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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-benzene-tricarboxylate) with high porosity and low pressure gas sorption, followed by the development of chromium(III) terephthalate (MIL-101) with high chemical stability, MOF-74 (Zn₁(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.

<table>
<thead>
<tr>
<th>Application</th>
<th>MOF</th>
<th>Metal</th>
<th>Ligand</th>
<th>Year</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drug delivery</td>
<td>MIL-101 [Cr_3O(OH,F,H_2O)_(1,4-bdc)_3]</td>
<td>Cr</td>
<td>1,4-benzenedicarboxylate moieties (bdc) or H_3btc: Benzene-1,3,5-tricarboxylate</td>
<td>2006</td>
<td>Patricia Horcajada et al. [4]</td>
</tr>
<tr>
<td>Methane Storage</td>
<td>MOF-5 Zn_(1,4-bdc)_3</td>
<td>Zn</td>
<td>bdc</td>
<td>2002</td>
<td>Li and Eddaoudi, et al. [5, 6]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>HKUST( Hong Kong University of Science and Technology)-1 Cu_(3H_2O)_3(CO_2)_4</td>
<td>Cu</td>
<td>H_3btc</td>
<td>2006</td>
<td>Rowsell and Yaghi [7]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>IRMOF-9 Zn_3O(bpdc)_3</td>
<td>Zn</td>
<td>4,4’-biphenyldicarboxylate (bpdc)</td>
<td>2006</td>
<td>Rowsell and Yaghi [7]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>MOF-74, Zn_3(C_8H_2O_6)</td>
<td>Zn</td>
<td>2,5-dihydroxybenzene-1,4-dicarboxylic acid</td>
<td>2006</td>
<td>Rowsell and Yaghi [7]</td>
</tr>
<tr>
<td>Drug delivery</td>
<td>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)</td>
<td>Zn</td>
<td>Bix: 1,4-bis(imidazol-1-ylmethyl)benzene</td>
<td>2010</td>
<td>Inhar Imaz et al. [9]</td>
</tr>
</tbody>
</table>
## 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.

### Table 1. Some examples of MOFs and their applications.

<table>
<thead>
<tr>
<th>Application</th>
<th>MOF</th>
<th>Metal</th>
<th>Ligand</th>
<th>Year</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antibacterial</td>
<td>Cu-BTC(MOF-199)</td>
<td>Cu</td>
<td>H\textsubscript{3}btc</td>
<td>2014</td>
<td>Rodriguez et al.</td>
</tr>
<tr>
<td></td>
<td>Co-TDM</td>
<td>Co</td>
<td>H\textsubscript{3}tdm: tetrakis[(3,5-)dicarboxyphenyl)-oxamethyl] methane</td>
<td>2012</td>
<td>Wenjuan et al.</td>
</tr>
<tr>
<td></td>
<td>MIL-100(Fe or Cr) and MIL-127(Fe)</td>
<td>Fe, Cr or</td>
<td>tricarboxylate or tetracarboxylate</td>
<td>2014</td>
<td>Eubank et al.</td>
</tr>
<tr>
<td></td>
<td>Ag\textsubscript{5}(PYDC\textsubscript{2})(OH)</td>
<td>Ag</td>
<td>HO-H\textsubscript{3}ipa = 5-hydroxyisophthalic acid and H\textsubscript{3}pydc = pyridine-3, 5-dicarboxylic acid</td>
<td>2014</td>
<td>Xinyi Lu et al.</td>
</tr>
<tr>
<td></td>
<td>Mn\textsubscript{3}(HCOO)\textsubscript{6}·DMF</td>
<td>Mn</td>
<td>3-nitrophthalic acid (H\textsubscript{2}npta) and 4,4′-bipyridine (4,4′-bipy)</td>
<td>2014</td>
<td>Ying-Ping Zhao et al.</td>
</tr>
</tbody>
</table>

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**Introductory Chapter: Metal Organic Frameworks (MOFs)**

http://dx.doi.org/10.5772/64797

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**Soft coupling-deprotection sequence**

*fluorenylmethyloxycarbonyl group (Fmoc), a base-label protecting group for amines

**Antibacterial**

Cu-BTC(MOF-199)

Cu

H\textsubscript{3}btc

Cu

2014

Rodriguez et al.

**Highly potent bacteriocidal activity**

Co-TDM

Co

H\textsubscript{3}tdm: tetrakis[(3,5-)dicarboxyphenyl)-oxamethyl] methane

2012

Wenjuan et al.

**Delivery of nitric oxide**

MIL-100(Fe or Cr) and MIL-127(Fe)

Fe, Cr or

tricarboxylate or tetracarboxylate

2014

Eubank et al.

**Antibacterial**

Ag\textsubscript{5}(IPA)(H\textsubscript{2}O)-(H\textsubscript{3}O) and Ag\textsubscript{5}(PYDC\textsubscript{2})(OH)

Ag

HO-H\textsubscript{3}ipa = 5-hydroxyisophthalic acid and H\textsubscript{3}pydc = pyridine-3, 5-dicarboxylic acid

2014

Xinyi Lu et al.

**Adsorption of CO\textsubscript{2} over N\textsubscript{2}**

Mn\textsubscript{3}(HCOO)\textsubscript{6}·DMF

Mn

3-nitrophthalic acid (H\textsubscript{2}npta) and 4,4′-bipyridine (4,4′-bipy)

2014

Ying-Ping Zhao et al.
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.
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, anticancerous 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].

<table>
<thead>
<tr>
<th>Application</th>
<th>BioMOF</th>
<th>Metal</th>
<th>Ligand</th>
<th>Year</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar and CH₄ sorption</td>
<td>[Cu(trans-fum)]</td>
<td>Cu</td>
<td>Fum: Fumaric acid</td>
<td>2001</td>
<td>K. Seki et al [18]</td>
</tr>
<tr>
<td>Reversible H₂O sorption/desorption</td>
<td>[Ni₇(suc)(OH)₆(H₂O)₃]·7H₂O</td>
<td>Ni</td>
<td>Suc: Succinic acid</td>
<td>2002</td>
<td>Forster et al. [19]</td>
</tr>
<tr>
<td>– Sorption of more than 30 kinds of guests (e.g. DMF, benzene, etc.); structural change</td>
<td>[Mn₃(HCOO)₆(CH₃OH)·(H₂O)]</td>
<td>Mn</td>
<td>Formic acid</td>
<td>2004</td>
<td>Wang et al. [21]</td>
</tr>
<tr>
<td>Selective CO₂ and H₂ sorption</td>
<td>Mn₃(HCOO)₂·1/3(C₃H₅O₂)</td>
<td>Mn</td>
<td>Formic acid</td>
<td>2004</td>
<td>Dybtsev et al. [22]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Fe₃O₃MeOH₃(fum)₅(CO₂·CH₃)·4.5MeOH</td>
<td>Fe</td>
<td>Fum</td>
<td>2004</td>
<td>Serre et al. [23]</td>
</tr>
<tr>
<td>1,3-Butanediol sorption</td>
<td>[Ni₂O(L-Asp)(H₂O)·4H₂O</td>
<td>Ni</td>
<td>Amino acid L-Asp: L-Aspartic acid</td>
<td>2004</td>
<td>Anokhina et al. [24]</td>
</tr>
<tr>
<td>Enantioselective separation and catalytic</td>
<td>Zn₂(bdc)·(L-lac)(DMF)</td>
<td>Zn</td>
<td>bdc: 1,4-benzendicarboxylic acid and L-lac: L-lactic acid</td>
<td>2006</td>
<td>Dybtsev et al. [25]</td>
</tr>
<tr>
<td>Application</td>
<td>BioMOF</td>
<td>Metal</td>
<td>Ligand</td>
<td>Year</td>
<td>Author</td>
</tr>
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</tr>
<tr>
<td>CO₂ sorption</td>
<td>[Ni₂(L-Asp)₂(4,4'-bipy)]₂H₂O</td>
<td>Ni</td>
<td>L-Asp and 4,4'-bipy : 1,2-bis(4-pyridyl)ethane</td>
<td>2006</td>
<td>Vaidhyanathan et al. [26]</td>
</tr>
<tr>
<td>H₂ sorption</td>
<td>Co₂(L-Asp)₂(4,4'-bipy)₂H₂O</td>
<td>Co</td>
<td>L-Asp and 4,4'-bipy</td>
<td>2008</td>
<td>Zhu et al. [27]</td>
</tr>
<tr>
<td>Heterogeneous asymmetric catalysts for the methanolysis of rac-propylene oxide</td>
<td>Ni₂(L-Asp)₂(4,4'-bipy)-(HCl)1.8(MeOH)</td>
<td>Ni</td>
<td>L-Asp and 4,4'-bipy</td>
<td>2008</td>
<td>Ingleson et al. [28]</td>
</tr>
<tr>
<td>Heterogeneous asymmetric catalysts for the methanolysis of rac-propylene oxide</td>
<td>Cu₂(i-Asp)₂(bpe)(HCl)₂(H₂O)₂</td>
<td>Cu</td>
<td>i-Asp and bpe: 1,2-bis(4-pyridyl)ethane</td>
<td>2008</td>
<td>Ingleson et al. [28]</td>
</tr>
<tr>
<td>Cation exchange capabilities, including cationic drugs and lanthanide ions</td>
<td>Zn₈(Ado)₄(bpdc)₆O·2Me₂NH·8DMF·11H₂O</td>
<td>Zn</td>
<td>Nucleobases: Adenine:Ade and bpdc: biphenyl dicarboxylate</td>
<td>2009</td>
<td>An et al. [29]</td>
</tr>
<tr>
<td>Selective CO₂ sorption</td>
<td>Co₂(Adeo)(CO₂CH₃)₃·2DMF·0.5H₂O</td>
<td>Co</td>
<td>Ade</td>
<td>2010</td>
<td>An et al. [30]</td>
</tr>
<tr>
<td>Drug delivery and imaging</td>
<td>Fe₃O(MeOH)₃(fumarate)₃·(CO₂CH₃)₄·4.5MeOH and [Fe₃O(MeOH)₃(C₆H₄O₈)₃Cl·6MeOH</td>
<td>Fe</td>
<td>Fumarate and C₆H₄O₈ is galactarate</td>
<td>2010</td>
<td>Horcajada et al. [31]</td>
</tr>
<tr>
<td>Therapeutic agent</td>
<td>BioMIL-1</td>
<td>Fe</td>
<td>Nicotinic acid (pyridine-3-carboxylic acid, also called niacin or vitamin B3)</td>
<td>2010</td>
<td>Miller et al. [32]</td>
</tr>
<tr>
<td>Reversible flexible structure; CO₂, MeOH and H₂O sorption</td>
<td>[Zn(GlyAla)₂]·(solvent)</td>
<td>Zn</td>
<td>Peptide, Glycine-adenine</td>
<td>2010</td>
<td>Rabone et al. [33]</td>
</tr>
<tr>
<td>(γ-CD)</td>
<td>K</td>
<td>Saccharides</td>
<td>2010</td>
<td>Smaldone et al. [35]</td>
<td></td>
</tr>
<tr>
<td>(γ-CD)</td>
<td>Rb</td>
<td>γ-CD: cyclodextrins</td>
<td>2010</td>
<td>Smaldone et al. [34]</td>
<td></td>
</tr>
<tr>
<td>Application</td>
<td>BioMOF</td>
<td>Metal</td>
<td>Ligand</td>
<td>Year</td>
<td>Author</td>
</tr>
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<td>---------------------------------</td>
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<td>-------------------------</td>
</tr>
<tr>
<td>4-phenylazoplenol, etc.</td>
<td>CD-MOF-2</td>
<td>Rb</td>
<td>γ-CD</td>
<td>2011</td>
<td>Jeremiah J. Gassensmith et al. [35]</td>
</tr>
<tr>
<td>Highly selective adsorption of CO₂</td>
<td>CD-MOF-2</td>
<td>Rb</td>
<td>γ-CD</td>
<td>2011</td>
<td>An et al. [36]</td>
</tr>
<tr>
<td>Photostable O₂ sensor</td>
<td>Zn₈(Ade)₄(bpdc)₆ · O₂Me₂NH₂ loaded with lanthanide cations (Tb(III), Sm(III), Eu(III) and Yb(III))</td>
<td>Zn and lanthanide</td>
<td>Ade and bpdc</td>
<td>2011</td>
<td>Saines et al. [37]</td>
</tr>
<tr>
<td>Porous</td>
<td>α-CD-MCF</td>
<td>Rb</td>
<td>α-CD</td>
<td>2012</td>
<td>Gassensmith et al. [38]</td>
</tr>
<tr>
<td>Adsorption</td>
<td>CD-MOF-1 and CD-MOF-2</td>
<td>K, Rb and Cs</td>
<td>γ-CD</td>
<td>2012</td>
<td>Forgan et al. [39]</td>
</tr>
<tr>
<td>Drug storage and release or for the immobilization and organization of large biomolecules</td>
<td>Bio-MOF-100</td>
<td>Zn</td>
<td>Ade</td>
<td>2012</td>
<td>Jihyun An et al. [40]</td>
</tr>
<tr>
<td></td>
<td>MIL-151 to -154</td>
<td>Zr</td>
<td>H₄gal</td>
<td>2014</td>
<td>Cooper et al. [41]</td>
</tr>
<tr>
<td>Antibacterial carrier</td>
<td>BioMIL-5</td>
<td>Zn</td>
<td>AzA: azelaic acid</td>
<td>2014</td>
<td>Tamames-Tabar et al. [42]</td>
</tr>
<tr>
<td>Antioxidant carrier</td>
<td>Mg(H₄gal)</td>
<td>Mg</td>
<td>H₄gal</td>
<td>2015</td>
<td>Cooper et al. [43]</td>
</tr>
<tr>
<td>Inclusion and</td>
<td>CD-MOF-1</td>
<td>Na</td>
<td>β-CD</td>
<td>2015</td>
<td>Lu et al.</td>
</tr>
<tr>
<td>Application</td>
<td>BioMOF</td>
<td>Metal</td>
<td>Ligand</td>
<td>Year</td>
<td>Author</td>
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</tr>
<tr>
<td>Loading the drug molecules</td>
<td>MOF-525</td>
<td>Zr</td>
<td>H₄tcpp: meso-tetra-(4-carboxyphenyl) porphine</td>
<td>2015</td>
<td>Kung et al.</td>
</tr>
<tr>
<td>Electrochemical nitrite detection</td>
<td>Al-PMOF</td>
<td>Al</td>
<td>H₄tcpp</td>
<td>2015</td>
<td>Wilcox et al.</td>
</tr>
<tr>
<td>Ammonia uptake</td>
<td>[Zn(ain)(atz)],</td>
<td>Zn</td>
<td>[Zn(ain)(atz)], Hatz: 5-aminotetrazole and Hain: 2-amino-4-isonicotinic</td>
<td>2016</td>
<td>David Briones et al.</td>
</tr>
</tbody>
</table>

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 Sharmin and Fahmina Zafar

*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

References


