

Multifunctional nanoscale metal-organic frameworks-polymer composites for biomedical applications

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Tahir Rasheed^a, Fahmeeda Kausar^b, Muhammad Tuoqeer Anwar^c,
Ayesha Jahangir^d, Muhammad Bilal^e, Hafiz M. N. Iqbal^f

Abstract: Metal-organic frameworks (MOFs) are an emerging class of materials with unique properties such as extensive surface area, good stability, and high porosity, which facilitate their deployment in various fields of science, including nanomedicine. Numerous strategies have been proposed for designing nanoscale MOF-polymer composites with tailored properties. Polymers can be incorporated inside and outside of the MOF pores to prepare such composites. Polymers are directly grafted to the MOF wall via covalent linkages or physical coordination with the host. Though MOFs are associated with drawbacks like unrestrained liberation, placing of biomolecules/drugs, and less resilience under various physical conditions, a set of advantageous attributes have also been noticed, such as tuning capability and pore size of undecorated MOFs. Novel strategies have been developed to improve MOFs' functioning for bio-imaging, cancer treatment, and drug delivery. For this, the introduction of polymers has proved helpful in expanding the functionalities and diversities of MOFs. Owing to the benefits like a controlled release of drugs in response to extrinsic stimuli, boosted inclination towards targeted cells, intensified MOF durability, and increased biocompatibility, MOF-polymer composites are excellent sources of helpful implementation in the biomedical field. This study provides insight into the synthesis and performance of MOF-polymer composite as a novel candidate in the biomedical sector.

Keywords: MOF-polymer composites; Polymeric ligands; MOF self-assembly; Nanomedicine; MOF stabilization.

^a Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia. Corresponding author: tahir.rasheed@kfupm.edu.sa

^b School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

^c 3Department of Mechanical Engineering, COMSATS University Islamabad, Sahiwal Campus, Off G.T. Road, Sahiwal, 57000, Pakistan.

^d University of Sargodha, Sargodha, Pakistan.

^e Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, PL-60695 Poznan, Poland. Corresponding author: muhammad.bilal@put.poznan.pl

^f Tecnológico de Monterrey, School of Engineering and Sciences, Monterrey, 64849, Mexico. Corresponding author: hafiz.iqbal@tec.mx

1. INTRODUCTION

Chemistry research studies have led to the compounds with facile and controllable properties, modifiable porous structure, and unparalleled exterior locality. They are known as metal-organic frameworks (MOFs) that constitute interlinking organic ligands, joining metal-ions/metal-ion aggregates. Unlimited MOF arrangements could be produced owing to the wide range of construction units multifariously. Twenty-thousands compounds have been synthesized and reported in the previous thirty years to up till now due to fast and extensive research studies (Furukawa *et al.*, 2013). Many implications like a storehouse for gas, chemical sensors, drug transportation, liquid/gas detachment, and catalytic process are germane to such compounds following the guest-host chemical approach. Following improved post/

pre-synthesis strategies, architecture complications of MOFs could be identified clearly in the presence of diversified construction units (Yin *et al.*, 2019).

Additional compounds consisting of substructures are affixed at metals/ligand-mainstay. For example, there is also a fair chance for post-synthetic replacement of metals and ligands. Additionally, variant functional groups laid over the ligand's mainstay, constituting several organic ligands residing similar metal connecting abilities, up-ranked intricated multifaced-MOF which have been described in the literature (Mon *et al.*, 2019). Furthermore, non-native moieties were attached to the exterior and interior areas of MOF for these compounds, intensifying architectural complications of composites' fabrication, besides modifying and arranging raw MOFs. These improvements are made to upgrade available characteristics and put external functional groups in MOFs' distinctive family. Presently, available literature can elaborate on the combination of MOF and SiO₂, ribonucleic acid, deoxyribonucleic acid, and enzymes being examples of the biomolecule, polymeric compounds, clusters, NPs' host, and graphene (Shang *et al.*, 2016; Kitao *et al.*, 2017; Yu *et al.*, 2017; Li *et al.*, 2018; Teplensky *et al.*, 2019). In addition, pyrolysis leads to the derivative of MOF carbon composites, where an outstanding level of durability is needed for particular applications (Jiao *et al.*, 2019).

Polymers are considered to be employed for increasing the execution capability of MOF, external

functional groups, inculcating inclination and augmenting the porous structure of MOF. Thus, MOF-polymers are getting great fascination out of assorted MOF-supported compounds. Furthermore, a wide variety of rational implications for guest-host approach could be achieved in consequence of modeling various novel structures with demandable pore size, and, enormously efficient compounds can be utilized given this novel chemical concept. Constructing units of polymers and MOFs has considerable importance for producing various products. This review describes reports from the last decade related to synthesis, stabilization and practical utilization of MOF-polymer composites.

2. FORMATION OF MOF-POLYMER COMPOSITES

Commonly diverse and varied approaches have been offered in the previously reported works as a limelight for the fabrication of MOF-polymer composites. These kinds of compounds are synthesized accompanied by polymers via utilizing the whole porous surface (interior and exterior) of MOF. Reduced inhibited intact communications of polymer (guest) 1 and MOF (host) results in the regulation of polymer. Moreover, covalent bonds could be generated with direct intact grafting of polymers to MOF surface. In addition, an overview of MOF synthesis, properties, and applications is shown in Figure 1 (Bilal *et al.*, 2019; Yang *et al.*, 2021).

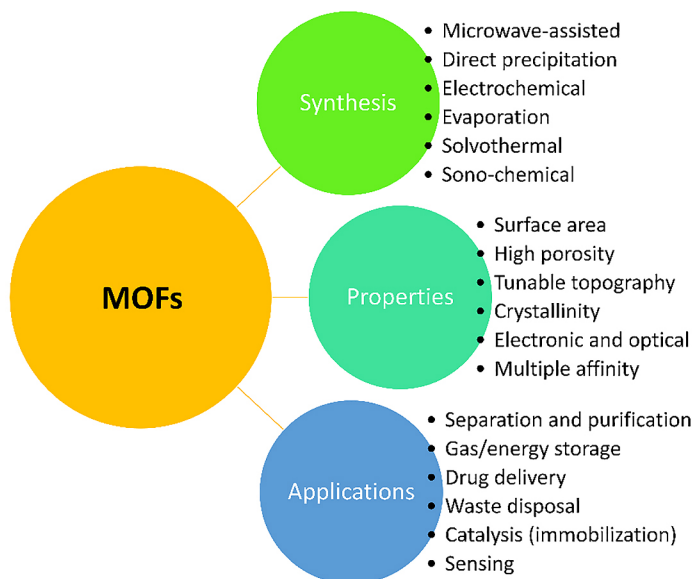


Figure 1. A schematic overview of MOF synthesis, properties, and applications. Reprinted from ref. (Bilal *et al.*, 2019) with permission under the Creative Commons CC-BY-NC-ND license.

2.1. On-site polymerization methodologies

Initially, the foremost technique applied to porous MOF consisted of polymerizing monomers and occurred on-site/in situ. The entrance of the monomer may be in a liquid or gaseous state. After the entry, polymerization can be initiated by a direct reaction between MOF structure and monomers. Other polymerization-initiating factors may be heat, light and chemical initiators. Such monomers can enter the pore via the liquid or gas phase. The ship-in-the-bottle approach is employed for stabilizing the formed polymer in MOF pores, MOF pores are dimensions which are trapped inside due to extended growth of the polymer chains. The polymers are stabilised by producing the sharp intermolecular interactions among the MOF walls and nonnative guest's species. The output of mentioned methodology will be a linear polymer with controlled monomers. To produce different commercial polymers, the initiators driving bulk polymerization are of significance (Cowie and Arrighi, 2007). Firstly, Kitagawa *et al.* employed the initiator-driven polymerization inside the MOFs in 2005 (Uemura *et al.*, 2005). The researcher described and discovered styrene polymerization in the MOFs' pores. They developed a convenient method to produce polystyrene having a lesser polydispersity index (PDI) and higher molecular weight. Due to the confinement factors of MOFs' pores, the radical living species, which play a role in styrene polymerization, have a significant role in polymerization.

Polyacrylonitrile, poly(vinyl acetate) and poly(methyl methacrylate) are vinyl polymers introduced into MOFs due to these research outcomes of this research. The above-mentioned are the polymer with great mono-dispersity due to the enhanced "living radical" lifetime. Cation initiators and anion initiators play a pivotal role in the subsequent growth. For example, 3D-polymer dispersity, like poly glucose can be efficiently regulated by regulating the cationic polymerization in the MOF (Kobayashi *et al.*, 2016). It was also mentioned that polyacetylene is introduced in Cu-based MOF (Uemura *et al.*, 2006). The anionic carboxylate species can also initiate the polymerization of the MOF ligand. The part of MOF itself can be employed for the starting of the polymerization and is mentioned in research studies.

Researchers are focusing on inventing methods of producing MOFs having an active site without employing the external initiator, which will initiate the polymerization itself. However, such innovative

methods of in situ polymerization has been adopted by other researchers as well. Moreover, porous polymer production is initiated using MOF templates. The property that leads to the high carbon dioxide capacity and carbon dioxide or nitrogen gas selectivity is achieved by forming the 1,2-diethynylbenzene (DEB) in-situ polymerization, which is later employed to divide the MOFs in hydrophobic chambers as cited by Wang's group. Heating the pure styrene for many hours at 65 °C in the MOF-5 crystal produced uniform polystyrene as reported by Matzger (Ding *et al.*, 2016). Sun *et al.* (2018) studied that the ferrous metal ion, active redox ion present inside the MOF surface, can initiate the in-situ polymerization. Iron-supported MOF involves the process of transferring electrons between ferrous ions and is called Fe-BTC (alternatively known as MIL-100(Fe); BTC-1,3,5 — benzenetricarboxylate; MIL— materials of the institute of Lavoisier) and through anaerobic oxidation monomer dopamine is polymerized into polydopamine (PDA).

In another study, it is reported that MOFs containing no active redox metal can produce the PDA by treatment with aqueous ammonia, which permits dopamine to diffuse into MOF pores. (a method of using double solvent (Peng *et al.*, 2018). The advantages and disadvantages of in-situ polymerization are also considered in such polymerization. Firstly, the in-situ polymerization of the MOF can be applied to many frameworks. All such in-situ polymerizations are feasible in MOFs due to chemical and thermal stability of MOFs (Ding *et al.*, 2016).

Moreover, the 3D polymer chains are the output when the MOF template of 3-dimensional pores is involved in situ polymerization. A porous free-standing polymer will be output as studied and first reported by the Kitagawa group. A porous polypyrrole was produced by using 3-D MOF called HKUST-1(Hong Kong University of science and technology $\text{Cu}_3(\text{BTC})_2$) as the sacrificial template (90 m^2/g) (Uemura *et al.*, 2009). By using a similar sacrificial template, the high-quality polyaniline with a porous structure (986 $\text{m}^2 \text{g}^{-2}$) was prepared by Lu *et al.* (2014).

In-situ polymerization is considered as easy to drive. Still, the disadvantages of the in-situ polymerization are also considerable, e.g., the in-situ polymerization may become uncontrollable in a few cases. The evenly and homogenous diffusion of the monomers in the MOF template is also questionable in in-situ polymerization. In some conditions, the composite show inhomogeneity diffusion in the

template of MOF (Zhang *et al.*, 2015). However, blockage of the pore might occur if the in-situ polymerization occurs on the surface of MOF pores. The selection of the initiator or chemical species must be studied with MOF. Moreover, the choice of the initiator or the chemical specie for in-situ polymerization must be studied earlier. Decomposition of the MOF is observed if the reaction between the initiator and MOF becomes unfeasible.

2.2. Application of polymeric ligands for synthesizing MOF

The term polyMOFs is also coined by Seth and Chen after introducing the methodology of producing the MOF polymer composite by another method in 2015 (Allen *et al.*, 2013). In this study, pre-designed polymeric ligands are added to the polymer naturally within the framework upon crystallization, which is employed in MOF synthesis. The properties of the polymer and the MOFs are inculcated in the poly-MOFs, like the processing ability of the polymer, enhanced chemical stability of the MOF, porosity and crystallinity. Cohen group reported that repeating the 2-amino-1,4-benzene carboxylic acid and diacyl dichloride with many numbers of alkyl space produces the first polymer-based ligand.

Many kinds of IRMOF-1 (isoreticular-IR) analogue is produced when the polymeric ligand is isolated by heating in the presence of a salt of zinc ion (Allen *et al.*, 2014; Zhang *et al.*, 2016; Ayala *et al.*, 2017). By employing a different kind of MOF architecture, several polyMOFs can be formed by this group of researchers. The polyMOF analogue having stability like UiO-66 (University of Oslo) is produced by employing the 1,4-benzenedicarboxylic acid subunit polymeric building block. The structure of the UiO-66 polyMOF is rooted on the $Zr_6O_4(OH)_4$ chain, which is interconnected by poly-2,5-bis(hex-x-en-yloxy)terephthalic acid(pbdca-u) ligand (Schukraft *et al.*, 2017). The presence of alkyl spacer in pores results in the less surface area (200-400 m^2/g), and in some cases, no surface area of composites is mentioned. This group also studies the expansion of the polyUiO-60 structure.

Biphenyl and triphenyl analogs of 1,4-benzenedicarboxylic acid ligands are extensions of polymeric ligands. The output structures obtained are poly UiO-67 and polyUi-68 (Gu *et al.*, 2019), with the highest surface area in the range of 1626 m^2/g . The colloidal stability, size, and shape of polyMOFs are controlled by different strategies (Tanabe and Cohen,

2011; MacLeod *et al.*, 2017; Ayala *et al.*, 2019). For instance, polymeric benzene dicarboxylic acid ligand having 8 methyl spacer (pbdc-8a) is polymerized with modified alkene polyethylene glycol (PEG). The block co-poly IRMOF and block co-polyUiO-66 were yielded by reacting the new polymeric ligand and metal precursors. The size, shape and colloidal stability of MOF-polymer are varied depending on the molecular weight of PEG and loading level.

Several MOF composites are produced using polyMOFs with new and promising methodologies. The advantage of employing the polymeric ligand is that we can control the polymer composition and molecular weight. Moreover, loading is under control in MOF. In the near future, the MOF processability is upgraded by an innovative approach which can control the size, colloidal stability, and shape of MOF. MOF plays a vital role in synthesizing the polymeric ligand, but the MOF crystallization conditions must be examined periodically. The employment of the polymeric building is challenging due to the kinetic and entropic challenges compared to the MOFs, which form crystalline and organized polymer using ligands. Moreover, polymeric ligands may cause irregular structure and entangled chains. It is promising to use the MOF because it forms ligands and small ligands whose structures are organized and crystallized.

Considering the safe use of the polymeric ligand, it may lead to an intractable and amorphous solid. The architecture of MOF can be checked by studying the molecular weight and function of polymeric ligands. Chemists are keenly interested in the yielding of new polyMOF structures like analog to IRMOFs, $[Zn_2(BME-bdc)2(bpy)]_n$ (BME-bdc- 2,5-bis(2-methoxyethoxy)-1,4-benzenedicarboxylate; bpy = 4,40-bipyridine) and UiO. Chemists are keenly interested in MOF-polymer production with alkyl spacers or long alkyl-chain with the versatility of MOF framework.

2.3. Reactive ligands surface grafting with polymer covalently adopted post-synthesis

Grafting the polymer synthetically on MOF ligand is also an innovative way to study MOF-polymer. Using the reactive functional group, double-bonded carbons, nitride, amino, hydroxyl, chlorine, bromine and -CHO MOFs can be synthesized (Nagata *et al.*, 2015). MOF can be synthesized from ligands. The polymer grafting in MOF is done by employing

synthetic techniques to synthesize organic compounds. As mentioned in the literature, many polymers are grafted onto the MOF surface by using this methodology. This methodology also justifies the chemical properties, new functionality, and reactivity of grafted polymer. The external surface of the UiO-66-NH₂ is grafted with poly(N-isopropylacrylamide) (PNIPAM), a thermo-receptive polymer (Liu *et al.*, 2014). The amines of 2-amino-1,4-benzene dicarboxylate ligand undergo a reaction with polymer at a large surface area to make its diffusibility possible into MOF pores. For the under-control production of polymer, the practical opening and closing of MOF structure must be adequately studied. In the thermo-responsive polymer, the transition temperature is crucial for regulating the opening and closure of the MOF structure. Under the polymer transition temperature, the MOF remain open for the entrance and exit of guest particle. Above transition temperature, the guest species movement is halted, polymer coils up, and pores get closed.

The grafted polymer and NH₂-MIL101(A1) are yielded by possessing the transition property that changes from hydrophilic to hydrophobic upon application of temperature (Li *et al.*, 2018). The MOF crystal dispersion or aggregation in solution is controlled by the team. The methodologies mentioned above of grafting are easy to use. Polymer appendages are done using multi-step complex methodologies, as noted by Li and co-workers. It was the initial approach to combine click chemistry, ATRP (atom-transfer-radical-polymerization) and PSM (post-synthetic modification) (Zimpel *et al.*, 2016). The modification of the amine of UiO-66-N₂ having alkynyl functionality is done by click reaction, which will functionalize the surface of MOF with azide-terminated tetra butyl methacrylate (PtBMA). The UiO-66-NH₂@PtBMA is yielded by the reaction of Ui-66-NH₂@tPMAA (PMAA = polymethacrylic acid) with trifluoro-acetic acid.

The polyanionic coating upgrades the MOF dispersion in water and interactions with amines at the surface of enzymes. Moreover, the immobilization of the pectinase enzyme by interacting with the specific amines is also improved. The enzyme immobility can be due to the extraordinary matrix of the MOF-polymer composite. The pectinase in free form and immobility causes the upgraded pectinase with more excellent stability and wide temperature and pH range. Moreover, the storage and recycling ability is also improved compared to its non-mobilized counterpart. The chemists are looking forward

to innovative polymer grafting methodologies in which MOF's limitations and functionality are applied. For instance, the use of unsaturated ligands on the surface of MOF is reported to be more advantageous. On the surface of MOF, the amidation reaction on carboxylate functional group is carried out. Moreover, the Fe-BTC nanoparticles (NPs) are also synthesized by this group. The carboxylate-based MOF can be produced if the PEG5000 and Stp 10-C form a covalent bond, and the framework surface can be enlarged by involving a number of carboxylate-based functionalities (Hou *et al.*, 2016).

In aqueous media, the colloidal stability of MOF NPs is the objective of the study. An easy and universal method was mentioned by Dong *et al.* in their research. Solvent-containing monomer is soaked in versatile MOFs, like MOF-5, UiO66, UiO-66-NH₂, MIL-125(Ti), IRMOF-3, ZIF-8 and [Cy(BTCA) 0.5(H₂O)₃]2H₂O(BTCA = 1,2,3,4-butanetetracarboxylic acid). After some period, the sample is radiated with the help of UV light. The porosity of MOF is undisturbed by using polymer brushes. Polymer brushes will significantly upgrade MOF's thermal and chemical stability (Zhang *et al.*, 2014). The immobility of the initiator and pre-modification is not applied to the photo polymerization approach.

The polymer grafting range by post-synthetic approach has been less reported. The property of MOF can be altered with less effort and in a short period. Due to such MOF, new building blocks can be designed. Several properties can be upgraded by coating, like chemical stability, colloidal stability, the processability of MOF and aimed performances of MOF. The bio-based products are the aim of studies. The production of biomolecules keeping the temperature and pH in view are significantly critical. The versatile properties can be achieved by external grafted coating (Zimpel *et al.*, 2016). The cell transfection and specificity or imaging purpose inside the cell is due to tagging of several species like fluorophores (Hou *et al.*, 2016). The area of improvement is also present in post-synthetic grafting reaction at the MOF surface, and it becomes limited due to the demand for reactive ligands. The limitations of the applied coating of MOFs are being studied universally (Ejima *et al.*, 2013). Approaches are made to control polymer density, thickness and desired properties without changing the surface of MOF (Uemura *et al.*, 2010). Changing in polymer thickness or surface affect the porosity and performance of the polymer. Chemists are making substantial endeavours to explore novel approaches in this regard.

2.4. Preformed polymers' inception for post-genesis

This strategy has been applied as the substitute when MOFs could not be achieved using polymeric ligands, or the polymerization could not be proceeded due to unfavorable parameters for MOFs' exterior or interior pores. Polymer-melt processing demonstrated this approach and was presented by Uemura and coworkers for the 1st time to the extent of our information. Additionally, polyethylene glycol (PEG) was reported (Le Ouay *et al.*, 2018) along with poly(methylpropylsilane). It was heated at an elevated temperature (more than m.p. of polymer) to combine pre-synthesized MOF and pre-synthesized polymer (Kitao *et al.*, 2015). Polymeric strings invaded MOF by passing across pores and were confirmed by applying molecular-dynamics (MD) simulations. Following the indicated crucial work, considerable literature revolves around solvent/melt-based polymer embodiment. Owing to the feasible market approach, volatile nature and greater compactness because of amine, carbon dioxide could be collected directly by polyethyleneimine (PEI) combined with MIL-101(Cr) and was reported by Darunte and team members (2016). In addition, polymers' entrance to MOF was restricted by implementing branched structures. Therefore, diffusibility was not facile. Despite many disadvantages, applying the given approach could prove auxiliary to explain the genesis of MOF-polymer composites.

2.5. Polymers surrounded with MOF self-assembly

Eventually, polymers decorated wholly with MOFs are acquired using different approaches and described here. MOF could enclose the polymers in its core. On the other hand, MOF furnishes its interior surface with polymers' attachment. Blocked pores of MOF and heterogeneous polymeric properties could be diminished with the help of this technique, some of the antecedent predicaments. Biomimetic mineralization directs the application of this strategy to elevated dispersity and heavy Mw biopolymers and biomolecules. MOF fabrication involves the immediate addition of a capped-protein, polyvinylpyrrolidone, succeeding Zeolitic-Imidazolate-Framework-8 (ZIF-8) that submerged proteins inside (Lyu *et al.* 2014; Liu *et al.*, 2018). Figure 2 and Figure 3 show the strategy for the ZIF-8-based catalyst development by the deposition-redispersion method (Liu

et al., 2018). An composite architecture includes crystallization of submerged capped proteins, while 2-methylimidazole linking agents connected nodes of zinc metal, thus constructing MOF. In addition, ZIF-8 embraced protein in the form of bovine albumin-serum and was presented by Doonan and team members to expand this ideology (Liang *et al.*, 2015). For this purpose, MOF production was carried out through the head-on incorporation of uncapped biomolecules. Following this trend, ribonuclease A, oligonucleotide and ovalbumin have been extensively studied to clear apprehension. The volume and area of biomolecules dynamically explain the genesis of novel chambers in MOF and confirm the existence of biomolecules. As a result, MOFs guarded biomolecules from the unfavorable external conditions.

3. POLYMER INCORPORATION FOR IMPROVING MOF STABILIZATION

Generally, stability properties are of great concern for the in-field utilisation of MOF because of less strong coordination bonding. Simultaneous application of heat and pressure, MOFs experience state transformation, architecture shattering and liquefaction in the existence of varied participating moieties. Considering the implication of compounds, thermal, mechanical, and chemical stabilizations are essential to be elaborated. The description of the stabilization of MOFs is explained as follows:

3.1. Chemical stabilization

The consequence of ligand-protonation is its putrefaction and transfiguration. Also hydrolyzation of metal needs to be attained in the presence of water, hydrogen and hydroxyl ions inhabiting in the solution form which are responsible for the chemical stabilization of MOFs. Swift transition in H₂O was observed. For instance, vivid structure synthesized using copper-peddled wheel aggregates mutually attached through ligands like 1,3,5-benzenetricarboxylate (BTC) transformation. The porous-crystalline framework could be shattered when hydrolyzation of copper oxide bonds engenders the separation of RCOO-ligands (Todaro *et al.*, 2016). Improvements were implemented for the chemical stabilization of MOF by introducing several techniques succeeding many decades. Coordination bonding of ligand is achieved, and metal is reinforced employing construction units that enhance the bonding sites, and it is a general method for modeling MOFs with good durability (Ding *et al.*, 2019).

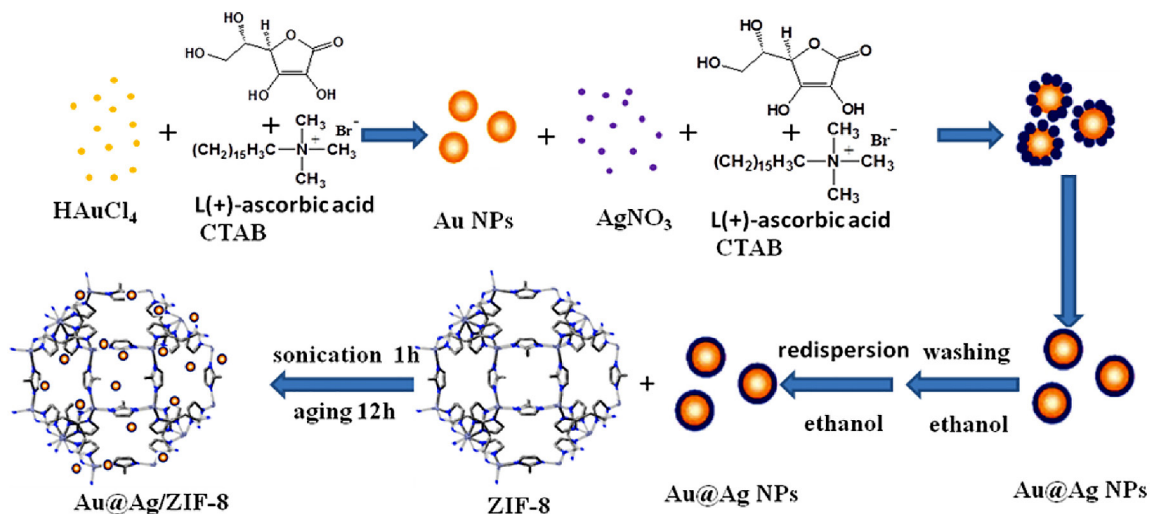


Figure 2. The strategy for the Au@Ag/zeolite imidazolate framework Zn(2-methylimidazole)₂·2H₂O (ZIF-8) catalyst by the deposition-redispersion method. Reprinted from ref. (Liu *et al.*, 2018) with permission under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

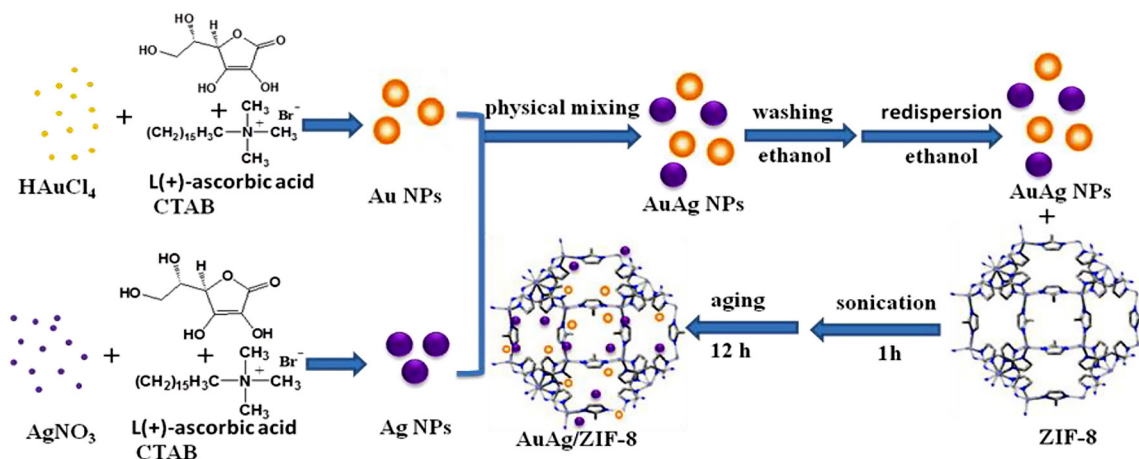


Figure 3. The strategy for the AuAg/ZIF-8 catalyst by the deposition-redispersion method. Reprinted from ref. (Liu *et al.*, 2018) with permission under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

Pyrazoles, triazoles and tetrazoles are the ligands with elevated pK_as. However, some MOFs' rods were detected that exhibit lower pH, e.g., -COOH. The compound that can show resistance to saturated NaOH for twenty-four hours at higher temperatures (100°C) is pyrazolate-supported porphyrinic-Ni-MOF (PCN601) which was reported by Wang and coworkers (2016). Conventionally, polymers' surface laminating materials could be synthesised using several versatile techniques (Takashima *et al.*, 2018). ZNBT and HKUST-1 indicated augmented angles of 130°, and MOF-5 was detected with 128° in the presence of H₂O following post-lamination.

Furthermore, the exterior surface of ZNBT was noticed to reduce from 1845 m² to 1417 m² per gram, HKUST-1 experienced a reduction from 1544 m² to 1515 m² per gram, and armored coating of MOF was lessened from 3195 m² to 2871 m² per gram, each specie was observed for three days in 55% RH environment. Nevertheless, the same parameters were scrutinized to cause the reduction of MOFs' exterior surface to a minimum (zero) when exposed without coating (Zhang *et al.* 2014).

Using copper ions with an acidic nature furnished active-sites, while trimethylsilyl cyanide (TMSCN) and C₆H₅CHO underwent cyanosilylation in

liquid-state and catalytic reactions place in laminated HKUST-1, because of the ability of PDMS to permeate in lamination. At temperature 333 kelvin, the procedure was executed for forty-eight hours $\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_3$. When uncovered cuprous ions pores were charged with H_2O , the yield swiftly reduced to 19.6% even within two min, owing to the presence of saturated- H_2O vapors. However, the parent yield was 48.2% for pristine-MOF after catalysis. In the moisture and dry climate, 49.1% and 50.1% yields of painted-MOFs were conserved, respectively. Although reusability and the improved catalytic functionality could be attributable to humidity for a long duration, the boosted functionality was strongly deemed reusability and the improved catalytic functionality could be attributable to humidity for a long duration, the boosted functionality was strongly considered stabilized hydrolysis. In addition, only thermally resistant MOFs at elevated temperatures (235°C) could be appropriate for this methodology.

Many other techniques have been introduced to enhance the MOFs' stabilization and durability. Organosilicon (-SH) hydrophobic polymer, for instance, was painted over HKUST-1, ZIF-67, NH_2 -MIL-125 (Ti) and MOF immersed in $\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_3$ solution by Qian and team members with the purpose to observe variation in carbon dioxide storage efficacy after five days (Qian *et al.*, 2017). Thirty days' observation revealed that the applied ambiance of sodium hydroxide (pH = 12) and sulfuric acid (pH = 2) for 24 hours did not affect the appearance, crystallinity, and pore sizes of HKUST-1@PDA-SF loaded with 16.2% polymer, except increment in contact angle. In the consequence, these details would be very beneficial to instigate facile improvements to stabilize MOFs' chemistry, avoiding any remarkable degradation in reachable exterior areas and leading to proficiency in useful implications with the addition of hydrophobic-polymers to MOFs' surfaces (interior and exterior).

3.2. Mechanical stabilization

Material science has described a little regarding the mechanical durability of MOFs, one of the excellent properties, although several research works have been reported for enhancing the chemical stability of MOFs. Polydopamine (PDA) was attained spontaneously with submerged dopamine's polymerization, succeeding preparation of M2-NDISA. In contrast, M referred to nickel, cobalt, magnesium,

and zinc ions. At the same time, NDISA stands for naphthalene diimide salicylic acid that acted as a ligand, a member of MOFs' class with the same design and meso-porosity. With the application of dynamic-vacuum at 150°C temperature polymer injection, reachable MOFs' exterior-areas were noticed with excellent increment from five to fifty (Peng *et al.*, 2019).

At ambient temperature, the forerunner MOFs' architecture was detected vulnerable to collapsing notwithstanding separation from the mother-liquor. The π - π communication entanglements among surrounding ligands were considered responsible for the shattered architecture of M2-NDISA, and were proved from molecular-dynamics (MD) measurements. Destruction of π - π communications made upgraded porous-compounds that could resist and endure intense vacuum and elevated temperature resulting from the addition of PDA. Furthermore, reflectivity FT-IR was diffused promptly, and transgendered observations employing carbon monoxide as a probing agent caused enhancement in achievable metal-positions along with increment in hole sizes and inner exposed layer.

Presently, Uemura and coworkers utilized DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane) as supporting rods betwixt 2-dimensional zinc-carboxylate sheets, protecting $[\text{Zn}_2(\text{BDC})_2(\text{-DABCO})]_n$, the MOF, polystyrene (guest). Fig 4b demonstrates the restricted building of shattered and densely packed structure which arranges the vicinal sheets firmly at positions in the turbo-stratified state stabilized by a polymer. Moreover, thermal therapy was applied to eliminate DABCO columns and was observed after simultaneously polymerizing styrene (Le Ouay *et al.*, 2019). In addition, the implications demanding elevated pressure could remarkably enhance MOFs' designing architecture and have been less elaborated on in the literature.

3.3. Thermal stabilization

MOFs exhibit a predominant property of thermal stabilization along with mechanical and chemical stabilization. The available attachment sites on MOF-node and bonding capability between ligand and metal are considered as the most critical factors like remaining stabilization kinds. To improve MOFs' thermal-stability, parameters perform a vital character together. Investigations were carried out as thermogravimetric-analysis (TGA)

under elevated temperatures for decomposing compounds. However, numerous carboxylate-supported connection sites bonded with higher central metal atom nodes of tetra- and tri-valent metal-cations (Canivet *et al.*, 2014), azolate-supported linking agents joined with divalent metal cations (Colombo *et al.*, 2011).

For enhancing MOF composites' thermal stabilization, Shen and coworkers (2015) for example, reported graphene-oxide (GO) for the protection of USTA-16 (University of Texas San Antonio), a $\text{CoC}_6\text{H}_5\text{O}_7$ -supported MOF. Powder X-ray diffraction (PXRD) analysis proved that 340°C temperature would be needed to decompose USTA-16 when GO-19 (GO = 19 mg) was laminated over it. In comparison, only 139°C temperature can decompose it without coating. No remarkable intensified work has been found due to the lower thermal degradation temperature of externally added polymer and less noticeable reports about MOF-polymer decomposition temperature (Yang *et al.*, 2019). Therefore, advanced investigations related to this horizon can make many useful discoveries and inventions possible.

4. UTILIZATION OF POLYMERS FOR INTENSIFYING MOF FUNCTIONALITY

Previously, MOF-polymer composites have efficiently been manipulated with several techniques that could be employed in many beneficial branches. Furthermore, because of the incredible variety in host designing, the past reported methodologies are enough to support the complete apprehension of MOF-polymer composite stabilization ideology. Therefore, more endeavors would be needed to intensify the fabrication techniques. This segment has been devoted to explaining some typically reported research.

5. ION AND MOLECULE IDENTIFICATION USING MOF-POLYMER COMPOSITES

For probing the targeted small ionic moieties, MOF-polymer composites have been implemented in chemical sensors. Different observable variations like hindrance, mass expansion and contraction, radiance, and color confirm tested moieties. For a long time, there have been assorted composites prepared for utilization in chemical sensors. MOF-453, for example, was submerged within a thick vitreous-matrix that quenched the emission

intensity intending to prob ferric ions residing in aqueous-solution applying MOF-polymer, constructed by Du and team members (Liu *et al.*, 2017). Following this concept, carboxylates consisting of ligands i.e., 2-aminoterephthalic acid and 1,3,5-triyltri-p-aminobenzoic acid were placed as linkers to connect different zinc oxide nodes of MOF-453, prepared hydrothermally which is an optimal technique. The red-shifted emission spectra of MOF-453 unveiled the enhanced detection ability for ferric ions, attributable to novel bonding between PUA and MOF.

Moreover, chromium, cobalt, silver, nickel and cuprous ions were capable of quenching emission intensity partly. In contrast, ferric ions were efficiently quenched due to radiance to a maximum level, even in a composite sensor's existence of these combative ions. Therefore, it is strongly expected that these investigations would be highly fruitful for implementing MOF-polymer composites in chemical sensing, observing surroundings, etc.

6. Biomedical implications of MOF-polymer composites

A considerable amount of literature is available, referring to a wide range of potential applications of MOFs in biomedicine (Figure 4) (Ma *et al.*, 2021). Although MOFs display some disadvantages like unrestrained liberation, placing of biomolecules/drugs and less durability under physical conditions, various merits have also been noticed, for instance, tuning capability and pore size of undecorated MOFs. MOFs have been fabricated not only through alterations in available spongy materials but also novel strategies have been presented to improve the functioning of bio-imaging, treatment of cancer photothermally and drug delivery-like applications. For this purpose, polymers have been introduced that considerably enhance a variety of MOFs. Owing to the benefits like regulated liberation of drugs in response to extrinsic stimuli, boosted inclination towards particular cells, intensified MOF durability and increased biocompatibility, MOF-polymer composites are excellent sources of application in the biomedical-branch.

In favor of the biomedical field, various excellent techniques are deployed for preparing MOF-polymer composites. Quick drug transport and remediation of tumor photothermally could be achieved through collegial interactions of polymers

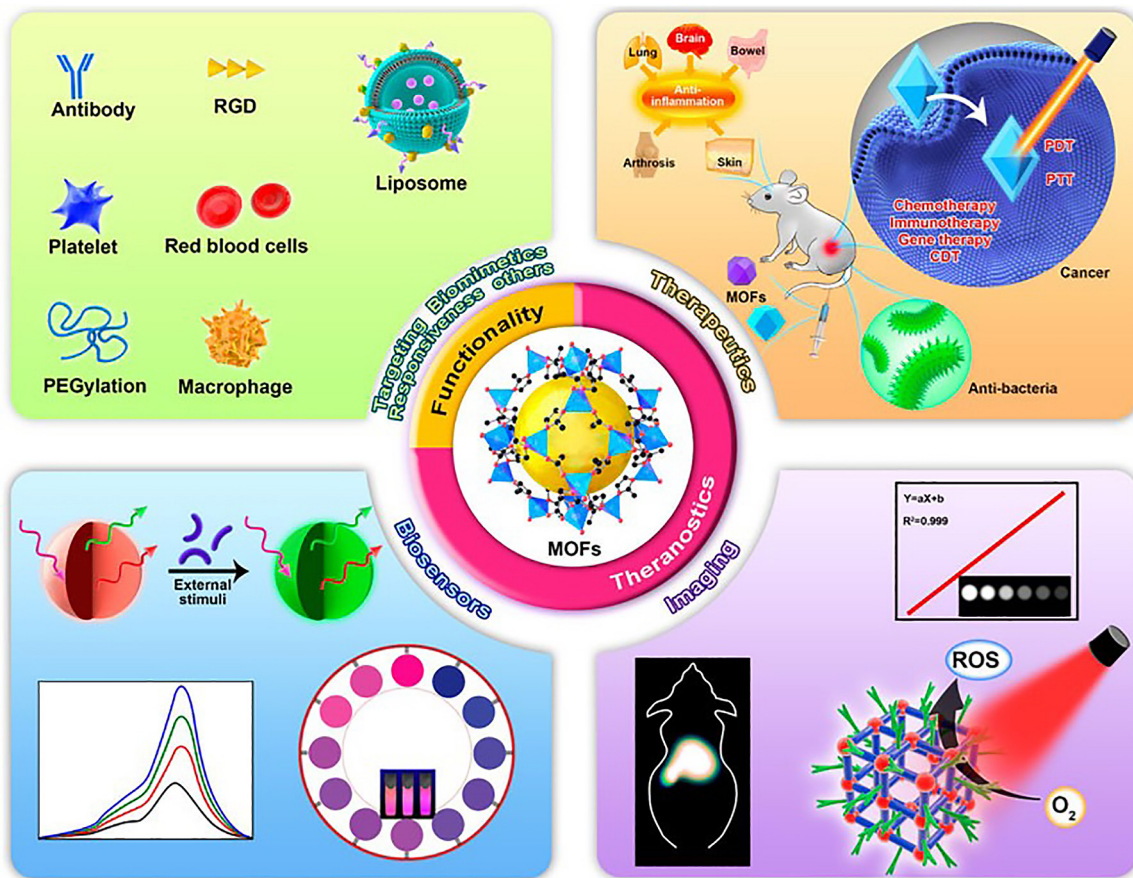


Figure 4. Schematic illustration of functionalities and biomedical applications of metal-organic frameworks (MOFs). Reprinted from ref. (Ma *et al.*, 2021) with permission under the terms of the Creative Commons Attribution License (CC BY).

and MOFs. Ibuprofen was carried via MIL-101 and iron-supported MIL-100, and Horcajada and co-workers were the foremost to demonstrate in favor of MOF application in delivering drugs (Horcajada *et al.*, 2006). Later, they applied a core-corona (MOF-polymer) approach to estimate the impact of lamination of exterior area of MOF employing polymers, numerous derivatives of MIL, such as MIL-101, -100, -89, -88, and -53 were also scrutinized for imaging-capabilities and efficient drug transmission (Horcajada *et al.*, 2010).

Some endeavors were made to enhance tissue identification and bio-dispensation obtained using chitosan and poly(ethylene-glycol) like polymers adhered to the exterior area of MOF. The corona-polymers revealed only advantageous impact of restriction to proliferating clusters of nano-sized crystals. However, researchers presented various cosmetic compounds such as benzophenone 4 and 3, NH_2CONH_2 and $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, etc. They encapsulated

a vast number of anti-viral/cancer medicines, for example, doxorubicin (DOX), cidofovir (CDV), azidothymidine-triphosphate (AZT-TP) and busulfan (Bu). Moreover, deliberating securing characteristics like bio-adhesion and enzyme degradability presented in applying chitosan over MIL-100 nanoparticles to enhance oral drug conveyors (Hidalgo *et al.*, 2017).

There is a wide range of versatile reports following many previous literary compositions. Poly-aniline (PANI), for instance, was painted over fabricated UiO-66 nanoparticles. Colon cancer could be treated by utilizing engendered UiO-66@PANI composite (Wang *et al.*, 2016). The procedure of polymerization exhibits dual tactics: (1) MOF adsorbed monomer due to the existence of electrostatic communication that was supported with monomer comprising a solution in which MOF was placed. (2) Further execution of polymer synthesis was achieved utilizing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidizer

in the reaction mixture. Furthermore, the produced composite with favorable size was scattered in the water while illuminating with 808 nm laser light. Later, various characteristics were determined photothermally and were confirmed to cause the death of virulent cells through hyperthermia. Afterwards, researchers investigated colon cancer by employing UiO 66@PANI internally to the tumor while phosphate buffered saline was used as a solvent. Moreover, cell identification of polymers was augmented through lamination of utilized polymers (Kim *et al.*, 2019).

Ligands have many fascinating properties like photo-responsiveness, biocompatibility, and durability owing to the existence of interlinking porphyrin rings with clusters of $Zr_6(O)_4(OH)_{12}(H_2O)_6$ of discriminated PCN-224 and MOF, and have been

presented here. At ambient conditions, anticancer drug DOX was introduced on PCN-224 through absorption by soaking for twenty-four hours after preparation of PCN nanoparticles. Afterwards, hyaluronic acid (HA) was implemented to cover exterior area bio-compatibly. Polymers furnished the restriction of drug spillage prior to cell-transfection and selectivity for aimed cancerous parts. Electrostatic forces held the adjoined polymer and zirconium together, leading to coordinated bonding and communications between polymers and MOF. Nevertheless, the applicable compounds remarkably increased in variety when polymers are treated with MOFs, as MOFs are accepted as valuable utilization in bio-medical science as drug carriers. A summary of different applications of MOF-polymer composites is represented in Table 1.

MOF-polymer used	Application/Function	References
NCO-MOF-453	To prob ferric ions	Liu <i>et al.</i> , 2017
BTC-MIL-100, BDC-MIL-101	Drug delivery	Horcajada <i>et al.</i> , 2006
PEG-MIL-88, PEG-MIL-89	Drug delivery, imaging capabilities	Horcajada <i>et al.</i> , 2010
CS-MIL-100	Oral drug-conveyers	Hidalgo <i>et al.</i> , 2017
UiO-66@PANI	Colon-cancer treatment	Wang <i>et al.</i> , 2016
HA-PCN-224	Cancer therapy	Kim <i>et al.</i> , 2019

Table 1. Application of MOF-polymer composites.

7. CONCLUSIONS

Rapid development in nanoscience and nanotechnology approaches has enabled the design and fabrication of nanoscale MOFs-based composites with multifunctional attributes for a range of scientific and technological applications. As has been inspected in this work, MOF-polymer composites with exceptional features, such as the controlled release of drugs in response to extrinsic stimuli, increased inclination towards targeted cells, intensified MOF durability and increased biocompatibility, render these nanoconstructs as excellent candidates for applications in the biomedical field. To date, many MOF-polymer composites with structural diversity and unique characteristics have been synthesized via different fabrication techniques. These hybrid materials are likely to retain the individual benefits of each constituent and offer unprecedented advantages over the use of a single system, further expanding the potential prospects for multiple biological applications.

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Conflict of interests

The authors declare no conflicting interests

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