



Review article

Metal-Organic Polyhedra (MOPs) as emerging class of metal-organic frameworks for CO₂ photocatalytic conversions: Current trends and future outlook

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ABSTRACT

Metal-Organic Polyhedra (MOP) is a relatively new class of metal-organic frameworks, and their budding application as photocatalysts for catalytic conversion of CO₂ with high activity and specificity has been reported in the last five years. However, challenges such as catalytic stability, the deactivation of active sites, and reusability concerns limit their industrial application. To mitigate these challenges, post-synthetic modifications (PSM) of MOP have proven useful without significantly altering the catalytic activity of the metal-organic framework. PSM can occur at metal centres, organic linkers, and via salt metathesis/ion exchange. These three scenarios are discussed, and useful photosensitive modifiers are highlighted. This study also highlights the potential for homogeneous catalysts to form chemical bonds with or within heterogeneous MOPs to improve CO₂ transformation to CO and formic acid with 131 h⁻¹ and 76 h⁻¹ turnover frequencies, respectively. There is a surge in published articles on the application of functionalized MOPs in energy storage, sensors, and membrane separation in the form of hydrogels, dendrimers, hybrid composites and other heterostructures. This suggests the enormous potential of MOPs as building blocks for porous materials. Hence, the development of stable MOP via one-pot synthesis techniques and industrial-scale applications in green energy production and environmental remediation should be further investigated.

1. Introduction

Metal-organic-based materials are a growing class of composite materials developed when metal ions and multitopic organic linkers with the correct coordination numbers interact [1,2]. Many self-assembled materials have been produced by interacting with metal ions and organic molecules [3]. MOPs have gained massive attraction lately because they can be applied in numerous scientific developments [4,5]. However, compared to other industrially relevant

metal-organic-based composites like zeolites, the thermo-chemical and hydrothermal stabilities of MOPs have been the significant challenges for relevant applications such as gas separation, ion exchange, water treatment, biomedical applications, photocatalysis, etc. [6–9]. Since coordination complexes are unstable, especially in an aqueous environment and other processes that include solvation, future research should address stability issues of MOPs in solution and solid states.

MOPs with large surface areas and other adaptable physicochemical features for photocatalysis have reportedly been produced by the

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interaction of many organic building blocks and appropriate metals [10]. Along with the traditional hydrothermal/solvothermal procedures, there are alternative ways to prepare MOPs, such as mechanochemical, electrochemical, microwave, and sonochemical techniques [11,12]. The development of multimetallic complexes is rapidly replacing monometallic complexes in the field of coordination chemistry. Multimetallic coordination complexes have been produced in large quantities thus far [11]. Metal-organic polyhedra are recent multimetallic coordination complexes with clearly defined topologies (MOPs). MOPs are distinct, porous structures that function at the molecular level and exhibit complex surface chemistry due to their reactive surface sites (Fig. 1).

The advancement of scientific research adaptable for CO₂ recovery/capture/separation and re-use has been deemed essential to lessen atmospheric pollution and address the threat of global warming as carbon dioxide emissions rise. Reaching net zero CO₂ emissions, where anthropogenic events/activities even out or lead to a net reduction of CO₂ in the atmosphere, are best-case scenarios for environmental sustainability and protection. Direct utilization techniques, like mineral carbonation and CO₂-improved exploration of crude oil, naturally adapt their processes for prolonged CO₂ storage and work towards overall negative emissions. Manufacturers of beverages, fire extinguishers, foaming agents, and gas propellants use CO₂. Utilizing CO₂ indirectly by converting it into useful chemicals is also an alternative to direct utilization. To achieve CO₂ transformation with high turnover frequency, both heterogeneous and homogeneous catalysis require the development of highly efficient, selective and robust catalysts. In particular, photoactive catalysts that use visible light to transform CO₂ into useful hydrocarbon products are becoming more crucial for solving energy and environmental issues.

This comprehensive review captures the five-year journey in developing the budding class of metal-organic frameworks (metal-organic polyhedra- MOPs), post-synthetic modification strategies to achieve stable heterostructures and improved structural properties and highlights their emerging application in CO₂ conversion. Advances in MOP synthesis, post-synthesis modifications, and prospects were holistically discussed.

2. Synthesis of metal-organic polyhedra (MOPs) and post-synthesis modification

MOPs appear similar to well-known coordination cages developed by many research groups, such as the Fujita and Stang groups, in terms of morphology and structure [13–16]. MOPs are a subcategory of these cages that may be described as having strong coordination linkages

typically made of metal-carboxylates and intrinsic porosity in the solid state. With a polyhedral nature and structural characteristics that set them apart from other MOFs, MOPs show vast and adjustable structural chemistry [10]. The primary distinguishing structural features of MOPs include: (1) It has one interior cavity that is reachable through windows in the cages; (2) It has two distinct surfaces (interior and exterior surfaces); (3) modular solubility, and (4) It has orthogonal reactive sites that are directional, finite and distributed across the interior and exterior surfaces (i.e., organic moieties and metal sites) [17].

2.1. Overview of conventional MOP synthesis

Material scientists/chemists have paid close attention to the self-assembled coordination polyhedra, which not only showcase the elegance of chemistry and the art of synthesis but also offer insight into possible uses at the cutting edge of materials science and chemistry. MOPs are highly significant due to their capacity to operate as catalysts for chemical transformation, bioprocess microenvironment mimics, and stabilizers of reactive species and metastable compounds [18]. Numerous variables, including the kinetics of crystallization—which should result in nucleation and crystal growth, reaction time, temperature, solvent type, organic ligand, and metal ion types, node size and structural characteristics, and counter ions presence; all affect the synthesis of MOPs and other MOFs [19]. Ligand and metal salt solutions are often mixed to create MOPs in solvent media.

Solid-state synthetic techniques have been applied in certain instances despite challenges with single crystal development [20]. The process of slowly evaporating the reaction solution has been widely employed in the growth of metal-organic architectures. Often, metal-organic frameworks are created at high pressure and temperature via solvothermal/hydrothermal processes [21]. While the basic ideas behind building the simplest platonic polyhedron are well known, many obstacles still exist in synthesizing novel and stable MOPs. The use of secondary building units (SBUs) for the development of rigid polyhedral frameworks with paddle-wheel cluster have been explored to address these challenges (Fig. 2) [22,23]. Other alternative synthetic techniques have been developed in recent years, including electrochemical, microwave-assisted, mechanochemical, and sono-chemical techniques [24]. These techniques are quicker, less expensive, and generate high-purity coordination compounds.

MOPs were reportedly prepared by the solvothermal process using Cp₂ZrCl₂ and tetramethyl terephthalic and formic acid as precursors, producing a rhombohedral MOP [25]. Other metals such as Mo, Rh, Cu, and Zn have also been reported to synthesize paddle-wheel type MOPs [22,26]. MOPs architecture contains building units (such as the

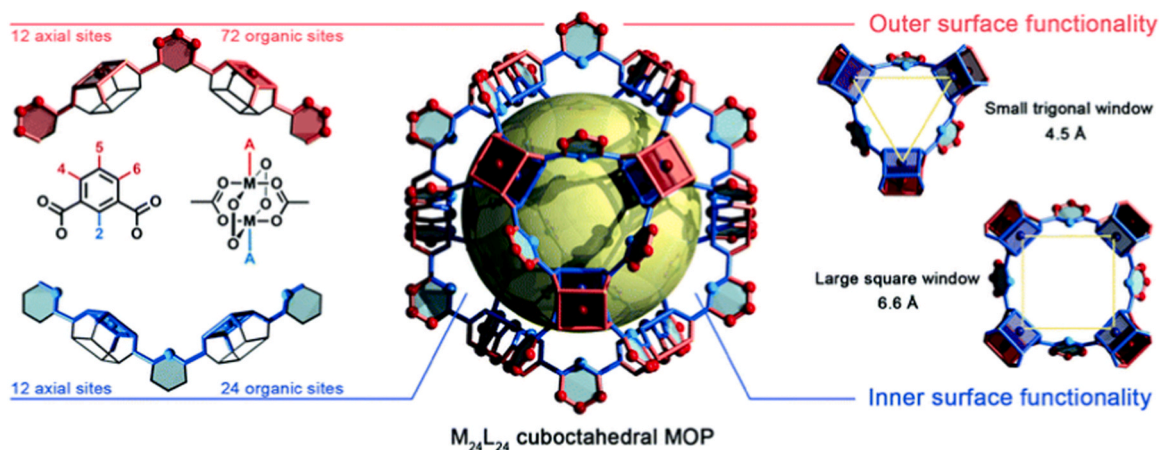


Fig. 1. The typical M₂₄L₂₄ metal-organic polyhedra's interior and exterior orthogonal active sites are shown schematically. MOP structure reveals several organic functional groups and axial open-metal sites (Left). Trigonal and square windows provide access to the cage's interior hollow (right). Reprinted with permission from [10].

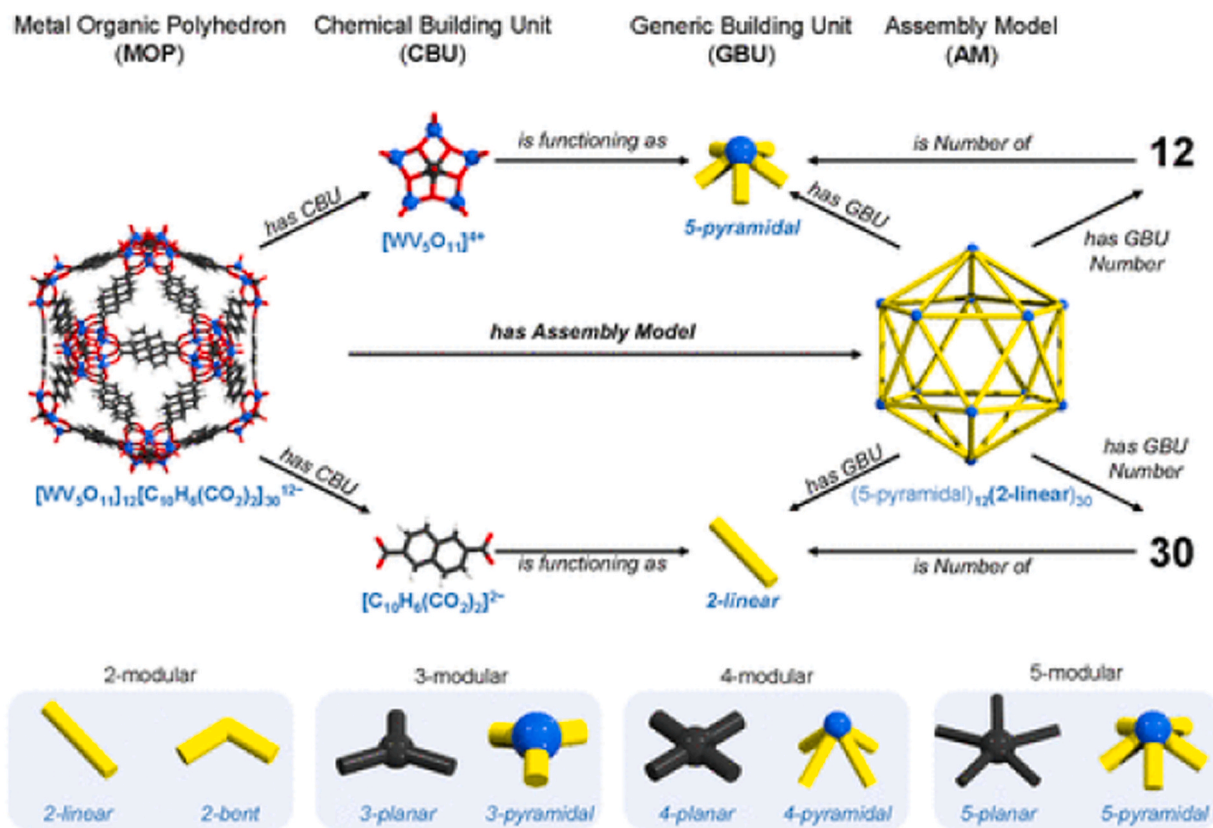


Fig. 2. The relationships among assembly models, MOPs, CBUs, and GBUs (four main kinds of GBUs). Icosahedral MOP $[WV_5O_{11}]_{12}[C_{10}H_6(CO_2)_2]_{30}^{12-}$, made up of 12 inorganic $[WV_5O_{11}]^{4+}$ CBUs functioning as "5-pyramidal" GBUs and 30 organic moieties $[C_{10}H_6(CO_2)_2]^{2-}$ CBUs functioning as "2-linear" GBUs [23].

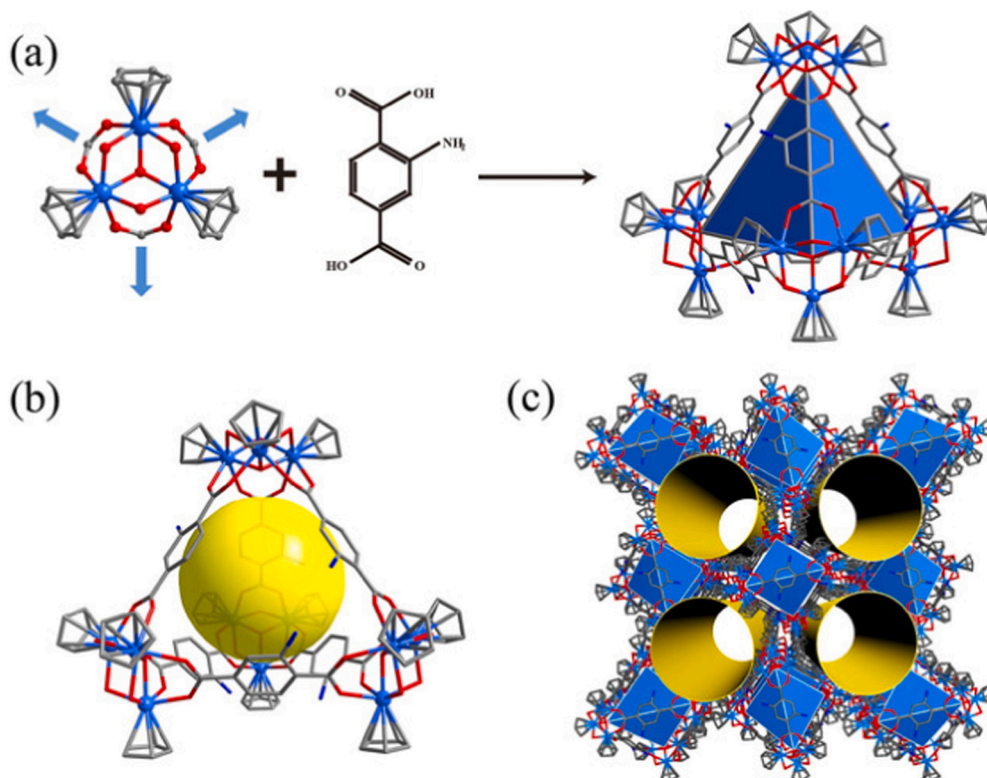


Fig. 3. (a) Zr-MOPs are constructed through the slow hydrolysis of Cp_2ZrCl_2 , which results in a trinuclear Zr-cation polyhedron bridged by BDC/NH₂-H₂BDC ligands, (b, c) crystal structure and packing mode of Zr-MOPs, respectively [28].

paddlewheel) connected by identical moieties derived from four-connected cages with planar vertex alignment where all links are equivalent (quasiregular) [27]. In the case of polyhedral structures, the augmentation process is known as truncation, and there are three possible polyhedral structures: The truncated octahedron with 6 squares, the truncated cuboctahedron with 12 squares, and the truncated icosidodecahedron with 30 squares [22]. Authors have used 1,4-benzenedicarboxylate (BDC) with 180° (straight) links to generate an infinite periodic structure.

Similarly, 1,3-benzenedicarboxylate (m-BDC) with 120° between functional moieties can serve as SBUs for a finite truncated cuboctahedron structure with 12 linked paddlewheels and many other molecular frameworks that have been designed using these principles [11]. Furthermore, the in situ method was first reported by Liu et al. to develop isostructural supramolecular structures of the coordination tetrahedra of Zr-based MOPs (Fig. 3). Bis(cyclopentadienyl)zirconium dichloride was hydrolyzed in water and carboxylate acid to form a trinuclear ligand-bridged cluster, which resembles a 3-connected secondary building unit (SBU) with pyramidal geometry that creates a suitable platform to construct coordination polyhedral [28]. Solvent medium plays a huge role in the development of MOPs, i.e., the solvent's reactivity, solubility, and redox potential must be considered because the solvent significantly influences the reaction's thermodynamics and activation energy.

2.2. Stable MOP synthesis via self-assembly

The self-assembly technique spontaneously develops more complex structures from simpler ones [29]. MOPs that are stable in an aqueous medium are important in coordination chemistry. Material scientists' main challenge is designing soluble MOPs with chemical and thermal

stabilities [30]. The nodes, or metal-organic bonds, which result in either protonated organic linkers or hydroxide-ligated nodes, are the chemically vulnerable points in MOPs. The acid solution may protonate linkers, while the basic solution speeds up the production of hydroxide-ligated nodes [7,10,31]. Thus, choosing the right metal clusters and organic moieties is very sacrosanct to successfully preparing stable MOPs (Fig. 4).

According to Pearson's hard/soft-acid/base concept, hard/soft bases combined with hard/soft metal ions often produce stable metal-ligand complexes. In contrast to the monodentate model complex, $[\text{Pd}(\text{py})_4](\text{OTf})_2$ (py = pyridine), Fujita's group showed that the ligand exchange rate ($k_{\text{obs}} = 1.9 \times 10^{-7} \text{ s}^{-1}$) is substantially slower in a cuboctahedron MOP made up of 48 Pd(II)-pyridine in close interaction [32]. Progressively stable supramolecular structures have been developed by improving the strength of the metal-organic interactions in sphere-in-sphere structures instead of ring-in-ring structures [33]. According to the kinetics of the ligand exchange of self-assembled $M_{12}L_{24}$ spherical complexes, there are three steps to the multicomponent self-assembly (Fig. 5). Although selecting suitable metal ions and organic linkers played the most significant roles in producing stable MOPs, processing conditions/variables may also impact the stability of MOPs.

In summary, the increased bond strength between metal and ligand, the use of suitable counter anions with water-soluble substituents or functional groups with charges during self-assembly, the introduction of organic linkers with chelating functionalities, post-synthesis modification techniques, and the use of hyaluronic acid are a few simple and affordable ways to synthesis thermo-chemically stable MOPs [10]. The utilization of "inert" metallic species during self-assembly is a common strategy for producing MOPs that display good stability. Another approach involves using pre-synthesized, kinetically locked components

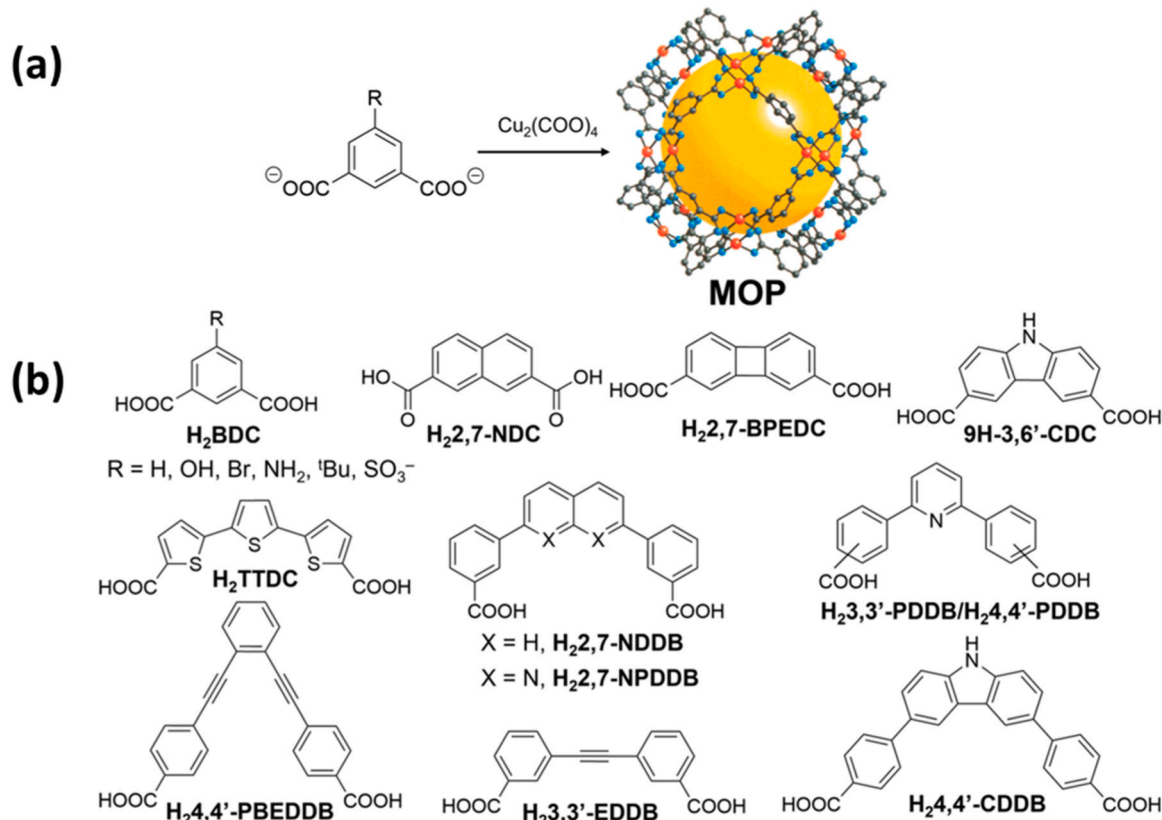


Fig. 4. (a) Conventional self-assembly method for MOPs using metallic cluster and 5-substituted benzene 1,3-dicarboxylate (ditopic organic acid linkers); (b) Several types of ditopic organic acid linkers used to generate different MOPs. Adapted from Samanta [11].

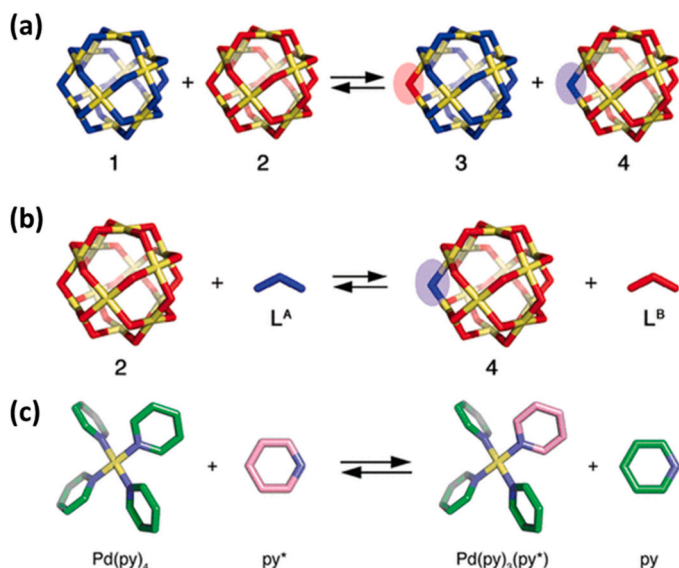


Fig. 5. (a) Shows the exchange of ligands between complexes 1 and 2; (b) the exchange of ligands between complexes 2 and L^A ; (c) the exchange of ligands between $[Pd(py)_4]^{2+}$ and free pyridine.

Adapted with permission from Sato et al. [32].

to build advanced structures. In that respect, hard bases often create very strong complexes with metallic elements positioned towards the top periodic table. This is because the interaction between metal and ligand is electrostatic (or ionic) for alkaline earth, alkali metals, and lanthanides (with filled d-orbitals). Due to the enhanced ligand field energy, transition metal ions often lead to the formation of stable metal-monodentate ligand complexes [34].

2.3. Stable MOP synthesis via post-synthesis modifications

In contrast to pristine MOPs, stable MOPs can be created via post-synthetic procedures because they have functional moieties attached to the outer surface that protect the metal ions from being attacked by water or other chemicals [35]. The structural fragility that made the early MOPs, such as those based on Cu(II), susceptible to degradation by water, heat, reactive species, or acids/bases is the primary disadvantage

associated with MOPs [36]. These difficulties may be addressed through surface functionalization of MOP's interior and exterior surfaces. Post-synthesis modification might be categorised based on the targeted subunit and the chemistry used in each instance (Fig. 6). Researchers have been able to use more effective chemistries to create functionalized MOPs for a variety of applications [36–38]. The invention of novel modifiers and the formation of more durable cages with MOPs based on Cr(II), Mo(II), Rh(II), or Zr(IV) have facilitated progress in stable MOP development.

2.3.1. Modification at metal centres

Through the ligand-exchange method, Zhou's group showed that it was possible to react to the equatorial locations in Cu(II)-based paddlewheel MOPs [39]. With soluble metal-organic polyhedra, they showed how the replacement of bridging ligands creates novel MOPs with improved characteristics. The insertion of organic binding agents with properties that vary from the initial MOP may enhance the size and stability of the MOP [39,40]. After the MOP is formed, the equatorial metal linker is not "blocked," and post-synthetic techniques can take advantage of their dynamic reactivity further. Modifying MOPs by substituting the respective linkers with different moieties containing the dicarboxylate group made it possible to take advantage of the reversible nature of MOPs and create stable functionalized isostructural MOP [41, 42]. The two main driving forces behind this post-treatment approach are the displacement of linkers and the precipitation of new MOPs from the reaction medium. Cage topology was altered by choosing a replacement ligand with the proper bending angle for ligand exchange (Fig. 7). As a result, they changed their original lantern-type cages into cuboctahedral cages and octahedral cages [39].

Recently, Su and Furukawa presented Rh(II)-based MOPs, claiming that these materials exhibited remarkable thermal and chemical stability [43,44]. Strong intermetallic Rh-Rh connections and chemically inert equatorial regions in the paddlewheel worked together to increase stability. Surprisingly, despite the dirhodium paddlewheel's equatorial orientation being "chemically locked," its axial metal sites remain extremely reactive without distorting the nodes. As a result, it's easier to host a wide variety of nucleophiles at the axial metal sites [44]. N-donors are the most well-researched of these nucleophiles. However, others, such as S-donors, P-donors, and O-donors, can also bind with these sites [17]. This study opened the door for further investigation into the molecular functionalization of MOPs' open-metal sites.

Consequently, coordinating linkers with various polarities, charges,

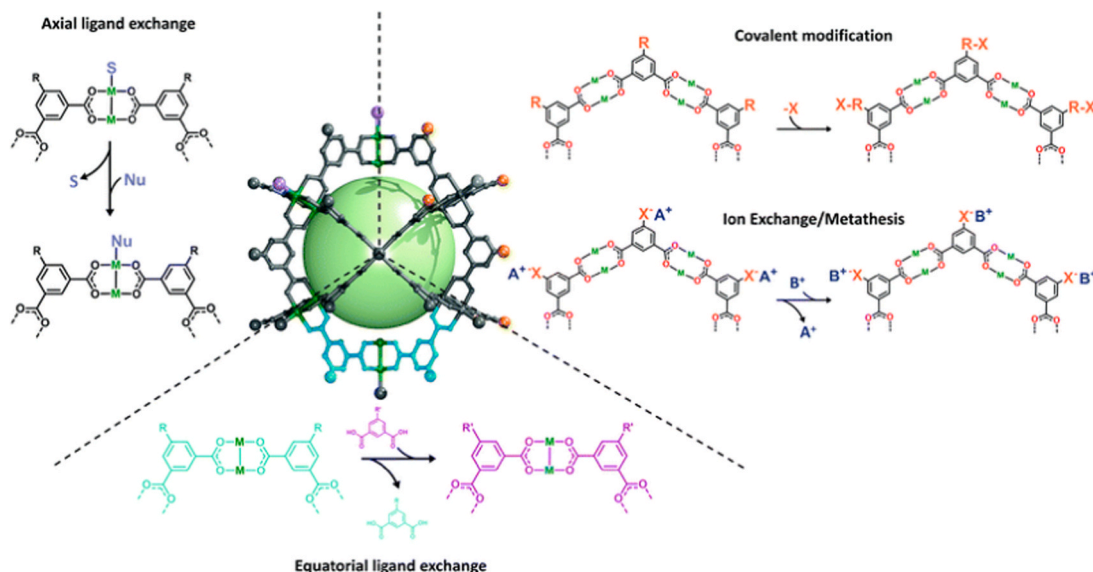


Fig. 6. The typical $M_{24}L_{24}$ metal-organic polyhedra's surface reactivity is shown schematically. Nu is a nucleophile, and S is the solvent.

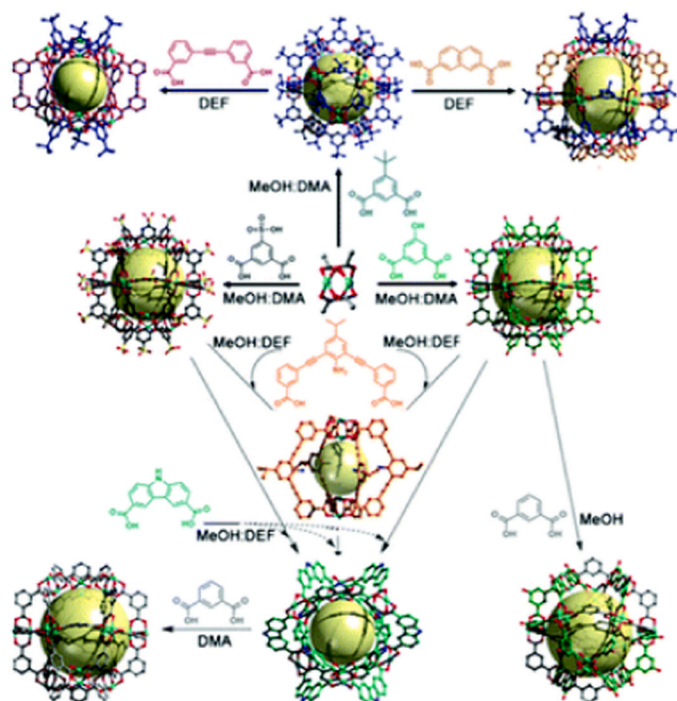


Fig. 7. Linker-exchange mechanisms are illustrated schematically as modifying the exterior surface of MOPs. New ligand(s) react in excess with MOP in an appropriate medium at ambient temperature.

Adapted with minor modifications from Li and Zhou [39].

and chiralities may be functionalized at the axial locations of MOPs. As a result, inherent physicochemical characteristics, such as hydrophilicity, solubility and chirality, may be modified in a reversible and controlled reaction without negatively impacting the porous structure of the material [10,17]. By attaching the appropriate pyridine derivatives to the open-metal sites, solubility adjustments of several MOPs were possible in weakly polar solvents (i.e., diethyl ether), halogenated solvents (i.e., dichloromethane and chloroform), polar aprotic solvents (i.e., dimethylformamide and dimethylsulfoxide), and protic (i.e., water and alcohols) [45]. By anchoring (up to twelve) pyridinyl nucleophiles, a coordinative solubilizer technique can change the surface characteristics of insoluble MOP platforms, increasing their solubility. On the other hand, their solubility can be altered by anchoring organic substrates to MOP surfaces with established solubility profiles.

The hybrid character of MOP surfaces is interesting because it gives these metal-organic building blocks a distinct orthogonal platform for separate and irreversible attachments while preserving the other interior and exterior active sites.

2.3.2. Modification at organic linkers

As a result of MOP supramolecular nature and complexities of MOP heterostructure, in comparison to organic molecules, post-treatment of MOPs at their organic sites is hampered by two significant issues. First and foremost, the functional groups inside the organic binders must remain active under the process conditions for cage formation, either in solvothermal couplings in basic solutions or crystallization at ambient temperature [46,47]. Secondly, the reaction conditions that can be used for covalent functionalization are those that do not impact the structure's other components, particularly the highly susceptible equatorial metal-COO bonds [48,49]. Thankfully, progress in organic-based synthesis has led to the development of several techniques to rearrange, cleave or assemble covalent bonds on delicate MOP substrates. Alkene polymerization, click chemistry (azide-alkyne cycloadditions), and condensation reactions (e.g., production of imine, amide, or ester bonds) have been the main focuses of covalently driven post-modification of

MOPs (Fig. 8) [35,50–52].

Researchers must create alternate paths to increase the variety of peripheral moieties that are useful for and can withstand cage synthesis conditions to increase the adaptability of MOPs further. Due to their nucleophilicity and affinity for metals, organic linker moieties containing primary amine or carboxylic acid groups have been challenging to integrate into MOP heterostructures [53]. Using ligands containing functional groups with steric hindrance with no coordinative tendency is one approach to get around these problems. It has been reported that the interior cavity of a lantern-shaped MOP known as OMe-CuMOP(L)-NH₂ was functionalized via direct assemblage of Cu(II) and a linker with free NH₂ groups [53,54].

Two conflicting approaches have been discovered to overcome the nucleophilic behaviour of free NH₂ groups during MOP preparation; both involved temporarily preventing undesirable reactivity with masking agents [10]. Furukawa et al. [55] reported a procedure that prevented the axial reactivity of Cu(II), which allowed them to be the first to add free amino groups to the MOP surface. They created the first-ever M₂₄L₂₄ NH₂-functionalized MOP by taking advantage of copper(II) acetate's affinity for nitrogen donors to mask the axial sites with large monodentate supplementary ligands. Recently, cuboctahedral Rh(II)-based MOPs with 24 attached NH₂ and COOH moieties were synthesized for the first time using a two-step synthesis that involved temporarily masking the linker moieties during cage assemblage, accompanied by chemoselective demasking [56]. Since the protective compounds and the demasking process can be modified to mitigate challenges regarding the stability of MOPs and compatibility of reactive functional groups, these two examples presented above provided the foundation for integrating reactive groups at the surface of MOPs, even if they contain amine groups.

Furthermore, other methods for synthesizing stable MOPs via surface functionalization with suitable organic linkers/moieties include the use of hard metals that will not react with these susceptible groups, leading to what is called NH₂-tagged MOPs (i.e., Zr(IV)-based MOPs) [57]. Researchers have also prepared stimuli MOPs (srMOPs) that respond to stimuli like light, temperature, and/or solvent changes by adding stimuli-sensitive moieties (i.e., azobenzene groups attachment) to the MOP framework [58–60]. In our opinion, the aforementioned illustrations show that careful adjustments of organic subunits and covalent bonding interaction are the most effective post-synthetic methods for modifying and transforming MOPs into specialized and stable heterostructures.

2.3.3. Modification by salt metathesis/ion-exchange

A different kind of reaction based on salt metathesis can post-synthetically modify MOPs with a charged backbone. The counter ions on the surface of molecules influence their surface properties, which in turn affects how they behave in solutions like the activity of charged inorganic nanoparticles (i.e., solubility and reactivity) [61]. Several research groups have systematically used the ion exchange approach to vary the solubility of coordination cages [62–64]. Moreover, neutral MOPs can now have charges. For example, neutral paddlewheel-based MOPs became charged with the support of pendant pH-responsive groups that are either positively or negatively charged when protonated/deprotonated. The first negatively-charged MOP, known as SO₃X-CuMOP, with the formula X₂₄[Cu₂(5-SO₃-bdc)₂]₁₂, was synthesized by the inclusion of sulfonic groups [39]. Subsequently, porous salts were prepared using SO₃X-CuMOP as a charged monomer [65,66]. However, due to the structural fragility of SO₃X-CuMOP in solution, particularly in water, its tunability in solution-phase metathesis has not yet been investigated.

The negatively-charged ONa-RhMOP (Na₂₄[Rh₂(5-O-bdc)₂]₁₂) can also be produced by deprotonating the hydroxyl groups attached to the surface of OH-RhMOP with NaOH [67]. The precursor, OH-RhMOP was soluble in straight-chain alcohols, but its negatively charged derivative, containing 24 hydrophilic Na⁺ cations on its peripheral, was highly

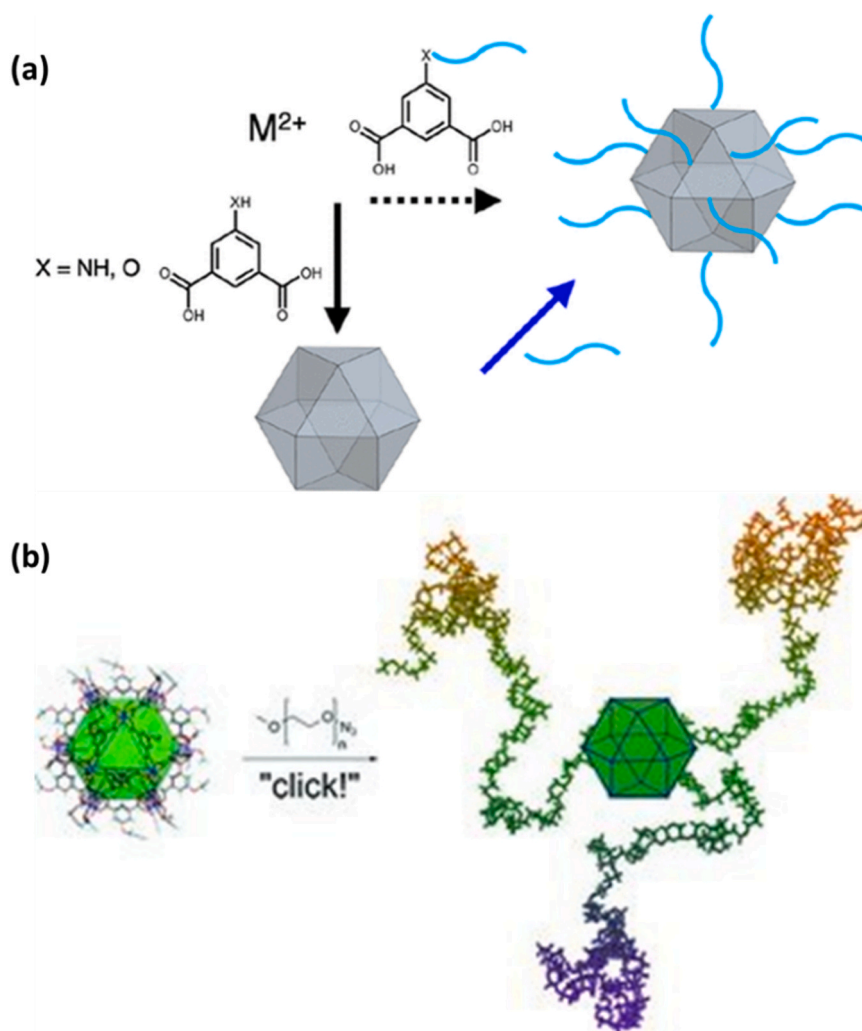


Fig. 8. (a) Surface functionalization at the organic linker using amide/esters, (b) Surface functionalization with polyethylene glycol with an azide end through a click reaction. Adapted from [35,50].

stable and soluble in an alkaline solution. Rapid surface hydroxyl group deprotonation made it possible to transfer Rh-MOPs in situ from the organic phase to the aqueous phase and vice versa (Fig. 9). Furthermore, ONa-RhMOP responded to both cation-exchange processes and pH changes [10,67,68]. Consequently, a soluble MOP (CTA₂₄[Rh₂(5-O-BDC)₂]₁₂) was synthesized by quantitatively exchanging the 24 Na⁺ ions with organic hydrophobic cations, such as cetyltrimethylammonium (CTA). Other successful attempts have been made with Zr-MOPs to tune their solubility in organic solvents (i.e., methanol) and water using ion exchange and leverage on zirconocene-cluster [57, 65,69].

The surface chemistry of MOPs can be drastically altered by salt metatheses, which are quick and quantitative reactions that also allow for in-situ tuning of the solubility and reactivity of MOPs. These new frameworks for molecular separation, transport, and phase-transfer photocatalysts are particularly appealing because of the synergistic interaction of ionic exchange processes, MOPs porosity and reactivity.

2.4. General perspectives on MOPs synthesis, modifications and characteristics

MOPs have a remarkable range of other structural characteristics that can be exploited in addition to their porosity, such as tunable solubility and clearly defined surface functionalities and active sites. Unfortunately, the scarcity of reliably modified MOPs and poor

compatibility with coordination chemistry has kept their practical application to a minimum. Fortunately, researchers have been able to harness the surface characteristics of MOPs to adjust their solubility, which creates alternative coordinative pathways for the development of stable MOPs [45,47,70]. This has been made possible by the development of functionalized MOPs via post-synthetic modification. Yet, a lot can still be done to create stable MOPs and include them in mega structures.

MOPs' intrinsic capabilities have not been fully utilized. A burgeoning area of research in materials science is the utilization of MOPs as building blocks of porous heterostructures/composites. The development of well-defined molecular precursors with intriguing structural features can be achieved due to recent developments in MOP surface modifications towards achieving thermally and chemically stable MOP. Researchers have been able to functionalize MOPs with remarkable diversity, thanks to recent improvements in the overall stability of MOPs and methods that introduce functionality without harsh synthetic approaches. Post-synthetic modification techniques and the development of functionalized Zr(IV)- or Rh(II)-based MOPs [56,71], among other less-represented sources of strong metals, have paved the way for advanced applications of MOPs.

Recently, carboxylate-tagged MOP cages were prepared [72]. Incorporating the carboxylate functional group at the surface of an Rh-based cage has paved the way for preparing crystalline, hierarchically porous MOF heterostructures with unique structural properties

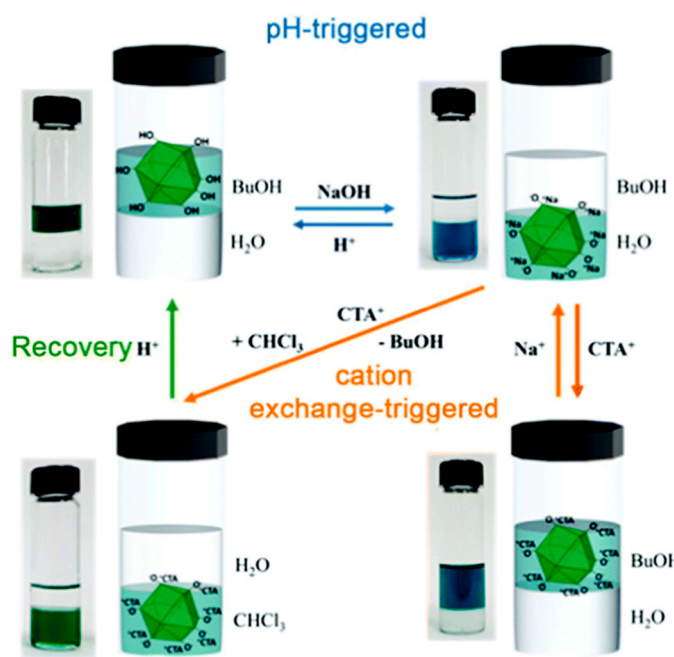


Fig. 9. Scheme showing reversible phase transfer of OH-RhMOP that is both pH- and cation exchange-triggered (blue arrows and orange arrows). Adapted with minor modifications from [10].

and organized hybrid metal sites. Therefore, subject to further investigation, fascinating discoveries will be made when alkyne and other equally reactive moieties are investigated for surface functionalization of MOPs.

3. CO₂ photoreduction using functionalized MOPs

MOPs have demonstrated promising applications in adsorption, sensing and separation and have been utilized as host frameworks to control the properties of several guest molecules. MOP is often used as nanocontainers to encapsulate catalytically active materials or as nanoreactors with organocatalysts attachments or inorganic complexes bound to their framework. The use of MOP as a secondary building block for photocatalysts or pristine MOPs as photocatalysts is rare. This is partly because the heterogenization of photocatalytic compounds often promotes stability at the expense of activity. Hence, a new strategy of preparing stable catalysts on a molecular level without jeopardizing their inherent catalytic characteristics is greatly desired.

One of the promising methods to reduce CO₂ emissions and environmental concerns is the solar-driven conversion of CO₂ into chemical feedstocks [73]. Because CO₂ reduction requires numerous electron transfer processes and can simultaneously yield multiple products, such as CO, formic acid, methane, methanol, oxalate, etc. [74,75], it is more complex than the effective reduction of water into H₂. The high activity, selectivity, and well-defined, customizable structure of molecular catalysts like Fe, Co, Ni, and Mn complexes help to clarify the photocatalytic reaction mechanism. However, the poor stability of MOFs generally makes industrial use of these frameworks very difficult [76,77]. But successfully building molecular heterogeneous photocatalysts such as MOPs would be preferable since it combines the advantages of homogeneous and heterogeneous catalysts.

Metal-organic polyhedra (MOPs) are a new family of well-organized composites with desirable properties because of the large number of accessible metal sites around their interior cavity [78,79]. Dirhodium paddlewheels have recently been encapsulated within Rh-MOP, and their three-dimensionally formed heterostructures have proven to be effective photocatalysts for the selective photochemical conversion of

CO₂ to formic acid [80]. Unusually, the catalytic activity per Rh atom is higher in the heterostructure than in the molecular subunit Rh-MOP and this results in turnover frequencies (TOF) of up to 60 h and production rates of about 76 mmol formic acid per gram of the catalyst per hour, which are record-breaking in heterogeneous photocatalysis. The high photocatalytic performance relative to other materials is mainly driven by the high amount of Rh active sites per gram of the catalyst and high accessibility within the heterostructure. A three-stage mechanism involved photoexcitation and reductive quenching of photosensitizer⁽ⁱ⁾, electron transfer from photosensitizer to Rh photocatalyst⁽ⁱⁱ⁾, and CO₂ reduction to formic acid⁽ⁱⁱⁱ⁾ (Fig. 10). The electron-rich N-ligands in Rh-MOP heterogenized its active center and enhanced the overall stability of the MOP [80]. Electrochemical characterization and X-ray photoelectron spectroscopy revealed an increase in electron density around the active metal site due to the electron-donating N-ligands, leading to a higher stability and thermodynamically driven conversion process.

Similarly, CO₂ reduction to CO has reportedly been carried out with the aid of passivated and functionalized MOP. An interesting aspect of this project is that a homogenous photocatalyst ReTC- (Re^I(CO)₃(BPYDC)(Cl)) was heterogenized by Zr-based MOP for both enhanced stability and catalytic activity [81]. Zr-based MOP stabilized the photocatalytic compound (ReTC) without impairing its catalytic activity. ReTC was chemically linked to discrete cages of the MOP with strong CO₂ to CO transformation activity (660 h⁻¹ turnover frequency (TOF)) for a minimum of 24 h under exposure to visible light. The free molecular form of the compound (H₂ReTC) achieved 131 h⁻¹ TOF in only 2 h. The accumulated turnover ratio of ReTC-MOP was 42 times the value for molecular ReTC. ReTC-MOPs improved absorptivity, non-static nature, and stability in solution are credited for their excellent photocatalytic activity and stability (Fig. 11). The high stability and catalytic activity of ReTC-MOP are due to the very small framework of MOP, which facilitated a high degree of motional freedom, binding of ReTC, improved absorption of light, and chemical stability in the reaction solution. We suggest researchers consider applying this strategy to other molecular catalysts for improved stability without affecting their functionality/reactivity in certain catalytic processes.

The use of a MOP designed by employing Ir(III) as a singular molecular cage in Zr-MOC (Ir(III)-MOC-NH₂) has been recently reported for CO₂ photoreduction [82]. A V₄E₆-type cage is formed by four secondary building units (Cp₃Zr_{3μ₃}-O(μ₂-OH)₃) coordinating to six linkers of bpdc-NH₂ and Ir-ppyc (Fig. 12). Under visible light, Ir(III)-MOC-NH₂ achieved high conversion and selectivity (99.5%) for producing CO. A TOF of 120 h⁻¹ was also achieved with a 6.71% apparent quantum yield. Due to the incorporation of MOC-NH₂, the aggregation-induced deactivation of Ir(III) was limited as the -NH₂ group can stabilize the metal's transition state. It is conjectured that Ir(III) is the active site for the reduction of CO₂, which involves the Cl from leading to a penta-coordinated structure (Fig. 10). According to DFT calculations, mass spectrometry, and in situ IR, the excellent catalytic performance of the MOP is related to the Ir-ppyc as the catalytic center and cage arrangement around it, which stabilizes the metal transition state and the CO₂ adduct during photocatalysis [82]. This also leads to a decline in Gibbs

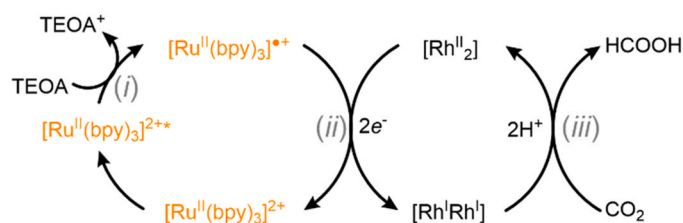


Fig. 10. Proposed mechanisms for CO₂ conversion to formic acid using Rh₂ paddlewheel-based cuboctahedral metal-organic polyhedra (Rh-MOP). Adapted with permission from [80].

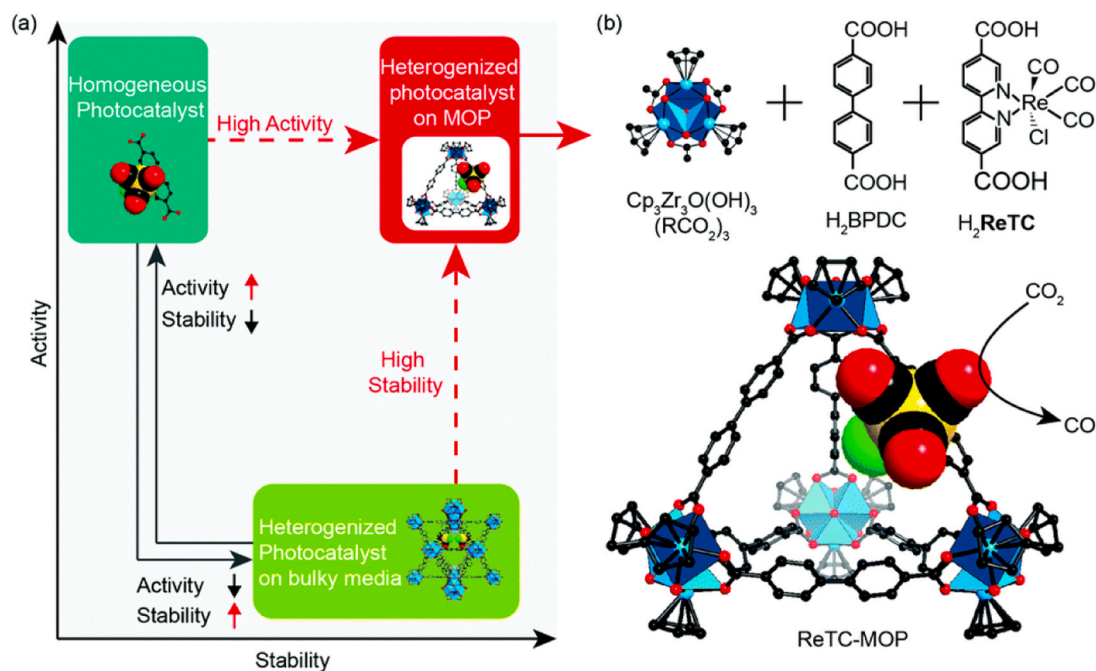


Fig. 11. Illustration of a photocatalyst's heterogenization on MOP. The photocatalyst heterogenized on the MOP showed better stability without losing activity ^(a). The ReTC-MOP structure for the photocatalytic conversion of CO₂ to CO ^(b). C is "black," O is "red," Zr is "blue polyhedra," Re is "yellow," Cl is "green," and H atoms are excluded.

Adapted with permission from [81].

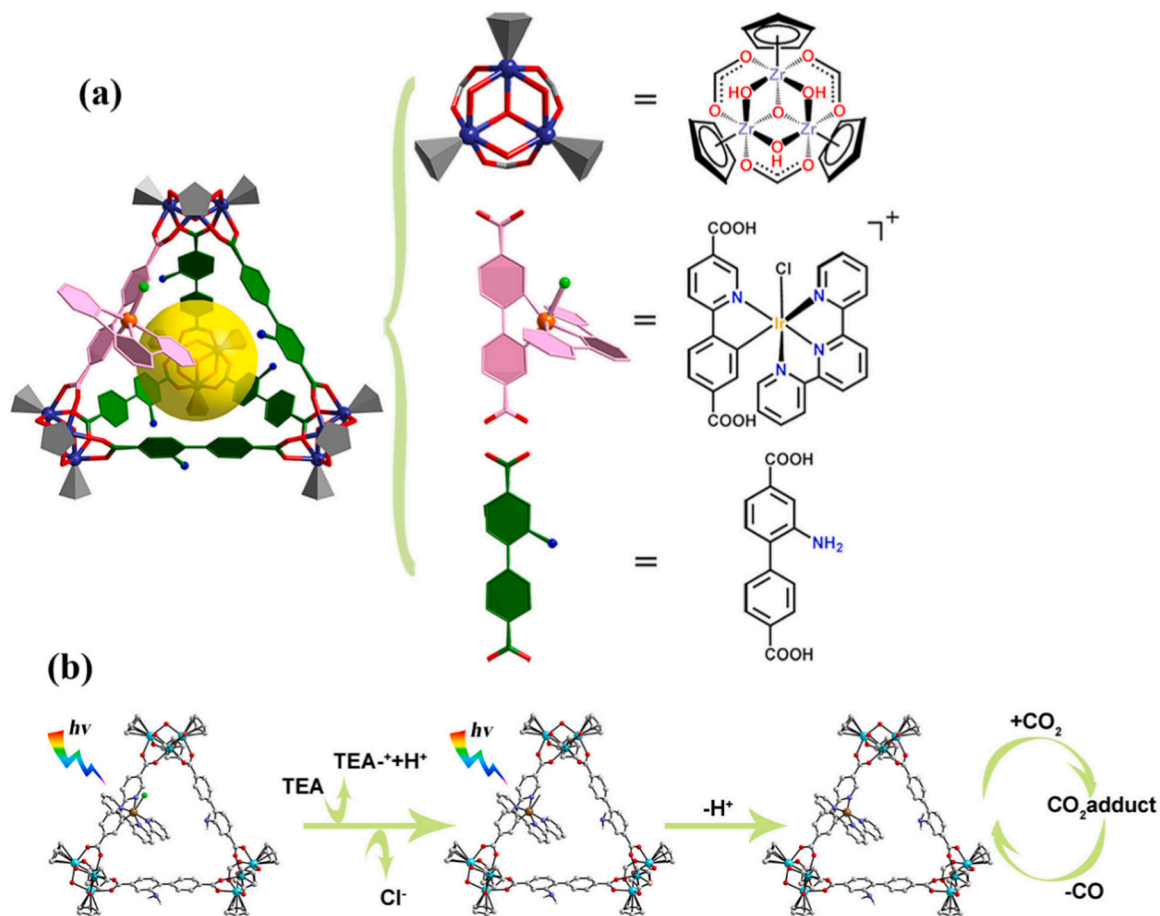


Fig. 12. Structure of Ir^{III}-MOC-NH₂ showing bridging ligands and trinuclear zirconium clusters ^(a). Mechanism of the photocatalytic conversion of CO₂ to CO ^(b). Adapted with permission from [82].

reaction energy and the activation barrier, thereby catalyzing the conversion of CO₂.

Yang et al. [83] synthesized two polyoxometalate-based metal-organic complexes under hydrothermal conditions for application in CO₂ photoreduction. The first complex was [Co(H₂O)₂DABT]₂[CrMo₆(OH)₅O₁₉] denoted as Co-CrMo₆ and the second was [Zn(H₂O)₂DABT]₂[CrMo₆(OH)₅O₁₉] denoted as {Zn-CrMo₆} (where DABT is 3,3'-diamino-5,5'-bis(1*H*-1,2,4-triazole)). Both complexes have similar structures. Co-CrMo₆ is fan-shaped and possesses one DABT ligand, one half of a CrMo₆ anion, one Co(II) ion and a coordinated water molecule (Fig. 11). Co-CrMo₆ had a higher performance than Zn-CrMo₆, achieving 1935.3 μmol g⁻¹ h⁻¹ CO formation. Co-CrMo₆ was more interesting as it also showed good performance in sulfur oxidation. MeCN/triethanolamine (TEOA) is added as a photosensitizer to help the catalyst. During CO₂ photoreduction with Co-CrMo₆, TEOA is a sacrificial agent that combines with the photogenerated holes so the electron does not quickly recombine and can participate in photocatalysis (Fig. 13). The Co(II) active site captures the photogenerated electrons and utilizes them for photocatalysis. Yang et al. attributed the excellent chemical and stability of the synthesized MOP to the anionic metal-oxide nanoclusters of polyoxometalates. The abundance of the terminal and bridging oxygen atoms serves as nodes to coordinate to metal ions and organic, and high surface areas provide the basis for the stability and overall performance of the POM-based MOPs [84].

There is a paucity of literature focused on the application of MOPs for CO₂ photoreduction and conversions. The major studies discussed above were only published in the last three years. Hence, there is a need for more environmental protection and sustainability research, particularly MOP utilization for CO₂ separation and/or conversion to valuable

products, in consonance with sustainable development goals (SDGs). The application of stable MOPs or derivatives for the photocatalytic conversion of CO₂ to other products, such as methane (CH₄), methanol (CH₃OH) and ethanol (C₂H₅OH), etc., should be investigated towards addressing the need for renewable energy sources.

4. Research gaps in the application of MOPs for CO₂ utilization and photoreduction

Metal-organic polyhedra have strong potential for resolving the long-standing environmental CO₂ emission challenges since they are efficient, affordable, visible-light responsive materials with adjustable properties. MOPs should be investigated for the conversion of CO₂ to solar fuels, for CO₂ adsorption, and more research on the photoreduction of CO₂ due to the inherent large surface areas, high porosity, good chemical stability (especially after post-synthetic modification), and variable topology.

Modified MOPs' optical absorption characteristics might be precisely adjusted by choosing the right light-harvesting linker/components. Iron is one of the metal ions that can be used to create metal clusters that act as semiconductors. In general, organic compounds may absorb light energy, and depending on their functionality, they may already be light-responsive [85,86]. Alternatively, the useful ligands may be infused with photo-sensitivity by incorporating photoactive metalloligands or dyes through post-synthetic modifications [87]. A list of light harvesters that may be investigated for MOPs is presented in Table 1. Furthermore, enhanced photocatalytic activity may be facilitated by increasing the concentration of active light-responsive ligands.

MOPs can produce simultaneous double or triple excitations at the

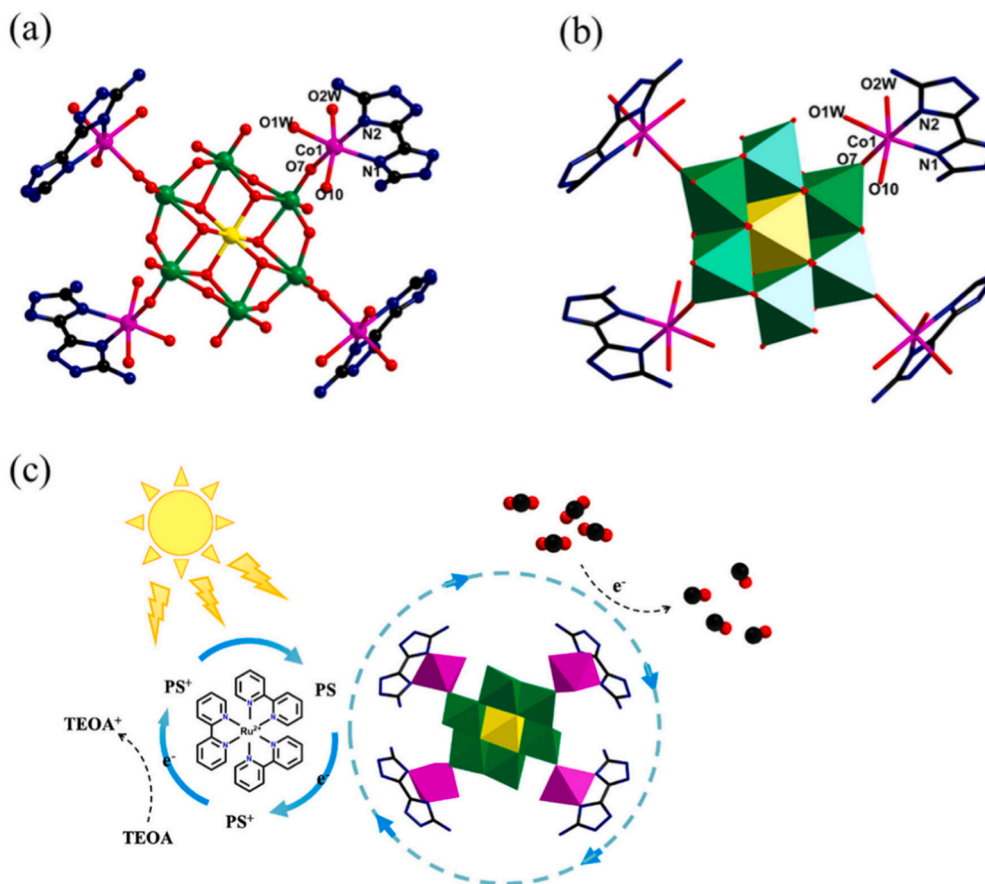
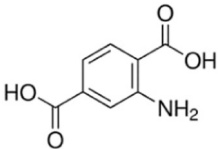
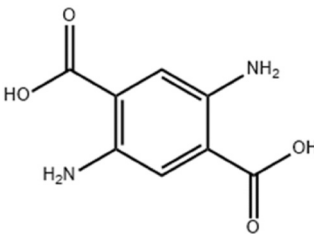
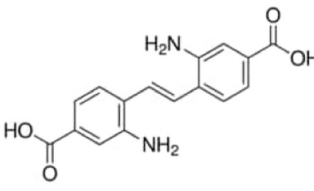
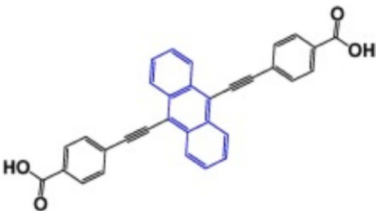
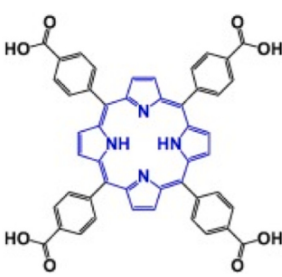


Fig. 13. Ball-and-stick diagram of the fan-shaped unit of {Co-CrMo₆}^(a). Polyhedral diagram of {Co-CrMo₆}^(b). Mechanism of CO₂ photoreduction by {Co-CrMo₆}^(c). MoO₆ octahedra is "bottle green", Cr(OH)₆ octahedron is "yellow", Co is "purple", C is "black", N is "blue", O is "red", and H is excluded. Adapted with permission from [83].

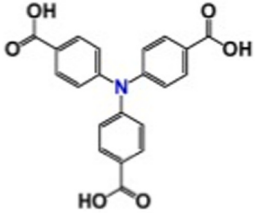
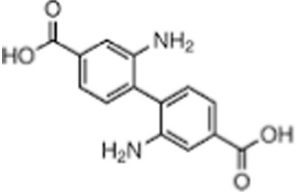
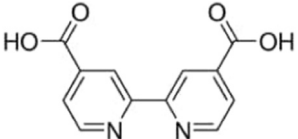
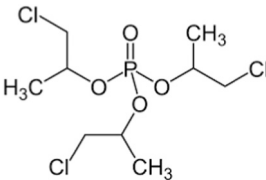
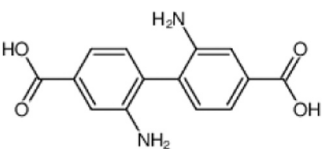
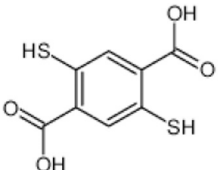
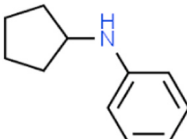
Table 1

Efficient light harvesters/responsive ligands that may be explored for MOP synthesis, modification and application as photocatalysts.

Ligands	Structure	References
2-aminoterephthalic acid		[90]
Diaminoterephthalic acid		[91]
2,2'-diamino-4,4'-stilbenedicarboxylic acid		[92]
4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid		[93]
Tetraphenylporphyrin		[94]

(continued on next page)

Table 1 (continued)

Ligands	Structure	References
4,4',4''tricarboxyltriphenylamine		[95]
3,3''-diamino-1,1':4',1''-terphenyl-4,4''-dicarboxylate		[96]
2,2'-bipyridine-4,4'-dicarboxylic acid)(CO) ₃ Cl		[97]
Tris (chloroisopropyl) phosphate		[98]
Biphenyl-4,4'-dicarboxylic acid		[99]
2,5-dimercapto-1,4-benzenedicarboxylic acid		[100]
N-cyclopentyl-N-cyclobutylformamide		[101]

metal node, organic linkers, and pores [88,89]. Unlike zeolite and other conventional catalysts, MOPs are modular and can combine the benefits of inorganic and organic chemistry. Therefore, MOP photocatalytic sites can be easily immobilized in organic ligands, metal nodes, and the cavity, opening up a wider range of possible applications. Furthermore, researchers should look into avenues to reduce the number of synthesis steps and the need for post-treatment of MOPs. Facile, quicker and eco-friendly routes for preferably one-pot synthesis of stable MOPs are desirable.

MOP stability in the presence of water is a key issue, mainly because water is typically used as a proton donor in photocatalytic CO₂ reduction. However, using the appropriate post-synthetic modifications may solve this problem. Moreover, the mechanism of photocatalytic reduction using MOP needs to be fully understood. The structure-activity relationship should, therefore, be thoroughly explored to design MOP photocatalysts for higher performance in the reduction of CO₂. Advanced characterization methods like transient absorption techniques and Density functional theory tools should also be employed to facilitate optimization studies. The conversion of CO₂ to hydrocarbon, which can yield more valuable products, is another area that needs further exploration with MOPs. Photothermal and photo-electrocatalytic methods can be integrated with photocatalysis as a strategy for effective CO₂ transformation or removal.

In summary, MOP, an emerging molecular heterogeneous catalyst, is one of the most attractive candidates for CO₂ photoreduction to fuels and other value-added products because of their flexible coordination geometry and atomically distributed catalytic sites [73]. MOPs, notably Zr-based MOPs, can provide viable alternatives to conventional MOFs for stabilising reactive species/intermediates, metal complexes, greenhouse gases, etc [18,102]. Non-covalent bonding combined with suitable cavity shape, size, and hydrophobic nature of MOPs is germane to this aim. MOPs could encapsulate target species within their cages to inhibit the interaction of reactive species with the surroundings, thus ensuring chemical stability. While smaller MOFs utilize covalent bonds to form stable coordination compounds [103–105], MOPs with larger cavities open several alternative pathways, including non-covalent interactions. With respect to CO₂ conversion, the distinct structure of MOP offers a framework for customizing the CO₂ conversion reaction pathway and comprehending the mechanisms involved. However, their potential applicability is limited by the use of organic sacrificial reagents and photosensitizers based on noble metals. Hence, future works should consider building bifunctional cages that function as co-catalyst and photosensitizers. Furthermore, significant advancements in catalyst design and reaction optimization will be necessary for the practical implementations of MOP-based photocatalytic reduction of CO₂.

5. Concluding remarks

High activity and product selectivity are two of the most interesting characteristics of the few MOP photocatalysts explored to date. Still, they have also faced difficulties with catalytic stability, the deactivation of active sites, and reusability concerns. According to some findings, a metal-organic polyhedra cage with an organic linker and an inorganic node can sustain MOP photocatalysts without losing its initial catalytic activity with the proper post-synthetic modifications. Also, we have identified quite a few photosensitive organic molecules that have not yet been investigated for MOP photocatalysts but have proven effective in other similar metal-organic frameworks. This review also emphasizes the possibility of chemical bond/entrapment between homogeneous catalysts with/within heterogenous MOPs to maintain and enhance the cumulative CO₂-to-CO conversion activity.

Finally, the increase in published studies on the usage of functionalized MOPs in hydrogels, hybrid composites, hairy dendrimers, and other heterostructures indicates the vast potential of MOPs as building blocks for the design and assembly of porous materials. Thus, future research should focus on developing stable, efficient, regenerable,

reusable, and cheap MOP photocatalysts and MOP-based membranes using facile methods for the adsorption, separation, and photoreduction/transformation of CO₂.

CRedit authorship contribution statement

Nomngongo Philiswa N.: Formal analysis, Funding acquisition, Project administration, Supervision, Validation, Writing – review & editing. **Kyesmen Pannan I.:** Data curation, Formal analysis, Writing – original draft. **Ighalo Joshua O.:** Data curation, Formal analysis, Writing – original draft. **Adeola Adedapo O.:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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