Synthesis and Thio-Functionalization of Metal Organic Frameworks of Isonicotinate Ligands and Their Removal of Dye from Aqueous Solution

Comment [i1]: Their application for fluorescein removal from aqueous solution

ABSTRACT

Mechanochemical syntheses of four (4) know metal organic frameworks (MOFs) [1 - 4] were obtained by grinding stoichiometric amounts of metal salts [Zn(II) and Cu(II)] and corresponding carboxylate ligands [Fumaric and Isonicotinic acids] in a mortar with a pestle. Also, Solvent-based syntheses of MOFs [5 - 14] were carried out with the reaction of metal salts and each carboxylate ligand by mixing in the presence of solvents. The compounds were characterized by the comparison of melting point, elemental analysis, FT-IR spectroscopy and XRPD results with those of the free ligands and literature. The analytical and spectroscopic data of the compounds prepared via the two different methods gave the expected product.

The presence of coordinatively unsaturated metal centers in the synthesized MOFs provides an accessible way to selectively functionalize them through coordination bonds. In this work, thiol-functionalization of MOFs were described by choosing six well known MOFs in which three (3) are Zn-based while the other three (3) are Cu-based MOF, by a facile coordination based postsynthetic strategy. The obtained thiol-functionalized MOFs were characterized by powder X-ray diffraction, CHN and infrared spectroscopy. The analytical and spectroscopic data of the unmodified and modified compound were different.

A series of [Cu(Ina)$_2$] samples stoichiometrically decorated with thiol groups has been prepared through coordination bonding of coordinatively unsaturated metal centers with –SH group in thioglycolic acid. [Cu(Ina)$_2$].H$_2$O and [Cu(Ina)$_2$]-TH were investigated for the adsorptive removal of fluorescein from aqueous solution. The parameters that affect the dye sorption such as contact time, solution pH, initial fluorescein concentration and temperature, have been investigated and optimized conditions determined. Equilibrium isotherm studies were used to evaluate the maximum sorption capacity of MOFs and experimental results showed that the removal efficiency decreases in the order of [Cu(Ina)$_2$]-TH > [Cu(Ina)$_2$].H$_2$O both in adsorption rate and adsorption capacity. The Langmuir, Freundlich, Temkin and Dubinin Radushkevich models have been applied and the

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data correlate well with Dubinin Radushkevich model. The adsorption mechanism may be explained with a simple electrostatic interaction and π- π interaction. Finally, it can be suggested that modification of MOFs can be use to improve their adsorption capacity and rate, making them a better adsorbent to remove emerging dyes contaminants from waste water.

INTRODUCTION AND LITERATURE REVIEW

1.1 GENERAL INTRODUCTION

During the past century particularly around 1960, extensive work was done on crystalline extended structures (Porous materials) in which metal ions are joined by organic linkers containing Lewis base–binding atoms such as nitriles and bipyridines [1]. These were recognized as coordination polymers and were first reported by Tomic [2]. The metal ions which act as the center connector are usually chosen from Cu, Zn, Mn, and Co. The connectors-linkers building blocks form continuous porous network structures that can be classified by porous structure as dots (0 D cavity), channels (1D space), layers (2D space), and intersecting channels (3D space). Based on the porous structure, coordination polymer can be applied in separation, storage, and heterogeneous catalysis. However, a more general term Metal-Organic Frameworks was introduced, and has attracted great attention after the group of Yaghi O.M. published a simulation on MOF-5 structure in 1995 as shown in figure 1 [3].

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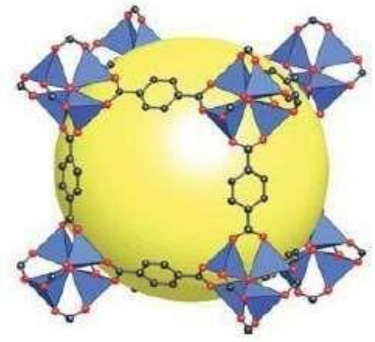

Figure 1: A typical structure of MOF

The superior characteristics and properties of porous MOF [6] when compared to traditional porous carbon materials and inorganic zeolites is the drive behind its rapid development in science world. These include the possibility to design the structures and sizes of their pore by carefully choosing metal ions and organic ligands because of the wide variety of coordination geometries offered by transition and lanthanide metal ions; and the varsity of structures and reactive functionalities that can be incorporated into organic linkers via organic synthesis [7]. Also, unlike zeolites, which form channels ranging from 3-12 Å in diameter, MOFs allow for much greater internal void space and larger channels (up to 20- 30Å) in which guests can resides.[8, 9]

1.2POROUS MATERIAL

Porous solids are group of materials that have pores or channels that run through their structures that are permeable to the diffusion of guest molecules such as air or water. Most porous solids have porosities from 0.2 to 0.95, defined by the fraction of void accessible to guests to the total volume occupied by the solid material itself [10]. Porous solids can be generally divided into two broad classes, amorphous (disordered) solids and ordered (crystalline) solids.

1.2 METAL ORGANIC FRAMEWORKS

Metal-Organic Frameworks are crystallinecompounds consisting of metalionsor clusterscoordinated to rigid organic moleculesto form one-, two-, or three-dimensional structures that can be porous[36]. Metal-Organic Frameworks (MOFs) are a class of hybrid materials which are constructed by metal nodes and organic linkers forming highly porous structures. The careful selection of MOF building blocks such that their properties are retained by the framework can yield unique materials with a host of physical and optical characteristics and applications. The nature of the linkers often leads to voids present in the structure; these are usually occupied by guest molecules, which interact with the framework and need to be removed or exchanged for the MOF to be activated.

One of the most important properties of MOFs is their high structure porosity exhibiting high pore volume (up to 90 % of the crystal volume) and high specific surface area (up to several 2 -1 [36-40] thousand m g). The wide-open MOF structures with well-defined pores with internal diameters of up to 48 Å provide extra-large free space for loading with guest molecules making MOFs promising host materials for applications in energy (H /CH gas) storage molecule adsorption and separation, nano particle in-pore assembly, catalysis. MOFs are also of great importance in their use as drug delivery agent due to their properties; exceptionally high surface area and large pore sizes.

1.5 MOFs STRUCTURE

A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are typically mono-, di-, tri-, or tetravalentligands.[53] The choice of metal and linker has significant effects on the structure and properties of the MOF, for example, the metal's coordinationpreference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which [54] orientation. As shown in Fig.2, the metal nodes (metal ions or metal-including clusters) serve as connecting points and the organic ligands serve as bridging molecules to coordinately connect metal nodes forming a three-dimensional framework.

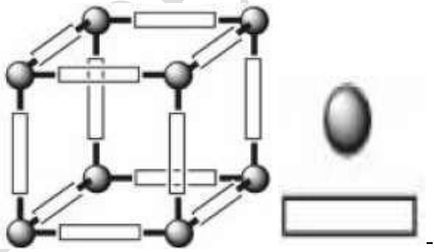

Fig 2 Connection of metal nodes and organic linkers leads to a three-dimensional frameworks.[54]

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Although varying valency of the transition metals may seem to expand the number of potential structures to be produced with diminishing ability to predict structural architecture, this problem can be solved by carefully changing reaction conditions to favour a particular coordination number and geometry.[53, 54]Recently the generation of frameworks with new and unusual network topologies has seen the emergence of lanthanides as metal centres. Lanthanide metal ions commonly have the oxidation state 3^+ and possess large ionic radii. Therefore binding is non-directional and electrostatic with steric factors often directing the coordination geometries of resulting frameworks.

1.10 CHARACTERIZATION OF MOFs

1.10.1 ELEMENTAL ANALYSIS

Elemental analysis is an experiment that determines the amount (typically a weight percent) of an element in a compound. Just as there are many different elements, there are many different experimental methods for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds). The elemental analysis of a compound enables one to determine the empirical formula of the compound. The empirical formula is the formula for a compound that contains the smallest set of integer ratios for the elements in the compound that gives the correct elemental composition by mass.

1.10.2 INFRARED SPECTROSCOPY

IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible Vibrational and rotational states. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.

1.10.3. ULTRAVIOLET-VISIBLE SPECTROSCOPY

Ultraviolet- visible spectroscopy is referred to as absorption spectroscopy or reflectance spectroscopy in the ultra violet visible region. UV- Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compound, and biological macromolecules. This spectrophotoscopic technique is commonly carried out in solutions however; solids and gases may also be studied.

1.10.4 NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance (NMR) is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms; in practical applications, the frequency is similar to VHF and UHF television broadcasts (60–1000 MHz). NMR allows the observation of specific quantum mechanicalmagnetic properties of the atomic nucleus. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through NMR spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

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1.10.5 X-RAY SINGLE CRYSTAL

X-ray diffraction (XRD) is a material characterization technique that can be useful for analyzing the lattice structure of a material. X-raycrystallographyis a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions. From the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

1.10.6 X- RAY POWDER DIFFRACTION

This is a scientific techniques using X-ray neutron or electron diffraction on powder or microcrystalline samples for structural characterization of materials. Many new materials can be accessed only via mechanochemical preparation procedures, in which suitable solid starting materials are subjected to mechanical grinding. In general, materials prepared by such processes are microcrystalline powders, and the product phase usually does not contain single crystals of suitable size and quality to allow structure determination by single-crystal X-ray diffraction. Instead, the most suitable strategy for determining the structural properties of new materials prepared in this way is to use powder X-ray diffraction [89]

1.11ADSORPTION APPLICATION OF MOFs

1.12 ADSORPTION

Adsorption is a process whereby a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural, biological, physical and chemical systems, and is widely used in industrial applications such as synthetic resins, activated charcoal, MOFs etc. Adsorption is a selective process which is affected by the molecular weight of adsorbate, and the porosity and the shape of the adsorbent. The polarity and electrostatic charge of the adsorbent- adsorbate also affect adsorption process. Adsorption is widely used as effective physical method of separation in order to eliminate or lower the concentration of wide range of dissolved pollutants (organics or inorganics) in the effluent [109]

1.2.1 TYPES OF ADSORPTION

(i) **Physisorption** is the adherence of adsorbate to the surface of an adsorbent through Van der Waals (weak intermolecular) interactions. It also known as physical adsorption which is responsible for non- ideal behavior of real gases, characterized by low temperature of the order of 5 – 10 kCal per mol of the gas, always under the critical temperature of the adsorbate.

(ii) **Chemisorption** which is an irreversible process. This is a highly selective process whereby a molecule adheres to a surface through the formation of a chemical bond. Many a time, chemisorptionsis accompanied by much higher heat changes from 10 kCal to 100 kCal per mole of the gas.

1.13.5 THIOGLYCOLLIC ACID

Thioglycolic acid (TGA), its IUPAC name is 2-sulfanylacetic Acid, is the organic compound $HSCH_2CO_2H$. TGA is often called mercaptoacetic acid (MAA). It contains both a thiol(mercaptan) and carboxylic acidfunctional groups. It is a colourless liquid with a strongly unpleasant odor. TGA is miscible with polar organic solvents like water.TGA, usually as its dianion, forms complexeswith metal ions. Such complexes have been used for the detection of iron,molybdenum,silver, and tin. TGA reacts with diethyl acetylmalonate to form acetylmercatoacetic acid and diethyl malonate, the reducing agent in conversion of Fe(III) to Fe(II).[123]

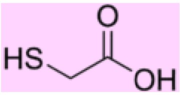

Figure 3: Structure of Thioglycolic Acid

1.14.1 FUNCTIONALIZATION OF MOF

The presence of coordinatively unsaturated metal centers in metal-organic frameworks (MOFs) provides an accessible way to selectively functionalize MOFs through coordination bonds. In this work, we describe thiol-functionalization of MOFs by choosing a well known MOFs. Precise chemical modifications can especially endow MOFs with specific functions and offer the possibility of designing a new generation of enhanced MOFs.[124]

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1.16 AIM AND OBJECTIVES

The primary aim of this research project is to functionalize metal-organic framework (MOFs) initially synthesized and also to apply both the functionalized and unfunctionalized MOFs for environmental remediation.

The objectives of this research work are to:

i. Use room temperature solvent based and mechanochemical solvent free synthetic methods to prepare some of the MOFs that had been synthesized previously by hydrothermal/solvothermal methods thereby allowing large scale production of MOFs in industries.

ii. To characrerize the synthesized MOFs using Melting point, Elemental Analysis, IR spectroscopy and XRPD.

iii. Use the functionalized and unfunctionalized MOFs for removal of dyes from aqueous solution.

1.17 JUSTIFICATION

A principal challenge of modern chemistry is to develop new energy, solvent and atom efficient approaches to chemical synthesis in order to aid the chemical industry in managing the global problem of pollution, growing energy demand and a shortage of raw materials.

Environmental problem associated with disposal of waste in most chemical reactions have led chemists to consider alternative environmental friendly preparative methods. For instance, one of the major targets of green chemistry is to limit the excessive use of solvents or even better to carry out the synthetic reactions in absence of solvents.

MOFs are a new class of crystalline materials which are currently of great interest for sorption, separation, drug delivery and catalysis. MOFs have been mainly synthesized at relatively high temperature by hydrothermal or solvothermal methods using conventional heating. However, these methods suffer from several drawbacks such as high temperature, long reaction times, excess organic solvents, lower product yields and harsh refluxing conditions. Solvothermal conditions are unsuitable for thermally- sensitive starting materials. Due to the aforementioned drawback of the solvothermal and hydrothermal syntheses, this research was focused on the use of room temperature solution based synthesis which does not require heat for the synthesis of MOFs.

2.4. THIOL-FUNCTIONALIZATION OF THE SYNTHESIZED MOFs

To prepare the thiol-functionalized MOFs samples, the method used by Ling-Guang *et al.*[124]was modified. The schematic illustration of the thiol-functionalization of MOFs is shown below

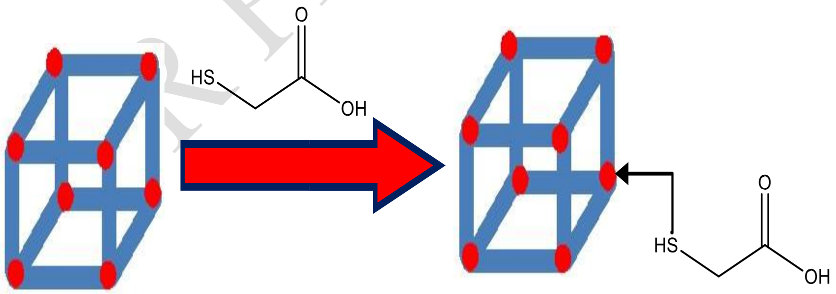

Fig. 4. Schematic illustration of the thiol-functionalization of MOFs through coordination bonding between one thiol group of Thiogluconic Acid and coordinatively unsaturated metal centers (UMCs) in MOFs.

2.4.1. THIOLATION OF [Cu(INA)$_2$]

[Cu(INA)$_2$] (0.620 g, 2 mmol) was dehydrated at 150 ◦C for 12 h and then suspended in 10 mL of anhydrous ethanol. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was refluxed magnetically for 12 h at 80 ^{o}C. Cream flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis. This was done in batches to produce the quantity needed for the removal of dyes.

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2.4.2. THIOLATION OF [Zn(INA)$_2$

[Zn(INA)$_2$] (0.619 g, 2 mmol) was dehydrated at 100 ◦C for 12 h and then suspended in 10 mL of anhydrous toluene. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was stirred magnetically for 12 h at 150 ^{o}C. Light yellow flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis.

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2.4.3. THIOLATION OF [Zn(fum)(H$_2$O)$_2$]

[Zn(fum)(H$_2$O)$_2$] (0.431 g, 2 mmol) was dehydrated at 150 ◦C for 12 h and then suspended in 10 mL of anhydrous toluene. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was refluxed magnetically for 12 h at 150 ^{o}C. Yellow flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis.

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2.4.4. THIOLATION OF [$Zn_2(fum)_2(bpy)$]

[$Zn_2(fum)_2(bpy)$] (1.030 g, 2 mmol) was dehydrated at 150 ◦C for 12 h and then suspended in 10 mL of anhydrous toluene. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was stirred magnetically for 12 h at 150 °C. Yellow flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis.

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2.4.5. THIOLATION OF [$Zn_4O(bdc)_3$]

[$Zn_4O(bdc)_3$] (2.932 g, 2 mmol) was dehydrated at 150 ◦C for 12 h and then suspended in 10 mL of anhydrous toluene. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was refluxed magnetically for 12 h at 150 °C. Yellow flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis.

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2.4.6. THIOLATION OF [$Cu_3(BTC)_2$]

[$Cu_3(BTC)_2$] (2.932 g, 2 mmol) was dehydrated at 150 ◦C for 12 h and then suspended in 10 mL of anhydrous toluene. Thiogluconic (0.091 ml, 1 mmol) was added to the suspension and the mixture solution was stirred magnetically for 12 h at 150 °C. Black flake crystal was obtained which was recovered by filtration, washed with ethanol (15 mL × 5) and then dried overnight at room temperature in vacuum. The relative content of S in the functionalized sample was determined by elemental analysis.

Comment [i13]: Correct the spelling

2.5. PHYSICAL AND INSTRUMENTAL CHARACTERIZATION METHODS

2.5.1 Melting Point – The melting point of the synthesized metal-organic frameworks were determined using a Gallen-Kamp melting point apparatus at the department of Chemistry, University of Ilorin.

2.5.2 Element Analysis – The elemental analyses were performed on a Perkin-Elmer CHN Analyzer 2400 series II at Medac Ltd, Brunnel Science Centre, Egham, United Kingdom.

2.5.3 Infrared Spectra – The infrared analyses were done using the SHIMADZU scientific model FTIR 8400s Spectrophometer at Redeemer‘s University, Ogun State. IR spectra on the range of 4,000-400 cm^{1}were obtained from samples in the form of KBr pellets.

2.5.4 X-ray Powder Diffraction Analysis –XRPD analyses were carried out at the Chemistry Department, University of Cape town, South Africa. Powder XRD analysis were measured on a Bruker D8 Advance X-ray diffractometer operating in a Da Vinci geometry equipped with Lynxeye detector using a CuKα-radiation(λ= 1.5406 Å).X-rays were generated by an accelerating voltage of 30kV and a current flow of 40mA. A receiving slit of 0.6mm and a primary secondary slits of 2.5mm were used. Samples were placed on a zero background sample holder and scanned over a range of 4^o to 40^{o}with a step size of 0.01^{o}s^{-1}.

2.6. DYES ADSORPTION PROCEDURE.

Comment [i14]: Include the result and graph of dye removal studies like effect of contact time, pH, dye concentration and temperature. In the abstract it is mention that the Langmuir, Freundlich, Temkin and Dubinin Radushkevich were applied include the graph of this isotherm and mention the parameters of each in tabular format. Justify the application of Dubinin Radushkevich model for the present study
Also mention the optimum pH for the removal and the adsorption capacity of the adsorbent.

Batch equilibrium technique was used to study adsorption of fluorescein on [Cu(Ina)$_2$].H_2O and [Cu(Ina)$_2$]-TH. An aqueous stock solution of fluorescein (100 ppm) was prepared by dissolving 100mg of fluorescein in 1L of deionized water. Aqueous dye solutions with different concentrations of the fluorescein (3 - 21 ppm) were prepared by successive dilution of the stock solution with deionized water. The concentration of fluorescein was determined using the absorbance (at λ_{MAX} = 490nm) of the solutions after getting the UV spectra of the solution with a spectrophotometer (SHIMADZU UV-1650pc UV-VIS spectrophotometer). The calibration curve was obtained from the spectra of the standard solutions (3 - 21 ppm) at a pH of 7.8.

Before adsorption, the Adsorbents ([Cu(Ina)$_2$].H_2O and [Cu(Ina)$_2$]-TH) were activated by drying overnight under vacuum at 150^{O}C and kept in a desiccator. An exact amount of the adsorbents (2mg) were put into the aqueous solutions (50mL) with the fixed dye concentration from 3 ppm to 21 ppm. The aqueous fluorescein solutions containing adsorbents (MOFs) were mixed well with an incubator shaker at 165 rpm and were maintained for a fixed time (10 min to 6 h) at 32 ± 2 ^{O}C. After adsorption for a pre-determined time, the solutions were separated from adsorbent (MOFs) using syringe filter, and the dyes concentration was calculated with the absorbance that would be obtained from the UV spectrophotometer.

3.0 RESULTS AND DISCUSSION

3.7. METAL ORGANIC FRAMEWORKS OF THIOGLYCOLIC ACID

Compound were synthesized by the modification of the solvent based method described by Debajyoti*et al*[125]. The solvent-based synthesis of its Compound was carried out in basically ethanol and methanol and all the MOFs show similar coordination point except some in which water coordinate with the metal. During the room temperature synthesis, the starting materials were dissolved in ethanol and methanol and stirred for about two hours at room temperature. Clear solutions of different colours were gotten depending on the metal present and left standing to evaporate slowly. The melting points of the MOFs were different from those of the ligands. Analysis of FTIR and CHN analysis clearly show the formation of the compounds**.** The compounds were insoluble in water and methanol but soluble in solvents having pronounced donor properties e.g. DMSO, DMF and DMA.

All the MOFs were characterized and different results were obtained for the melting point test, IR and elemental analysis. The synthesized compounds have colours which are different from those of the ligands and the melting points of the MOFs are in the range of 100 ^{O}C -250^{O}C which is different from those of the parent ligands.

The physical and analytical data of the MOFs are given in Table 1 below:

Table 1: Physical and Analytical Data of Thioglycolic acid, Some dicarboxylic acid, Nicotinamide and their Cu(II) and Cd(II) MOFs.

Ligand/MOFs	Appearance	Yield (%)	Molecular weight (g/mol)	Melting point (^{o}C)	Elemental analysis % found (% calculated)		
					C	H	N
Thioglycolic acid	Light yellow liquid	-	92	96	- (26.09)	- (4.35)	- (0.00)
Isonicotinic acid	White powder	-	123	300	- (78.08)	- (4.06)	- (11.38)
Nicotinamide	White powder	-	122	130	- (59.02)	- (4.92)	- (22.95)
[Cu(Thg)(Nic)] (9)	Pale yellow powder	55	275.5	123	39.50 (38.35)	2.20 (2.18)	4.99 (5.08)
[Cu(Ita)(Thg)(H_2O)$_2$] (10)	Brown powder	32	317.5	146	26.42 (26.46)	3.21 (3.15)	<0.10 (0.00)
[Cu(Fum)(Thg)] (11)	Brown powder	69	267.5	205	26.50 (26.92)	1.37 (1.50)	<0.10 (0.00)
[Cu(mal)(Thg)] (12)	Pale yellow powder	54	255.5	112	23.42 (23.48)	1.64 (1.57)	<0.10 (0.00)
[Cd(Oxa)(Thg)(H_2O)$_2$] (13)	Cream powder	58	326.4	153	14.72 (14.71)	1.84 (1.84)	<0.10 (0.00)
[Cd(Ina)(Thg)(H_2O)$_2$] (14)	Cream powder	61	361.4	223	26.54) (26.56)	1.84 (1.66)	4.00 (3.87)

3.7.1 FT-IR Spectroscopy Result of Thioglycolic acid, dicarboxylic acid, Nicotinamide and their MOFs with Cu(II) and Cd(II)

It can be seen from Table 2 and Appendix 1 that FT-IR spectra of the MOFs synthesized are different from those of the ligands. The relevant IR and frequencies of the ligands and the MOFs are presented in Table 2below:

Table 2 : Selected FT-IR absorption band for Thioglycolic acid, Some dicarboxylic acid, Nicotinamide and their Cu(II) and Cd(II) MOFs.

Ligand/MOFs	ν(O-H) (cm^{-1})	ν(N-H) (cm^{-1})	ν(S-H) (cm^{-1})	ν(C=O) (cm^{-1})	ν(C=N) (cm^{-1})	ν(C=C) (cm^{-1})	ν(C-O) (cm^{-1})	ν(C-S) (cm^{-1})	ν(M-O) (cm^{-1})
Thioglycolic acid	3200br	-	2569w	1716s	-	-	1298s	671w	-
Fumaric acid	3417br	-	-	1674s	-	1427m	1274s	-	-
Isonicotinic acid	3437br	-	-	1716s	1616m	1564m	1028s	-	-
Nicotinamide	-	3367m 3163m	-	1710m	1681m	1620m 1595m	-	-	-
[Cu(Thg)(Nic)] (9)	-	3404m 3184m	2397w	1708m	1678m	1602m	1201s	688w	443w
[Cu(Ita)(Thg)(H_2O)$_2$] (10)	-	-	2364w	-	-	1645m	1141s	707w	426w
[Cu(Fum)(Thg)] (11)	-	-	2364w	1734m	-	1616m	1197s	682w	486w
[Cu(mal)(Thg)] (12)	-	-	2372w	1627m	-	-	1118s	696w	399w
[Cd(Oxa)(Thg)(H_2O)$_2$] (13)	-	-	2364w	1614m	-	1456m 1440m	1224s	715w	501w
[Cd(Ina)(Thg)(H_2O)$_2$] (14)	-	-	2364w	-	1116m	1552m	1226s	707w	453w

br= broad, m= medium, s= strong, sh= sharp, w= weak

The infrared spectra of the MOFs in the far IR region 4,000 – 400 cm^{-1} were compared with those of the ligands as shown in Table 3. The infra-red spectra of the MOFs were found to be different from those of the ligand and showed either a shift or disappearance of some characteristic frequencies and appearance of some new frequencies. The carboxylate protons were all deprotonated in all the carboxylate acids present. Carboxylic acid always have coordination sites at only the carboxylic acid functional groups, Nicotinamide is an amide having coordination sites at different functional groups (C=N and C=O) while Thioglycolic acid is a thiol having coordination site at different functional groups (H-S, O-H and C=O). From table 3above, peaks characteristics of various ligands are obtained in the spectra of the MOFs, an indication that the ligands are coordinated to the metal ion. The broad band at 3068 cm^{-1}(due to the O-H) present in thioglycolic and dicarboxylic acid disappeared in MOFs all the MOFs, this is an indicative of the deprotonation and coordination through the O-H group.[145] These NH bands in the MOFs are split and appear in the 3450–3150 cm^{-1} region at higher wave number than comparable bands in free nicotinamide because of hydrogen bonding. The absorption bands of the ν(C-O) shifted from their initial bands for all the MOFs. This clearly indicates a bidentate mode of O$^-$ in this MOF indicating that the bicarboxtlate ions function as bridging moieties. [152]

3.7.2 Proposed Structures of the MOFs of Thioglycolic Acid

From the analytical data and the spectroscopic studies, it was found that the Copper ion coordinates via the nitrogens of the amide & pyridine ring in the Nicotinamide, oxygen of the hydroxyl group & sulphur on the thiol group in thioglycolic acid and oxygen of the hydroxyl group in dicarboxylic acid to form a tetrahedral compound mainly while some have two molecule of water inside the coordination sphere to make them octehedral. **Fig 5: Proposed structure of synthesized MOFs obtained through room temperature solvent-based syntheses.**

Comment [i15]: Include fig 5

3.8. THIOL-FUNCTIONALIZATION OF THE SYNTHESIZED MOFS

Thiol-functionalizations of the MOFs were carried out as described in the experimental section. Each of the MOFs was modified chemically by Thiolation as previously described by Ling-Guang *et al.*[124] After modification with acidic functional group all the MOFs undergo significant change both physical and chemical. The colour, texture and melting point of the modified MOFs were totally different from those as-synthesized. The change in the chemical composition of the MOFs as thiolation was confirmed by CHN, FT-IR and XRPD.

3.8.1 *THIOLATION of [Cu(INA)$_2$]*

The thiolation of ***[Cu(INA)$_2$]*** was carried out by refluxing ***[Cu(INA)$_2$]*** with thioglycolic acid at 80 ^{o}C. Analysis of XRPD, FTIR and CHN analysis clearly shows the thiolation of ***[Cu(INA)$_2$].*** The elemental analysis (CHN), XRPD and FT-IR spectra data obtained for the functionalized

[Cu(INA)$_2$] was compared with that of the unfunctionalized and it can be inferred from the results that the functionalization was successful.

Table 3.: FT-IR band frequencies of *[Cu(INA)$_2$]* and thiol-modified *[Cu(INA)$_2$]* MOFs

MOFs	**ν(O-H) (cm^{-1})**	**ν(S-H) (cm^{-1})**	**ν(C=O) (cm^{-1})**	**ν(C=N) (cm^{-1})**	**ν(C=C) (cm^{-1})**	**ν(C-O) (cm^{-1})**	**ν(C-S) (cm^{-1})**	**ν(M-N) (cm^{-1})**	**ν(M-O) (cm^{-1})**
[Cu(INA)$_2$]	3460br	-	1722m	1550m	1419m	1232s	-	578w	457w
[Cu(INA)$_2$]-TH	-	2366	1734m	1612m	1436m	1290s	821w	617w	505w

The above shows FT-IR data of the thiol-functionalized samples, as well as the unfunctionalized [Cu(INA)$_2$] powered. The functionalized [Cu(INA)$_2$] shows most of the bands on the unfunctionalized [Cu(INA)$_2$] have shifted to higher wave number. The bands around 2366 and 821 cm^{-1} observed in thiol functionalized samples can be attributed to the presence of ν (S– H) and ν (C–S) vibrations respectively indicating the presence of thioglycolic acid. Although the peak at 2366 cm^{-1} corresponding to ν(S–H) is not very strong, obvious shift of the aliphatic ν(C–H) stretching vibrations at 2800–3000 cm^{-1} to larger values was found, as observed when the molecule is coordinated to a Lewis acid center[153, 154]. The result clearly reveals that thioglycolic acid molecule(s) were successfully grated onto the UMCs in channels created in the framework, rather than adsorbed on external surface of [Cu(INA)$_2$].

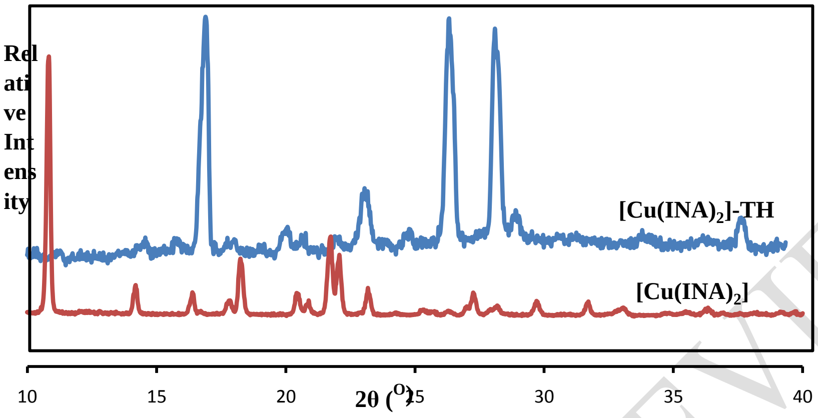

Fig. 6: XRPD pattern of *[Cu(INA)$_2$]* and thiol-modified *[Cu(INA)$_2$]*

It can be observed in Figure 6that the XRPD of the as-synthesized [Cu(INA)$_2$] differ from that of the thiol-functionalized [Cu(INA)$_2$], this is an evidence of modification of product. High intensity Bragg diffraction peaks are observed at 10.22^{O}, 20.84^{O} and 21.92^{O}with low intensity peaks at 13.66^{O} 15.98^{O}, 17.78^{O}, 18.26^{O}, 20.14^{O} and 26.84^{O} for as-synthesized [Cu(INA)$_2$] while High intensity Bragg diffraction peaks are observed at 16.92^{O}, 26.33^{O} and 28.09^{O}with low intensity peaks at 13.66^{O}, 14.59^{O}, 15.90^{O}, 20.17^{O}, 21.76^{O}, 23.05^{O}, 24.82^{O} and 28.91^{O} for thiol-functionalized [Cu(INA)$_2$]. The observed XRPD pattern of the functionalized *[Cu(INA)$_2$* obtained in the solvent based reaction was totally different form that of the unfunctionalized [Cu(INA)$_2$] which confirmed the successful functionalization of [Cu(INA)$_2$].

3.8.6. *THIOLATION of* [Cu$_3$(BTC)$_2$]

The thiolation of **[Cu$_3$(BTC)$_2$]**was carried out by refluxing **[Cu$_3$(BTC)$_2$]**with thioglycolic acid at 150 ^{o}C. Analysis of FTIR and CHN analysis doesn‘t shows the thiolation of **[Cu$_3$(BTC)$_2$].**The elemental analysis (CHN) and FT-IR spectra data obtained for the functionalized **[Cu$_3$(BTC)$_2$]** was compared with that of the unfunctionalized **[Cu$_3$(BTC)$_2$]** and it can be inferred from the results that the functionalization was unsuccessful.

3.9 ADSORPTION OF FLORESCEIN DYES ON THE AS-SYNTHESIZED AND THIOL FUNCTIONALIZED $[Cu(Ina)_2].H_2O$

Dye products correspond to a number of chemical compositions/constituents, which are widely used in our everyday life. Several research works have demonstrated the presence of dye in the effluent of wastewater treatment plants, rivers, lakes and occasionally, ground water. In the previous sections, the effect of the discharge of effluents from textile, paper, printing and dyestuff industries have been discussed. Also, various means of environmental remediation and the drawbacks of each of these techniques were given, thus the need for adsorptive techniques for the removal of these effluents. MOFs have been proven to be effective adsorptive materials due to the properties they possess i.e. large pores and surface area which make them better off than the existing adsorbents. Out of the synthesized MOFs reported,$[Cu(Ina)_2].H_2O$is a known MOFs and was functionalized used as an adsorbent for the adsorption of fluorescein dye.

Here, the adsorption of fluorescein dye onto as-synthesized and thiol functionalized $[Cu(Ina)_2].H_2O$ was carried out and reported. The objective of this section was to investigate the possible use of the synthesized MOFs as an alternative adsorbent material for the removal of fluorescein dyes from aqueous solution and to see if thiol functionalized $[Cu(Ina)_2].H_2O$ with adsorb better that the unfunctionalized $[Cu(Ina)_2].H_2O$.

3.11 CONCLUSION

Metal Organic frameworks and metal complexes constructed from Zn(II), Cu(II) and Ni(II); and carboxylic acids (Fumaric acid, Glutaric acid, Isonicotinic acid, Terephtalic acid, Thioglycolic acid and Trimesic acid) have been synthesized using mechanochemical and room temperature solvent- based methods. The compounds obtained from both methods were characterized using elemental analysis, FT-IR spectroscopy and XRPD. The results showed that the good products were obtained. It was discovered that most these carboxylate ligands coordinated to the metals in a bidentate fashion thereby exhibiting tetrahedral geometry for MOFs.

Six of the synthesized MOFs were functionalized (with thioglycolic acid) using Solvent- based methods, but just five of the functionalization was successful. The compounds obtained from the thiolation were characterized using elemental analysis, FT-IR spectroscopy and XRPD. The results showed that the products form were totally different from that of the as-synthesized -MOFs. ($[Cu(Ina)_2].H_2O$ and $[Cu(Ina)_2]$-TH).

. This research on metal-organic frameworks (MOFs) for dye removal from water is a vital advancement in environmental remediation. It aligns with themes of predictive analysis in resource management (11), highlighting the importance of comprehensive strategies in complex challenges (12). The principles of data-driven decision-making (13) and the significance of organizational culture in fostering innovation (14) are also applicable in the development and implementation of MOFs. Additionally, the need for foundational groundwork in technology development (15) parallels the research efforts required for effective MOF applications in environmental solutions.

3.12 RECOMMENDATION

It is recommended that further analytical methods such as BET analysis to determine the pore sizes of the adsorbents, thermogravimetris analysis, NMR and mass spectroscopies should be done to further elucidate the morphologies and porosity of the thio-functionalized MOFs. More researches should be done on the functionalization of MOFs using other functionalizing agent most especially Copper trimasate which has show a negative result with thiolation. Also, more researches should be done on other applications of MOFs, most especially in military and security sector on how it can be used for loading and detecting of explosive.

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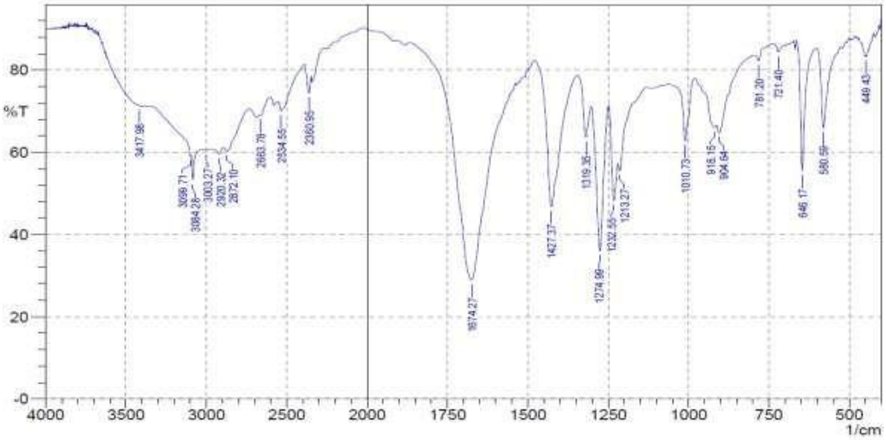
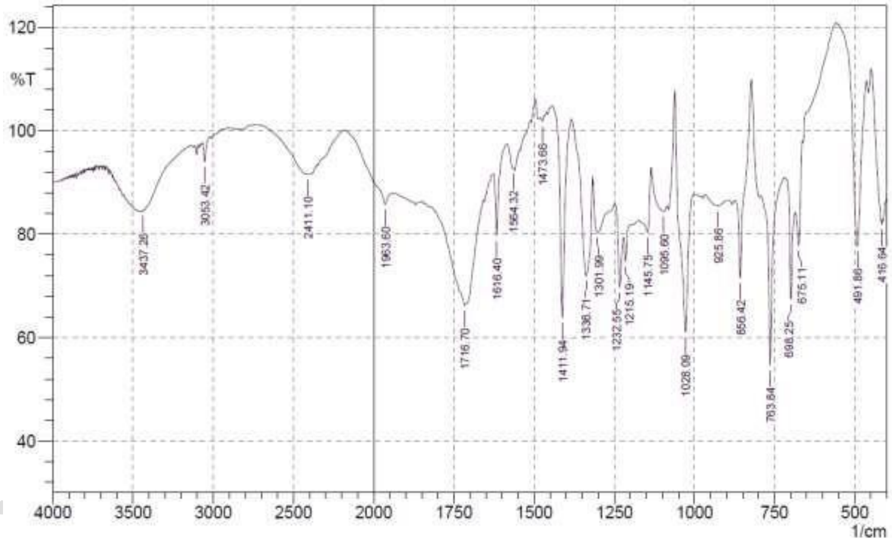
APPENDIX ONE

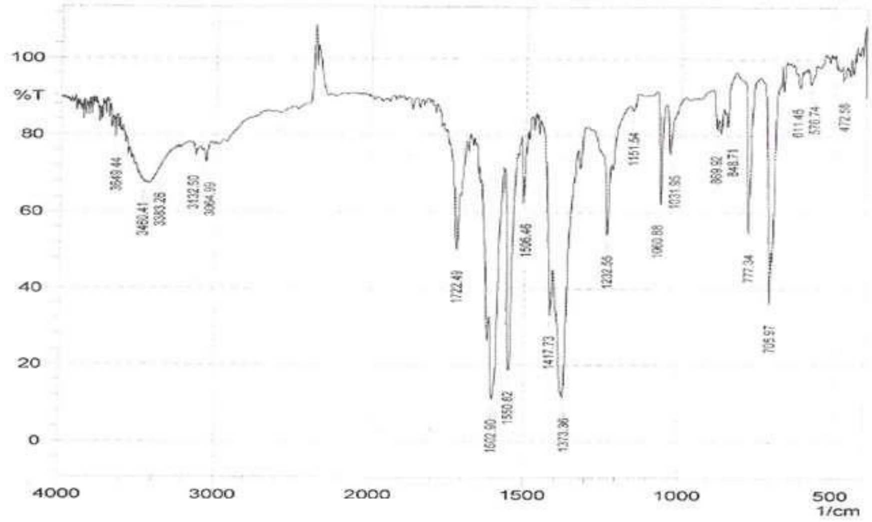
1. FT-IR SPECTRA OF MECHANOCHEMICALLY SYNTHESIZED MOFs.



FT-IR spectrum of Fumaric acid

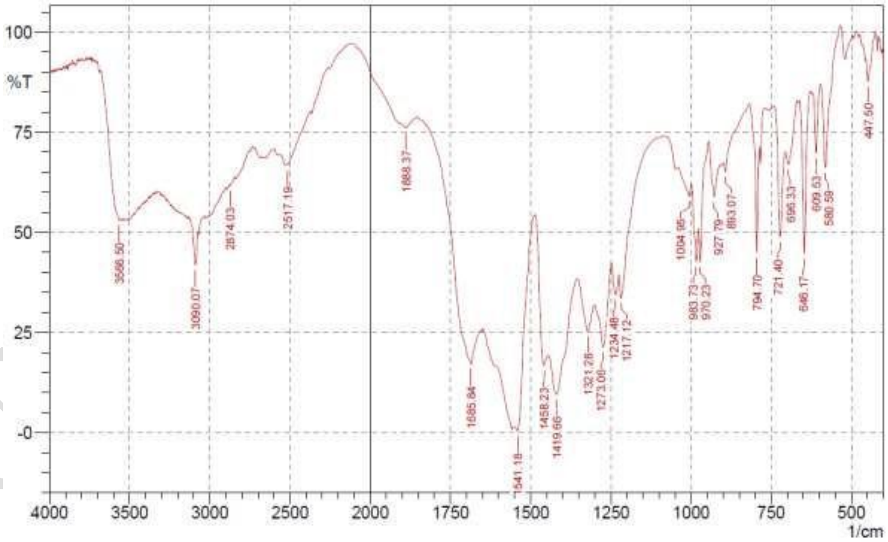


FT-IR spectrum of isonicotinic acid

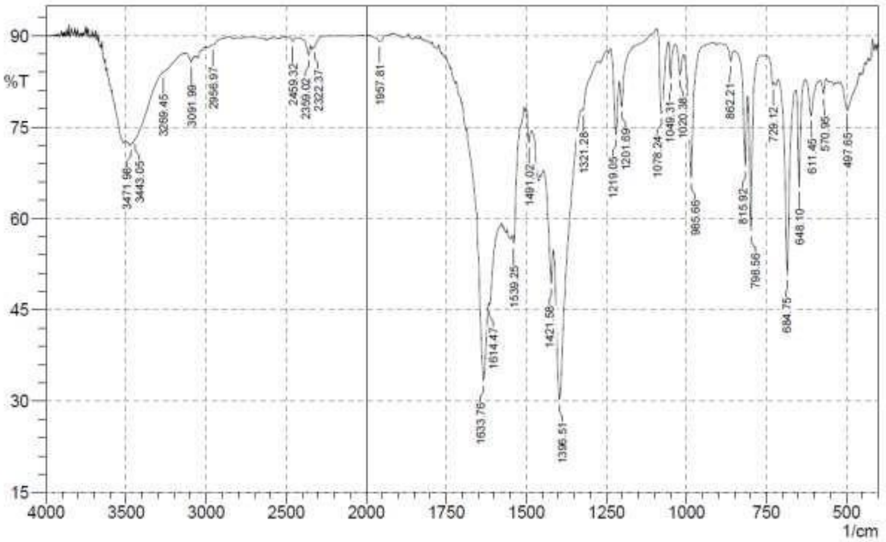


FT-IR spectrum of $[Cu(Ina)_2].H_2O$

6. FT-IR SPECTRA OF ZINC FUMARATE AND ITS DERIVATIVE..

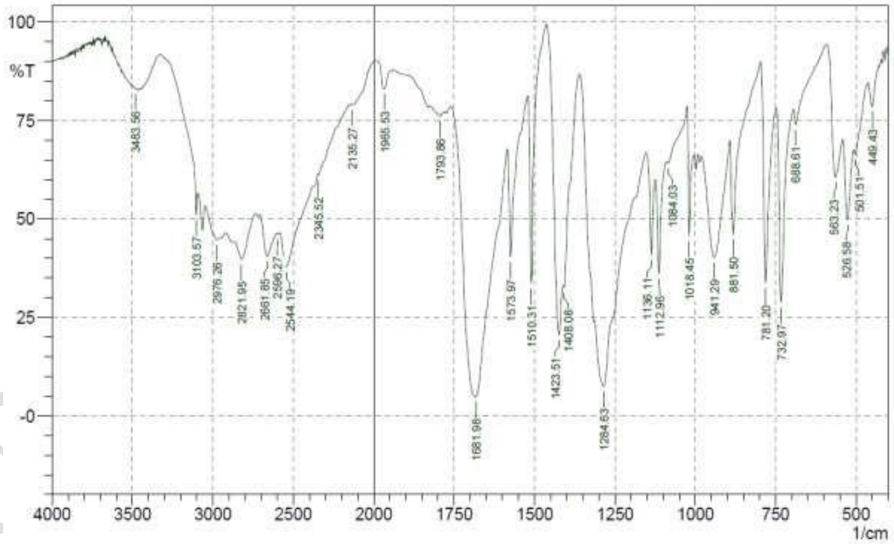


FT-IR spectrum of $[Zn(Fum)(H_2O)_2]$

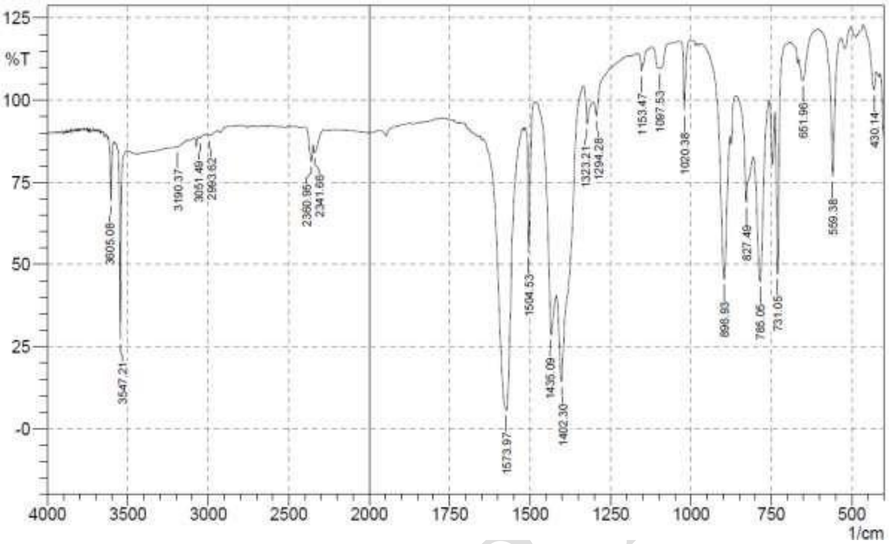


FT-IR spectrum of $[Zn_2(Fum)_2(bpy)]$

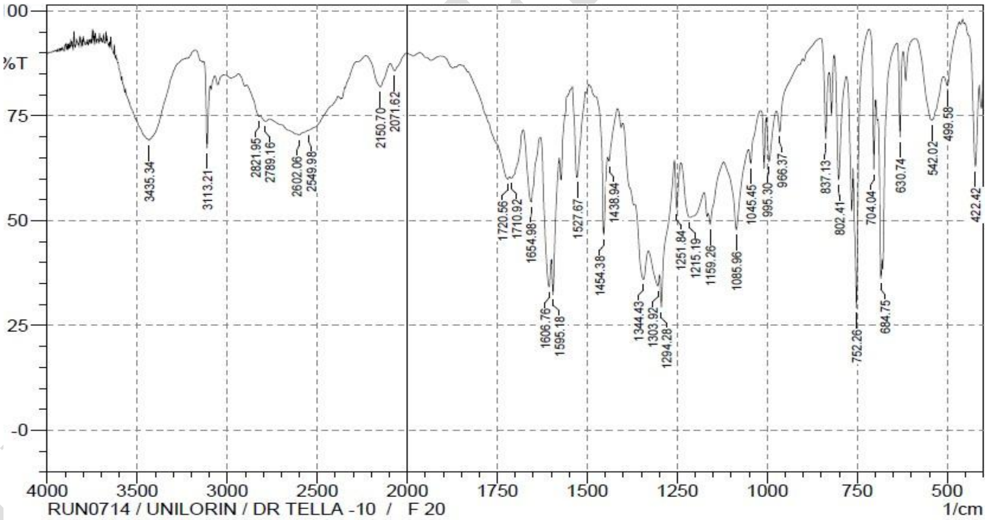
2. FT-IR SPECTRA OF SOLVENT-BASED SYNTHESIZED MOFs.



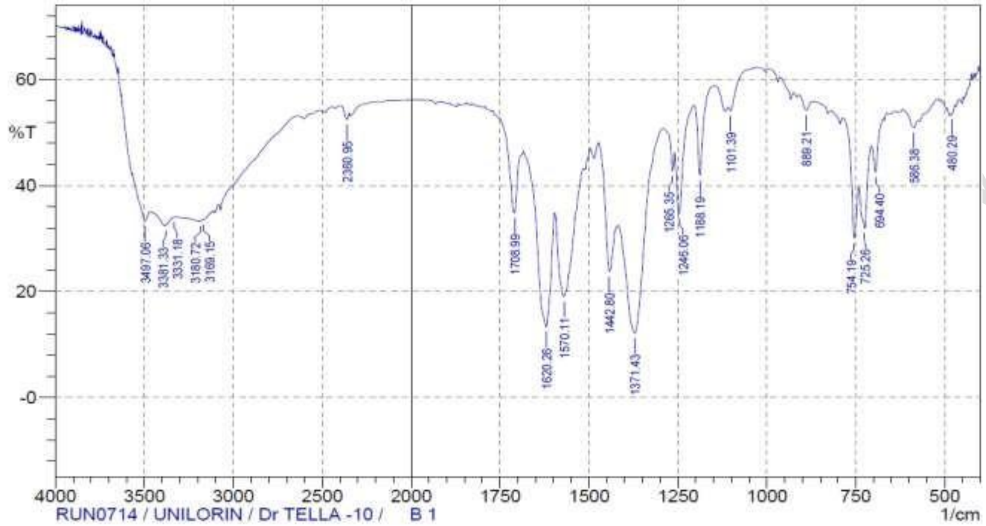
FT-IR Spectrum of Terephthalic acid.



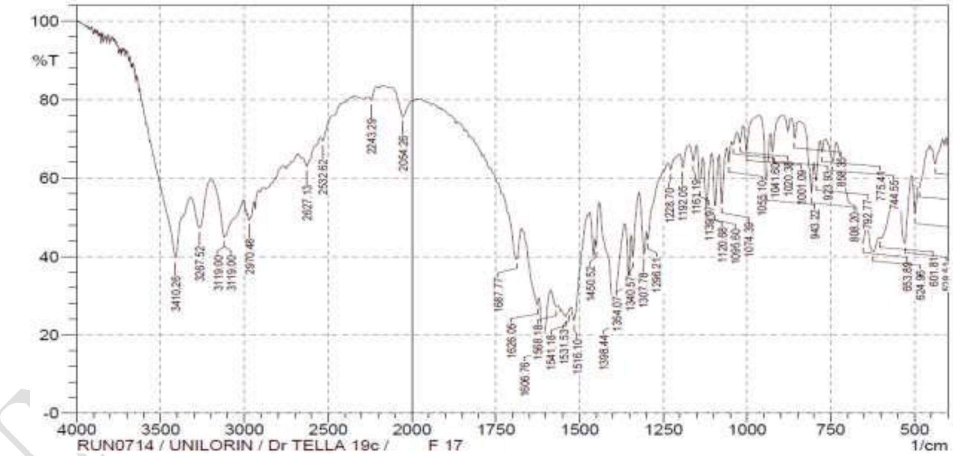
FT-IR spectrum of [$ZnO_4(BDC)_3$]



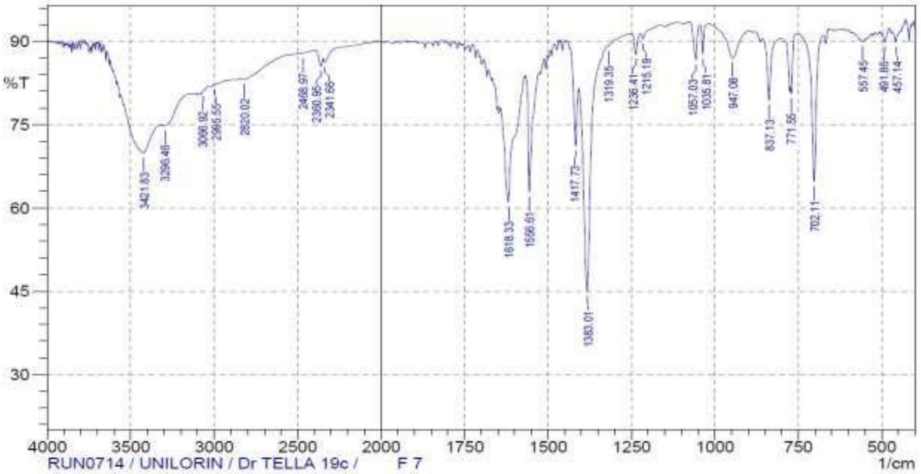
FT-IR spectrum of trimesic acid



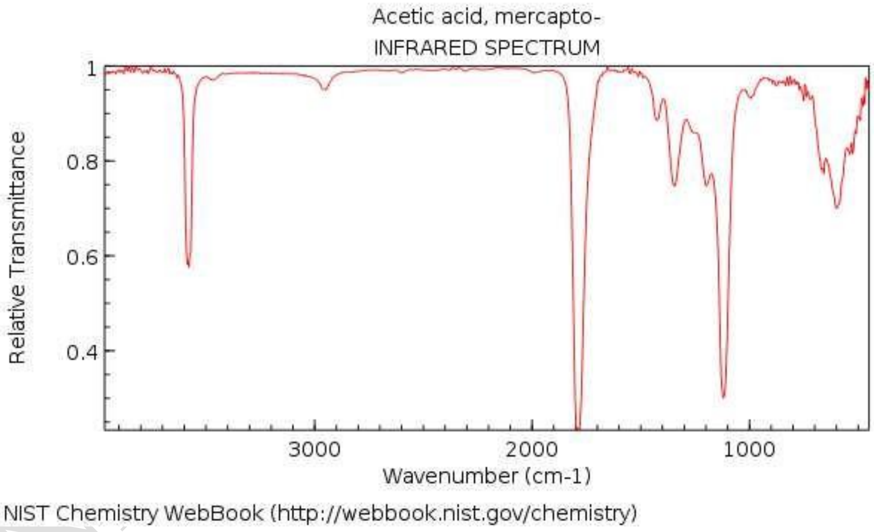
FT-IR spectrum of $[Cu_3 (BTC)_2]$



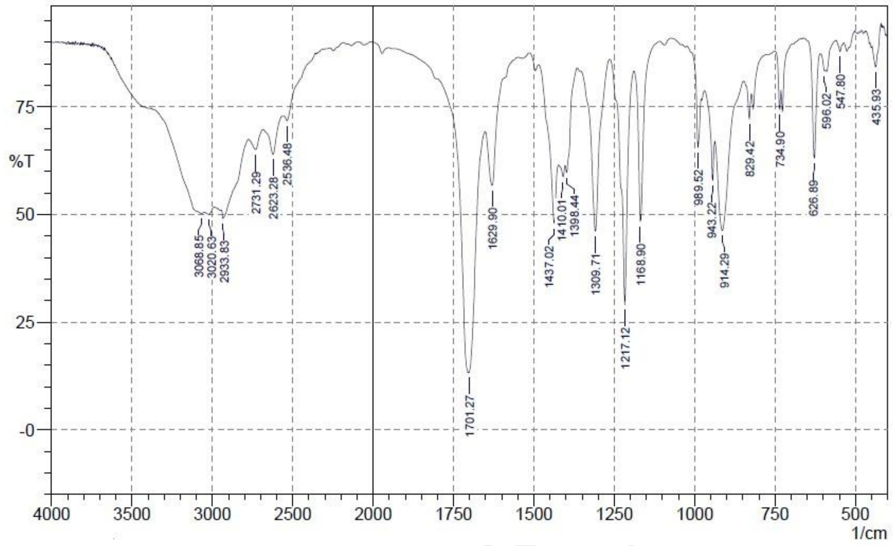
FT-IR of Glutaric acid



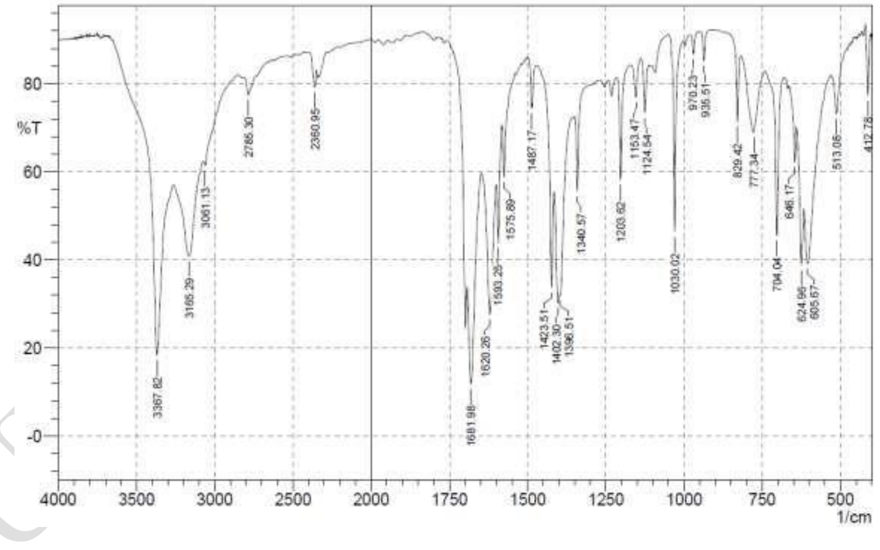
FT-IR of [(Cu(Ina)(Glut)(H_2O)$_2$]



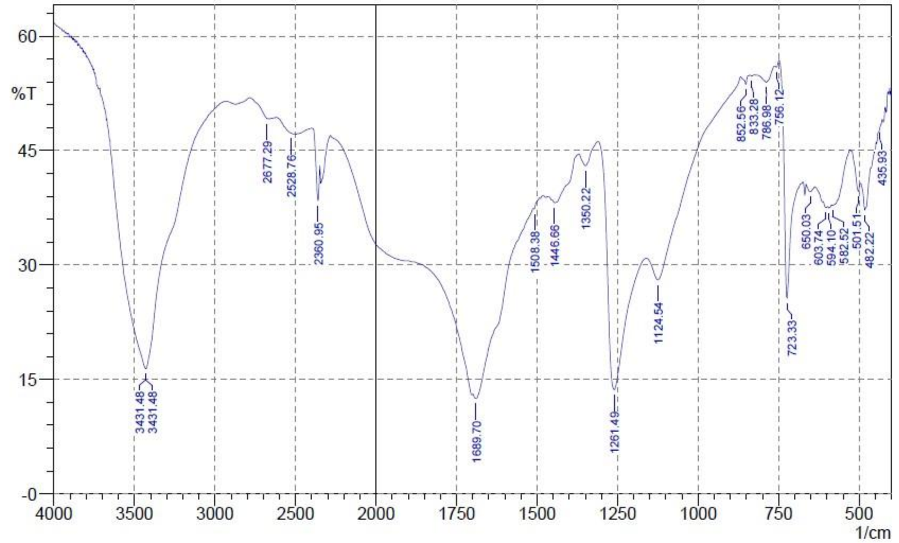
FT-IR of Thioglycolic acid



FT-IR spectrum of Itaconic acid



FT-IR spectrum of Nicotinamide



FT-IR spectrum of Oxalic acid

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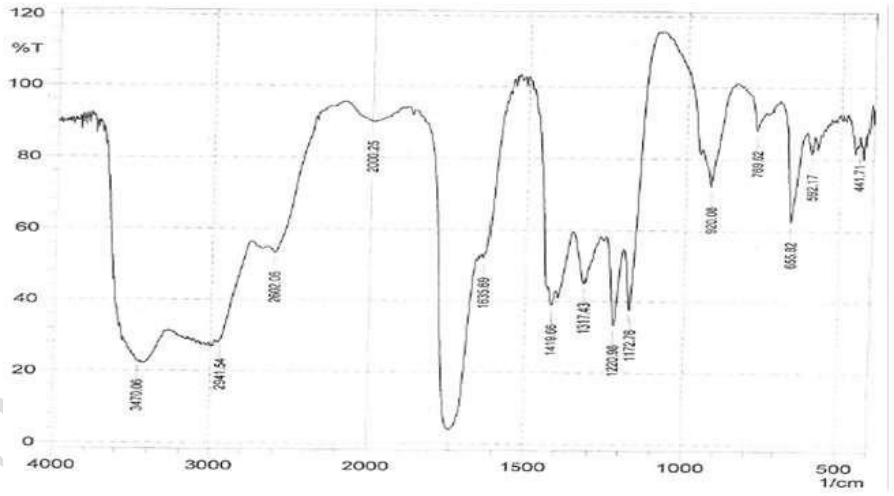
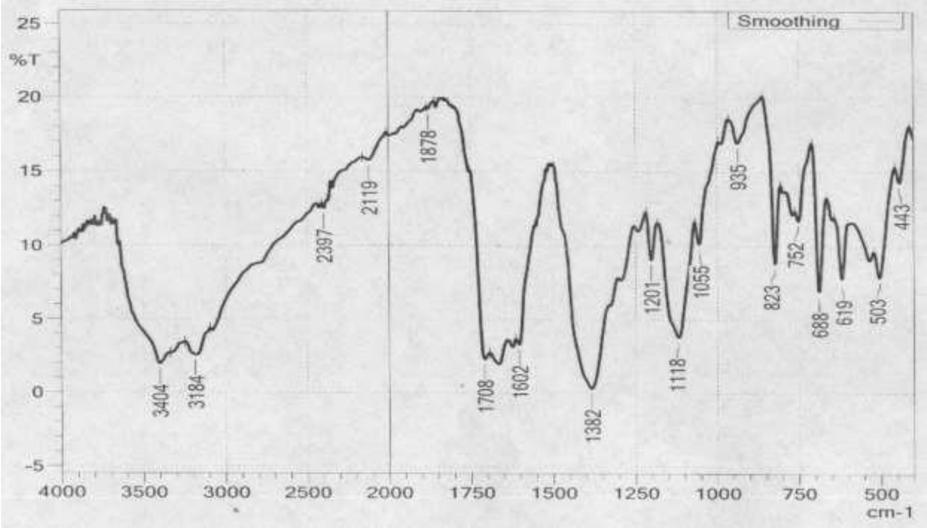
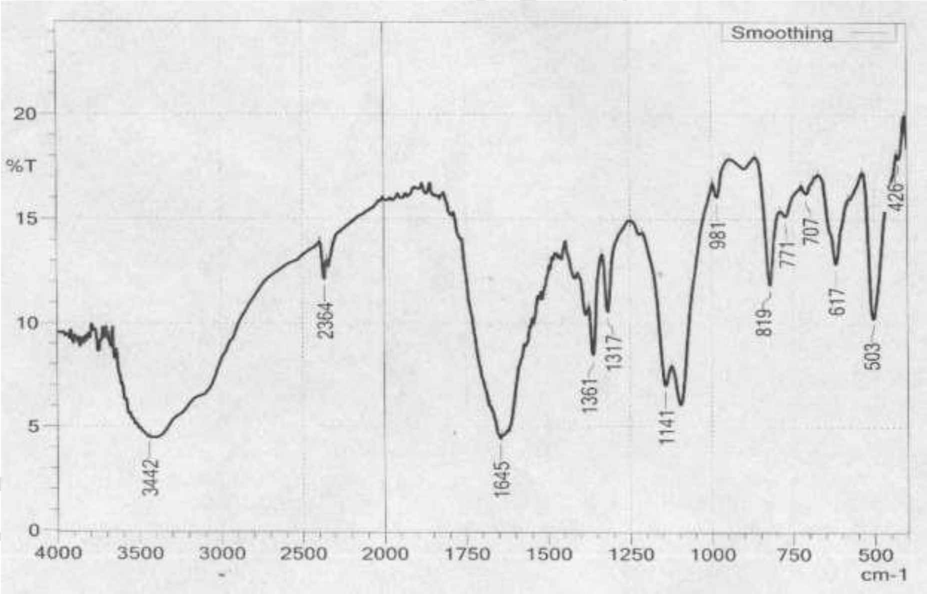


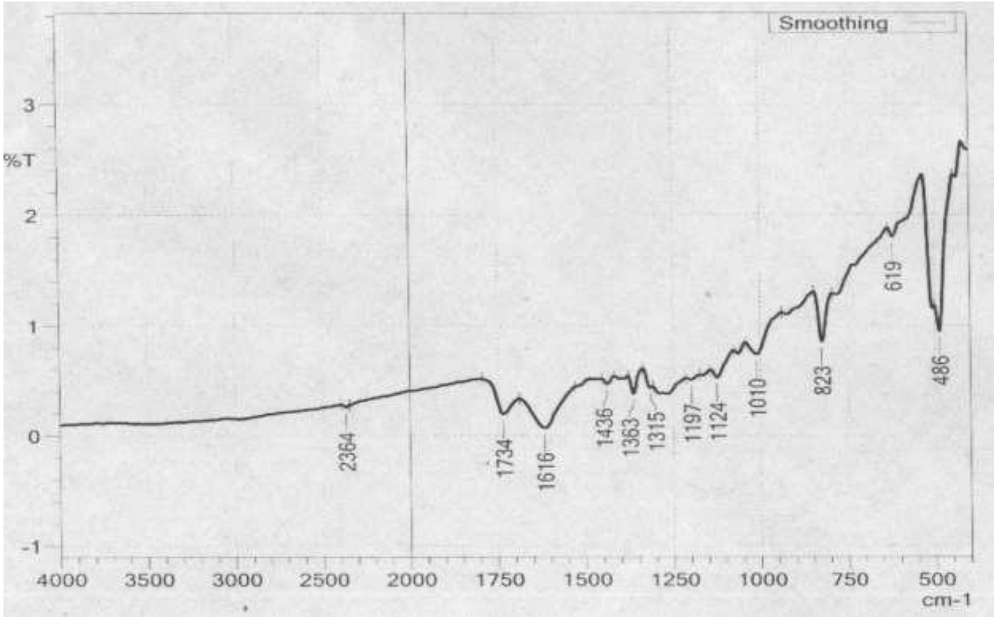
FT-IR spectrum of Malonic acid



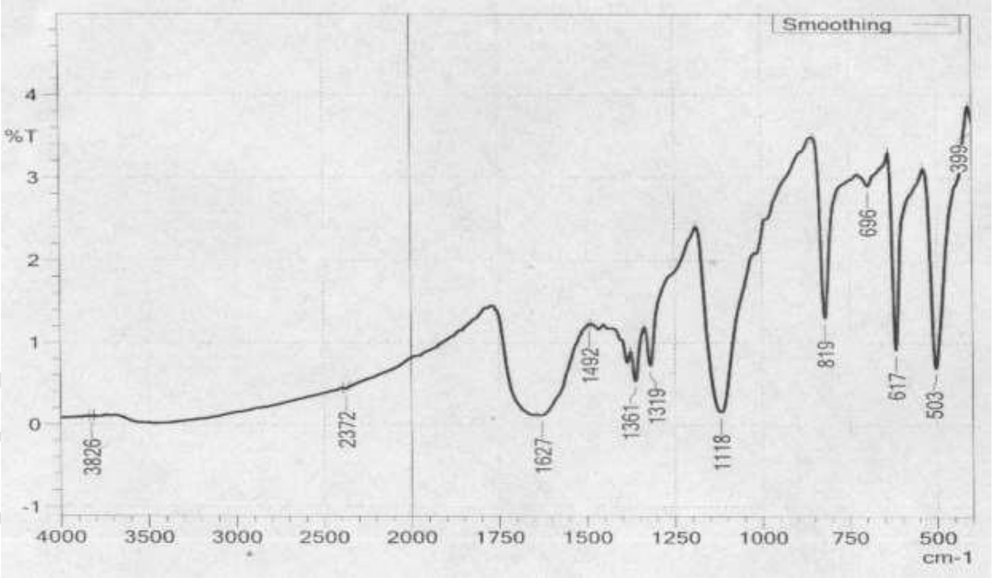
FT-IR spectrum of [Cu(Thg)(Nic)]



FT-IR spectrum of [Cu(Ita)(Thg)$(H_2O)_2$]

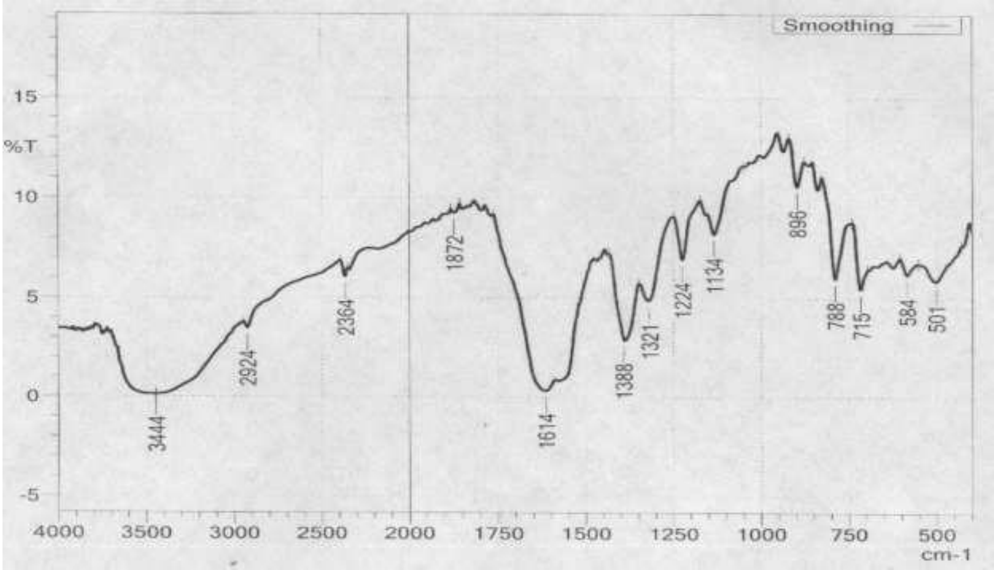


FT-IR spectrum of [Cu(Fum)(Thg)]

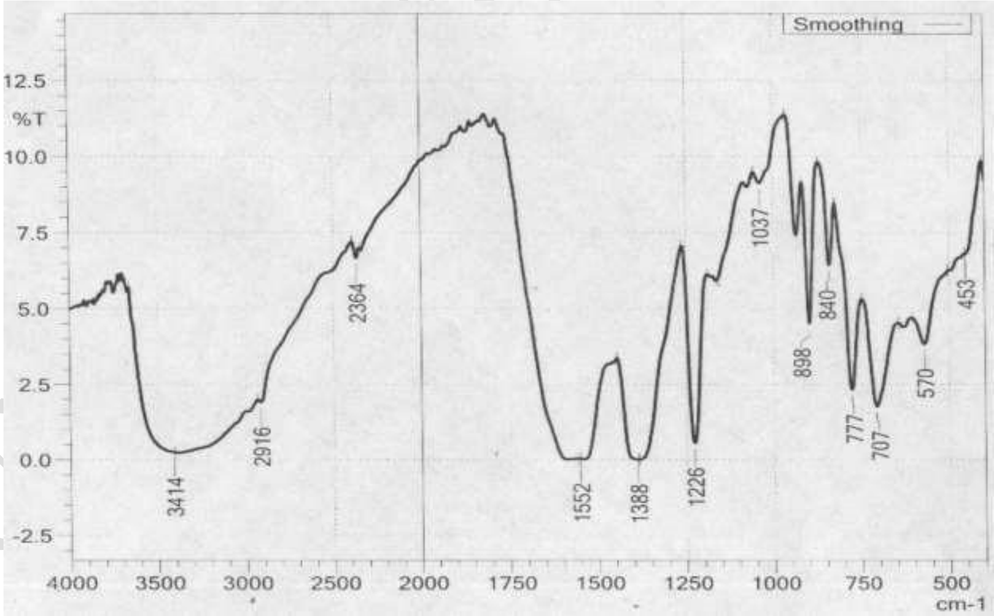


FT-

IR spectrum of [Cu(mal)(Thg)]



FT-IR spectrum of [Cd(Oxa)(Thg)$(H_2O)_2$]



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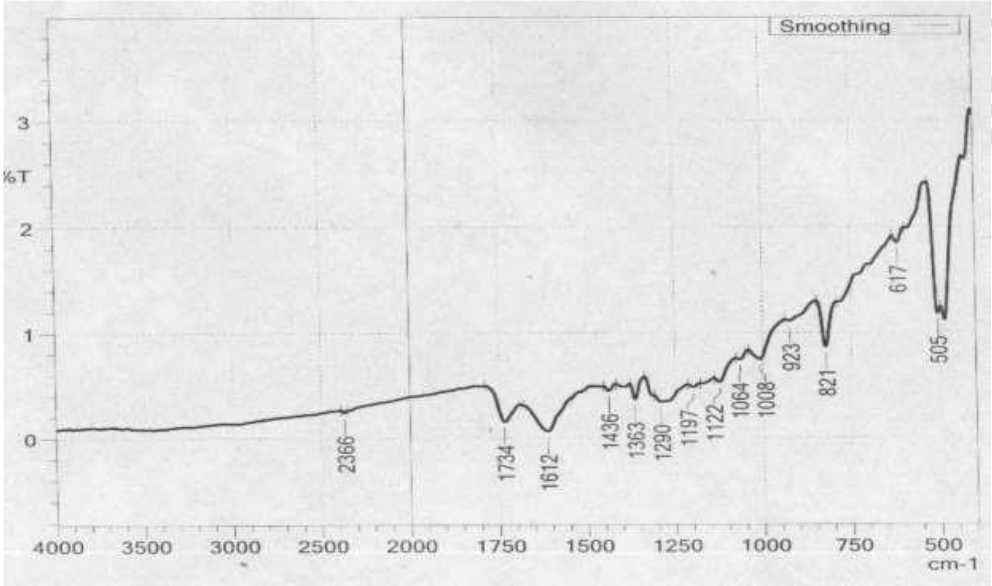
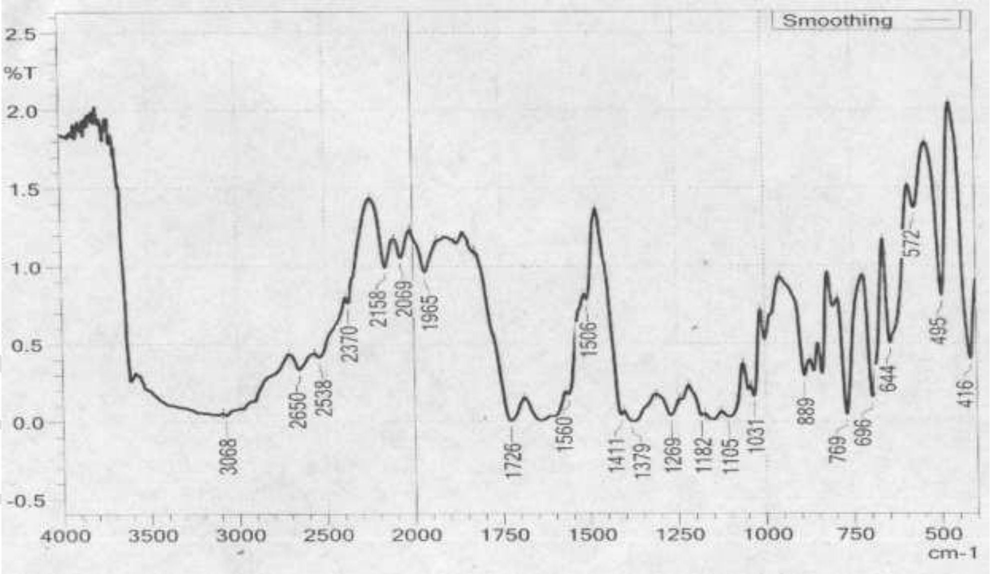
IR spectrum of [Cd(Ina)(Thg)(H_2O)$_2$]

3. FT-IR SPECTRA OF THIO-FUNCTIONALIZED MOFs.

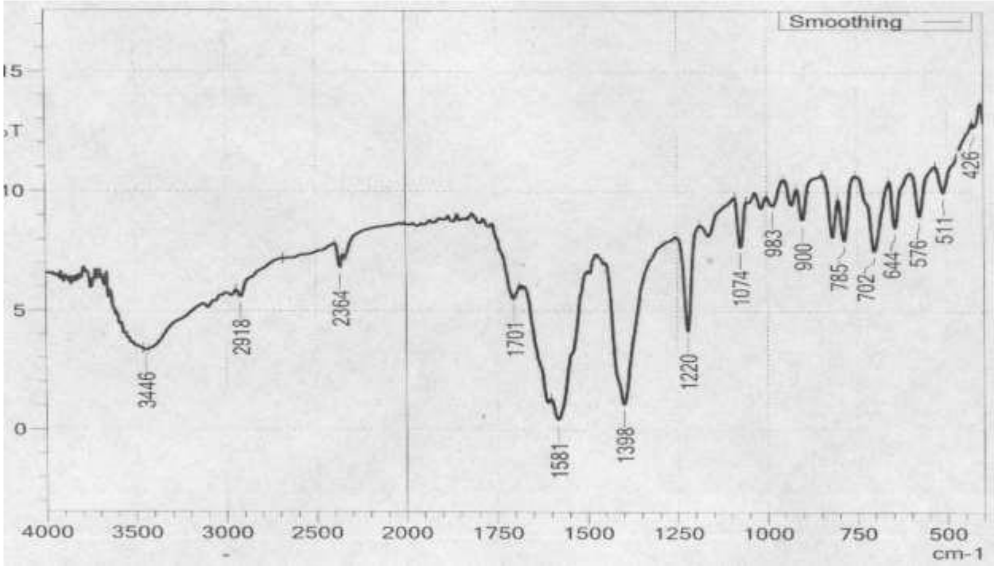


FT-IR spectrum of [Cu(INA)$_2$]-TH



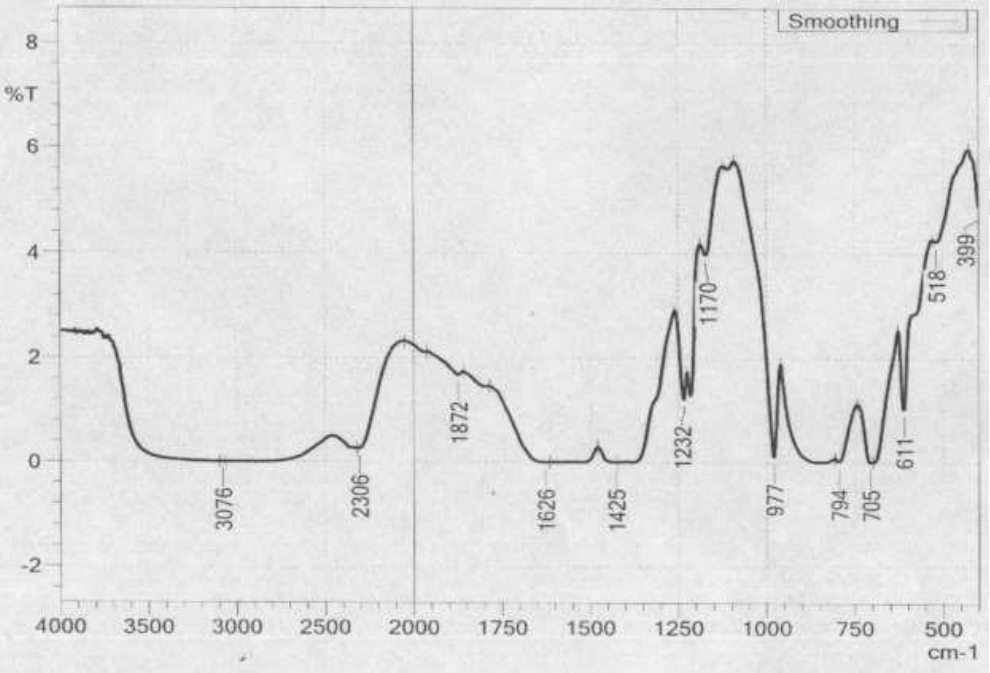
FT-

IR spectrum of [$Zn(INA)_2$]-TH



FT-IR spectrum of [$Zn(fum)_2(byp)$]-TH

FT-



IR spectrum of $[Zn(fum)(H_2O)_2]$-TH

FT-