

Ti(IV) ions into UiO-66 to enhance CO<sub>2</sub> capture by 81 % via postsynthetic exchange with Ti(IV) ions, the full effect was seen with 50 % Ti loading (Figure 14 a).[82] Co and Ni were observed to be incorporated more favourably into the Mg-MOF-74 framework from solution than Mg, the effects of these substitutions on CO<sub>2</sub> adsorption and kinetic water stability properties.[85] substitution of Mn, Fe, and Co into Cu-BTC (HKUST-1), at various levels and the effect of that substitution was studied on preferential gas sorption.[88] Ag was doped into MIL-101 to enhance its adsorption capacity (Figure 14 b).[90]



Figure 14. (a) Zr-based MOF UiO-66 undergoing postsynthetic exchange with Ti (IV) to deliver heterometallic MOF; (b) The formation of Ag (II) because of the existence of F and Ag (II) coordinate within the framework of MIL-101. Reproduced with permission (*Chem. Commun.*, 2013, **49**, 3634-3636; *J. Solid State Chem.*, 2016, **237**, 274-283)

# **Review of Past Work and Project motivation**

*Bertmer et al.* (2012) showed the formation of bimetallic Cu-Zn-BTC in which Zn<sup>2+</sup> partially replaced Cu<sup>2+</sup> from its framework up to 21% in the HKUST-1(Figure 15a).[95] Similarly, *Kleist et al.*(2015) reported bimetallic Cu-Ru-BTC by partial substitution of Cu<sup>2+</sup> centres by Ru<sup>3+</sup> in the paddlewheel structure of HKUST-1 (Figure 15b).[36]



Figure 15. (a) Representation of  $Cu^{2+}$  partially replaced by  $Zn^{2+}$ ; (b)  $Cu^{2+}$  partially replaced by  $Ru^{3+}$  in HKUST-1. Reproduced with permission (*J. Phys. Chem. C*, 2012, **116**, 20866-20873)

On the other hand, *Jian Zhang et al. (2012)*, reported the incorporation of  $Cu^{2+}$  in ZIF-67 to tune gas sorption and photocatalytic property of ZIF-67, although the incorporation content was very low in amount (0.12 to 5.04 %).[72]  $Cu^{2+}$  doped ZIF-8 frameworks were

shown by *Schneider et al.* (2015) and the resultant material was used as a catalyst for cycloaddition and condensation reactions. However, they attempted to increase the doping percentage but unfortunately failed above 25%. As at highest doping percentage i.e. 25 % of  $Cu^{2+}$  a decrease in the porosity was observed and at 50% of  $Cu^{2+}$  doping, ZIF-8 framework couldn't resist to keep the framework intact (Figure 16 a).[41] *Wang et al.* (2014) tried to modify the ZIF-8 framework in a different way by the incorporation of six-coordinated nickel clusters into ZIF-8 structure via a one-pot mechanochemical synthesis under liquid assisted grinding (LAG) conditions. This framework was further inked for alcohol sensing and photocatalytic reaction under visible light irradiation. This Ni-substituted ZIF-8 was seen to selectively pick different alcohol molecules according to their shapes and undergo a decoordination to form stable four-coordinated Ni clusters (shown in Figure 16 b).[60,99]



Figure 16. (a) Formation of Cu<sup>+2</sup> doped ZIF-8; (b) six-coordinated nickel ZIF-8. Reproduced with permission (*Catal. Sci. Technol.*, 2015, **5**, 1829-1839; *J. Mater. Chem. A*, 2014, **2**, 5724-5727).

Recently, *Jiang et al.* (2015) showed the formation mixed bimetallic CoZn-ZIF-8 frameworks, using a methanol based synthetic route. These frameworks were employed as a template to synthesise highly porous carbon materials.[98]

An interesting fact about ZIF-8 and ZIF-67 is that they share similar topology, sodalite type zeolitic structure which intuitively offer the maximum fortunate chances of blending  $\text{Co}^{2+}$  in the ZIF-8 frameworks. Furthermore, the ionic radius of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  is quite comparable which facilitate the high solubility of  $\text{Co}^{2+}$  ions in the ZIF-8 frameworks. These facts, very recently lead to the formation of Codoped ZIF-8 by *Lu et al. (2016)*. Unfortunately, only 10 % of doping of cobalt was possible. It was studied as precursor for the synthesis of porous Co-ZnO nanoparticles and the effect of Co doping on the magnetic properties of ZnO.[96]

Being motivated from these recent reports, we have synthesized a mixed bimetallic CoZn based zeolitic imidazole framework, in water at room temperature, with varying Co to Zn ratios (1:3, 1:1, 3:1). Interestingly, the resulting cobalt substituted ZIF-8 (Co<sub>100%</sub>-ZIF-8) framework, displayed high porosity as implied from the enhancement of surface area by ~40% and pore volume by ~33% as compared to the ZIF-8 framework. Further, these bimetallic CoZn-ZIF-8 with improved porosities displayed enhanced CO<sub>2</sub> uptake capacity at 298 K and 1 bar compared with ZIF-8.

### **Experimental section**

#### 3.1. Reagents and Chemicals

All of the chemicals were of analytical grade and used as received without further purification. These chemicals included zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ , 96% purity, Merck), Cobalt nitrate hexahydrate ( $Co(NO_3)_2 \cdot 6H_2O$ , 98% purity, SDFCL) and 2-methyl imidazole (Hmim 99%, purity, Sigma Aldrich).

#### **3.2.** Characterization

The powder X-ray diffraction (PXRD) patterns of the samples were recorded using Rigaku smart lab automated multipurpose X-ray diffractometer system with CuK $\alpha_1$  radiation ( $\lambda = 1.540593$  Å) in 20 range of 5-40 ° at scanning speed of 3 ° per minute and 0.01 ° scan step size. Scanning electron microscopy (SEM) and energy dispersive Xray spectroscopy (EDS) were taken using a Carl Zeiss Supra-55, scanning electron microscope and EDS Oxford instruments model X-Max, energy dispersive X-ray spectroscopy. Images were captured under 5 kV acceleration voltage and scale (100 nm and 200 nm). Sample preparation was done by dispersing the material into methanol by sonication and a drop of resulting suspension was placed on a sample holder disk, dried at room temperature and coated using gold sputter coating for SEM analysis. EDS analysis of materials were obtained by increasing the acceleration voltage up to 20 kV. To check the thermal stability, Thermo gravimetric analysis (TGA) was done using Mettler Toledo TGA/DSC 1 analyser. The apparatus was loaded with approximately 4 mg samples under flow of nitrogen gas at a heating rate of 5 °C/min from room temperature to 800 °C. Transmission electron microscopy (TEM) images were obtained using a JEM-1400 microscope (JEOL) operated at 100-120 kV. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was

performed using ARCOS, Simultaneous ICP Spectrometer. The N<sub>2</sub> gas adsorption isotherms were performed at 77 K on automatic volumetric adsorption equipment (Belsorp max). The equipment used for the CO<sub>2</sub> adsorption experiments was Autosorb IQ, Quantachrome sorptometer. Samples were out gassed prior to measurements being taken. Some adsorption experiments were also conducted after the samples were outgassed at 160 °C for 6 h (increasing rate 5 °C/min). The data was collected at 298 K from 0.025 bar to 1 bar (40 point system).

# **3.3.** Synthesis of ZIF-8, CoZn-ZIF-8 and Co<sub>100%</sub>-ZIF-8

#### i) Preparation of ZIF-8

ZIF-8 was prepared according to the previously reported procedure of Zhiping Lai *et al.*[100] An aqueous solution of zinc nitrate hexahydrate  $Zn(NO_3)_2 \cdot 6H_2O$  (0.2925g, 0.98 mmol) was prepared in 2 mL of distilled water. Another aqueous solution was prepared by dissolving 2-methyl imidazole (5.675g, 69.11 mmol) in 20 mL distilled water and filtered it through whatmann filter paper into a 50 mL round bottomed flask. The molar ratio of 2-methylimidazole to zinc was 70:1. Material was synthesized via rapid pouring of aqueous solution of zinc nitrate hexahydrate into the aqueous solution of 2methyl imidazole, and the mixture was stirred at room temperature for 10 min. The product was collected by centrifugation (6500 rpm, 15-30 min) and washed with distilled water for 3 times. Further, it was dried at 65 °C overnight in a drying oven, after cooling to room temperature stored in tightly capped vials at room temperature.

### ii) Preparation of Co<sub>25%</sub>-ZIF-8, Co<sub>50%</sub>-ZIF-8, Co<sub>75%</sub>-ZIF-8

CoZn-ZIF-8 was prepared by slight modification made to the previously reported procedure of Zhiping Lai *et al.*[100] An aqueous solution of zinc nitrate hexahydrate Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and cobalt nitrate

hexahydrate  $Co(NO_3)_2 \cdot 6H_2O$  (total 0.98 mmol, according to Table 1) was prepared in 2 mL of distilled water along with the aqueous solution of 2-methyl imidazole (5.675g, 69.11 mmol in 20 mL distilled water, filtered it through whatmann filter paper). The molar ratio of 2methylimidazole to zinc and/or cobalt was 70:1 in this case, as well. Material was synthesized via rapid pouring of aqueous solution of zinc nitrate hexahydrate and cobalt nitrate hexahydrate into the aqueous solution of 2-methyl imidazole, and the mixture was stirred at room temperature for 10 min. The product was collected by centrifugation (6500 rpm, 15-30 min) and washed with distilled water for 3 times. Further, it was dried at 65 °C overnight in a drying oven, after cooling to room temperature stored in tightly capped vials at room temperature.

**Table 1** Experimental data used for the preparation of the Co25%-ZIF-8, Co50%-ZIF-8, Co75%-ZIF-8.

Entry	Material	Cobalt (grams)	Zinc (grams)
1	Co <sub>25%</sub> -ZIF-8	0.0719	0.2203
2	Co <sub>50%</sub> -ZIF-8	0.1437	0.1468
3	Co <sub>75%</sub> -ZIF-8	0.2156	0.0735

#### iii) Preparation of Co<sub>100%</sub>-ZIF-8

Co<sub>100%</sub>-ZIF-8 was prepared by modifying the previously reported procedure of Zhiping Lai *et al.*[100] An aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2874, 0.98 mmol) was prepared in 2 mL of distilled water. Another aqueous solution was prepared by dissolving 2-methyl imidazole (5.675g, 69.11 mmol) in 20 mL distilled water and filtered it through whatmann filter paper into a 50 mL round bottomed flask. Rest of the procedure was same as discussed in i).

#### Chapter 4

# **Results and Discussion**

CoZn-ZIF-8 frameworks were synthesized via a simple one pot reaction methodology in water at room temperature.[100] Zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methyl imidazole (Hmim) mixed under stirring for 10 min at room temperature (Scheme 1). A white to violet colour solid was immediately precipitated out, which was collected by centrifugation. The Co: Zn molar ratio were altered by varying the initial concentration of  $Co(NO_3)_2 \cdot 6H_2O$  and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1:3, 1:1, 3:1 Co/Zn molar ratio) for the synthesis of CoZn-ZIF-8 frameworks with tuned Co to Zn ratio. ZIF-8 (with no Co content) and Co<sub>100%</sub>-ZIF-8 or ZIF-67 (with no Zn content) was also synthesized analogously using respective metal salts only.



Scheme 1 Schematic representation for the preparation of CoZn-ZIF-8 where red colour represents cobalt, blue colour represents zinc, blue colour represents nitrogen and sky grey colour represents carbon

Interestingly, a white coloured precipitate in case of ZIF-8 and violet precipitates were obtained for CoZn-ZIF-8, upon increasing the Co content in ZIF-8 as depicted in Figure 17.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) results were in good agreement with the initial molar concentration of Co and Zn used during synthesis, confirms that the intended content of  $Zn^{2+}$  and  $Co^{2+}$  was successfully incorporated in the frameworks without disturbing the ZIF-8 framework (Table 2). ICP-

AES results for  $Co_{25\%}$ -ZIF-8,  $Co_{50\%}$ -ZIF-8 and  $Co_{75\%}$ -ZIF-8 were 22.3, 48.9 and 74.8, respectively.



**Figure 17.** Photographs of the synthesized material, showing white to violet colour change with increase in molar percentage of cobalt in CoZn-ZIF-8 frameworks (a) ZIF-8, (b)  $Co_{25\%}$ -ZIF-8, (c)  $Co_{50\%}$ -ZIF-8, (d)  $Co_{75\%}$ -ZIF-8 and (e)  $Co_{100\%}$ -ZIF-8

Table 2 ICP-AES and EDS data in accordance with intended content of  $\text{Co}^{+2}$  in CoZn-ZIF-8

ZIF	Co content (mol%) based on	EDS	ICP-
frameworks	precursor materials used		AES
Co <sub>25%</sub> -ZIF-8	25	24.8	22.3
Co <sub>50%</sub> -ZIF-8	50	50.5	48.9
Co75%-ZIF-8	75	77.9	74.8
	ZIF         frameworks         Co25%-ZIF-8         Co50%-ZIF-8         Co75%-ZIF-8	ZIFCo content (mol%) based onframeworksprecursor materials usedCo25%-ZIF-825Co50%-ZIF-850Co75%-ZIF-875	ZIFCo content (mol%) based onEDSframeworksprecursor materials usedCo25%-ZIF-82524.8Co50%-ZIF-85050.5Co75%-ZIF-87577.9

Construction of CoZn-ZIF-8 framework by the substitution of the tetrahedral Zn<sup>2+</sup> by tetrahedral Co<sup>2+</sup>, while retaining the structural framework was well supported by UV/Vis diffuse reflectance spectroscopy (Figure 18). The comparable ionic radii of Co<sup>2+</sup> (0.72 Å) and Zn<sup>2+</sup> (0.74 Å), may enable high solubility of Co<sup>2+</sup> and Zn<sup>2+</sup> ions and hence there is a high chance of replacing of Co<sup>2+</sup> by Zn<sup>2+</sup> or viceversa. UV/Vis spectra showed characteristic bands of tetrahedral coordinated Co<sup>2+</sup> at 588 nm and 540 nm, suggesting the presence of Co<sup>2+</sup> in the synthesized CoZn-ZIF-8.[96,101] Moreover, the observed systematic shifts in the bands towards the pure ZIF-67 (Co<sub>100%</sub>-ZIF-8), with the increase in Co content in CoZn-ZIF-8, further supports the formation of CoZn-ZIF-8 framework with the substitution of  $Zn^{2+}$  by  $Co^{2+}$  ions.



**Figure 18.** UV-vis spectra of (a) ZIF-8, (b)  $Co_{25\%}$ -ZIF-8, (c)  $Co_{50\%}$ -ZIF-8, (d)  $Co_{75\%}$ -ZIF-8 and (e)  $Co_{100\%}$ -ZIF-8, (f)  $Co(NO_3)_2 \cdot 6H_2O$  and (g)  $Zn(NO_3)_2 \cdot 6H_2O$ 

Powder X-ray diffraction (PXRD) patterns of the synthesized CoZn-ZIF-8 displayed sharp and prominent peaks analogous to those of ZIF-8 (Figure 19).[60] A very sharp peak below 10 ° (with 20 of 7.3) and above 12 ° (with 20 of 12.6 °) was observed in the PXRD diffractogram for all the synthesized CoZn-ZIF-8 indicating that a highly crystalline material was achieved. These results suggest that the synthesized CoZn-ZIF-8 framework adopts the same crystalline frameworks as of ZIF-8 with sodalite topology. Notably, no structural damage or alteration was observed for the synthesized CoZn-ZIF-8 frameworks. Moreover no segregation of Co-ZIF-8 cluster and ZIF-8 cluster were observed in the PXRD of CoZn-ZIF-8.[60] Because, the ionic radii of Zn<sup>2+</sup> and Co<sup>2+</sup> in tetrahedral coordination are quite comparable (0.74 Å and 0.72 Å respectively), they are likely to interact well and therefore Co<sup>2+</sup> ions can substitute Zn<sup>2+</sup> ions. PXRD pattern of

 $Co_{100\%}$ -ZIF-8 matches well with that of reported ZIF-67 suggesting an altering route for the synthesis of ZIF-67.[102,103] Moreover a slight but systematic shift in the peaks of CoZn-ZIF-8 towards lower 20 value with respect to ZIF-8 were observed in the PXRD pattern of CoZn-ZIF-8, further support the substitution of Zn ion by Co ion in the synthesized CoZn-ZIF-8 framework.



Figure 19. Powder XRD pattern of (a) ZIF-8, (b)  $Co_{25\%}$ -ZIF-8, (c)  $Co_{50\%}$ -ZIF-8, (d)  $Co_{75\%}$ -ZIF-8 and (e)  $Co_{100\%}$ -ZIF-8

Consistent with PXRD pattern, SEM (Figure 20) and TEM images (Figure 21) of CoZn-ZIF-8 framework adopted well-defined truncated rhombic dodecahedral morphology.



**Figure 20.** SEM images at a scale of (a-e) 200 nm and (f-j) 100 nm of (a,f) ZIF-8, (b,g) Co<sub>25%</sub>-ZIF-8, (c,h) Co<sub>50%</sub>-ZIF-8, (d,i) Co<sub>75%</sub>-ZIF-8 and (e,j) Co<sub>100%</sub>-ZIF-8

TEM images of the CoZn-ZIF-8 framework suggesting the particle size is in the range of 150-300 nm. Moreover, a slight increase in the particle size of CoZn-ZIF-8 was observed with an increase in Co substitution, which suggests a kinetically controlled growth of the framework.[102,103] Energy dispersive X-ray spectroscopy (EDS) (Figure 21) results also accord well with the expected Co: Zn molar ratio in the synthesized CoZn-ZIF-8 frameworks (Table 2).



**Figure 21.** (a-c) TEM images and (d-f) EDS spectra of (a,d) Co<sub>25%</sub>-ZIF-8, (b,e) Co<sub>50%</sub>-ZIF-8, (c,f) Co<sub>75%</sub>-ZIF-8

Thermogravimetric analysis (TGA) showed analogous pattern of weight loss of ZIF-8 and CoZn-ZIF-8, suggesting their similar frameworks (Figure 22).[100,102,103] Initial weight loss of 2-6 % was observed from 135-155 °C, from the removal of residual  $H_2O$  or unreacted Hmim. The second weight loss observed from 420-518 °C corresponds to the structural decomposition of the ZIF framework. After Co incorporation, the thermal stability of CoZn-ZIF-8 enhance to the range of 450-520 °C, in comparison to 420 °C for ZIF-8 (Figure 22).[100,102,103]



**Figure 22.** TGA curves for (a) ZIF-8, (b) Co<sub>25%</sub>-ZIF-8, (c) Co<sub>50%</sub>-ZIF-8, (d) Co<sub>75%</sub>-ZIF-8 and (e) Co<sub>100%</sub>-ZIF-8

Surface area, pore volume and pore diameter of CoZn-ZIF-8 samples were determined by performing the N<sub>2</sub> adsorption-desorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) theory (Figure 23). All the CoZn-ZIF-8 samples showed Type I isotherm which revealed high BET surface area for Co<sub>25%</sub>-ZIF-8 (1160 m<sup>2</sup> g<sup>-1</sup>), Co<sub>50%</sub>-ZIF-8 (1518 m<sup>2</sup> g<sup>-1</sup>) and Co<sub>75%</sub>-ZIF-8 (1571 m<sup>2</sup> g<sup>-1</sup>) than that of analogously synthesized ZIF-8 and Co<sub>100%</sub>-ZIF-8 (1131 m<sup>2</sup> g<sup>-1</sup> and

1191 m<sup>2</sup> g<sup>-1</sup>) (Table 3).[54,58,99,104] The BET surface area and pore volume of  $Co_{75\%}$ -ZIF-8 were found to be highest than those having lower  $Co^{2+}$  content. Pore volume for  $Co_{25\%}$ -ZIF-8,  $Co_{50\%}$ -ZIF-8 and  $Co_{75\%}$ -ZIF-8 were 0.6086, 0.7435 and 0.7750 cm<sup>3</sup> g<sup>-1</sup>, respectively (Table 3). The pore size of CoZn-ZIF-8 framework are in the range of 1.9~2.1 nm which implies that the material is microporous (< 2 nm) in nature.



Figure 23.  $N_2$  sorption isotherm of (a) ZIF-8, (b)  $Co_{25\%}$ -ZIF-8, (c)  $Co_{50\%}$ -ZIF-8, (d)  $Co_{75\%}$ -ZIF-8 and (e)  $Co_{100\%}$ -ZIF-8 at 77K

Entry	ZIF frameworks	Pore volume	Pore diameter	Surface area
		$(cm^3 g^{-1})$	(Å)	$(m^2 g^{-1})$
1	ZIF-8	0.5819	20.6	1131.1
2	Co <sub>25%</sub> -ZIF-8	0.6086	21.0	1160.1
3	Co <sub>50%</sub> -ZIF-8	0.7435	19.6	1518.8
4	Co <sub>75%</sub> -ZIF-8	0.7750	19.7	1571.7
5	Co100%-ZIF-8	0.5776	19.4	1191.2

**Table 3** BET surface area, pore volume and pore diameter for ZIF-8,Co100%-ZIF-8 and CoZn-ZIF-8

The data obtained further compelled to investigate the CoZn-ZIF-8 frameworks for their CO<sub>2</sub> molecule uptake. To vacant the pores of the material, the materials were degassed at 170 °C for 6 hours before CO<sub>2</sub> uptake experiment and adsorption isotherm of CO<sub>2</sub> was obtained at 298 K up to 1.0 bar. The CO<sub>2</sub> adsorption capacities increased linearly with increase in the pressure for all the synthesized materials, CoZn-ZIF-8, ZIF-8 and Co<sub>100%</sub>-ZIF-8 (Figure 24 and Table 4).

Table 4 CO<sub>2</sub> uptake of CoZn-ZIF-8, ZIF-8 and Co<sub>100%</sub>-ZIF-8 at 298 K

Entry	ZIF frameworks	$CO_2$ uptake (mmol g <sup>-1</sup> )	
		0.15 bar	1 bar
1	ZIF-8	0.098	0.70
2	Co <sub>25%</sub> -ZIF-8	0.111	0.77
3	Co <sub>50%</sub> -ZIF-8	0.122	0.87
4	C075%-ZIF-8	0.126	0.90
5	Co100%-ZIF-8	0.124	0.85



Figure 24. (i)  $CO_2$  adsorption isotherm showing linear increase in adsorption capacity with increase in pressure for (a) ZIF-8, (b)  $Co_{25\%}$ -ZIF-8, (c)  $Co_{50\%}$ -ZIF-8, (d)  $Co_{75\%}$ -ZIF-8 and (e)  $Co_{100\%}$ -ZIF-8 at 298 K; (ii) corresponding magnified image at pressure range of 0.93 to 1 bar.

The synthesized bimetallic CoZn-ZIF-8 displayed enhanced  $CO_2$  uptake capacity than their monometallic analogous ZIF-8 and  $Co_{100\%}$ -ZIF-8 at 1 bar and 0.15 bar (flue gas partial pressure). The uptake capacity of ZIF-8 and  $Co_{100\%}$ -ZIF-8 or ZIF-67 are in good

agreement with the previously reported data.[52,58,99,105,106] Among all the CoZn-ZIF-8 investigated,  $Co_{75\%}$ -ZIF-8 exhibited the highest CO<sub>2</sub> uptake which is 30% higher than that of ZIF-8. The CO<sub>2</sub> uptake capacities were in the order Co<sub>75%</sub>-ZIF-8 > Co<sub>50%</sub>-ZIF-8 > Co<sub>100%</sub>-ZIF-8 > Co<sub>25%</sub>-ZIF-8 > ZIF-8 (Table 3). It is well establised that gas uptake capacity of the materials not only depends on the surface area but also depends on the favourable interactions between pore walls and guest gas molecules.[107] Therefore the enhanced CO<sub>2</sub> uptake capacities of CoZn-ZIF-8 framework was due to the combined effect of a) chemical heterogeneity in the pore and framework due to the presence of Co<sup>2+</sup> and Zn<sup>2+</sup>, b) enhancement of pore volume by ~33%, surface area by ~40%, and c) enhancement in micro porosity.

#### Chapter 5

### **Conclusion and Scope for Future Work**

In a nutshell we can say, a bimetallic Co-Zn based Zeolitic imidazole frameworks have been successfully synthesized in aqueous medium at room temperature. We observe that a framework can withstand a high content of metal ion in them as the resultant material (CoZn-ZIF-8) was synthesized by adjusting the molar ratios of Co to Zn precursors (Co:Zn 1:3, 1:1, 3:1), along with monometallic ZIF-8 and Co<sub>100%</sub>-ZIF-8. Notably, the synthesized CoZn-ZIF-8 frameworks showed no structural damage or alteration for which inferred that Co<sup>2+</sup> was successfully incorporated in the framework without interrupting the ZIF-8 framework. The pore volume and surface area increases with increase in the Co<sup>2+</sup> concentrations up to Co<sub>75%</sub>-ZIF-8 as compared to the monometallic ZIF-8 and Co<sub>100%</sub>-ZIF-8. The surface area of Co<sub>25%</sub>-ZIF-8, Co<sub>50%</sub>-ZIF-8 and Co<sub>75%</sub>-ZIF-8 were calculated to be 1160, 1518, 1571  $m^2 g^{-1}$ , repectively which is higher than that of analogous synthesized ZIF-8 and Co<sub>100%</sub>-ZIF-8 (1131 m<sup>2</sup> g<sup>-1</sup> and 1191 m<sup>2</sup> g<sup>-1</sup>). The surface area showed an enhancement of 40% whereas pore volume showed an enhancement of 33%, as compared to ZIF-8. Among all the synthesized CoZn-ZIF-8, Co75%-ZIF-8 exhibited the highest CO2 uptake capacity with an enhancement of 30% in the uptake with respect to ZIF-8. The CO<sub>2</sub> uptake capacity for the CoZn-ZIF-8 was found in the decreasing order of  $Co_{75\%}$ -ZIF-8 >  $Co_{50\%}$ -ZIF-8 >  $Co_{100\%}$ - $ZIF-8 > Co_{25\%}$ -ZIF-8 > ZIF-8. These results suggest that the synthesis of the bimetallic organic frameworks may provide great opportunities for developing new nanomaterials based on MOFs for various industrial application.

#### **APPENDIX-A**

Poster - 12 Frontiers in Inorganic and Organometallics

Synthesis and Characterisation of Mixed Metal Co-Zn in Zeolitic Imidazole Framework (Co-ZIF-8)

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ZIFs an important sub-class of metal-organic framework (MOFs), often showed better thermal, hydrothermal and chemical stabilities. Hence, synthesis of different type of ZIFs or doping of ZIFs with analogous metals has attracted more and more attention in various applications such as gas storage, separations, catalysis and chemical sensors <sup>111</sup>. However, altering the framework of MOFs by mixing different ligands or metals has gained new efforts which are now in contention. Previously, doped Cu<sup>-2</sup> doped ZIF-8 has been reported, using methanol at room temperature up to 25% of Cu<sup>+2</sup> in the ZIF-8 framework, above which a decrease in porosity was observed <sup>121</sup>, on the other hand Ni<sup>-2</sup> substituted ZIF-8 is prepared by introducing six-coordinated nickel clusters into a zinc-based ZIF-8 structure via a one-pot mechanochemical synthesis under liquid assisted grinding (LAG) conditions <sup>[81]</sup>. This raise our curiosity to look carefully into the framework of ZIF-8 and notice the changes caused when the central metal Zn<sup>-2</sup> replaces by other metals and study their structural changes. In this work, a mixed metal Co-Zn based MOF with ligand 2-methyl imidazole has been prepared with different doping percentages of Co (25–75% of Co<sup>2+</sup>) along with monometallic ZIFs in mild reaction conditions. The tenability of pore size, pore volume and surface area of Co doped ZIF-8 has been extensively studied by Brunauer-Emmett–Teller (BET). The highest surface area and pore volume was observed with 75% doping of the Co in ZIF-8. The particle size of various doped Co-ZIF-8 particles by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that they were 200-400 nm in size. The synthesized material was characterized by powder X-ray diffraction (PXRD), thermo gravimetric analysis (TGA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).



Fig. a Schematic representation for the preparation of ZIF-8 and Co-ZIF-8; b Histogram depicting the trend of surface area with the increase Co<sup>+2</sup> doping

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