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1. Introduction

Over the past 50 decades, porous materials, from zeolites, coordination polymers to metal organic frameworks (MOFs), have gained considerable attention. The interesting feature is their porosity that allows the diffusion of guest molecules into the bulk structure. The shape and size of pores govern the shape and size selectivity of the guests to be incorporated. MOFs as defined by Yaghi et al. are porous structures constructed from the coordinative bonding between metal ions and organic linkers or bridging ligands (Figure 1) [1]. MOFs are formed by anchoring metal-containing units or secondary-building units (SBUs) with organic linkers, by coordination, yielding open frameworks that show exceptional feature of permanent porosity, stable framework, enormous surface area, and pore volume. The porosity is a consequence of long organic linkers that confer large storage space and numerous adsorption sites within MOFs. They also bear the ability to systematically vary and functionalize their pore structure [2, 3]. In the history of MOFs, a benchmark was represented by the synthesis of MOF-5 (Zn₄O(bdc))₃ bdc = terephthalate) and HKUST-1 (Cu₃(btc))₂ btc = 1,3,5-benzenetricarboxylate) with high porosity and low pressure gas sorption, followed by the development of chromium(III) terephthalate (MIL-101) with high chemical stability, MOF-74 (Zn₄(dhbdc), dhbdc = 2,5-dihydroxy-1,4-benzenedicarboxylate) with low pressure adsorption of CO₂, and several isostructural analogs of Mg-MOF-74 termed as IRMOF-74-I to IRMOF-74-XI, with large pore apertures to accommodate protein, NU-110E with acetylene-expanded hexatopic linker, having material highest experimental Brunauer-Emmett-Teller (BET) surface area of any porous material reported to date (7140 m² g⁻¹) Some examples of MOFs and their applications are given in Table 1 [1–15].
Figure 1. Structure of MOF.

| Application          | MOF                          | Metal | Ligand                           | Year | Author                      |
|----------------------|------------------------------|-------|----------------------------------|------|-----------------------------|
| Drug delivery        | MIL-101 [Cr₃O(OH,F,H₂O)₃(1,4-bdc)₃] and MIL-100 | Cr     | 1,4-benzenedicarboxylate moieties (bdc) or H₃btc: Benzene-1,3,5-tricarboxylate | 2006 | Patricia Horcajada et al. [4] |
| Methane Storage      | MOF-5 Zn₃(1,4-bdc)₃          | Zn     | bdc                              | 2002 | Li and Eddaoudi, et al. [5, 6] |
| Adsorption and storage | HKUST( Hong Kong University of Science and Technology)-1 Cu₅(H₂O)₃(CO₂)₄ | Cu     | H₃btc                            | 2006 | Rowsell and Yaghi [7]       |
| Adsorption and storage | IRMOF-9 Zn₃O(bpdc)₃          | Zn     | 4,4'-biphenyl dicarboxylate (bpdc) | 2006 | Rowsell and Yaghi [7]       |
| Adsorption and storage | MOF-74, Zn₄(C₈H₂O₆)  | Zn     | 2,5-dihydroxybenzene-1,4-dicarboxylic acid | 2006 | Rowsell and Yaghi [7]       |
| Drug delivery        | metal–organic Zn(bix) spheres with encapsulated DOX [DOX/Zn(bix)], SN-38 [SN-38/Zn(bix)], CPT [CPT/Zn(bix)] and DAU [DAU/Zn(bix)] Doxorubicin (DOX), SN-38, camptothecin (CPT) and daunomycin (DAU) | Zn     | Bix: 1,4-bis(imidazol-1-ylmethyl)benzene | 2010 | Inhar Imaz et al. [9]     |
2. Chemistry

MOFs consist of both inorganic and organic units. The organic units (linkers/bridging ligands) consist of carboxylates, or anions, such as phosphonate, sulfonate, and heterocyclic compounds (Figures 2 and 3). The inorganic units are the metal ions or clusters termed as SBUs. Its geometry is determined by the coordination number, coordination geometry of the metal ions, and the nature of the functional groups. A variety of SBU geometries with different number of points of extension such as octahedron (six points), trigonal prism (six points), square paddle-wheel (four points), and triangle (three points) have been observed in MOF structures (Figure 4). In principle, a bridging ligand (ditopic, tritopic, tetratopic, or multitopic linkers) reacts with a metal ion with more than one vacant or labile site. The final framework topology of MOF is governed by both SBU connectors and organic ligand linkers. Depending upon the nature of the system used, infinite-extended polymeric or discrete-closed oligomeric structures can arise (Figure 4). Metal-containing units and organic linkers can be varied resulting in a variety of MOFs, tailored for different applications [3]. MOFs with large spaces may result in the formation of interpenetrating structures. Thus, it is very important to inhibit interpenetration by carefully choosing the organic linkers. The pore size is allowed to be tuned and spatial cavity arrangement be controlled, by judicious selection of metal centers.
and organic ligands and also by adjusting their conditions of synthesis. The large porosity allows their applications in adsorption and separation of gaseous molecules, catalysis, microelectronics, optics, sensing applications, bioreactors, drug delivery, and others. MOFs have pore openings up to 2-nm size, which can accommodate small molecules. However, the pore openings rarely allow the inclusion of large molecules (e.g., proteins and enzymes). Attempts have been taken to increase the pore size to mesopore regime (pore size of 2–50 nm) and to decrease the crystal size to the nanometer scale. The large pore aperture benefits surface modification with a number of functionalities, without sacrificing the porosity of MOFs, also allowing the encapsulation of large molecule MOFs. The synthesis of MOFs involves reaction conditions and simple methods such as solvothermal, ionothermal, diffusion, microwave methods, ultrasound-assisted, template-directed syntheses, and others [2, 3].

An interesting and significant advancement in the field is to combine MOFs with functional nanoparticles, yielding new nanocomposite materials with unparalleled properties and performance. Nano-MOFs are advantageous over conventional nanomedicines owing to their structural and chemical diversity, high loading capacity, and biodegradability. The final properties are dependent on the particle composition, size, and morphology. These can be obtained as either crystalline or amorphous materials. As soft porous crystals, framework flexibility (triggered by an external stimulus, e.g., mechanical stress, temperature, light interactions) may be shown by MOFs, also in the absence of guests or with no involvement of adsorption and desorption [1–3, 16].

![Figure 2. Some examples of organic ligands with carboxylic functionality used for the preparation of MOFs.](image-url)
Figure 3. Some examples of ligands containing nitrogen, sulfur, phosphorous and heterocycles used for the preparation of MOFs.

Figure 4. MOFs resulting from different metal nodes and bridging ligands.
3. Metal biomolecule frameworks (BioMOFs)

Biomolecules are naturally and abundantly available. They are cost-effective, rigid, and flexible with different coordination sites, rendering structurally diverse, biologically compatible MOFs. MOFs have also been synthesized from nontoxic endogenous cations (such as Ca, Mg, Fe, and Zn) and ligands consisting of naturally occurring derivatives or biomolecules [17]. These BioMOFs are usually biocompatible and suitable for biomedical applications [17–47]. Such combinations of natural ligands with endogenous cations are also associated with several therapeutic effects (anti-allergic, anti-inflammatory, antimicrobial, anticarcinogenic activities). Table 2 shows some examples of BioMOFs and their applications [18–47]. Such biologically and environmentally compatible MOFs are designed and constructed based on specific composition criteria governed by judiciously selecting metal ions and organic linkers as building blocks, which are nontoxic and biologically and environmentally compatible. Biomolecules such as amino acids, peptides, proteins, nucleobases, carbohydrates, and other natural products such as cyclodextrins, porphines, and some carboxylic acids (Figure 5) serve as emerging building blocks for the design and construction of metal-biomolecule frameworks with novel and interesting properties and applications that cannot be obtained through the use of traditional organic linkers [17, 43, 44, 48, 49].

| Application | BioMOF                          | Metal | Ligand                  | Year | Author   |
|-------------|---------------------------------|-------|-------------------------|------|----------|
| Ar and CH₄ sorption | [Cu(trans-fum)]                  | Cu    | Fum:Fumaric acid        | 2001 | K. Seki et al [18] |
| Reversible H₂O sorption/desorption | [Ni₇(suc)₆(OH)₆(H₂O)₂]         | Ni    | Succ Succinic acid      | 2002 | Forster et al. [19] |
| –                      | [Ni₇(suc)₄(OH)₆(H₂O)₃]·TH₂O | Ni    | Succ                    | 2003 | Guillou et al. [20] |
| Sorption of more than 30 kinds of guests (e.g. DMF, benzene, etc.); structural change | [Mn₃(HCOO)₆]·(CH₃OH)·(H₂O) | Mn    | Formic acid             | 2004 | Wang et al. [21]  |
| Selective CO₂ and H₂ sorption | Mn(HCOO)₂·1/3(C,H,O) | Mn    | Formic acid             | 2004 | Dybtsev et al. [22] |
| Adsorption | Fe₄O(MeOH)₃(fum)₃(CO₂CH₃)·4.5MeOH | Fe    | Fum                     | 2004 | Serre et al. [23] |
| 1,3-Butanediol sorption | [Ni₂(O-L-Asp)·H₂O]·4H₂O | Ni    | Amino acid L-Asp: aspartic acid | 2004 | Anokhina et al. [24] |
| Enantioselective separation and catalytic | Zn₂(bdc)·L-lac(DMF) | Zn    | bdc: 1,4-benzenedicarboxylic acid and L-lac:Lactic acid | 2006 | Dybtsev et al. [25] |
| Application                               | BioMOF                                             | Metal | Ligand                      | Year | Author(s) |
|------------------------------------------|----------------------------------------------------|-------|-----------------------------|------|-----------|
| CO₂ sorption                             | [Ni₂(L-Asp)₂(4,4’-bipy)]₂H₂O                      | Ni    | L-Asp and 4,4’-bipy: 1,2-bis(4-pyridyl)ethane | 2006 | Vaidhyanathan et al. [26] |
| H₂ sorption                              | Co₂(L-Asp)₂(4,4’-bipy)₂H₂O                        | Co    | L-Asp and 4,4’-bipy         | 2008 | Zhu et al. [27] |
| Heterogeneous asymmetric catalysts for the methanolysis of rac-propylene oxide | Ni₂(L-Asp)₂(4,4’-bipy)(HCl)₁.₈(MeOH)              | Ni    | L-Asp and 4,4’-bipy         | 2008 | Ingleson et al. [28] |
| Heterogeneous asymmetric catalysts for the methanolysis of rac-propylene oxide | Cu₂(2-Asp)₂(bpe)(HCl)₁.₈(H₂O)₂ | Cu    | 2-Asp and bpe: 1,2-bis(4-pyridyl)ethane | 2008 | Ingleson et al. [28] |
| Cation exchange capabilities, including cationic drugs and lanthanide ions | Zn₆(Ade)₁(bpdc)₁₀₂(Me₂NH₅)₁₈(8DMF-1₁H₂O)       | Zn    | Nucleobases: Adenine: Ade and bpdc: biphenyldicarboxylate | 2009 | An et al. [29] |
| Selective CO₂ sorption                    | Co₂(Ade)₂(CO₂CH₃)₁₂·2DMF·0.5H₂O                   | Co    | Ade                         | 2010 | An et al. [30] |
| Drug delivery and imaging                | Fe₃O(MeOH)₃(fumarate)₁₃.₈(CO₂CH₃)₁₈·4.₅MeOH and [Fe₃O(MeOH)]₁₈(C,H₄O₈)₃Cl·6MeOH | Fe    | Fumarate and C₆H₄O₈ is galactarate | 2010 | Horcajada et al. [31] |
| Therapeutic agent                         | BioMIL-1                                           | Fe    | Nicotinic acid (pyridine-3-carboxylic acid, also called niacin or vitamin B₃) | 2010 | Miller et al. [32] |
| Reversible flexible structure; CO₂, MeOH and H₂O sorption | [Zn(GlyAla)₂]₁(solvent) | Zn    | Peptide; Glycine-adenine    | 2010 | Rabone et al. [33] |
| Inclusion of several molecules (e.g. Rhodamine B, ...) | (γ-CD)₁(KOH)₁(Pb₂₅(NO₃)₂) | K     | Saccharides γ-CD: cyclodextrins | 2010 | Smaldone et al. [35] |
|                                          | (γ-CD)₁(Rb₆O₇)₁(Pb₂₅(NO₃)₂) | Rb    | γ-CD is a (chiral) cyclic oligosaccharide | 2010 | Smaldone et al. [34] |
| Application                                      | BioMOF           | Metal | Ligand                              | Year | Author               |
|-------------------------------------------------|------------------|-------|-------------------------------------|------|----------------------|
| 4-phenylazoplenol etc.)                         |                  |       |                                     |      |                      |
| Highly selective adsorption of CO<sub>2</sub>    | CD-MOF-2         | Rb    | γ-CD                                | 2011 | Jeremiah J. Gassensmith et al. [35] |
| Photostable O<sub>2</sub> sensor                 | Zn<sub>8</sub>(Ade)<sub>4</sub>(bpdc)<sub>6</sub>·2Me<sub>2</sub>NH<sub>2</sub>] loaded with lanthanide cations (Tb(III), Sm(III), Eu(III) and Yb(III)) | Zn and lanthanide | Ade and bpdc | 2011 | An et al. [36] |
| –                                               | M(II/III) Gallates | Fe, Mn, Co and Ni | H<sub>4</sub>gal: gallic acid | 2011 | Saines et al. [37] |
| Porous                                          | α-CD-MCF         | Rb    | α-CD                                | 2012 | Gassensmith et al. [38] |
| Adsorption                                      | CD-MOF-1 and CD-MOF-2 and CD-MOF-3 | K, Rb and Cs | γ-CD                                | 2012 | Forgan et al. [39] |
| Drug storage and release or for the immobilization and organization of large biomolecules | Bio-MOF-100 | Zn    | Ade                                 | 2012 | Jihyun An et al. [40] |
| –                                               | MIL-151 to -154  | Zr    | H<sub>4</sub>gal                     | 2014 | Cooper et al. [41] |
| Antibacterial carrier                           | BioMIL-5         | Zn    | AzA: azelaic acid                   | 2014 | Tamames-Tabár et al. [42] |
| Antioxidant carrier                             | Mg(H<sub>4</sub>gal) | Mg    | H<sub>4</sub>gal                     | 2015 | Cooper et al. [43] |
| Inclusion and                                   | CD-MOF-1         | Na    | β-CD:                               | 2015 | Lu et al.             |
| Application                                      | BioMOF   | Metal | Ligand                                                                 | Year | Author                    |
|-------------------------------------------------|----------|-------|------------------------------------------------------------------------|------|---------------------------|
| loading the drug molecules                      | MOF-525  | Zr    | H₄tcpp: meso-tetra(4-carboxyphenyl) porphine                           | 2015 | Kung et al. [44]          |
| Electrochemical nitrite detection               | Al-PMOF  | Al    | H₄tcpp                                                                | 2015 | Wilcox et al. [45]        |
| Ammonia uptake                                  | [Zn(ain)(atz)]ₙ | Zn    | Hatz : 5-aminotetrazole and Hai: 2-amino-4-isonicotinic                | 2016 | David Briones et al. [47] |

Table 2. Some examples of BioMOFs and their applications.

Figure 5. Examples of organic linkers used for the synthesis of BioMOFs.
4. Summary

MOFs find versatile applications as drug-delivery agents, sensors, storage and separation systems, catalysts, and others. Nontoxic nano-MOFs bearing tailored cores and surfaces can be used as nanodrug carriers for antitumor and anti-HIV drugs (biomedicine, nontoxic, drug). MOFs with biomolecules as organic linkers are still in cradle stage in contrast to their counterparts bearing traditional organic linkers. However, biomolecules confer biological compatibility and easy recyclability to MOFs. They also confer unique characteristics such as chirality and specific recognition, self-assembly characteristic, separation, ion exchange, and catalytic properties, also rendering bioinspired structures. In future, a better understanding and control of chemistry and design of MOFs may provide plethora of opportunities towards their structures, properties, and applications in different fields.

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Author details

Eram Sharmin¹ and Fahmina Zafar²*

*Address all correspondence to: fahmzafar@gmail.com

1 Department of Pharmaceutical Chemistry, College of Pharmacy, Umm Al-Qura University, Makkah Al-Mukarramah, Saudi Arabia

2 Inorganic Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi, India

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