

A Project on

**“SYNTHESIS AND APPLICATIONS OF METAL-ORGANIC
FRAMEWORK (MOF) ”**

*Submitted in partial fulfillment of the requirement for the award of Degree of
BACHELOR OF TECHNOLOGY*



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CERTIFICATE

*I hereby certify that the work which is being presented in the project entitled “**Synthesis and Applications of Metal Organic Frameworks**”, in partial fulfillment of the requirements for the award of the degree of Bachelor in Technology in Chemical Engineering submitted in the school of Chemical Engineering in Galgotias University, Greater Noida is an authentic record of my work carried out under the supervision of **Mr. Gagnesh Sharma** refer works by other researchers that are properly cited in the reference section. This project’s subject area has not been proposed for any other degree from this or any other university.*

*(**Kriti Dubedi**)*

This is to attest that, to the best of my knowledge, the aforementioned claim made by the candidates is accurate and true.

Dr. Gagnesh Sharma

ACKNOWLEDGEMENT

Without the participation and support of a great number of people, many of whose names may not be listed, this undertaking would not have been able to be completed. I truly appreciate and gladly acknowledge their contribution. I would like to thank our faculty for their endless support in the completion of this research.

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ABSTRACT

Metal-organic frameworks are permeable materials made of metal ions or oligonuclear metallic complexes and organic ligands. They are a coordination polymer sub-class that can be stretched out into one, two, and three aspects. Hundreds of new MOFs have been successfully synthesized since the disclosure of the main MOF structure during the 1990s.

This material class is useful for a variety of ecological and biomedical applications, as well as catalysts, sensors, thermoelectric, and attractive materials due to the structural diversity of the framework and the multifunctionality of the pores.

In the current survey article underlying perspectives; techniques for amalgamation; properties and uses of MOFs have been examined.

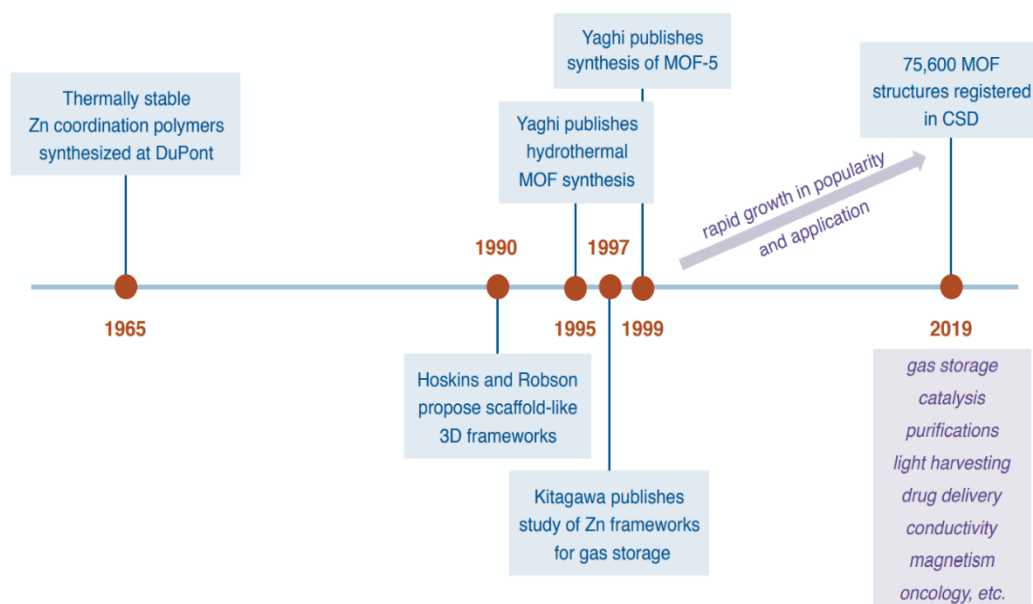


Fig. Brief History of Metal Organic Framework

INTRODUCTION

Metal-organic framework (MOF) materials are a promising class of materials that comprise of metal focuses or bunches and natural(organic) linkers. These are porous crystalline materials in which metal is locked into a position to produce rigid and porous geometry and is linked by various organic groups. They are a subclass of coordination polymers that can be reached out into one-dimension, two-aspect, and three aspects. Metal nodes (metal ions or metallic groups) serve as nodes of association and organic ligands connect the metal centres via coordination bonds, resulting in one-, two-, or three-dimensional networks. The term coordination polymers previously showed up in 1960, however huge headway in this field has been made starting around 1995 when Yaghi and partners begat the term metal-organic frameworks (MOFs). The idea of sub-atomic structure blocks connected together to shape foreordained structures serious areas of strength for through laid the reasonable and useful basis for reticular chemistry.

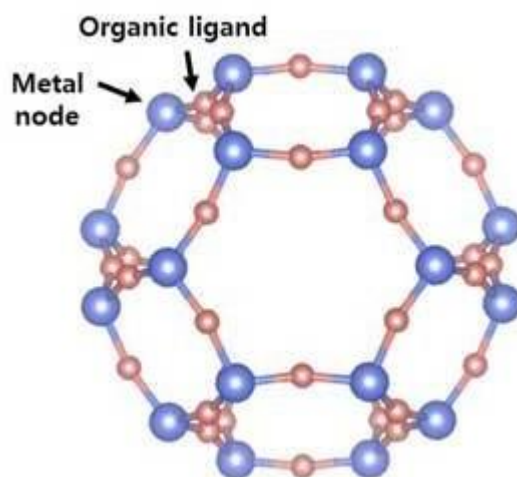


Fig. A metal-organic framework is depicted schematically (MOF).

BASIC STRUCTURE OF MOF

A metal ion or bunch of metal ions and an organic molecule known as a linker make up the two main parts of MOFs. Because of this, the substances are frequently referred to as hybrid organic-inorganic substances.

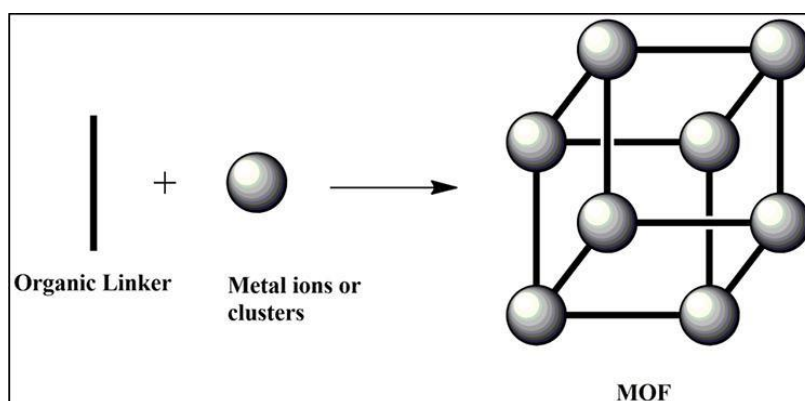


Fig. Basic structure of MOF

Metal ions (connectors) that connect the organic polymers (linkers) are the basic primary units that result in porous three-dimension structure MOFs. Thus, the "Primary Building Units" are the metal ions and organic compounds utilized in the formation of metal-organic frameworks. Metal ions from the first-row transition series, such as Cr^{3+} , Fe^{3+} , Co^{2+} , and Zn^{2+} , are ordinarily used as connectors in the evolution of MOFs. Organic linkers, through which the metal ions or nodes are connected, generally contain functional groups that are capable of forming coordination bonds such as carboxylate, phosphate, sulfonate, amine, nitrile, etc. The use of rigid or flexible organic ligands plays a vital part in designing a MOF in light of the fact that the flexible ligands offer increased degrees of

freedom as compared to the rigid ones and can lead to unpredictable crystal structures. MOFs connect organic linkers via metal-oxygen-carbon clusters rather than metal ions alone. "Secondary Building Units" refer to these metal-oxygen-carbon clusters (SBUs). SBUs have intrinsic geometric properties that aid MOF's topology.

MOFs have a three-dimensional structure formed by strong coordination bonds between metal particles and organic ligands, with cavities and internal surfaces involved by counterions, visitor particles, as well as solvate particles. Different sorts of cooperations, for example, hydrogen bonds, metal bonds, and π -connections, can likewise happen and add to the MOFs' strength. Coordination bonds, on the other hand, are stronger and provide more stable networks.

Properties

The main structural features of MOFs that are directly related to their properties and applications are:

- *High porosity,*
- *The enormous volume of pores that can reach 90% of the crystalline volume or more, Permanent pores are formed in porous solids and saturate the material's structure. Because the pores are large enough, guest molecules must diffuse into the structure.*
- *High thermal stability (250-500 °C) due to the presence of strong bonds.*

- *The metal ions form nodes that connect the arms of the linkers to form a repeating, cage-like structure. MOFs have an incredibly large internal surface area due to their hollow structure. The large surface area provides more room for chemical reactions and molecule adsorption.*
- *Metals and organic linkers, the framework's building blocks, can be combined in nearly infinite ways to create novel materials. As a result, by tuning the basic materials according to their application, unique structural characteristics can be achieved.*
- *MOF surface region and pore volume can be constrained by altering organic ligands that go about as spacers and make an open permeable design.*
- *Large specific surface area*

FEW EXAMPLES OF MOF

MOF-5

Metal-organic framework compound MOF-5, also known as IRMOF-1, has the formula $Zn_4O(BDC)_3$, where $(BDC)^2$ is 1,4-benzodicarboxylate (MOF-5).^[1] The finder was Omar M. Yaghi. MOF-5's unit cell structure. The yellow sphere is a representation of the pore's volume. Red for oxygen, black for carbon, and white for hydrogen. The coordination of BDC with the zinc core is shown by tetrahedrons.

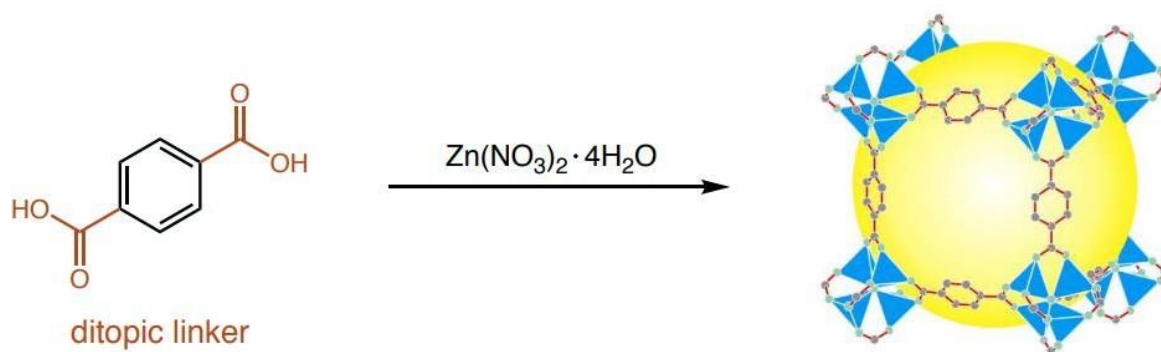


Fig.3. Unit cell structure of MOF-5

HKUST-1

Other names for HKUST-1 include Cu-BTC, MOF-199, and Basolite (TM) C300. A blue cubic crystal made on an ultra-microporous metal framework based on copper is called HKUST-1 (MOF). Nearly 2200 m^2/g of surface area is possible. It is a hybrid porous solid that has crystallised from inorganic subunits joined by organic linkers like carboxylates or phosphonates.

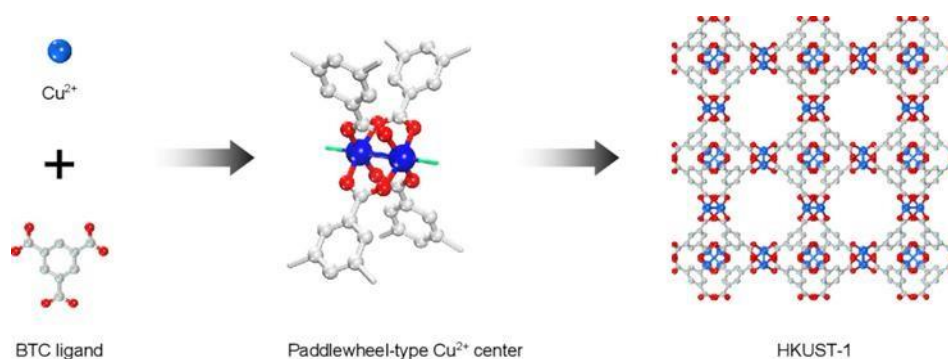


Fig. Unit structure of HKUST-1

Ui-O66

UiO-66 is an archetypal metal-organic framework (MOF) with exceptionally high surface area and thermal stability. UiO-66 is a crystal containing metal nodes made of a zirconium oxide complex connected by terephthalic acid ligands. Terephthalic acid is 1,4-benzenedicarboxylic acid (condensed as BDC). The figure below shows the crystal structure of UiO-66 where (a) shows the Six-centre octahedral zirconium oxide unit and (b) is the structural unit of UiO-66; blue atom for Zr, red atom for O, white atom for C, and H atoms.

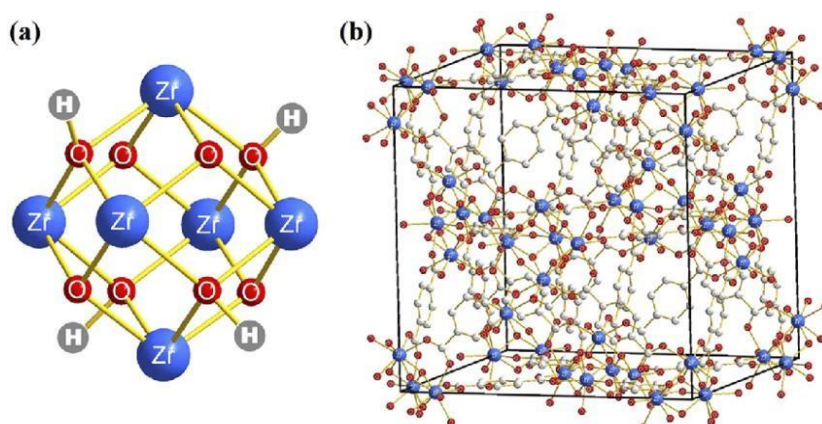
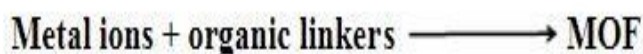


Fig. Crystal structure of UiO-66

METHODOLOGY

MOFs are traditionally created by combining metal ions and organic linkers in mild conditions to create a crystalline and porous network. This is known as "Modular Synthesis."



SYNTHESIS OF MOF

The synthesis of MOFs is determined by many factors related to the reaction time and temperature, the solvent used, the nature of the metal ions and the organic ligands, the size of the nodes and their structural characteristics, the presence of counterions, and the kinetics of the crystallization, which should lead to nucleation and crystal growth.

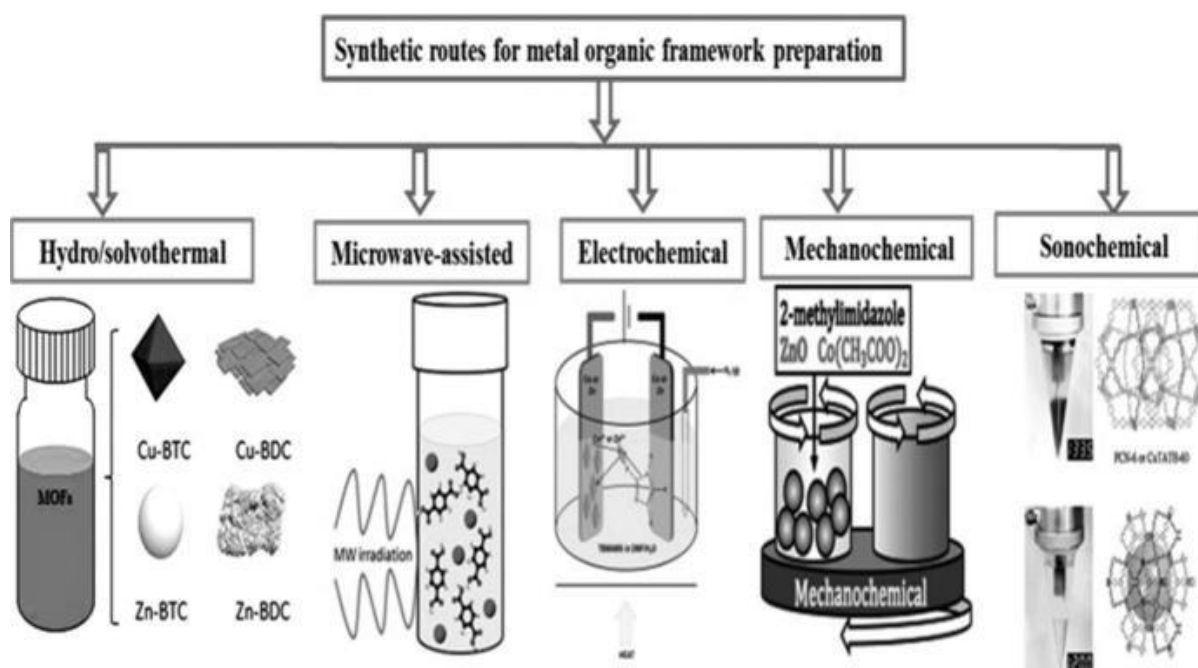


Fig. Different synthetic routes for preparation of MOF

- ***Solvothermal***

MOFs are typically synthesised at high temperatures and pressures under solvo(hydro)thermal conditions. This is the 'traditional' method of preparing MOFs. Metal precursors and organic linkers are typically dissolved in a solvent and set in a closed reaction vessel to form and self-assemble MOF crystals. If water is used as solvent this method is termed the hydrothermal method. The reactions typically take place in closed vessels (autoclaves) with polar solvents at temperatures between 50 and 260 °C, and they take a lot of time (hours and sometimes days). For reactions at high temperatures greater than 400 °C, teflon-lined autoclaves are utilised. The common solvents used include N, N-dimethylformamide (DMF), N, N-dimethylformamide (DEF), methanol, ethanol, and acetonitrile. When the temperature of the reaction is higher than the boiling point of the solvent, then the reaction is referred to as a solvothermal reaction and when the temperature is lower than the boiling point of the solvent it is referred to as a non-isothermal reaction.

- ***Mechanochemical***

A mixture of metal salt and organic linker is ground without the use of a solvent in a mortar pestle or a ball mill. After grinding, the mixture is gently heated to evaporate water or other volatile molecules formed as by-products in the reaction mixture [46]. This technique is known

as the mechanochemical method. Mechanical force is used to break intramolecular bonds in this method, which is followed by a chemical transformation. Because no solvent is used, the technique is harmless to the ecosystem and can produce a high yield of products.

- ***Sonochemical***

Sonochemistry is concerned with the chemical transformations of molecules in the presence of high-energy ultrasonic radiation (20 kHz–10 MHz). When a reaction solution is irradiated with ultrasound radiation, the bubbles form local hot spots with a short lifetime and high temperature and pressure, promoting chemical reactions and the immediate formation of crystallization nuclei [37,38,39]. In the presence of 1-methyl-2-pyrrolidone as a solvent, high-quality crystals of MOF-5 and MOF-177 with sizes of 5-25 nm and 5-20 nm, respectively, were prepared using the sonochemical method in a significantly reduced reaction time.

- ***Electrochemical Method***

Metal ions, rather than metal salts, are used as a metal source in the electrochemical synthesis of MOFs, which react with the dissolved linker molecules and a conducting salt in the reaction medium. Protic solvents are used to avoid metal deposition on the cathode, but H₂ is produced in the process. These synthesis procedures were used for

producing some MOFs using Zn, Cu, Mg, and Co as cathode material and 1,3,5-H3BTC and 1,2,3-H3BTC, H2BDC, and H2BDC-(OH)₂ as linkers.

- ***Microwave-assisted Synthesis***

Microwave (MW) radiation is used to provide energy for the reaction in this method. It is commonly used in organic synthesis, but it also has a wide range of applications in the rapid synthesis of nanoporous materials. MOF formation has been reported to occur under MW radiation at temperatures above 100 C and reaction times exceeding 1 hour. MOFs can be formed more quickly with MW irradiation than with conventional electrical heating. The highly pure and micropore with high volume (0.79 cm³gm⁻¹) HKUST-1 is prepared in 30 minutes by MW synthesis.

MOF APPLICATIONS

In MOFs there is a concurrent appearance of three qualities viz. crystallinity, porosity and existence of solid metal-ligand interaction. The unique combination of these properties makes MOFs a very special class of materials for environmental and biomedical applications, such as catalysts, sensors, toxic gas absorbers, and metal ions.

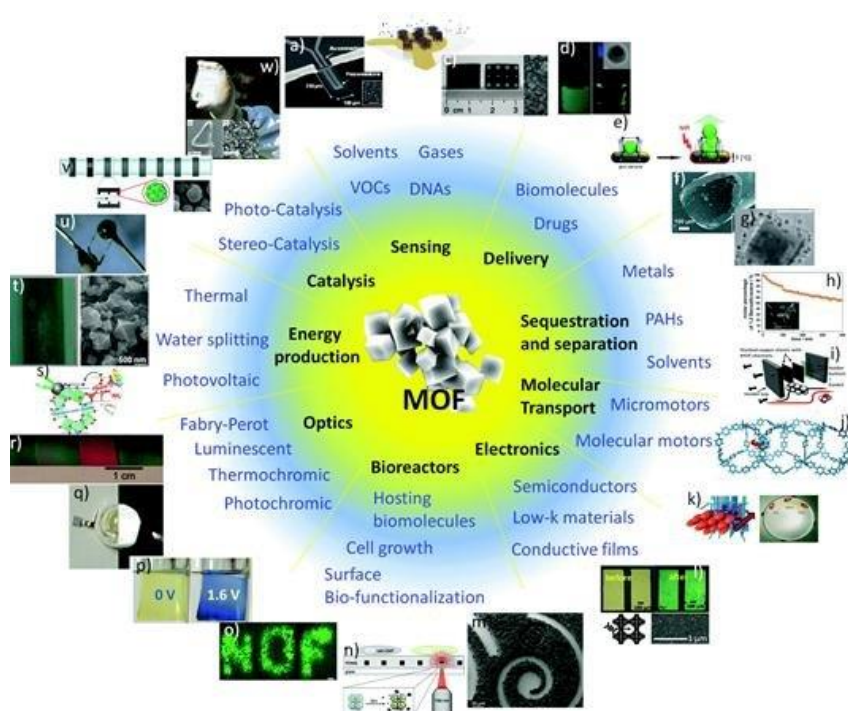


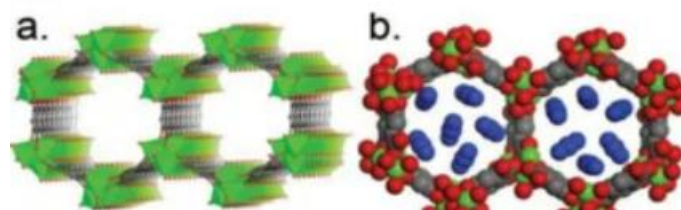
Fig. Various fields of MOF Applications

- **Gas Storage and Separation**

MOFs have been extensively researched for gas storage applications. H₂ and CH₄, for example, are alternative energy resources for future vehicles, and their effective utilization remains a challenge for the automotive industry. The capture of toxic industrial gases such as

NH₃ and H₂S, as well as volatile hydrocarbons such as benzene, and the removal of SO₂ and NO_x from flue gas are critical for environmental protection. The separation of gas mixtures, such as CO₂ capture and CO₂/CH₄, CO₂/N₂ separation, O₂ purification, and so on, is a critical step in the chemical industry.

More than 300 MOFs have been tested for H₂ storage. One of the promising MOFs for this purpose is MOF-177 which consists of [Zn₄O] clusters and 4,4',4''-benzene-1,3,5-triyltribenzoate (BTB) to form (6,3) net [117]. Due to its high surface area (~5000 m²g⁻¹) and large pore volume it shows a gravimetric H₂ uptake of 7.5 wt.% at 70 bar and 77 K. In general, MOFs with open metal sites have a large surface area, which allows for a stronger interaction between the metal ion and the H₂ molecule. This is the primary reason for MOFs' high H₂ uptake. At 56 bar and 77 K, NU-100 [120] has the highest excess H₂ storage capacity, 99.5 mg-g⁻¹. MOF-210 [121] has the highest total H₂ storage capacity of 176 mg-g⁻¹ at 80 bar and 77 K. CO₂ is the main greenhouse gas and is responsible for global warming and water acidification. MOF-74-Mg, which is the magnesium analog of MOF-74, shows the highest CO₂ uptake capacity of 228 and 180 cm³·g⁻¹ at 273 and 298 K and 1 bar, respectively [57]. The exceptional CO₂ uptake by MOF-74-Mg is attributed to the increased ionic character of the Mg-O bond, which imparts additional uptake beyond weight effects while maintaining the reversibility of adsorption.



**Fig. (a) The 1D channels of MOF-74-Mg, Mg-DOBDC
 (b) Space-filling model of the pore structure of MOF-74-Mg
 (Mg, green. C, grey. O, red)**

- **Catalytic Applications**

MOFs have been widely used as heterogeneous catalysts in fine chemical synthesis. The hearty idea of MOFs, which is expected for catalysis under outrageous circumstances, the porosity and enormous surface region, which facilitated catalytic activity, as well as the presence of pores and channels, which are required for catalytic selectivity, and the organic ligands that can tune the catalytic reactivity and selectivity, are the properties that make MOFs suitable for heterogeneous catalysts. Metal nodes, functionalized ligands, and structure pores might be for the most part artificially powerful areas for MOFs. The MOFs, in which metal centers are not completely blocked by organic ligands or unsaturated, i.e., labile ligands are introduced, are good catalysts because when labile ligands are generally solvent molecules, and when they are removed leave a free coordination position on the metal. For example, $[Cu_3(BTC)_2]$ (BTC = 1,3,5- benzenetricarboxylate) material HKUST-1, in which coordinated water molecule leaves a coordination vacancy on Cu upon thermal activation.

- **Biomedical Application**

MOFs have a very high drug loading capacity as well as a very long release time. MOFs can load four times more drug, ibuprofen, than mesoporous silica materials (up to 1.4 gm per gram of MOFs) with a longer release time (up to 21 days). MOFs that are non-toxic can be used in targeted drug delivery. Iron (III)carboxylate MOFs such as MIL-88A, MIL-8, MIL-100and MIL-101 can entrap anticancer [163], antitumor, and antiretroviral drugs as well as cosmetic agents. The problem of bio toxicity is among the most crucial ones for the use of MOFs as possible medication delivery systems. That is, MOFs might be dangerous to people. The presence of strong electrostatic interactions due to existence of charge compensating ions in MOFs enhances the adsorbate-adsorbent interaction which leads to higher drug loading at low pressure. In BioMOF-100,dimethylammonium cations present in the pores reinforce the attractive interaction with ibuprofen molecules

- **Sensing**

An enormous number of MOFs have been accounted for to be photoluminescent because aromatic units of linkers in most of the MOFs lead to excitation by absorbing UV-visible light and provide luminescence. MOFs as luminescent materials or phosphors can find application in cathode ray tubes, projection television, fluorescent tubes and X-ray detectors[149], small-

moleculesensors[150,151], pH sensors[152]. MOFs are particularly alluring as novel sensing materials. The Ln MOFs co-doped with multiple Ln³⁺ ions can be used as bimodal (or multicoloured) light emitters. Bimodal emission may be applied in multiplexed detection and imaging of therapeutic cells [154]. In contaminated ambient fluids, a bimetallic Eu-Tb MOF containing 1,4-benzenedicarboxylate ligands demonstrated Pb²⁺ selectivity. By doping the MOFs with various Tb/Eu ratios, it was possible to fine-tune the colour of the luminous Ln-MOFs from green to red. When Pb²⁺ is present, the MOF's emission colour switches from red-orange to green, which can be seen with the naked eye.

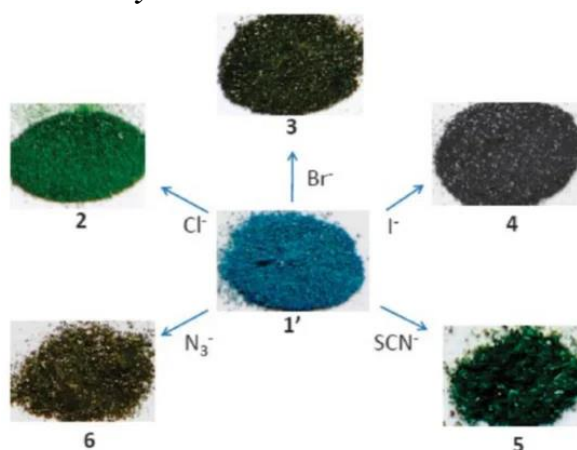


Fig. Color change of [CuL₂(H₂O)_{0.5}](NO₃)₂ (1') upon exchange of nitrates by the indicated anion

- **Magnetism And its Applications**

MOF materials show magnetism when paramagnetic 3d transition

metal nodes are utilized alongside appropriate diamagnetic organic linkers and MOFs having magnetic properties are named magnetic metal-organic frameworks (MMOFs). One more justification for magnetic behaviour of MOFs is the system structure, which might include layered calculation with a more limited formed distance between metal bunches. Organic linkers have likewise been utilized for the union of MMOFs, where radicals present in organic linkers are answerable for magnetic properties. A Ni-Glutarate-based MOF[Ni₂₀(H₂O)₈(C₅H₆O₄)₂₀.40H₂O] showed ferromagnetic behavior with a curie temperature of 4K due to weak ferromagnetic interactions of Ni-O-Ni angle. HKUST-1 is antiferromagnetic at high temperatures and below 65K shows weak ferromagnetism. MIL-9[144] [Co₅(OH)₂(C₄H₄O₄)₄] is reported to possess ferrimagnetic properties.

- **Electric Property and Its Application**

MOFs have been demonstrated to be compelling gadget materials for energy capacity. Electrical storage capacity of MOFs in Co-doped MOF-5, i.e., Co₈-MOF-5[167], as a supercapacitor electrode has been reported. In 2014, a series of 23 different nanocrystalline MOFs (nMOFs) were reported for their electrochemical energy storage capacity. Among these, a zirconium-based MOF i.e., nMOF-867 exhibited high capacitance. An Mn-based MOF is used as the active coating material. This surface-modified oxide material demonstrated a high discharge capacity, good thermal stability without compromising

cycle stability, high initial coulombic efficiency, and high-rate capability.

FUTURE SCOPE

Although there have been advancements in the structure optimization and performance improvement of MOFs to date, it is hoped that additional basic research and industrial use of MOFs will consider further headway. The advancement of new materials for perfect and arising advancements in the automobile area, energy age, clean air and water, and wellbeing can extraordinarily profit from MOFs; multifunctional properties and the composite materials they produce. Another scope of utilizations is currently being explored by changing over translucent MOFs into fluid and additionally lustrous states.

Researchers are now able to learn what happens at the molecular level when some MOFs are heated to their melting point and subsequently cooled to create a glass-like state thanks to technological advancements. Researchers are examining how engineering MOFs to hold a lot of refrigerant gases will assist cut energy consumption for air conditioning in a manner similar to the carbon capture application. The core of the clever materials expected to develop the fourth modern transformation all through our century is MOFs and subsidiary materials.

Future patterns will include the planning of powerful MOFs and MOF-based gadgets utilizing an effortless, green, and efficient methodology.

CONCLUSION

Metal-organic frameworks have acquired prevalence because of their interesting underlying properties, like their permeable nature and huge explicit surface region, as well as their high thermal stability. MOFs can be effortlessly blended under surrounding or outrageous circumstances at high temperature and strain, as well as utilizing green science techniques, for example, mechanochemical, electrochemical, and sonochemical strategies.

The investigation of MOFs has become one of the examination problem areas in many fields, attributable to the wide potential applications anticipated for these materials in different regions. MOFs show application in catalysis, drug delivery, gas storage, nanoparticle precursor, luminescence, electrochemistry, biomedicine, magnetism and sensing technology.

It stays a huge test to completely use the chemically versatile MOFs' novel arrangement of properties and functionalities and understand their application potential in different recognized areas.

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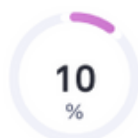
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