

Review

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Metal-organic frameworks as promising flame retardants for polymeric materials

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How to cite this article: Hou B, Pan YT, Song P. Metal-organic frameworks as promising flame retardants for polymeric materials. *Microstructures* 2023;3:2023039. <https://dx.doi.org/10.20517/microstructures.2023.37>

Received: 19 Jul 2023 **First Decision:** 10 Aug 2023 **Revised:** 24 Aug 2023 **Accepted:** 11 Sep 2023 **Published:** 10 Oct 2023

Academic Editor: Zhanxi Fan **Copy Editor:** Fangyuan Liu **Production Editor:** Fangyuan Liu

Abstract

This article presents a vision for advancing the development of next-generation flame-retardant materials through the utilization of metal-organic frameworks (MOFs). The proposed vision is centered on four key areas: industrialization, multifunctionality, ligand synthesis, and derivatives. By optimizing production processes, customizing MOFs for specific properties and applications, and developing novel ligands and derivatives, the effectiveness and versatility of MOFs as flame-retardant materials can be significantly enhanced. This vision represents a promising direction for the field that has the potential to address critical safety concerns across various industries.

Keywords: Microstructures, metal-organic frameworks, multifunction, industrialization, flame retardant

INTRODUCTION

Metal-organic frameworks (MOFs) are a type of porous material composed of metal ions or clusters linked by organic ligands. Their development can be traced back to the 1990s when researchers were exploring



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novel approaches for synthesizing materials with large surface areas and high porosity. The initial MOF structure, designated as MOF-5, was synthesized in 1999 by researchers at the University of Michigan. This material comprised Zn^{2+} ions coordinated with 1,4-benzenedicarboxylate (H_2BDC) ligands and exhibited a remarkable surface area exceeding $2,900\text{ m}^2/\text{g}$ ^[1]. In 2013, MOFs were introduced as fillers into the polymer matrix for the first time, thereby enhancing low-humidity proton conductivity^[2]. This breakthrough sparked a surge of interest in MOFs, prompting researchers to explore their potential for diverse applications such as gas storage, catalysis, and drug delivery. Since then, thousands of MOFs have been synthesized using various metal ions and ligands to create materials with distinct properties and functions. MOFs have garnered attention as potential flame retardants due to their high surface area, tunable pore size, thermal stability, abundance of transition metals, and flexible structure.

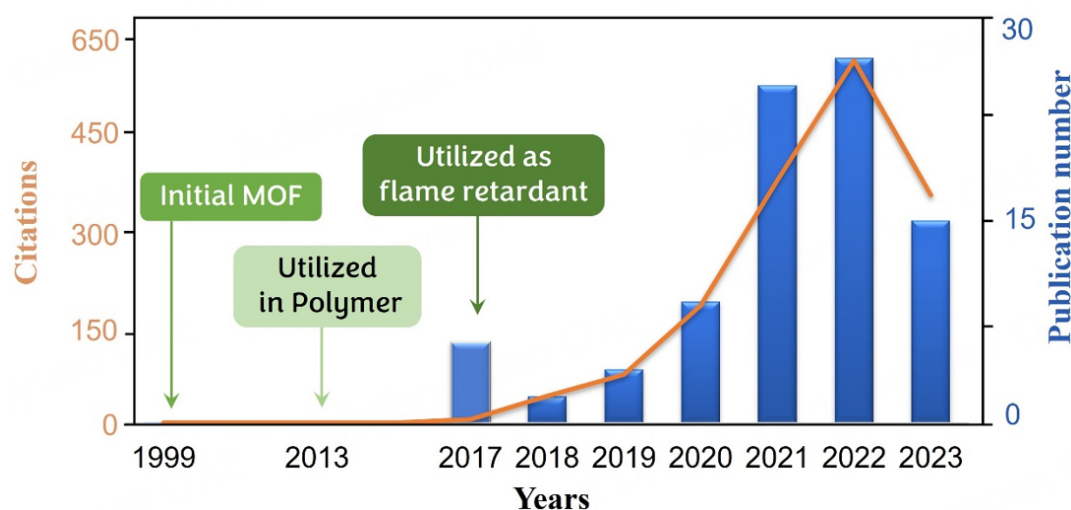
The application of MOFs as flame retardants can be traced back to research conducted in the late 2010s. In 2017, Hou *et al.* successfully synthesized iron-based and cobalt-based MOFs, which were subsequently incorporated into PS as flame retardants. The results demonstrated a significant improvement in both the thermostability and flame retardancy of the PS composites^[3]. Subsequently, researchers have investigated diverse categories of MOFs for their flame-retardant properties^[3-10]. Table 1 summarizes some MOF flame retardants for different polymer matrices^[11-23]. Recently, (zeolite imidazolate framework) ZIF series of MOFs have been intensively explored as potential flame retardants in various polymer matrices due to their ease of synthesis. MOFs contain flammable organic ligands in their structures, leading to limited efficiency, and therefore, modification or co-blending with other flame retardants is often required to boost their fire-retardant efficiency, e.g., performing better in UL-94 testing, especially at lower loading levels. It is accepted that MOFs usually reduce heat release rates and slow the combustion process of polymers via catalytic carbonization of transition metals within MOFs during combustion. However, there remain some unknowns on the impacts of structural compositions of MOFs on their catalyzing carbonization and modes of action. Additionally, they have explored the potential of incorporating MOFs as additives into existing flame-retardant materials to enhance their efficacy [Figure 1]. The use of MOFs as flame retardants is a relatively new and emerging area of research, and there are still ongoing debates regarding their cost-effectiveness compared to traditional flame retardants.

However, MOFs have several advantages over traditional flame retardants, such as their high porosity, high surface area, and tunable properties. These properties allow MOFs to be tailored to specific applications and offer superior flame-retardant performance. While MOFs may be relatively expensive compared to traditional flame retardants, their unique properties and superior flame-retardant performance may outweigh these costs in certain applications. The flame retardancy of MOFs is attributed to two primary mechanisms: gas-phase and condensed-phase. The gas-phase mechanism involves the liberation of non-flammable gases, such as water, carbon dioxide, and nitrogen. These gases can dilute the flammable gases and reduce the concentration of fuel and oxidizer in the flame zone^[24,25]. The condensed-phase mechanism involves the formation of a protective layer on the surface of the polymer, which acts as a physical barrier and reduces the combustion rate. This protective layer is formed by thermal decomposition of MOFs, releasing metal oxides or metal phosphates that react with the polymer to form a char layer. The char layer functions as an insulating layer, reducing heat transfer between flame and polymer and preventing fire spread^[26-29].

One may consider the potential benefits of utilizing MOFs as flame retardants, such as their capacity to enhance fire safety without adversely affecting the properties of the applied material. However, there are still some challenges associated with large-scale production and application of MOFs as flame retardants, as well as potential risks that come with using these materials. In this review, we aim to provide valuable guidance

Table 1. MOF-based flame retardants for different polymer matrices

Type of MOFs	Adding amount (%)	Matrix	UL-94	LOI (%)	pHRR reduction (%)	Reference
ZIF-8	1.0	PLA	V-2	26.0	-	[4]
UiO-66	5.0	PS	-	21.0	26.8	[5]
ZIF-8	0.91	PUF	-	18.8	50.6	[6]
Zr-MOF@CeHPP	2.0	PC	V-0	27.6	45.4	[11]
ZIF-67	2.0	EP	-	23.6	28.7	[12]
Ni-MOF	1.7 + 3.3 APP	PLA	V-0	31.0	26.9	[13]
ZIF-8	3 + 27 DDGS	PP	V-2	25.0	-	[14]
Fe-MOF	2.0	EP	-	-	18.6	[15]
Co-MOF	1.5 + 4.5 APP	TPU	V-0	28.2	81.1	[16]
ZIF-11	12.0	PUF	-	-	21.3	[17]
ZIF-8	0.75 + 2.25 EG	PUE	V-1	30.2	83.5	[18]
BP@MIL-53	1.0	PC	V-0	30.5	49.3	[19]
MIL-88B	1.0	PET	V-2	27.0	23.0	[20]
TEP@MIL-53	3.0	PS	-	-	24.7	[21]
ZIF-8/RGO	2.0	EP	V-1	26.8	49.66	[22]
Zr-MOF	4.0	PC	V-0	28.2	47.4	[23]

**Figure 1.** Data obtained with the keywords “MOF flame retard” or “MOF fire safety” in the Web of Science on August 14, 2023.

for researchers in this field by sharing our insights. One crucial aspect of MOFs is their adjustable structure, which enables precise manipulation of their physical and chemical properties. Ligand synthesis plays a pivotal role in fine-tuning the properties of MOFs, as ligands act as organic linkers that connect metal nodes and determine the framework structure. Therefore, the development of novel ligands and derivatives is imperative to enhance the versatility and performance of MOFs.

Furthermore, the industrialization of MOFs represents a crucial milestone toward their widespread commercial utilization. This entails scaling up the synthesis of MOFs, optimizing their properties for specific applications, and devising cost-effective production methods. Finally, the multifunctionality of MOFs is a key advantage that renders them suitable for a diverse range of applications. MOFs can be tailored to exhibit specific properties, such as antibacterial activity, gas storage capacity, and selective

adsorption.

The future of MOFs holds immense potential for innovation and impact across various industries. To advance the field of next-generation flame-retardant materials, we present a concise vision for industrialization, versatility, ligand synthesis, and MOF derivatives. This perspective is both timely and forward-looking, offering new insights and inspiration for senior researchers, deepening the understanding of young researchers, and providing guidance for those in related fields interested in the development of flame-retardant materials. Our work aims to provide valuable insights for a wide range of researchers and facilitate future advancements in this crucial field. We are confident that our article will make a significant contribution to the ongoing efforts toward developing safer and more sustainable materials for diverse applications.

INDUSTRIAL APPLICATION OF MOF-BASED FLAME RETARDANTS

Larger scale synthesis of MOF-based flame retardants

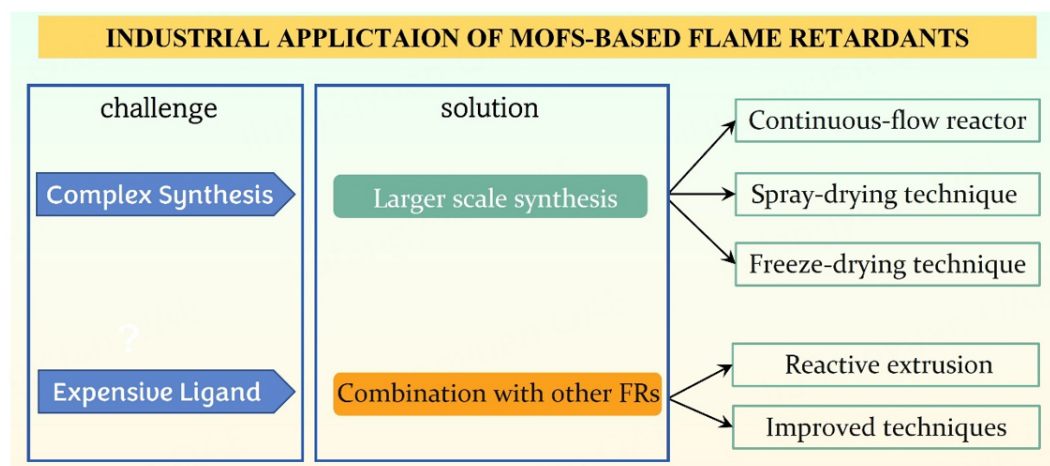
MOFs are typically synthesized in small quantities in a laboratory setting due to the intricate nature of their synthesis. For instance, the UIO and MIL series of MOFs necessitate a hydrothermal synthesis process followed by a high-temperature reaction in a reaction vessel^[30,31]. Achieving the desired MOF structure and properties requires meticulous control of reaction conditions, including temperature, pressure, and solvent composition. This process requires a significant amount of time. Even zeolite imidazolate skeleton materials (ZIFs), synthesized by facile methods, necessitate prolonged aging for the attainment of a flawless crystal structure^[32,33]. The aging process is essential for the formation of intermolecular hydrogen bonds between metal ions and ligands, which stabilize the MOF structure and prevent collapse. The duration of aging can vary from several hours to several days, depending on the specific MOF being synthesized and the desired crystal quality.

To achieve commercial viability, MOFs must be produced on a large scale [Table 2]. Despite the challenges associated with their synthesis, recent advances in synthetic methods have facilitated industrial production of MOFs, enabling scaling up to gram or even kilogram quantities [Figure 2]. Continuous-flow reactors are a commonly employed strategy for the large-scale synthesis of MOFs^[34-36]. In this approach, the reactants are continuously fed into the reactor and undergo controlled mixing and reaction, resulting in a steady-state production of MOFs. This method offers several benefits, including precise regulation of reaction parameters, rapid mixing, heat transfer, and continuous product output. A further approach is to employ the techniques of spray-drying or freeze-drying^[37-39]. The spray-drying technique involves the atomization of a liquid MOF precursor into small droplets, which are subsequently dried using a stream of hot air. As these droplets traverse through the drying chamber, the solvent evaporates, leaving behind solid MOF particles. The method is highly efficient in the production of MOF powders and can be readily scaled up for large-scale manufacturing.

Freeze-drying involves freezing a liquid MOF precursor and subsequently eliminating the solvent under vacuum conditions. The frozen specimen is then placed in a vacuum chamber where the solvent sublimates directly from the solid to the gas phase, resulting in a desiccated MOF powder. Freeze-drying is a more time-consuming process compared to spray-drying; however, it has the ability to maintain the crystalline structure of MOFs intact, which can prove crucial for certain applications. Both methods are capable of producing MOFs with high surface area, porosity, and thermal stability, rendering them highly versatile for a wide range of applications. Additionally, they facilitate the production of MOFs in powder form, which is more manageable and storable. Apart from that, the cost of MOFs can significantly affect large-scale production. Generally, the higher the cost of ligands, the greater the expense of producing MOFs. The price

Table 2. Industrial methods of MOF-based flame retardants

Method	Description	Example applications
Continuous flow reactors	MOFs are synthesized in a continuous flow system, where reactants are continuously pumped through a reactor	Large-scale production of MOFs
Spray-drying	A solution of MOF precursors is atomized into a hot drying gas, allowing rapid solvent evaporation and MOF formation in the form of dry powder	Production of MOF powders for various applications such as coatings and composites
Freeze-drying	MOF precursors are dissolved in a solvent, frozen, and then subjected to a vacuum, causing the solvent to sublime. The resulting solid is a porous MOF	Production of highly porous MOFs with preserved crystallinity

**Figure 2.** Industrial application of MOF-based flame retardants.

of MOF ligands can be influenced by a range of factors, such as the availability of raw materials used for synthesizing the ligands, the complexity involved in their synthesis, and the demand for MOF materials across various industries. With the advancement of novel and more efficient synthesis techniques, there is a possibility for a reduction in the cost of MOF ligands. As scientists have gained an enhanced comprehension of the structure and characteristics of MOFs, they have been able to optimize the production process of organic ligands that are utilized in creating these materials^[40,41]. This has resulted in more efficient and cost-effective approaches to synthesizing MOF ligands, thereby contributing to a reduction in their price. By reducing costs through economical synthesis and purification methods, MOFs can become more competitive with other materials, leading to increased adoption in industrial applications.

Combination of MOFs with other flame retardants

In this context, the commercial potential of incorporating MOFs as flame retardants into polymers has been demonstrated due to the decreasing cost of synthetic organic ligands. Recent unpublished work and conference papers have reported on MOFs acting as synergists with traditional flame retardants [Table 3]. MOFs can be added to other flame-retardant materials to enhance their performance^[18,42-48].

For example, MOFs can be added to intumescent coatings, which expand when exposed to heat, forming a protective layer that insulates the underlying material and delays its ignition. The thermal stability of the expanded coatings can be improved by adding MOFs; the coking property can be increased by transition metal catalysis, and the flame-retardant property can be enhanced. Shen *et al.* investigated the use of MOFs as a synergist for intumescent flame retardants in polypropylene (PP). The aim was to utilize ZIF-8 for enhancing char formation and improving fire retardancy of PP. It was discovered that the incorporation of ZIF-8 facilitated better char formation and reduced the emission of flammable gases during combustion^[42].

Table 3. Combination of MOFs with other flame retardants

MOF	Other flame retardants	Example applications
Ni-MOF ^[43]	Ammonium polyphosphate	Flame-retardant additives for polymers and textiles
MOF-Cu ^[44]	Ammonium polyphosphate	Flame-retardant additives for plastics and textiles
ZIF-67 ^[46]	Ammonium polyphosphate	Flame-retardant coatings and polymer formulations
ZIF-8 ^[47]	Phosphorus-based flame retardants	Flame-retardant coatings, textiles, and polymer matrices
UiO-66 ^[48]	Cyclotriphosphazene	Flame-retardant composites and polymer formulations

Xu *et al.* employed a solvothermal method to synthesize a specific type of MOF using cobalt ions and organic ligands, resulting in a porous material with high surface area and thermal stability. Subsequently, the Co-MOF was compounded with PP after being mixed with melamine polyphosphate (MPP), which is another flame retardant. The results indicate that the incorporation of Co-MOF into MPP/PP composite significantly enhances its flame retardancy, as compared to PP alone or with only MPP. This improvement is attributed to the release of water and gases from Co-MOF upon heating, which can effectively cool and dilute flames^[43]. Quan *et al.* explore the synergistic effects of ZIFs (ZIF-67 and ZIF-8) with different transition metals on intumescent flame-retarded PP composites^[49]. Overall, MOFs have the potential to be used as a synergist for intumescent flame retardants in polymers, which could lead to the development of more effective and efficient flame-retardant materials for a wide range of applications.

Escobar-Hernandez and Quan *et al.* provided valuable insights into the large-scale synthesis of MOFs^[50,51]. They present a promising method for the sustainable and efficient production of MOF-based polymer nanocomposites^[52]. The process utilized for the production of these materials is known as reactive extrusion, which involves blending MOF particles and polymers in an extruder. During this mixing procedure, chemical reactions take place between the MOFs and polymers, leading to the formation of robust chemical bonds between both materials. The sustainability and efficiency of this manufacturing process are emphasized by researchers. Reactive extrusion was utilized to produce MOF-based polymer nanocomposites with reduced energy consumption and waste generation compared to conventional methods for similar materials. Moreover, the incorporation of MOFs in these composites enhances their sustainability as they can be easily recycled and reused.

Despite their unique properties and potential for industrial applications, there are several challenges that must be overcome before MOFs can be widely adopted in the industry. MOFs are often susceptible to degradation or collapse when exposed to environmental factors such as moisture, heat, or mechanical stress. This can limit their long-term stability and durability, which is a crucial consideration for industrial applications. The cost of MOFs can be relatively high compared to traditional materials, which can limit their adoption in certain applications. Additionally, the cost of MOF synthesis and production can vary depending on the specific MOF and the synthesis method used, which can further complicate cost considerations. Addressing these challenges will require continued research and development in the synthesis, characterization, and integration of MOFs into industrial applications.

The industrialization of MOFs may follow a trajectory similar to that of graphene, which has demonstrated unique properties and potential for various industrial applications such as electronics, energy storage, and biomedical devices since its discovery in 2004^[53]. However, the slow pace of industrialization can be attributed to challenges in achieving mass production and cost-effective synthesis. Nevertheless, recent advancements in graphene research have resulted in the development of various scalable production methods, including chemical vapor deposition^[54], liquid-phase exfoliation^[55], and reduction of graphene oxide (GO)^[56]. These methods have enabled the production of high-quality graphene in large quantities at a

relatively low cost, making it possible for industries to incorporate graphene into their products. Furthermore, collaborations between academia and industry have facilitated the transfer of graphene research from the lab to the factory floor. Companies, including Samsung, Nokia, and IBM, have invested in graphene research and development, leading to the creation of new graphene-based products such as flexible displays, sensors, and batteries^[57]. In addition, the EU-funded Graphene Flagship project has played a crucial role in the industrialization of graphene^[58]. The project, launched in 2013, aims to accelerate the commercialization of graphene by bringing together over 150 academic and industrial partners from across Europe to develop new graphene-based technologies. Overall, the combination of advancements in research, scalable production methods, industry-academia collaborations, and funding initiatives has paved the way for the industrialization of graphene. Consequently, MOF-based products are increasingly prevalent across various industries, with expectations that MOFs will continue to play a significant role in future technology development.

MULTIFUNCTION OF MOF-BASED FLAME RETARDANTS

Due to the exorbitant cost of MOF-based flame retardants, their industrialization is still in its infancy. However, as a versatile material, it can also serve other purposes, such as wastewater adsorption, while retaining its flame-retardant properties [Figure 3]. This design has become a focal point of scholarly attention. Zhou *et al.* utilized MOF-derived layered double hydroxide (LDH) and 3-amino-propyl triethoxy-silane to modify hydroxylated boron nitride, resulting in polyurethane foam (PUF) composites with exceptional thermal stability, fire safety, and high absorption capacity. The incorporation of flame retardants significantly decreased the amount of combustible gas and toxic CO gas generated during PUF pyrolysis. The inhibition of smoke release was evidenced by a significant decrease in the emission of aromatic compounds. Moreover, the incorporation of 1 wt.% additive resulted in PUF composites with excellent pump oil adsorption capacity, achieving a removal rate of as high as 95%, which outperformed other PUF-based materials for oil and water separation^[59]. Piao *et al.* provided a growth site for ZIF-67 by *in-situ* polymerization of a polydopamine film on the surface of a polyurethane sponge. Then, ZIF-67 was etched with copper nitrate to form CuCo-LDH, and a high-performance oil-water separation flame retardant polyurethane sponge was obtained. The polyurethane composites demonstrate exceptional superhydrophobicity and superlipophilicity while also enhancing thermal stability, exhibiting excellent flame retardancy, and inhibiting the generation of toxic smoke. As such, they represent a highly efficient, sustainable, and safe material for emergency treatment of oil/organic solvent spills^[60].

Under the influence of this trend, we believe MOFs can be designed as a “one-pack” material with specific functionalities that allow them to serve multiple roles simultaneously. In the latest reports, MOFs can be functionalized with antimicrobial agents, ultraviolet (UV) stabilizers, or other additives to provide additional properties to the material. This can be particularly useful in applications where multiple properties are required, such as in the construction of buildings or in the aerospace industry. MOFs can exhibit antimicrobial activity through the release of metal ions. Besides, their high surface area and porous nature can facilitate contact between the MOFs and microorganisms, allowing for efficient antimicrobial action.

One example is the report by Zhao *et al.* on the synthesis of a novel antibacterial material based on silver nanoparticle-modified 2D MOF nanosheets. The authors first synthesized the MOF nanosheets using a solvothermal method and then modified them with silver nanoparticles using a simple deposition-reduction process. The resulting hybrid nanosheets exhibited excellent stability and could be easily dispersed in water. Then, they investigated the antibacterial properties of the hybrid nanosheets against *Escherichia coli* and *Staphylococcus aureus* and found that the nanosheets exhibited excellent antibacterial activity, which was

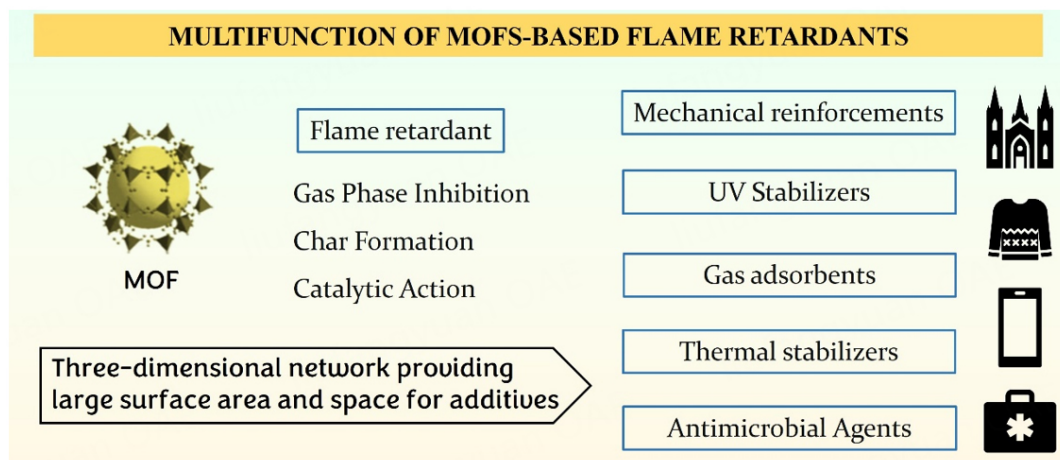


Figure 3. Multifunction of MOF-based flame retardants.

significantly enhanced under near-infrared light irradiation due to the photothermal effect of the silver nanoparticles. The authors also demonstrated that the antibacterial activity of the nanosheets could be further improved by increasing the silver content^[61]. This study provides a new strategy for the design and development of antibacterial materials based on 2D MOF nanosheets modified with silver nanoparticles. The use of near-infrared light to enhance the antibacterial activity of the material could have important implications for the development of new antibacterial therapies.

Another potential application of MOFs is as UV stabilizers. UV stabilizers are compounds that are added to polymers and plastics to protect them from the damaging effects of UV light, which can cause discoloration, degradation, and ultimately failure of the material. MOFs can be functionalized with UV stabilizers to improve their efficacy. Majidi *et al.* dispersed the GO nanoflakes in ethanol solvent and added the precursor solution of ZIF-7. The mixture was then stirred and sonicated to ensure that the ZIF-7 coated the surface of the GO nanoflakes. The resulting modified GO nanoflakes (GO-ZIF-7) were then incorporated into a polyurethane clear-coating^[62]. The researchers tested the weathering resistance and UV-shielding properties of the GO-ZIF-7-modified clear-coating and compared it to unmodified clear-coatings and coatings containing unmodified GO nanoflakes. The results showed that the GO-ZIF-7 modified clear-coating had significantly improved weathering resistance and UV-shielding properties compared to the other coatings. The MOF coating on the GO nanoflakes helped to absorb UV radiation, preventing it from penetrating the clear-coating and causing damage. Additionally, the MOF coating provided a barrier against other environmental factors, further improving the longevity of the clear coating. Therefore, the functional MOFs will continue to be developed in the future. In addition to their flame-retardant properties, MOF-based flame retardants can also influence specific functionalities to everyday applications.

MOF-derived carbon materials are synthesized by heating MOFs under controlled conditions in the absence of oxygen, resulting in the removal of the organic ligands and the formation of carbon structures^[63-66]. The resulting carbon materials inherit the unique properties of the original MOFs, such as high surface area, tunable pore size, and surface functionality. The prospect of MOF-derived carbon materials is significant due to their unique properties and potential applications. Some of the advantages of these materials include: (1) High surface area: MOF-derived carbon materials have a high surface area due to their porous nature, which makes them ideal for applications such as gas storage, catalysis, and energy storage; (2) Tunable properties: By controlling the composition and pyrolysis conditions, the properties of

the MOF-derived carbon materials can be tuned to meet specific application requirements; (3) Low cost: MOF-derived carbon materials can be synthesized from abundant and inexpensive precursors, making them cost-effective alternatives to other carbon materials and (4) Versatility: MOF-derived carbon materials can be synthesized in various forms, including powders, fibers, films, and monoliths, which makes them suitable for a wide range of applications.

In summary, the prospects for the multifunctionality of MOFs are very promising. Their unique properties make them highly versatile materials that can be tailored for a wide range of applications. We expect that future MOF-based flame retardants can show their functions in more aspects while ensuring fire safety. As research in this field continues, we can expect to see even more exciting applications of MOFs in the years to come.

LIGAND DESIGN OF MOF-BASED FLAME RETARDANTS

Traditional MOFs typically lack flame retardant properties due to the flammability of their organic components and the absence of other inherent flame-retardant elements, except for transition metals in metal frameworks. However, researchers have started to try to improve the flame-retardant properties of MOFs by different methods [Figure 4]. A commonly employed strategy involves the functionalization of ligand precursors with flame retardant moieties, such as phosphorus or nitrogen-containing groups, prior to their utilization in MOF synthesis^[67,68]. Phosphorus is an effective flame retardant because it can capture reactive radicals upon heating, which can dilute and quench the flame. Phosphorus-containing ligands, such as phosphonic acid and phosphonate derivatives, can act as flame retardant additives by releasing phosphoric acid and other phosphorus-containing species upon thermal decomposition, which promotes the formation of an expanded carbon layer. To achieve this, phosphonate or phosphonate groups can be incorporated into the organic linkers used to construct the MOF. In addition, transition metal ions that can coordinate with phosphorus-containing ligands can be used to enhance the flame-retardant properties of the MOF. Lu *et al.* synthesized an organic ligand containing P/N and combined it with Co to form a novel P-MOF^[69]. The researchers found that adding the P/N-treated cobalt MOFs to the lignin-based epoxy resins (EP) significantly improved their flame retardancy, as demonstrated by reduced peak heat release rates and decreased total heat release.

Bio-functional MOFs (Bio-MOFs) are biocompatible and biodegradable porous materials made from organic and inorganic building blocks with tunable porosity and high surface area. They can be functionalized with biological molecules to enhance selectivity and specificity, making them useful in biotechnology and environmental science^[70]. Nabipour *et al.* used adenine as an efficient adsorbent for *in situ* removal of zinc ions, resulting in the formation of a bio-MOF. The as-prepared bio-MOF was then added to the EP matrix to investigate its impact on the thermal stability, smoke suppression, and flame retardancy of the EP composites. The results showed that the addition of a boom improved the flame retardancy and smoke suppression properties of the EP composites^[71]. Zhou *et al.* present a study on a sustainable approach for simultaneously achieving flame retardancy, UV protection, and reinforcement in polylactic acid (PLA) composites using fully bio-based complexing couples. The authors used two bio-based complexing couples, tannin acid/ferric salt (TAF_e) and chitosan/phytic acid (CTSPA), to fabricate the composites. The thermal and burning properties of the composites were evaluated by various tests, including TGA, limiting oxygen index (LOI), UL-94 test, and cone calorimetry. The results showed that the composites with TAF_e and CTSPA had an earlier mass loss and higher char residue than pristine PLA. CTSPA also enhanced the LOI value of PLA from 19.6% to 30.5%. The study demonstrates a promising approach for developing sustainable composite materials with multiple desirable properties^[72].

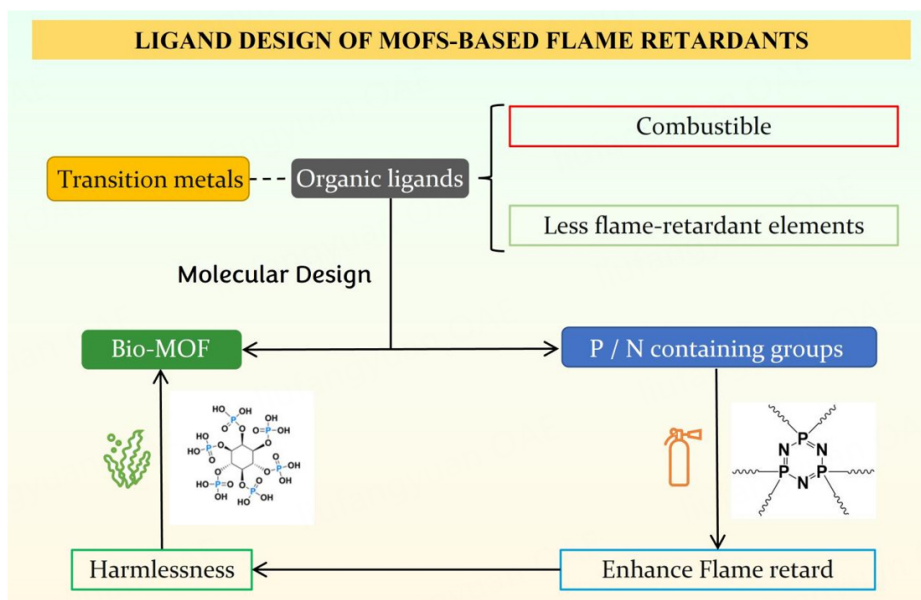


Figure 4. Ligand design of MOF-based flame retardants.

Harmlessness to the human body and environment-friendly recycling have become the prerequisites for the future development of flame retardants. Traditional flame retardants, such as halogenated compounds, have been found to be detrimental to both human health and the environment. Phosphorous flame retardants are commonly utilized in a diverse range of consumer goods, such as electronics, furniture, and construction materials, to mitigate the risk of fire. Nevertheless, these compounds have been associated with various potential hazards: (1) Phosphorus-based flame retardants have been found to accumulate in the environment, including soil, water, and air samples. They can also bioaccumulate in aquatic organisms and pose a toxic threat to fish and other wildlife; (2) Evidence suggests that exposure to certain phosphorus-based flame retardants may negatively impact human health. Therefore, developing effective ligands without the use of phosphorus or halogen presents a significant challenge. Overall, the utilization of biofunctional MOFs as flame retardants presents a promising avenue for research that could result in the development of safer and more environmentally sustainable materials. However, further investigation is necessary to comprehensively comprehend the properties and potential applications of these materials.

MOF DERIVATIVES TREATMENT AS FLAME RETARDANTS

As previously mentioned, the flammability of MOF ligands is a limiting factor in their inherent flame-retardant properties. Therefore, post-treatment techniques are often required to enhance their fire-resistant capabilities [Figure 5].

One common post-processing technique for MOFs involves the modification or removal of organic ligands. In MOFs, ligand removal can be achieved through an acid-base reaction between the MOF and solvent, which entails protonation of the organic ligand by a strong acid followed by detachment from the metal center. Generally, metal ions or clusters are linked by organic ligands in MOFs. These ligands usually contain carboxylic or amino functional groups that can serve as proton acceptors or donors, respectively. When a MOF is exposed to an acidic solution, the protons in the acid can interact with the functional groups on the ligands, resulting in protonation of the ligand. Subsequently, weakened affinity for metal centers allows easy detachment from metal ions or clusters. The liberated metal sites are then available for

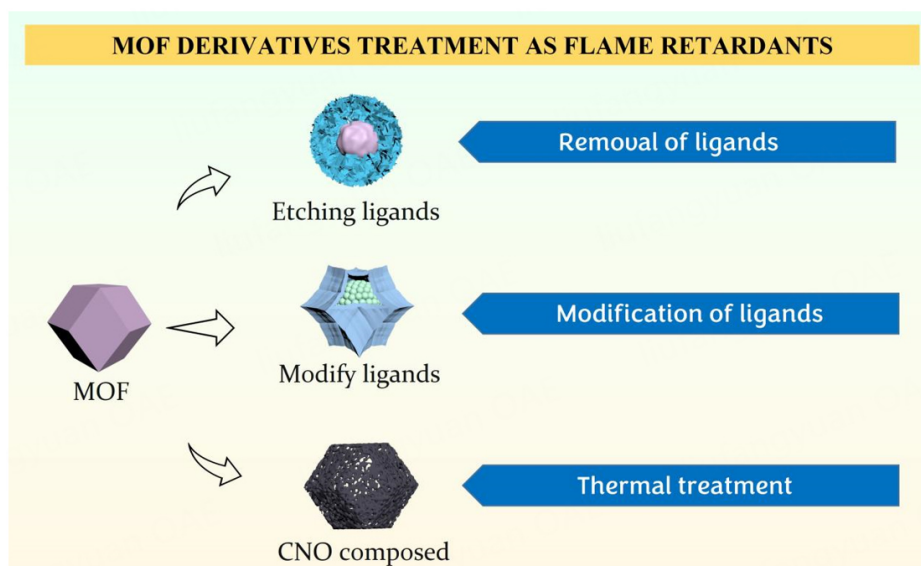


Figure 5. MOF derivatives treatment as flame retardants.

re-coordination with other ligands or functional groups, leading to a new MOF with altered properties^[73]. The acid-base theory of ligand removal in MOFs has found diverse applications, ranging from the synthesis of novel MOFs to the functionalization of existing ones with guest molecules and the recovery of metals from them^[74-76]. The judicious selection of acids and solvents can significantly impact both the extent and selectivity of ligand removal, rendering this approach highly versatile and tunable.

Previously, Pan's group have done a series of work to derive LDH by etching ZIF [Figure 6]^[77-82]. We incorporated mesoporous zinc hydroxystannate (ZHS) nanoparticles into NiCo-LDH nanocages that were derived from ZIF-67. The resulting composite material was then tested for its flame retardancy properties, and it was found that the LOI value of an epoxy composite containing 6 wt.% of these fillers increased to 27.2%. This improvement was significant enough to meet the UL-94 V-0 level, which is a widely recognized standard for flame retardancy. Subsequently, polyphosphazenes (PZS) is often used in modification and compounding of flame retardants because of its rich phosphorus and nitrogen, ZIF@LDH@PZS core-shell structures and LDH@PZS@NH trishell structures were synthesized through surface polycondensation on ZIF-67 using PZS, followed by ligand etching via nickel brine acidification. The interface of LDH was analyzed by adjusting the reaction time to enhance compatibility with the resin matrix. Recently, we have synthesized several hollow LDH nanocages with high thermal stability, featuring single-yolk shell nanostructures (s-CBC@LDH) and multi-yolk shell nanostructures (m-CBC@LDH). By incorporating phosphorus-based flame retardants, we have further enhanced their flame-retardant properties.

In the context of flame retardancy, LDHs are often used as additives to reduce the flammability of polymers. When LDHs are added to a polymer, they act as a physical barrier that prevents the diffusion of oxygen and other flammable gases to the surface of the material, thereby reducing the rate of combustion. One issue with the physical barrier effect of LDHs is that the thickness and width of the barrier layer are limited by the amount of the LDH that can be added to the polymer matrix without affecting its properties. Thicker barriers may be required to achieve adequate flame retardancy in some applications, but a small length-diameter ratio of LDH may not meet the flame-retardant demand. One of the main challenges in using LDHs as pure inorganic flame retardants is achieving proper dispersion in the polymer matrix. Inadequate dispersion can lead to the formation of voids or weak points in the barrier layer, which can compromise its

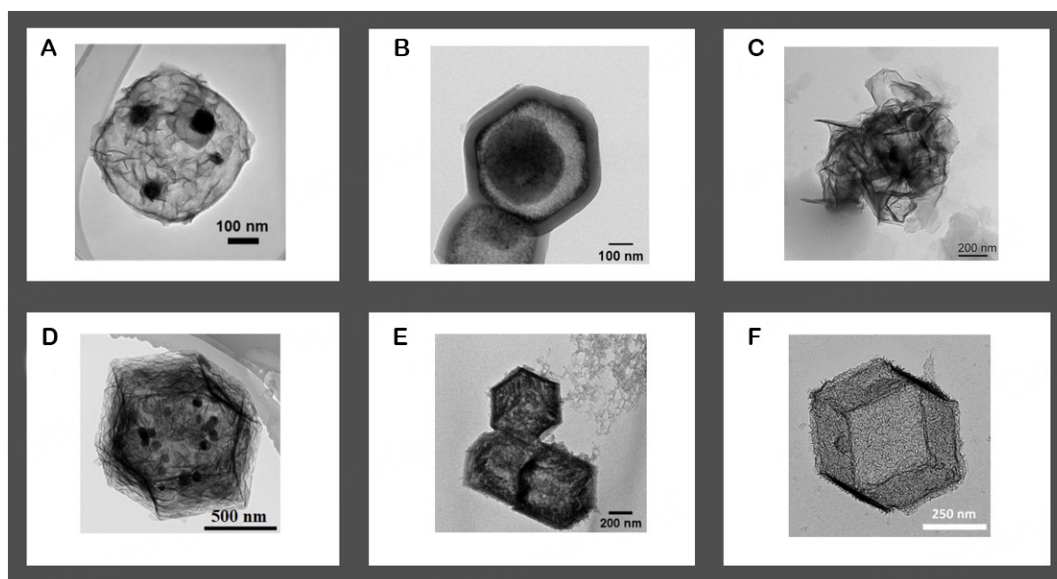


Figure 6. Microstructures of (A) ZHS@NCH (Reproduced with permission^[77]. Copyright 2019, American Chemical Society); (B) ZIF@LDH@PZS (Reproduced with permission^[78]. Copyright 2022, American Chemical Society); (C) m-CBC-P@LDH (Reproduced with permission^[79]. Copyright 2023, Elsevier); (D) m-CBC@LDH (Reproduced with permission^[80]. Copyright 2023, Elsevier); (E) MPOFs (Reproduced with permission^[81]. Copyright 2022, American Chemical Society); (F) ZNs-B/CP (Reproduced with permission^[82]. Copyright 2022, Elsevier).

effectiveness in preventing flame spread. Therefore, to enhance the compatibility of LDH, it is typically necessary to further modify or combine it with other flame retardants. Wang *et al.* modified LDH by toluene diisocyanate, 2-hydroxyethyl acrylate, and vinyl triethoxysilane (LDH-TDI-HEA-VTES) to improve its compatibility with organic matrix, resulting in better dispersion of modified LDH in matrix compared with LDH^[83]. The experimental results showed that with the increase of LDH-TDI-HEA-VTES content, the thermal stability, mechanical properties, flame retardant properties, and shear resistance of LDH-TDI-HEA-VTES-Acrylate composites were improved.

Moreover, acid etching can be employed to generate a novel ligand that substitutes the initial one. Wang *et al.* used a modified version of core-shell ZIF-67@ZIF-8, where phytic acid was added to the structure^[84]. The new phytate-metal ion hybrids are formed to improve the flame retardancy of EP. Our group also utilized carboxyl POSS to modify ZIF-67 and successfully synthesized Metal-POSS Organic Frameworks (MPOFs). Thioglycolic acid was employed to replace the original imidazole ligand and complex with metal ions. Additionally, We have synthesized hollow nanocage structures with a greater number of active sites by utilizing ZIF as a sacrificial template and employing stepwise etching in the sequence of phytic acid and boric acid. Another technique is thermal treatment. This involves exposing the MOF to high temperatures, which can cause structural changes that improve their ability to act as flame retardants. Hou *et al.* developed a method that involves utilizing HKUST-1, a MOF, as a sacrificial template to synthesize Oxygen-Rich Covalent C₂N (CNO) nanosheets through thermal treatment and chemical vapor deposition^[85].

In summary, conventional MOF ligands are often composed of organic compounds that possess flammability. Additionally, the limited presence of flame-retardant elements in MOFs may result in reduced flame-retardant effects and decreased practicality. The method of post-treatment MOFs is simple and controllable and has the following advantages: (1) Endowing MOFs with more flame-retardant elements: by

incorporating additional flame-retardant elements, such as phosphorus or nitrogen, into the MOF structure during post-treatment, their flame retardancy can be enhanced; (2) This method involves breaking the coordination bonds between the metal ions and the ligands in the MOF, which allows for the creation of a hybrid material that inherits some desirable properties of the original MOF, while also introducing new features; (3) Generating expanded pores: post-treatment of MOFs can create larger pores or expand existing ones, which can improve their ability to adsorb volatile organic compounds and harmful gases produced during polymer combustion. The expanded pores can be used as a carrier to load phosphorus-based flame retardants, which can further improve the flame retardancy of MOFs. Zhao *et al.* transformed the microporous structure of MIL-53 into macropores via ammonia water treatment under closed conditions, thereby enhancing its specific surface area and adsorption capacity^[21]. The excellent porous architecture was then utilized for triethyl phosphate (TEP) adsorption as a flame retardant in polystyrene and (4) Controlling morphology: multi-level pore structures can provide more active sites for catalytic reactions. Hollow structures can reduce the weight of flame retardants, which can improve their dispersion and increase the number of active sites available for flame retardancy. As a result, the flame-retardant efficiency has been significantly enhanced while minimizing any adverse effects on the mechanical properties of EP composites.

OUTLOOK

This perspective provides a concise overview of the latest research advances in MOF flame retardants and offers insights into their prospects. Compared to other commonly used fillers, such as platelet-like clay, carbon-based fillers, and silicates, MOFs offer several distinct advantages: In Gas-Phase, Certain MOFs containing nitrogen or phosphorus-containing organic ligands exhibit gas-phase action, effectively trapping active radicals and diluting combustible gases. This gas-phase action contributes to the overall flame retardancy of polymers by interrupting the combustion chain and reducing the availability of flammable gases. In the condensed phase, the metal ions or clusters present in MOFs act as catalytic centers, promoting char formation during combustion. This catalytic activity enhances the formation of a protective char layer, which acts as a barrier against heat and mass transfer, thereby improving the flame retardancy of the polymer. Furthermore, MOFs offer a high degree of tunability, allowing for the customization of their properties to suit specific applications. The pore size, surface area, and composition of MOFs can be tailored to optimize flame retardant performance and address specific requirements of the polymer matrix. These advantages position MOFs as promising alternatives to conventional flame-retardant fillers.

The cost outlook of MOF flame retardants is an important consideration for their widespread adoption in various industries. The cost of MOF flame retardants is influenced by several factors, including the cost of raw materials, the synthesis process, and the scale of production. One approach to reducing their cost is to optimize the synthesis process. The development of more efficient and scalable synthesis methods can reduce the cost of production and increase the yield of MOFs. Additionally, the use of cheaper starting materials and reagents can also lower the cost of MOF flame retardants. Another approach to improving the cost-effectiveness of MOF flame retardants is to increase their functionality and versatility. By designing MOFs with multiple functions, their value proposition can be increased, which can justify the higher cost. In addition to industrialization, researchers are also striving to develop multifunctional MOFs that can perform multiple tasks simultaneously. These types of MOFs can be engineered not only for flame retardants but also for gas absorption, antibacterial activity, or pollutant filtration. Ligand synthesis and derivatives are also important areas of research in the development of MOFs for flame retardant applications. By designing novel ligands and derivatives, researchers can precisely adjust the properties of MOFs to enhance their efficacy in fire suppression. Altering the structure of ligands or introducing new functional groups can elevate the thermal stability or augment the flame-retardant characteristics of MOFs.

The potential of MOFs in the field of flame retardancy is promising, with ongoing research expected to yield more effective and widely applicable flame-retardant materials that can address important safety concerns across a multitude of industries.

DECLARATIONS

Authors' contributions

Conceptual design and project supervision: Pan YT

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Availability of data and materials

Not applicable.

Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China (No.22005029) and the Australian Research Council (FT190100188; LP220100278).

Ethical approval and consent to participate

Not applicable.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Consent for publication

Not applicable.

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