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Introductory Chapter: Metal Organic Frameworks (MOFs)

Eram Sharmin and Fahmina Zafar

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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 ($\text{Zn}_4\text{O}(\text{bdc})_3$, bdc = terephthalate) and HKUST-1 ($\text{Cu}_3(\text{btc})_2$, 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 ($\text{Zn}_2(\text{dhbdc})$, dhbdc = 2,5-dihydroxy-1,4-benzenedicarboxylate) with low pressure adsorption of CO_2 , 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 ($7140 \text{ m}^2 \text{ g}^{-1}$) Some examples of MOFs and their applications are given in **Table 1** [1–15].

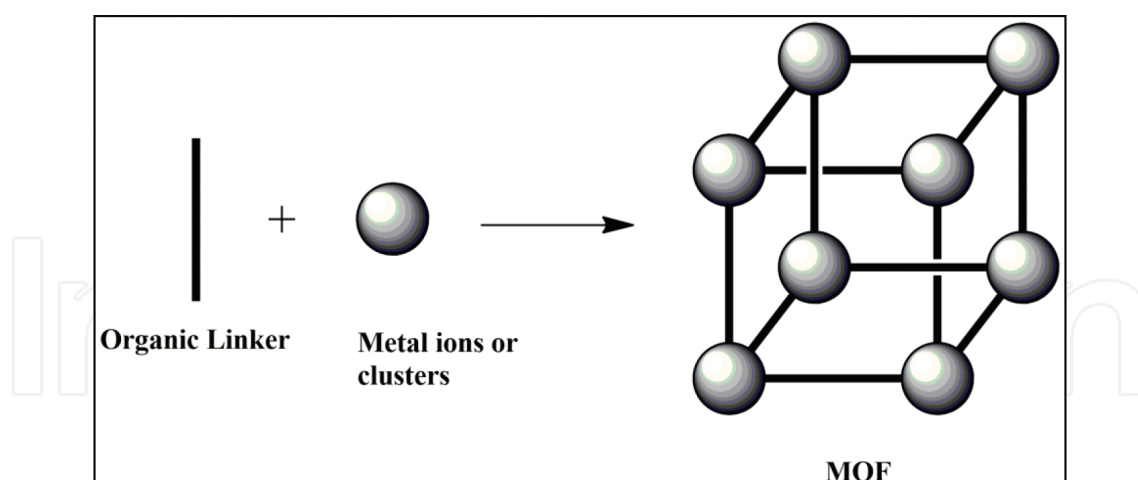


Figure 1. Structure of MOF.

Application	MOF	Metal	Ligand	Year	Author ^{Rf}
Drug delivery	MIL-101 [Cr ₃ O(OH,F,H ₂ O) ₃ (1,4-bdc) ₃ and MIL-100	Cr	1,4-benzenedicarboxylate moieties (bdc) or H ₃ btc: Benzene-1,3,5-tricarboxylate	2006	Patricia Horcajada et al. [4]
Methane Storage	MOF-5 Zn ₄ (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 Cu ₂ (H ₂ O) ₂ (CO ₂) ₄	Cu	H ₃ btc	2006	Rowsell and Yaghi [7]
Adsorption and storage	IRMOF-9 Zn ₄ O(bpdc) ₃	Zn	4,4'-biphenyldicarboxylate (bpdc)	2006	Rowsell and Yaghi [7]
Adsorption and storage	MOF-74, Zn ₂ (C ₈ H ₂ O ₆)	Zn	2,5-dihydroxybenzene-1,4-dicarboxylic acid	2006	Rowsell and Yaghi [7]
–	(In) MIL-68-NH ₂ or IHM-2	In	bdc-NH ₂ ; 2-aminoterephthalates	2011	Savonnet and Farrusseng [8]
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]

Application	MOF	Metal	Ligand	Year	Author ^{Rf}
Soft coupling–deprotection sequence	(In) MIL-68-NH-ProFmoc and (In) MIL-68-NH-Ala-FmocIn *fluorenylmethyloxycarbonyl group (Fmoc), a base-label protecting group for amines	In	Amino acid such as L-proline (Pro-OH) and D-alanine (Ala-OH)	2011	Jerome Canivet et al. [10]
Antibacterial	Cu-BTC(MOF-199)	Cu	H ₃ btc	2014	Rodriguez et al. [11]
Highly potent bacteriocidal activity	Co-TDM	Co	H ₈ tdm: tetrakis [(3,5-dicarboxyphenyl)-oxamethyl] methane	2012	Wenjuan Zhuang et al. [12]
Delivery of nitric oxide	MIL-100(Fe or Cr) and MIL-127(Fe)	Fe, Cr or Fe	tricarboxylate or tetracarboxylate	2014	Eubank et al. [13]
Antibacterial	Ag ₂ (O-IPA)(H ₂ O)·(H ₃ O) and Ag ₃ (PYDC) ₂ (OH)	Ag	HO-H ₂ ipa = 5-hydroxyisophthalic acid and H ₂ pydc = pyridine-3, 5-dicarboxylic acid	2014	Xinyi Lu et al. [14]
Adsorption of CO ₂ over N ₂	Mn ₃ (HCOO) ₆ ·DMF	Mn	3-nitrophthalic acid (H ₂ npta) and 4,4'-bipyridine (4,4'-bipy)	2014	Ying-Ping Zhao et al. [15]

Table 1. Some examples of MOFs and their applications.

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].

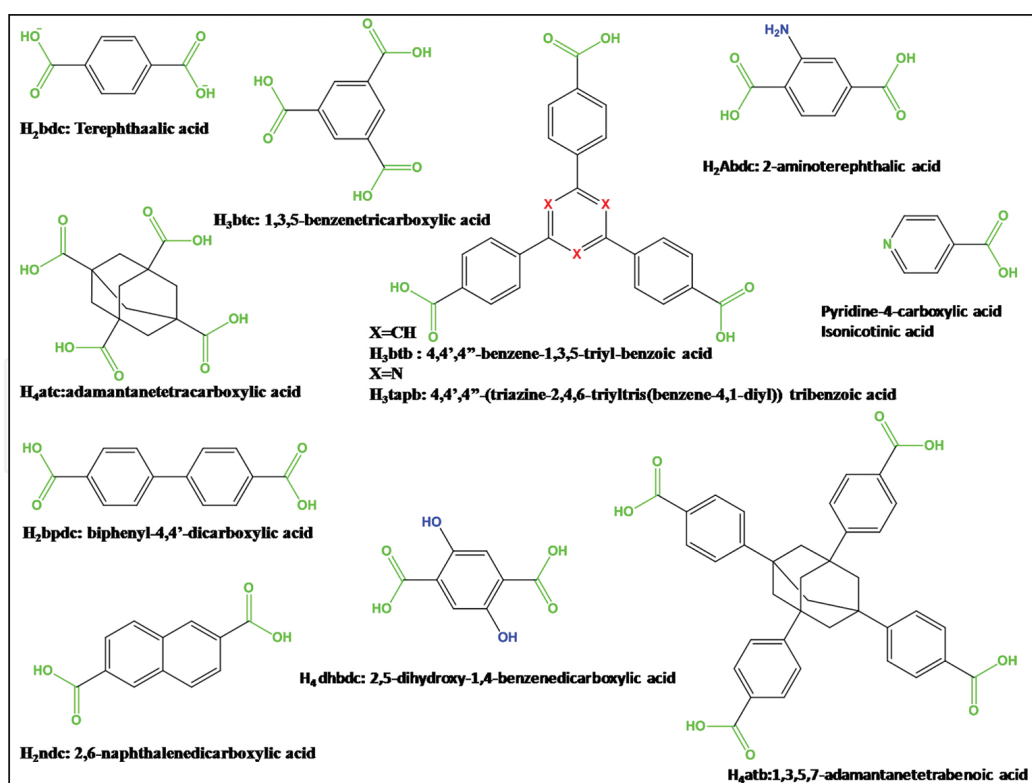


Figure 2. Some examples of organic ligands with carboxylic functionality used for the preparation of MOFs.

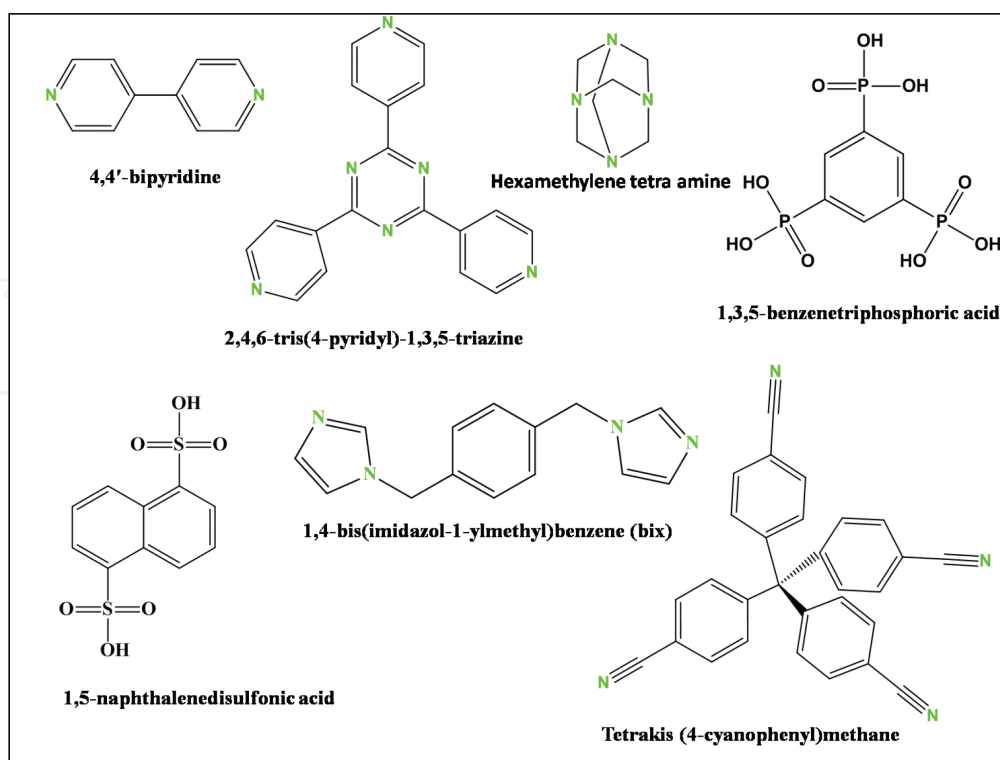


Figure 3. Some examples of ligands containing nitrogen, sulfur, phosphorous and heterocycles used for the preparation of MOFs.

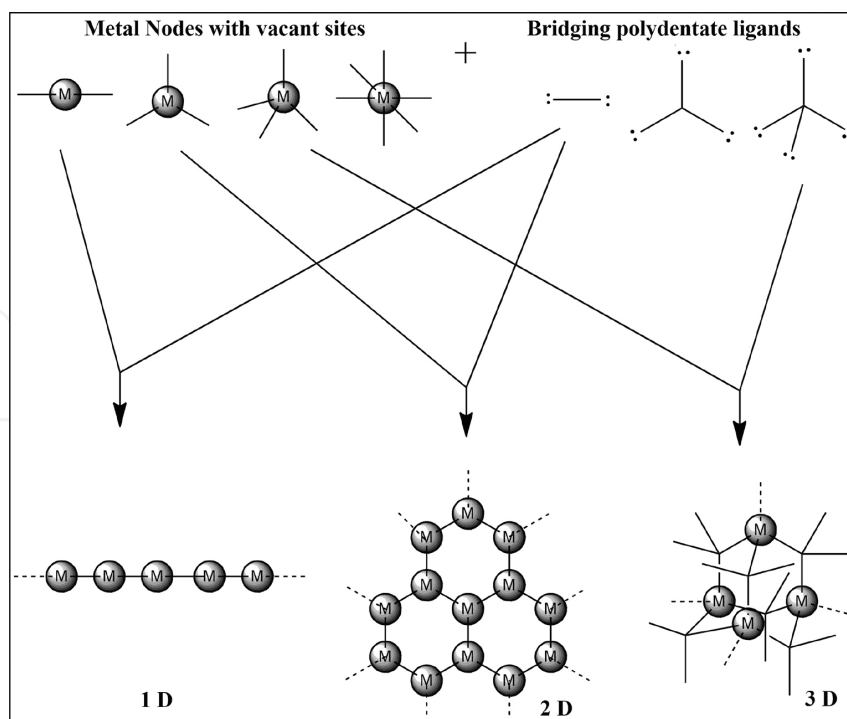


Figure 4. MOFs resulting from different metal nodes and bridging ligands.

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 ^{Rf}
Ar and CH ₄ sorption	[Cu(trans-fum)]	Cu	Fum:Fumaric acid	2001	K. Seki et al [18]
Reversible H ₂ O sorption/desorption	[Ni ₇ (suc) ₆ (OH) ₂ (H ₂ O) ₂ ·2H ₂ O]	Ni	Suc: Succinic acid	2002	Forster et al. [19]
–	[Ni ₇ (suc) ₄ (OH) ₆ (H ₂ O) ₃]·7H ₂ O	Ni	Suc	2003	Guillou et al. [20]
Sorption of more than 30 kinds of guests (e.g. DMF, benzene, etc.); structural change	[Mn ₃ (HCOO) ₆ ·(CH ₃ OH)·(H ₂ O)]	Mn	Formic acid	2004	Wang et al. [21]
Selective CO ₂ and H ₂ sorption	Mn(HCOO) ₂ ·1/3 (C ₄ H ₈ O ₂)	Mn	Formic acid	2004	Dybtsev et al. [22]
Adsorption	Fe ₃ O(MeOH) ₃ (fum) ₃ (CO ₂ CH ₃)·4.5MeOH	Fe	Fum	2004	Serre et al. [23]
1,3-Butanediol sorption	[Ni ₂ O(L-Asp)(H ₂ O)·4H ₂ O]	Ni	Amino acid L-Asp:L-aspartic acid	2004	Anokhina et al. [24]
Enantioselective separation and catalytic	Zn ₂ (bdc)(L-lac)(DMF)	Zn	bdc: 1,4-benzendicarboxylic acid and L-lac:Lactic acid	2006	Dybtsev et al. [25]

Application	BioMOF	Metal	Ligand	Year	Author ^{Rf}
CO ₂ sorption	[Ni ₂ (L-Asp) ₂ (4,4'-bipy)] ·2H ₂ O	Ni	L-Asp and 4,4'-bipy : 1,2-bis (4-pyridyl)ethane	2006	Vaidhyanathan et al. [26]
H ₂ sorption	Co ₂ (L-Asp) ₂ (4,4'-bipy)]·2H ₂ O	Co	L-Asp and 4,4'- bipy	2008	Zhu et al. [27]
Heterogeneous asymmetric catalysts for the methanolysis of rac-propylene oxide	Ni ₂ (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	Cu ₂ (L-Asp) ₂ (bpe)·(HCl) ₂ · (H ₂ O) ₂	Cu	L-Asp and bpe: 1,2-bis(4- pyridyl)ethane	2008	Ingleson et al. [28]
Cation exchange capabilities, including cationic drugs and lanthanide ions	Zn ₈ (Ade) ₄ (bpdc) ₆ O·2 Me ₂ NH ₂ · 8DMF·11H ₂ O	Zn	Nucleobases Adenine:Ade and bpdc: biphenyldicarboxylate	2009	An et al. [29]
Selective CO ₂ sorption	Co ₂ (Ade) ₂ (CO ₂ CH ₃) ₂ ·2DMF· 0.5H ₂ O	Co	Ade	2010	An et al. [30]
Drug delivery and imaging	Fe ₃ O(MeOH) ₃ (fumarate) ₃ · (CO ₂ CH ₃) ₃ ·4.5 MeOH and [Fe ₃ O(MeOH) (C ₆ H ₄ O ₈) ₃ Cl]·6MeOH		Fumarate and C ₆ H ₄ O ₈ 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; CO ₂ , MeOH and H ₂ O sorption	[Zn(GlyAla) ₂] ₂ ·(solvent)	Zn	Peptide, Glycine-adenine	2010	Rabone et al. [33]
	(γ-CD) (KOH) ₂	K	Saccharides γ -CD: cyclodextrins	2010	Smaldone et al. [35]
Inclusion of several molecules (e.g. Rhodamine B,	(γ-CD) (RbOH) ₂	Rb	γ-CD γ-CD is a (chiral) cyclic oligosaccharide	2010	Smaldone et al. [34]

Application	BioMOF	Metal	Ligand	Year	Author ^{Rf}
4-phenylazoplenol,etc.)			composed of eightR-1,4-linkedD-glucopyranosyl (R-1,4-D-Glup)		
Highly selective adsorption of CO ₂	CD-MOF-2	Rb	γ-CD	2011	Jeremiah J. Gassensmith et al. [35]
Photostable O ₂ sensor	Zn ₈ (Ade) ₄ (bpdc) ₆ ·O·2Me ₂ NH ₂] 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 ₄ gal: gallic acid	2011	Saines et al. [37]
Porous	α-CD-MCF	Rb	α-CD R-cyclodextrin (R-CD), comprised of sixR-1,4-D-Glupresidues portrayed in their stable 4C1 conformations	2012	Gassensmith et al. [38]
Adsorption	CD-MOF-1 and CD-MOF-2 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 ₄ gal	2014	Cooper et al. [41]
Antibacterial	BioMIL-5	Zn	AzA: azelaic acid	2014	Tamames-Tabar et al. [42]
Antioxidant carrier	Mg(H ₄ gal)	Mg	H ₄ gal	2015	Cooper et al. [43]
Inclusion and	CD-MOF-1	Na	β-CD:	2015	Lu et al.

Aplication	BioMOF	Metal	Ligand	Year	Author ^{Rf}
loading the drug molecules			cyclodextrins		[44]
Electrochemical nitrite detection	MOF-525	Zr	H ₄ tcpp: meso-tetra (4-carboxyphenyl) porphine	2015	Kung et al. [45]
Ammonia uptake	Al-PMOF	Al	H ₄ tcpp	2015	Wilcox et al. [46]
Highly active anti-diabetic activity	[Zn(ain)(atz)] _n	Zn	Hatz : 5-aminotetrazole and Hain: 2-amino-4-isonicotinic	2016	David Briones et al. [47]

Table 2. Some examples of BioMOFs and their applications.

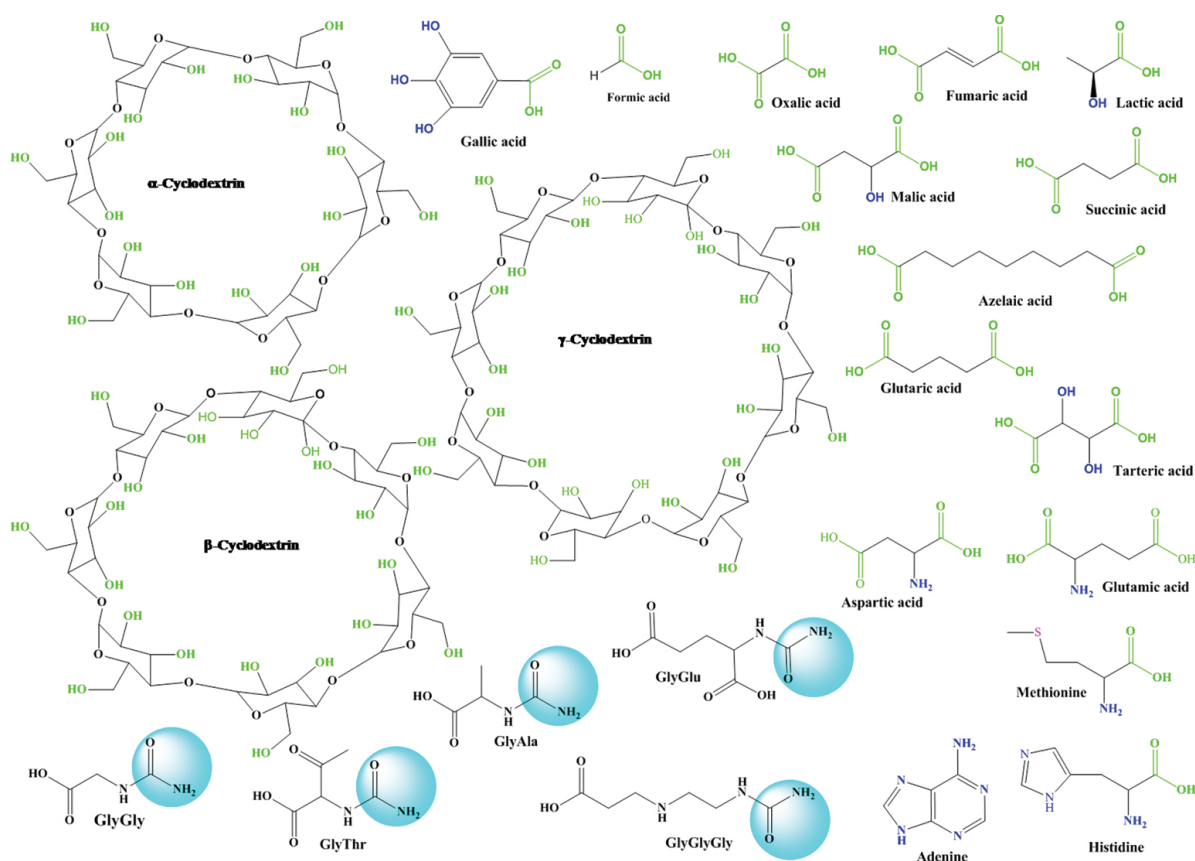


Figure 5. Examples of organic linkers used for the synthesis of BioMOFs.

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 Zafar^{2*}

*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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