DESIGN AND SYNTHESIS OF VARIOUS ORGANIC LINKERS FOR THE CONSTRUCTION OF CONDUCTING MOFS

M.Sc. Thesis

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DESIGN AND SYNTHESIS OF VARIOUS ORGANIC LINKERS FOR THE CONSTRUCTION OF CONDUCTING MOFS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree **of**

Master of Science

by **NISSAR HUSSAIN**



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DESIGN AND SYNTHESIS OF VARIOUS ORGANIC LINKERS FOR THE CONSTRUCTION OF CONDUCTING MOFS**, 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 2018 to June 2020 under the supervision of Dr. Shaikh M. Mobin, Associate professor, Discipline of Chemistry, IIT Indore.

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

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

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Dedicated to my Beloved Family

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ABSTRACT

Porous crystalline materials are one of the emerging and most promising branches of material chemistry, comprising of zeolites, metal organic frameworks, covalent organic frameworks and porous organic cages. The use of crystalline porous networks like **Metal Organic Framework (MOF)** have attracted enormous attention due to their porosity, tunable nature, chemical stability, long-range order, large surface area, high thermal and chemical stability, electronic interactions, charge carrier transport, efficient photocatalytic activity, tunable band gap, visible light absorbance and most important cost effectiveness etc.

The work described in this thesis concerns the synthesis of 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridin-1-ium)bromide (H₄L1), 5,5'-((naphthalene-2,6-diylbis(methylene)) bis(oxy)) diisophthalic acid (H₄L2), 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4carboxypyridin-1-ium) bromide (H₃L3), Characterization of 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridin-1-ium) phosph orouspenta flouride (H₃L4) and 5,5'-(oxybis(methylene))diisophthalic acid (H₄L5). These linkers have been characterized by ¹H NMR spectroscopy and Mass spectrometry. Further H₂L5 was utilized as linker in presence of Cu(NO₃)₂.3H₂O under room temperature condition gave **Cu-MOF** with 3D structure, respectively. This Cu-MOF was characterized by single crystal X- ray diffraction (SC-XRD).

TABLE OF CONTENT

LIST OF SCHEMES	XVI
LIST OF FIGURES	XVII-XIX
NOMENCLATURE	XX
ACRONYMS	XXI
Chapter 1: Introduction	1-19
1.1 Preamble	1-2
1.2 Metal-Organic Frameworks	(MOFs) 2
1.3 Design and Synthesis of M	OFs 3-6
1.4 Different methods for MOF	synthesis 6-9
1.4.1 Hydrothermal synthesis	5 7
1.4.2 Microwave Assisted sy	nthesis 7-8
1.4.3 Mechanochemical synthesis	hesis 8
1.4.4 Electrochemical synthe	sis 8
1.4.5 Sonochemical synthesis	8-9
1.4.6 Slow evaporation method	od 9
1.5 Application of Metal-Organic	Frameworks 9-19
1.5.1 Gas storage and separa	tion 10
1.5.2 CO ₂ conquestration	10-12
1.5.3 H ₂ adsorption	12-14
1.5.4 Water sorption applica	tions 14-16
1.4.5 Catalysis	16-19
1.6 Organization of the Thesis	19

Chapter 2: Experimental section	20-27
2.1 Materials	20
2.2 Methods and instrumentation	20
2.3 Synthesis of organic linkers	20
2.3.1 Synthesis of H ₄ L1	20-22
2.3.2 Synthesis of H ₄ L2	22-23
2.3.3 Synthesis of H ₃ L3	23-24
2.3.4 Synthesis of H ₃ L4	24-25
2.3.5 Synthesis of H ₄ L5	26-27
2.4 Synthesis of Cu-MOF	27
Chapter 3: Result and Discussion	28-35
3.1 Characterization of 1,1',1"-(benzene-1,3,5- triyltris(methylene))tris(4-carboxypyridin-1- ium)bromide (H ₄ L1)	28
3.1.1 NMR Spectroscopy	28
3.2 Characterization of 5,5'-((naphthalene-2,6- diylbis(methylene)) bis(oxy)) diisophthalic acid (H ₄ L2)	29
3.2.1 NMR Spectroscopy	29
3.3 Characterization of 1,1',1"-(benzene-1,3,5- triyltris(methylene))tris(4-carboxypyridin-1-ium) bromide (H ₃ L3)	30
3.3.1 NMR Spectroscopy	30
3.4 Characterization of 1,1',1"-(benzene-1,3,5- triyltris(methylene))tris(4-carboxypyridin-1-ium) phosphorouspentaflouride (H ₃ L4)	31
3.4.1 NMR Spectroscopy	31
3.5 Characterization of diethyl 5-((2-cyanobenzyl) amino)isophthalate	32
3.5.1 Mass Spectrometry	32
3.6 Characterization of 5,5'- (oxybis(methylene))diisophthalic acid	33
3.6.1 Mass Spectrometry	33

3.7 Crystal structure of Cu-MOF	34-36
Chapter 4: Conclusions and Scope for Future Work	37
APPENDIX A	38
REFERENCES	39-44

LIST OF SCHEMES

	Cu-MOF	
Figure 6	The synthetic scheme for the preparation of	27
Figure 5	The synthetic scheme for the preparation of H_4L5	26
Figure 4	The synthetic scheme for the preparation of H_3L4	25
Figure 3	The synthetic scheme for the preparation of H_3L3	24
Figure 2	The synthetic scheme for the preparation of H_4L2	22
Figure 1	The synthetic scheme for the preparation of H_4L1	21

LIST OF FIGURES

Figure 1.1	Scheme MOFs synthesis from metal centres and	2
	organic linkers to form 1D, 2D or 3D MOFs	
	depending on degree of extension.	
Figure 1.2	Components of MOFs.	4
Figure 1.3	Examples of linkers used in MOFs.	
Figure 1.4	Different methods for MOFs synthesis	7
Figure 1.5	Various applications of MOFs.	9
Figure 1.6	Improvement in the porosity of the MOFs during	10
	time according to their BET surface area	
	calculation.	
Figure 1.7	(a) Structure of Mg-MOF-74 that interacts with	12
	CO2 molecules.	
	(b) Structure of dimethylethylenediamine	
	functionalized $Mg_2(dobpdc)$. (c)Structure of	
	IRMOF-74 showing the interaction of amine	
	functionalized ligands with CO_2 molecules. (d)	
	Tetragonal crystal structures of [Cu(bpy-1)2(SiF ₆)]	
	(left) and $[Cu(bpy-2)_2(SiF_6)]$ (right). The	
	dimensions of these channels are controlled by the	
	bpy-1 and bpy-2 linkers.	
Figure 1.8	Representation of the solved structure of NU-100.	13
Figure 1 9	Working cycles of a sorption based chiller/heat	15
115010 117	pump.	

Figure 1.10	(a) Structure of UiO-66-NH ₂ an octahedral cluster 16		
	and related water sorption cycles. (b) Structure of		
	MIL-125 built up from a TiO ₆ octahedral cluster		
	and related water sorption cycles of MIL-125		
	(right).		
Figure 1.11	Cyanosilulation of henzaldehyde (above) and	16	
	rearrangement of g_ninene oxide to campholenic		
	aldehyde.		
Figure 1 12	Synthesis of USTC-253 and defect- engineering by	17	
rigure 1.12	adding TFA to the synthesis	1,	
Figure 1 13	Schematic Illustration of some representative	19	
i igui e i i i e	reactions catalysed by MOF supported iNPs		
Figure 3.1	The ¹ H NMR spectrum of H ₄ L1.	29	
Figure 3.2	The ¹ H NMR spectrum of H ₄ L2.	30	
Figure 3.3	The ¹ H NMR spectrum of H ₃ L3.	31	
Figure 3.4	The ¹ H NMR spectrum of H ₃ L4.	32	
Figure 3.5	ESI-MS spectrum of 5-((2-cyanobenzyl)	32	
	amino)isophthalate.		
Figure 3.6	ESI-MS spectrum of 5,5'-(oxybis(methylene))	33	
	diisophthalic acid (H4L5).		
Figure 3.7	Asymmetric unit of Cu-MOF.	34	
Figure 3.8	(a) Coordination environment of Cu(II) ions in Cu- 35		
	MOF, (b) paddle wheel structure adopted by Cu^{2+}		
	cations and H ₄ L5 anions within the Cu-MOF.		

Figure 3.9	Showing arrangement of atoms in Cu-MOF along	35
	(a) <i>b</i> -axis, (b) <i>a</i> -axis and (c) <i>c</i> -axis	

Figure 3.10Spherical cages in the supramolecular 3D35framework along c-axis.35

NOMENCLATURE

μ	mu
π	pi
σ	sigma
V	volume
%	percentage
θ	theta
λ	lambda
Å	Angstrom
S	second
h	Hour
g	gram
mmol	millimole

ACRONYMS

Ν	Nitrogen
0	Oxygen
С	Carbon
Н	Hydrogen
Cu	Copper
CDCl ₃	Deuterated chloroform
DMSO	Dimethyl sulphoxide
H ₂ O	Water
CH ₃ CN	Acetonitrile
NaOH	Sodium hydroxide
K_2CO_3	Potassium Carbonate
Na ₂ SO ₄	Sodium Sulphate
ESI-MS	Electron Spray Ionization- Mass Spectrometry
NMR	Nuclear Magnetic Resonance
SC-XRD	Single Crystal X-ray Diffraction

Chapter 1

Introduction

1.1 Preamble

The search for designing new materials has been a great challenge for researchers for particular applications aiming to address the urgent demands of real-world. To find the target and solution, major attention has been invest to develop new paths toward synthesizing and designing of materials for desirable properties. Therefore, in this way, efforts have been tackling to introduce higher functionality materials based on the combination of numerous components. Metal organic framework (MOFs), a new class of hybrid porous materials built up from metal ions or cluster and organic linkers which are linked through the coordination bonds to form networks in one-, two-, three dimensions and demonstrate to possess unprecedented potential for various applications i.e. storage energy, gas separation, drug delivery, catalysis, selective sensing etc. *[1-9]*

Metal Organic Frameworks are much attractive due to their tenability and significant structural diversity in the organic and inorganic units hold in their structures [10]. During assembly process the advantages on control of the components inorganic-organic attached with their distinctive physical properties are projected to motivate this field further into new realms of synthetic chemistry which can achieve astonishing materials [11]. Besides, "there is possibility to predict coordination geometries, to some extent, by choosing carefully the metal ions and organic linkers gives rise to generate a varied ambit of architectures framework" [12]. Many rational approaches of design have been arisen and developed to facilitate the building of the desired materials. This chapter will give a brief historical perspective of MOFs along with suitable terminologies.

1.2 Metal–organic Frameworks (MOFs)

In recent decades, Metal–organic frameworks or Porous Coordination Polymers a new class of porous crystalline materials have attracted tremendous interest. Generally, Metal-organic framework contains main two components (i) metal ions (clusters of ions) and (ii) organic ligands, which are accumulated via well-defined coordination bonds. MOFs are inorganic- organic- hybrids that coordinate metal ions to organic molecules to form 1D, 2D, or 3D structures (Figure1.1) [13]. In Metal-organic frameworks metal ion or cluster of metal ions called as node and organic molecules called as linkers. Usually metal ions include most of the metals from periodic table. The linkers involves organic components made up from aromatic, non-aromatic, aliphatic and coordinating carboxylate, imidazolate, triazolates, tetrazolate, pyridine based linkers, amino acids and its derivatives, etc. [14]



Figure 1.1 Scheme of MOFs synthesis from metal ions and organic linkers to form 1D, 2D or 3D MOFs depending on degree of extension.

1.3 Design and Synthesis of MOFs

Inorganic connectors and organic linkers are constructed from two key components of MOFs. By rational design, whole range of electrical, structural, magnetic, catalytic and optical properties can be incorporated into the metal-organic frameworks. Various metal ion having different geometries and coordination numbers such as linear, T- or Y-Tetrahedral, Square-pyramidal, shaped, Square-planar, Trigonalbipyramidal, Octahedral, Trigonal-prismatic, and Pentagonal-bipyramidal etc. (Figure 1.2). E.g. Cu (II) ions, having d⁹ configurations and having preference for tetrahedral and square-planar geometries, however depending on organic ligands and solvents it can also found with other coordination numbers [15]. Because of their large coordination numbers (usually 7 to 10), lanthanide ions, usually generate unusual and new topologies of network [16-19].

There are various varieties of selection for the organic linker. Rigid organic linkers are preferred often. Rigidity of organic linker defines the network geometry easily. After solvent removal the rigidity helps to withstand open-pore structure. The linkers can be cationic/anionic/neutral (**Figure 1.3**). For example 4,4 bipyridine (bpy) and pyrazine [20-22]. These are particularly used as pillars in the building for pillared- layer in 3D networks [23, 24]. Carboxylates are widely used anionic linkers, [25, 26] because they can accumulate metal ions to the clusters of ions and can form the stable frameworks. Due to low affinity for metal ions, cationic organic linkers are less used [27-29].



Figure 1.2: Components of MOFs.



Figure 1.3: Examples of linkers used in MOFs

Mostly, MOFs are synthesized by the hydrothermal or solvothermal methods [30-34] in which the reactions carried at hightemperature in closed vessels having an organic solvent or water. Though, these methods need long times of reaction (i.e. from hours to months) depend on reagent concentrations, MOF interest, reaction temperature, solvent, and many other factors. To allow the synthesis of MOFs in a few minutes, a microwave-assisted method has been developed [35-37]. It can control size of crystal from mm to sub-µm by controlling the reaction temperature and reactant conc. in solution.

Various researchers study that MOFs under solvent-free synthesis makes it environment friendly [38-40]. Mechano-chemical method of synthesis uses the mechanical forces to drive the reactions of metal oxides with organic linkers under solvent free at room temperature. BASF employ electrochemical synthesis of Metal-organic framework on commercial scale [45]. In this method, anodic dissolution is used for adding metal salts instead of adding metal salts. Its main advantage is to exclude unnecessary anions during synthesis, which further contribute in impurity, so complicate purification of synthesis.

1.4. Different methods for Metal-organic Framework synthesis

Different ways are used for the synthesis of Metal-organic framework. Each method makes compounds having different morphologies, size distributions, particle sizes, which lead to many applications. Few important methods of synthesis are follows [46].



Figure 1.4 Different methods for the synthesis of MOFs synthesis

1.4.1. Hydrothermal synthesis

It is a liquid-phase method for synthesis in which the reaction is performs at higher pressure and temperature (> $100 \, {}^{0}$ C) from hours to days in closed vessels. For this, Teflon-lined autoclaves usually used and in them high polar and high boiling solvents like DMSO, DEF, DMF, Water, acetonitrile, R-OH, acetones etc. Sometimes, solvents mixture is used to increase the solubility of the reactant in reaction. The polarity of the solution would be changed and lead to the intensity of the crystal growth. It forms good quality MOF crystals which are appropriate for structural characterization.

1.4.2. Microwave assisted synthesis

Microwave-assisted synthesis having higher nucleation rate due to this it is energy effective method for heating and also achieve the fast method of crystallization. Nowadays microwave-assisted method is generally used for nano scale with high purity very uniform distribution and identical morphology MOFs. When microwaves are used, the dipole moment of precursors in a Closed-vessel aligns itself with the field. That is conversion of electromagnetic energy into thermal energy is occurring, there is rise in kinetic energy in the sample due to frequent alignment collision between molecules. An important advantage of this method is adjustable pressure, power outputs and wide temperatures range.

1.4.3. Electrochemical synthesis

This method of synthesis has recently been applied for continuous and fast production of crystals of MOFs in large amounts. In this method, metal ions are used as metal source instead of metal salts. In anodic dissolution, the metal ions are reacting with electrolytes and organic ligands in the reaction medium. Through continuous process films and micro crystalline powders can be obtained.

1.4.4. Mechanochemical synthesis

Mechanochemical method is a solvent free synthesis. It is environmental friendly, economical and the simplest method comparing with other synthesis. Recently it is applied for the large scale production of MOFs. To grind the mixture of organic ligands and metal salts mechanical forces is used. Mechanical construction of new bonds and the breakage of intramolecular bonds occur. The advantages of this method are (1) room temperature is sufficient (2) organic solvents can be avoided, , (3 short reaction time and (4) side products formed are harmless.

1.4.5. Sonochemical synthesis

Nowadays sonochemical method of synthesis has efficiently applied for the fast synthesis of MOFs. By the application of ultrasound this method is very efficient to shorten the time of crystallization. Through a process of cavitation, ultrasound increases the physical or chemical changes in a liquid mode. After sonication subsequent destruction and growth of bubbles occur throughout the liquid. The collapse of bubbles leads to release of energy with pressure of 1000 atmospheres and temperatures of about 4000 K. This is environmental friendly and energy efficient method to create

homogeneous nucleation centers because there is no direct molecules interact with ultrasound.

1.4.6. The slow evaporation method

Slow evaporation or diffusion of solvents/solution in a reaction occurs in this method. It happens at room temperature with no external energy source. Metal salts are mixed with organic ligands in liquid phase without or with use of the additional molecules. This conventional method is very commonly used for **MOF** synthesis. Generally, highly soluble reactants are used which are concentrated by slowly evaporation. As compared to other methods of synthesis, it is time-consuming process.

In addition to these methods, numbers of other synthesis methods are also followed such as precipitation reaction followed by recrystallization, ionothermal method and layering methods of the solution.

1.5. Applications of Metal-Organic Frameworks

Some unique properties provided by MOF are structural diversity, high porosity, and high stability used in wide range of applications (**Figure.1.5**) *[47]*. Some of these applications will be given as a follows.



Figure.1.5 Various applications of MOFs.

1.5.1. Gas storage and separation

The main aim of gas storage and separation applications are control of toxic gases, dissemination of clean energy usage which would ultimately lead to environmental protection. Hence, CO_2 capture and separation is essential to decrease greenhouse effect. Moreover, methane and hydrogen gases are considered as greener energy sources. But, the best storage of the mentioned gases stills a great challenge. To overcome these problems, the MOFs are becoming source due to high surface area as compared with other porous materials (**Figure 1.6**). MOFs potential in gas separation and storage has given in sections below.



Figure1.6: Improvement in MOFs porosity during time according to their BET surface area calculation [48].

1.5.2. CO₂ sequestration

The effect of greenhouse gases on atmosphere is a serious global concern. So, an immediate solution is needed to express the CO_2 emission from plant or fossil fuel in a cost-effective and fast way. CO_2

capture are among the best solutions to overcome this problem. Due to lower density and higher surface area compared to other porous materials, Metal-organic framework has power to overawed current challenges in CO_2 sequestration. Due to their chemical tunability also to their porosity, MOFs are a good source for using CO_2 capture [49].

The adsorbent for CO_2 sequestration should be selectivity to CO₂ over other components such as H₂, N₂, and CH₄. This can be due to the pores size of MOFs which has chemical affinity of attached with CO₂. In this case, unsaturated metals can present in activated MOFs that shows Lewis acidity. The open metal centers coordinately act as binding sites where CO₂ molecules can bind to the pore surface by the dipole-quadrupole interactions. According to report, "Mg-MOF- 74, having unsaturated Mg ions, have the highest capacity of uptake (27.5 wt %) reported under standard conditions" [50]. The MOFs affinity towards CO₂ can enhance by Lewis basic groups such as imines, amines etc. To improve the adsorption of CO_2 . These groups provide the chemisorptive process to interact CO_2 with nitrogen lone pairs. A report was given by Hong and Long et al. through the Mg₂(dobpdc) where dobpdc = 4,4'-dioxidobipheny 1-3,3'dicarboxylate. After functionalization with N, N- dimethylethylenediamine (mmen), the capacity of adsorption of Mg₂(dobpdc) increases fifteen times as compared to other non-functionalized. Even $Mg_2(dobpdc)$ is a good CO_2 selective in moisture presence(Figure 1.7a-c) [51].

Finally, MOFs having non-metal inside the metal-organic framework can also increase the CO₂ capacity of adsorption by the interactions between the non-metallic groups and CO₂ molecules. For example MOFs prepared by the fluorinated M-XF₆ pillars (M = Cu, Zn, Co, and Ni; X = Ti, Sn, and Si) coordinated to the ligands having N-donor type. This types MOFs show high CO₂ uptake and is selectivite to the size of the network and interaction between fluorine atoms and CO₂ molecules. Moreover, SIFSIX-1-Cu (Cu(4,4'-bpy)2(SiF6), ,(dpa = 4,4'- dipyridylacetylene)) and (4,4'-bpy = 4,4'-bipyridine) SIFSIX-2-Cu-(Cu(dpa)2(SiF6) shows CO₂ uptake capacities at ambient pressure of 19.1 and 19.2 wt %. It is the utmost uptake for a MOF reported without unsaturated metal sites. (**Figure1.7d**) [52, 54]



Figure1.7: (a) Structure of Mg-MOF-74 that interacts with CO₂ molecules [52] (b) Structure of dimethylethylenediamine functionalized Mg₂(dobpdc). [51] (c) Structure of IRMOF-74 showing the interaction of amine functionalized ligands with CO₂ molecules. [47] (d) Tetragonal crystal structures of [Cu(bpy-1)2(SiF₆)] (left) and [Cu(bpy-2)2(SiF₆)] (right). The dimensions of these channels are controlled by the bpy-1 and bpy-2 linkers [53].

1.5.3. H₂ adsorption

The excellent replacement for gasoline and coal as a source of energy is water hydrogen because of its abundance, formation of nonhazardous combustion products and high combustion heat. As compared to other fuel sources, although H_2 has ultrahigh energy per mass its low density and ambient temperature end in a less energy per unit volume that needs new techniques for its transport, storage and increase its penetration [55]. In cryogenic conditions H_2 can be stored in the form of pressurized gas or using porous materials by chemisorption and physisorption process. Absorbent materials uses in this context produce fast desorption and adsorption condition of kinetics and energy and pressure need decrease. In this concern, MOFs having varied nature and highly porous have been shown good source [56].



Figure 1.8: Representation of the solved structure of NU-100.

Meanwhile, the surface area is greatly associated adsorption of gases; a first approach was varying the pore size and shape. E.g. A MOF based on copper paddle wheel (NU-100) having surface area of 6143 m² g⁻¹ have highest capacity to capture H₂ at 77 K and 56 bar (**Figure 1.8**). Zhou et al. reported in 2016, the MOF PCN-6, prepared by of Cu²⁺ and 4,4',4"-s-triazine-2,4,6-triyl-tribenzoic acid. This MOF has shown a adsorption capacity of H₂ as 72 mg g⁻¹ at 50 bar and 77 K [57]. As already described, the framework producing open metal sites can also enhance the capacity of H₂ adsorption. As example, in the report of Long et al. the synthesis of Mn₂ (dsbdc) where (dsbdc = 2,5-disulfido-1,4- benzenedicarboxylate)

coordinately to the unsaturated metal centers. Presence of Open metal sites also helps to enhance the H_2 uptake twice due the interaction with molecules of H_2 (1.6 wt% at 77 K and 1.2 bar) [58].

1.5.4. Water sorption applications

To increase the sorption capacity for gases like CH₄, CO₂ and H₂ in MOFs many investigations being conducted to produce special designs MOFs as the first discovered MOFs (MOF-5 and HKUST-1) were not stable in conditions of moistures. Later the water sorption features was discovered with the introducing of water stable metal-organic framework which show that type V isotherms present by MOFs for high water uptake (**Figure 1.9**), which is suitable in industrial applications like adsorption heat transformation (AHT) *[59]*. Environmental friendly and efficient cooling systems has been attempted many times to decrease the CO₂ power consumption

Desorption and Adsorption based methods are decent source to used as green refrigerating systems with solar collectors or waste heat of low temperature as energy source in the place of electricity. Metal-organic frameworks are the efficient materials used in these applications due to their stability under humid conditions. They have S-shaped adsorption isotherm (Figure 1.9) that provides with high working capacity on low regeneration temperatures and very narrow window of relative pressures [60]. To supply heat and cold, the AHT systems uses thermal energy. This happens in a cycle which starts with the water evaporation using heat from the surrounding. The water adsorption is an exothermic process because the adsorbent adsorbs water vapors and release heat into the surrounding at an intermediate temperature. Desorption of the adsorbed water starts at a high temperature relatively when the adsorbent start saturated with water. While heat release at an intermediate temperature, the desorbed water afterward condensed. This can work like adsorption cycle like heat pump forms heat at intermediate temperature, using adsorption or condensation or by using heat of evaporation to provide cold at very lower temperature (chiller) (Figure 1.9)[61]



Figure1.9: Working cycles of a sorption based chiller/heat pump. [62]

MOFs are efficient materials for AHT applications. sorption should present a isotherm of type V in the pressure range from 5% to 35% relative humidity, regeneration temperature lower than 120 °C with water sorption capacity > 0.2 gwater g⁻¹ and. Janiak and Henninger et al. reported CAU-10-H (Al(OH)(1,3-BDC)) that can be best source for this type of and application they performed the ten thousand water desorption/adsorption cycles with the sorption peak at relative humidity 25% and permanent capacity 0.34 g water $g^{-1}/63$. In other study, MIL-125-NH₂ and UiO-66-NH₂ have shown as good source displaying high stabilities and high water uptake even after forty cycles (Figure 1.10). Recently, Gordeeva et al. reported the MOF-801 (Zr-fumarate) that can be used as good source for application of air conditioning which shows low working range of temperature (up to 85 °C) and uptake up to 0.21 gwater g⁻ ¹ [64].



Figure1.10: (a) Structure of UiO-66-NH2 an octahedral cluster and related water sorption cycles. (b) Structure of MIL-125 built up from a TiO6 octahedral cluster and related water sorption cycles of MIL-125 (right). *[62]*

1.5.5. Catalysis

MOFs, having suitable chemical composition (both the inorganic and organic moieties) having high surface areas are useful for catalytic processes such as homogenous and heterogeneous catalysis. Different strategies have been developed to design MOFs for efficient catalysts, which include metal nodes, functionalized linkers, defective Metal-organic framework and the species supported by the frameworks *[65,*

66].



Figure 1.11: Cyanosilylation of benzaldehyde (above) and rearrangement of α -pinene oxide to campholenic aldehyde.

The first method is to take the benefit of metal nodes having unsaturated sites that plays a role of catalytic centers in the reaction of catalysis. These metal sites show character of Lewis acid so these materials use for desirable catalysts for reactions that catalyze by the Lewis acids. For example, in cyanosilylation reactions Metal-organic framework are useful. HKUST-1 is a useful catalyst for aldehydes cyanosilylation due to the intrinsic Lewis acidity by the unsaturated Cu (II) ions [67].



Fig.1.12: Synthesis of USTC-253 and defect- engineering by adding TFA to the synthesis.

HKUST-1 was used in cyanosilylation reactions as a catalyst for the terpene derivatives isomeration, such as rearrangement of α -pinene oxide to campholenic aldehyde and cyclization of citronellal to isopulegol (**Figure 1.11**) [68]. Also in MOFs the presence of the open metal sites generates defects in the structure of framework. For example, USTC-253 sulfone-functionalized MOF was synthesized by adding TFA (trifluoroacetic acid (**Figure 1.12**). The catalytic activity of this MOF studied in CO₂ cycloaddition to propylene oxide at 1 bar pressure and room temperature. USTC-253-TFA provide 81.3% conversion in presence of nBu_4NBr (TBAB) as co-catalyst at [69]. Introducing the functional linkers is the 3rd strategy to control the reaction of catalysis. Due to inductive effects of the metal nodes, functional groups on the aromatic linkers have a significant role in intrinsic catalytic activity. Addition of EWG such as – NO₂ and SO₃H increase the metal nodes Lewis acidity. Due to this, it increases catalytic activity. This was studied on MIL-101 and UiO-66 and was successfully used for different catalytic reactions such as oxidative coupling of benzylamines to imines and epoxide ring opening [70].

Finally, another approach of Metal-organic framework is used to support the active species such as inorganic nanoparticles (iNP). These materials are very active in catalysis. Though, they decrease or lose their reactivity and aggregate. Moreover, they have small size which prevents catalyst recollection from media and material recycling. These factors make a great challenge in industrial applications. In this case, MOFs with their large surface area and high stability are good source to be used as ease the iNPs collection from the reaction media and support in preventing aggregation. Many composites of MOFs have shown efficient catalysts for various reactions such as alcohol oxidation , CO oxidation and Carbon-Carbon coupling reactions (Suzuki, Ullman and Sonogoshira coupling). In general, UiO-66, ZIF-8, HKUST-1 and MIL-101 has revealed a good support for iNPs (Au, Pd, Pt, CeO2, Cu/Pd, Pt/Pd, Au/Pd, Au/CeO2). These composites have shown a good conversion percentage higher than 98% in the reactions (**Figure 1.13**) [71, 72].



Figure 1.13: Schematic Illustration of some representative reactions catalysed by MOF supported iNPs.

1.6 Organization of the thesis

The purpose of this project was to design and synthesis of functional linkers for the construction MOFs and their application in energy storage, drug delivery and catalysis.

Chapter 1: In this chapter, we have discussed about the introduction, Synthesis and applications of MOFs.

Chapter 2: This chapter includes materials, techniques and experimental procedure which were used to synthesize MOFs.

Chapter 3: In this chapter, we have discussed about the results that was obtained during synthesis of these compounds.

Chapter 4: In this chapter, we have concluded all the results of our work and their future aspects.

Chapter 2

Experimental section

2.1. Materials

All reagents were commercially available and were further used without purification. Cu(NO₃)₂.3H₂O (98%), 1,4 dichloromethyldurene, 2,6 dibromomethyl nepthalene, 5-hydroxyisophthalic acid, 5-hydroxymethyl isopthalic acid, 5-bromomethyl isopthalic acid were obtained from Sigma Aldrich. Other chemicals *i.e.* Na₂SO₄, HCl, K₂CO₃, KOH, NaOH and the solvents were purchased from Loba Chemie and S. D. fine Chemicals (India). All solvents were purified and dried earlier for using following standard methods.

2.2. Methods and instrumentation

All the reactions were monitored by TLC on Merck silica gel plates and spot were viewed under UV lamp. NMR spectra were recorded on a JEOL JNM-LA 400 FT (400 MHz) instrument in CDCl₃, D₂O, DMSO-*d6* with Si(Me)₄ as the internal standard. The patterns of splitting in ¹H NMR peaks are denoted as: s-singlet; d-doublet; t-triplet; q-quartet; m-multiplets. ESI-mass spectra were obtained by the WATERS Q-TOF Premier mass spectrometer.

2.3. Synthesis of organic Linkers

We have synthesized tri- and tetra- carboxylic acid based linker for the Metal-organic framework, described below.

2.3.1. Synthesis of H₄L1

The ligand H₄L1 was synthesized in several steps as shown in scheme 1.



Scheme 1: The synthetic scheme for the preparation of H4L1

Synthesisof5,5'-(((2,3,5,6-tetramethyl-1,4-phenylene))bis(methylene))bis(oxy))diisophthalic acid (H4L1)

Diethyl 5-hydroxyisophthalate (1g, 4.2 mmol) and K_2CO_3 (0.69 g, 5 mmol) in acetone (60 mL) were refluxed for 30 min. Then, 1,4 dichloromethyldurene (0.35 g, 1.5 mmol) added to the solution. Then the reaction refluxed for 6 h. After that the solution was concentrated under the rotary evaporator. Then the product was extract with DCM and Water and concentrated under rotary evaporator. White compound A was prepared

(2.1 g, yield 80%). This compound, A was further added to ethanol and H₂O (60 mL and 20 mL) and then add sodium hydroxide (0.79 g, 16.56 mmol) to it and refluxed for 12 h. After cooling, 6M HCl was added under stirring constantly to change the pH (1–2) of the solution under cold conditions. The resulting precipitates were filtered and washed with distilled water. The final product was dried in vacuo over for 48 h, (1.3 g, yield 75%); ¹H-NMR (DMSO- *d*₆, 400 MHz, Si (Me)₄): δ = 2.32 (s, 12 H, CH₃), 5.29 (s, 4 H, CH₂), 7.83 (s, 4 H, Ar-H); 8.18 (s, 2 H, Ar-H) ppm (**Figure 3.1**).

2.3.2. Synthesis of H₄L2

The ligand H₄L2 was synthesized in several steps as shown in scheme 2.



Scheme 2: The synthetic scheme for the preparation of H₄L2

Synthesis of 5,5'-((naphthalene-2,6-diylbis(methylene)) bis(oxy)) diisophthalic acid (H4L2)

Diethyl 5-hydroxyisophthalate (0.5 g, 2.1 mmol) and K₂CO₃ (0.34 g, 2.5 mmol) in acetone (60 mL) were refluxed for 30 min. Then, 2,6dibromomethylnepthalene (0.32 g, 1 mmol) was to be added. Then the reaction refluxed for 6 h. After that the reaction mixture was concentrated under rotary evaporator. Then the product was extract with DCM and Water and concentrated under rotary evaporator. White compound A was prepared, (1 g, yield 76%). This white compound, B was further added to ethanol and H₂O (60 mL and 20 mL) and then add sodium hydroxide (0.31 g, 7.96 mmol) to it and refluxed for 12 h. After cooling, 6M HCl was added in solution under stirring constantly to change the pH (1–2) under cold conditions. The resulting mixture was filtered and then washed with water .The final product was dried in vacuo over for 48 h, (0.75 g, yield 76%); ¹H-NMR (DMSO- *d*₆, 400 MHz, Si (Me)₄): $\delta = 5.47$ (s, 4 H, CH₂), 7.69 (d, 2 H, Ar-H); 7.85 (s, 4 H, Ar-H), 8.02 (d, 2 H, Ar-H), 8.09 (s, 2 H, Ar-H), 8.16 (s, 2 H, Ar-H) ppm (Figure 3.2).

2.3.3. Synthesis of H₃L3

The ligand H₃L3 was synthesized in several steps as shown in scheme 3.



Scheme 3: The synthetic scheme for the preparation of H₃L3

Synthesis of 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxy pyridin-1-ium) bromide (H₃L3)

1,3,5-tris(bromomethyl)benzene (0.543 g, 1.5 mmol) was added in DMF (30 mL). After that isonicotinic acid solution (0.555 g, 4.5 mmol) in DMF was to be added to this solution. The reaction mixture refluxed for 6 h. The resulting precipitates were filtered then washed with diethyl ether and DMF. The final product was dried in vacuo to give H₃L3 as a light yellow powder (0.411 g, yield 40.0%); ¹H-NMR (D₂O, 400 MHz, Si (Me)₄): δ = 5.91 (s, 6 H, CH₂), 7.63 (s, 3 H, Ar-H); 8.4 (s, 6 H, Ar-H), 9.0 (d, 6 H, Ar-H), ppm (**Figure 3.3**).

2.3.4. Synthesis of H₃L4

The ligand H₃L4 was synthesized in several steps as shown in scheme 4.



Scheme 4: The synthetic scheme for preparation of H₄L4

Synthesis of 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxy pyridin-1-ium) bromide (H3L4)

1,3,5-tris(bromomethyl)benzene (0.543 g, 1.5 mmol) was added in DMF (30 mL). After that isonicotinic acid solution (0.555 g, 4.5 mmol) in DMF was to be added to this solution. Then the reaction mixture refluxed for 6 h. Then the resulting precipitates were filtered, and then washed with diethyl ether and DMF to obtain C as white color sticky compound. Further the compound C was added with water and adds excess amount of KPF₆ stirred on R.T. After that white color precipitate ware formed which was further filtered and dried over vacuum to obtain white color H₃L4 (0.7 g, 79.0% yield);). ¹H-NMR (DMSO- *d*₆, 400 MHz, Si(Me)₄): δ = 6.11 (s, 6 H, CH₂), 7.79 (s, 3 H, Ar-H); 8.42 (t, 3 H, Ar-H), 9.16 (d, 3 H, Ar-H), 9.32 (d, 3 H, Ar-H), 8.16 (s, 3 H, Ar-H) ppm (**Figure 3.4**).

2.3.5. Synthesis of H₄L5



The ligand H₄L5 was synthesized in several steps as shown in scheme 5.

Scheme 5: The synthetic scheme for preparation of H4L5

Synthesis of 5, 5'-(oxybis(methylene))diisophthalic acid (H4L5)

diethyl 5-(hydroxymethyl)isophthalate (1 g, 3.96 mmol) and K₂CO₃ (0.65 g, 4.7 mmol) were added in DMF (40 mL). After that diethyl 5-(bromomethyl)isophthalate (1.24 g, 3.96 mmol) was to be added. The reaction refluxed for 24 h. The mixture was to be extracted with DCM and Water and also added brine solution. The organic layer was concentrated under rotatry evaporator to obtain compound D, (1.4 g, yield 74%). ESI-MS: $[M+Na]^+$ calculated for C₂₆H₃₀NaO₉: 509.18, found 508.827. Further white compound D (1.4 g, 2.90 mmol) was added to methanol and H₂O (60 mL and 20 mL) and NaOH (0.58g, 14.5 mmol) then mixture refluxed for 24 h. After cooling, 6M HCl was added under constant stirring to change the

pH (1–2) of the solution under cold condition. The resulting precipitates was filtered and dried in vacuo over for 12 h to obtain H₄L5 (0.81 g, yield 75%); ESI-MS: $[M+K]^+$ calculated for C₁₈H₁₄KO₉: 413.03, found 413.027.

2.5. Synthesis of Cu-MOF.

The Cu-MOF was synthesized by the slow evaporation method at room temperature. H₄L5 (37.4 mg, 0.1 mmol) and Cu(NO₃)₂·3H₂O (38.5 mg, 0.16 mmol) were dissolved in DMF (4 mL) and H₂O (2 mL), respectively, in two different flasks. These two solutions were heated on hot plate till the formation of a clear solution. Then these solutions were mixed together with the addition of 3 drops of 1 M HCl into the reaction mixture, which was stirred well. The reaction mixture was placed without disturbing for slow evaporation at ambient conditions. After 10 days, blue colour crystals were formed. Further the crystals were filtered, washed with DMF and H₂O. Yield = 27 mg, 80% (based on H₄L5 linker).



Scheme 6: Synthetic scheme for preparation of Cu-MOF

Chapter 3

Result and Discussion

Cu-MOF is synthesized by slow evaporation method at room temperature by reaction of Cu(NO₃)₂.3H₂O with H₄L5 in acidic medium in presence of DMF and H₂O as solvent. The presence of polydentate ligand and tendency of Cu(II) ion to form MOFs have led for the formation of an unreported MOF. The linker H₄L5 was characterized by mass spectrometry. The MOF was characterized by single crystal X-ray diffraction (SC-XRD) studies. We have also synthesized H₄L1, H₄L2, H₃L3, and H3L4 as linkers. These linkers were characterized by NMR spectroscopy.

3.1 Characterization of 5,5'-(((2,3,5,6-tetramethyl-1,4-phenylene))bis (methylene))bis(oxy)) diisophthalic acid (H4L1)

3.1.1 NMR Spectroscopy

NMR spectrums of H₄L1 were recorded in DMSO- *d6* using TMS as an internal standard. In ¹H NMR 2.32 ppm peak corresponds to the CH₃ group attached to the benzene ring, 5.29 ppm peak corresponds to the two proton present near to oxygen atom, 8.18 ppm corresponds to the proton present between the two carboxylic group and rest of the aromatic proton corresponds to the 7.83 ppm respectively (**Figure 3.1**).



Figure 3.1 The ¹H NMR spectrum of H₄L1.

4.2 Characterization of 5,5'-((naphthalene-2,6-diylbis(methylene)) bis(oxy)) diisophthalic acid (H4L2)

3.2.1 NMR Spectroscopy

NMR spectrums of H₄L2 were recorded in DMSO- d6 using TMS as an internal standard. In ₁H NMR 5.47 ppm peak corresponds to the two proton present near to oxygen atom , 8.16 ppm corresponds to the proton present between the two carboxylic group and rest of the aromatic proton corresponds to the 8.09, 8.02, 7.85 and 7.69 ppm respectively (**Figure 3.2**).



Figure 3.2 The ¹H NMR spectrum of H₄L2.

3.3 Characterization of 1,1',1''-(benzene-1,3,5-triyltris(methylene)) tris(4-carboxypyridin-1-ium) bromide (H₃L3)

3.3.1 NMR Spectroscopy

NMR spectrums of H_3L3 were recorded in D_2O using TMS as an internal standard. In ¹H NMR 5.91 ppm peak corresponds to the two proton present near to nitrogen atom , 9.0 ppm corresponds to the proton present ortho to carboxylic group, 8.41 ppm corresponds to the proton present meta to the carboxylic group and rest of the aromatic proton corresponds to the 7.63 ppm respectively (**Figure 3.3**).



Figure 3.3 The ¹H NMR spectrum of H₃L3.

3.4 Characterization of 1,1',1''-(benzene-1,3,5-triyltris(methylene)) tris(4-carboxypyridin-1-ium) phosphorous pentaflouride (H₃L4)

3.4.1 NMR Spectroscopy

NMR spectrums of H₃L4 were recorded in *d6*-DMSO using TMS as an internal standard. In ¹H NMR 6.1 ppm peak corresponds to the two proton present near to nitrogen atom, 9.2 and 9.32 ppm corresponds to the proton present ortho to carboxylic group, 9.16 ppm one proton near to the nitrogen atom, 8.42 ppm corresponds to the proton present meta to the carboxylic group and rest of the aromatic proton corresponds to the 7.79 ppm respectively (**Figure 3.4**).



Figure 3.4 The ¹H NMR spectrum of H₃L4.

3.5 Characterization of tetraethyl 5,5'-(oxybis(methylene)) diisophthalate

3.5.1 Mass spectrometry

ESI-MS data supports the formation of diethyl 5-((2-cyanobenzyl) amino)isophthalate with molecular ion peak at m/z 508.827 (100%) which corresponds to [M+Na]⁺ (Figure 3.5).



Figure 3.5 ESI-MS spectrum of 5,5'-(((2,3,5,6-tetramethyl-1,4-phenyl ene)bis(methylene))bis(oxy))diisophthalate.

3.6 Characterization of 5,5'-(oxybis(methylene))diisophthalic acid (H4L5)

3.6.1 Mass spectrometry

EI-MS data supports the formation of 5,5'-(oxybis(methylene))diisophthalic acid (H₄L5) with molecular ion peak at m/z is 413.02 (100 %)183 which corresponds to $[M+K]^+$ (**Figure 3.6**).



Figure 3.6 ESI-MS spectrum of 5,5'-(oxybis(methylene))diisophthalic acid (H₄L5)

3.7 Crystal structure of Cu-MOF

SCXRD study reveals that Cu-MOF crystallizes in C222₁ space group of the orthorhombic crystal system. **Figure 3.7** is the representation of asymmetric unit of Cu-MOF which consists of three Cu(II) ions, one and a half unit of H₄L5 ligand, three terminally coordinated H₂O molecules.



Figure 3.7: Asymmetric unit of Cu-MOF.

Figure 3.8(a) represents the coordination environment of Cu(II) ions within the framework showing distorted octahedral geometry where each Cu ion is coordinated to four carboxylate units of H₄L5 ligands at basal position, one copper ion and one H₂O molecule at apical position. Each H₄L5 ligand is coordinated to eight Cu(II) ions via carboxylate oxygen atoms. Paddle wheel structure is adopted by Cu(II) cations and H₄L5 anions taking Cu₂(COO)₄ as a node which additionally pillared by H₄L5 ligands into a 3D-MOF as shown in **Figure 3.8(b)**.



Figure 3.8: (a) Coordination environment of Cu(II) ions in Cu- MOF, (b) paddle wheel structure adopted by Cu^{2+} cations and H₄L5 anions within the Cu-MOF.



Figure 3.9: Arrangement of atoms in **Cu-MOF** along (a) *b*-axis, (b) *a*-axis and (c) *c*-axis.

The bond distances of Cu—O observed in **Cu-MOF** are in the range of 1.939 to 2.215 Å. The distance between two Cu(II) ions in each paddle

wheel unit is 2.648 Å. Figure 3.9 shows the packing of atoms within the supramolecular framework along a, b and c-axis.

Stable 1-D porous channels are present with dimensions of 12.654 Å along c-axis (Figure 3.10 a and b) in Cu-MOF.



Figure 3.10: Spherical cages in the supramolecular 3D framework along caxis.

Chapter 4

Conclusion and Future Scope

In this thesis, we have successfully synthesized various linkers such as $1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridin-1-ium)bromide (H_4L1), 5,5'-((naphthalene-2,6-diylbis(methylene)) bis(oxy)) diisophthalic acid (H_4L2), 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridin-1-ium) bromide (H_3L3), Characterization of 1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridin-1-ium) phosphorouspenta flouride (H_3L4) and 5,5'-(oxybis(methylene))diisophthalic acid (H_4L5). Their molecular structure was confirmed by mass spectrometry and NMR spectroscopy.$

A new CP/MOF (**Cu-MOF**) was synthesized utilizing Cu(II) metal ions with H₄L5 as linker respectively. This Cu-MOF was characterized by SC-XRD (single crystal X- ray diffraction). The structural study shows that the **Cu-MOF** is 3D metal-organic framework.

Cu (II) based MOFs are very good materials for the sensing applications viz. bio sensing, bio imaging, highly selective detection of nitro aromatic explosives, small molecules etc. Also, Cu-MOFs exhibits highest catalytic activity. There are many reports of Cu based MOF on supercapacitors, batteries, electrochemical sensing etc. Due to the porous network of our reported Cu-MOF, permeation of electrolyte could be easily allowed within the channels so it can be explored in electrochemical applications too.

APPENDIX-A

Crystal structure and refinement parameters for Cu-MOF`

Parameters	Cu-MOF
Empirical formula	$C_{26}H_{13}O_{16}Cu_3$
Formula wt.	771.638
Crystal system	orthorhombic
Space group	C 2 2 21 (20)
<i>a</i> , Å	18.5821(5)
b, Å	32.5900(7)
<i>c</i> , Å	19.9514(7)
a (deg)	90
β (deg)	90
γ (deg)	90
$V, Å^3$	12082.38(59)
Temperature (K)	293

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