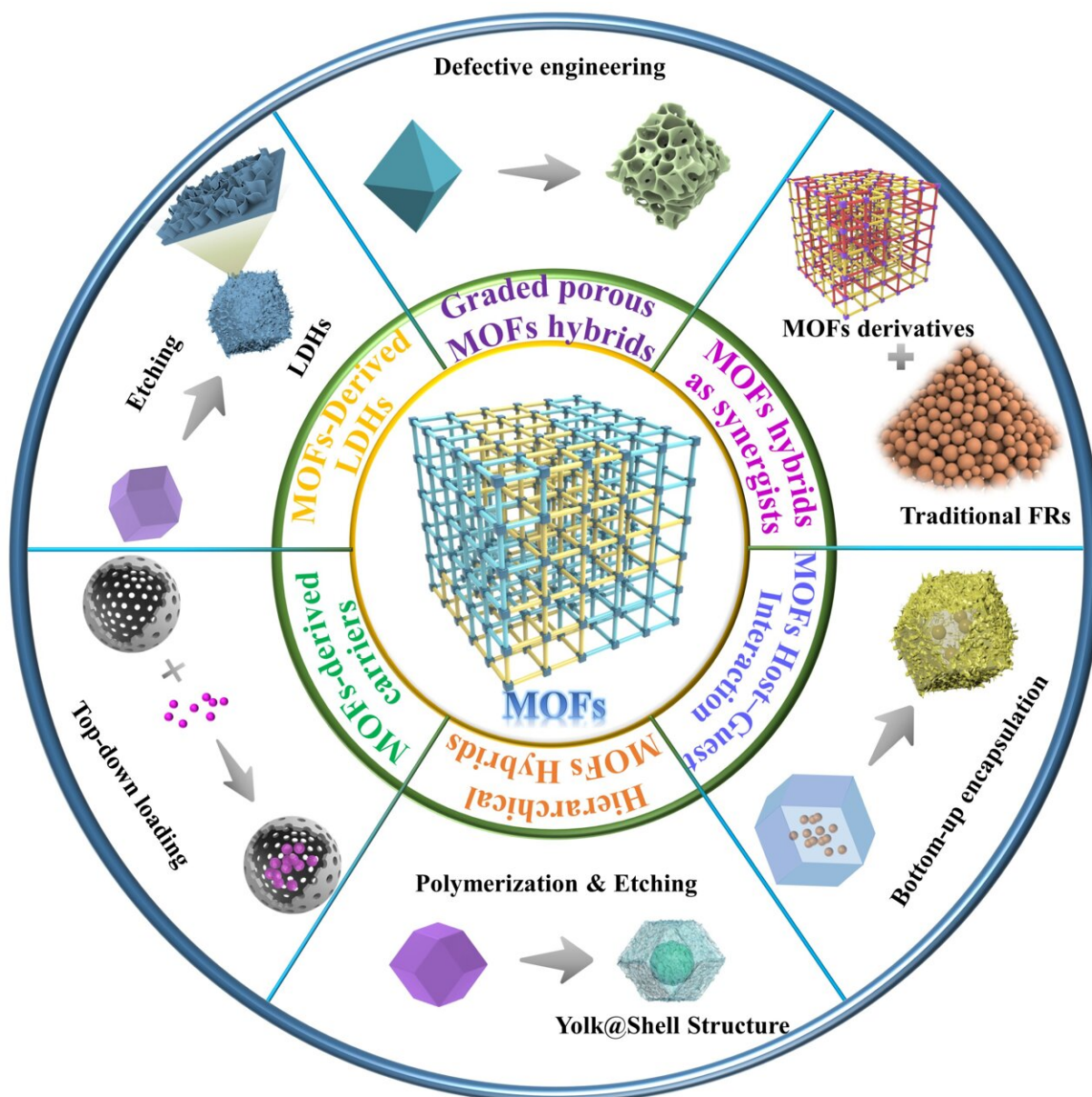


# Researchers conduct comprehensive review on preparation of MOF-based flame retardants via coordination bond cleavage

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Recent advances in the preparation of MOFs-based flame retardants based on coordination bond cleavage and their flame retardant applications. Credit: Ye-Tang Pan, Beijing Institute of Technology, China.

Since the first report of metal-organic framework (MOF)-based flame retardants in 2017, this research area has exploded. However, improving the flame-retardant efficiency of MOFs and expanding their application areas remain critical challenges. The physicochemical properties of MOFs are closely dependent on their topology, pore characteristics, and chemical composition, which can be modulated by targeted design.

Relative to direct synthesis, post-synthesis strategies for MOFs, including [ion exchange](#), ligand replacement, and acid/base etching have greatly increased their application scope and potential. Methods based on coordination bond cleavage of MOFs have proven to be very effective in modulating the structure and have attracted extensive research in the field of flame retardancy.

The team of Ye-Tang Pan at Beijing Institute of Technology (BIT) focuses on the design and preparation of MOF-based [flame retardants](#) and multifunctional flame retardant polymer nanocomposites. This work presents important progress of MOF-based flame retardants so far from three aspects: the development and challenges of MOF-based flame retardants, the design of efficient MOF-based flame retardants through coordination bond breaking, and the application of functionalized MOFs in flame retardant field.

The work is [published](#) in *Industrial Chemistry & Materials*.

MOFs applied alone do not confer high-limiting oxygen index (LOI) values and UL-94 vertical combustion ratings to polymer composites, due to the single flame-retardant element, low percentage of flame-retardant elements, flammability of ligands, and microporous-dominated pore structure that is difficult to fully utilize.

"In this review, we critically evaluate for the first time post-synthetic methods involving coordination bond cleavage in the flame-retardant field in order to tailor composites and structures with or without disrupting the reticulation chemistry of the parent matrix of MOFs," said Ye-Tang Pan, a professor at Beijing Institute of Technology, China, "We conclude with a critical outlook on the applications, challenges, and future prospects of this emerging and evolving field."

Template derivatization of MOFs is considered to be an effective strategy for the preparation of structurally functionalized materials; however, the typically generated metal-carbon compounds dramatically depend on uncontrollable heat treatments and are energy-consuming. Costly organic ligands are cracked into gases and spilled at high temperatures, accompanied by intrinsic structural contraction, leaving carbon structures with scarce functional components.

Therefore, the pseudomorphic cleavage of MOFs based on the ion/ligand exchange strategy is more facile, gentle and controllable, which is also increasingly investigated in many fields. MOFs possess inherent flame-retardant potentials, i.e., large specific surface area, well-defined pore structure, and tunable physicochemical properties, and the above strategies also provide feasible insights into the flame-retardant functionalization of MOFs.

Acid-base strength mismatch leads to the pH value far from 7 for the corresponding salt during hydrolysis. Alkaline imidazolate ligands in ZIFs are prone to protonation by the  $H^+$  released from the salt-contained

aqueous solution, followed by the collapse of the frameworks.

The group pioneered correlational research as early as 2017 in which honeycomb-like aluminum hydroxide flakes were fabricated by using aluminum nitrate (aq.) to attack ZIF-8 aggregates. The removal of rhombic dodecahedra with the residual of the outer coated layer resulted in mesoporous  $\text{Al}(\text{OH})_3$  that could be further loaded with phosphorous-based flame retardant to improve the fire safety of epoxy resin (EP), superior to the commercial counterparts.

A major reason that the flame retardancy of MOFs alone is not outstanding is that their structures contain a large number of flammable ligands. Flame-retardant functional substitution of pristine ligands by post-synthesis ligand exchange strategy provides a good idea to improve the flame-retardant performance of MOFs.

For ZIFs composed of basic ligands, acidic compounds are more likely to break their coordination bonds, which is caused by ionized  $\text{H}^+$  protonated ligands. The dissociation process of the coordination bonds of MOFs under alkaline conditions can be simplified as a ligand exchange process in which the coordination groups in solution are replaced by anions/molecules such as  $\text{OH}^-$  and  $\text{H}_2\text{O}$ .

Thermodynamically, MOFs are more inclined to remain in the crystalline state if the coordination bond between the metal ion and the ligand (M-L) is stronger than that between  $\text{OH}^-$  or other [ligand](#) anions.

Furthermore, inspired by the encapsulation strategy and the acid etching strategy, the group reported for the first time that the phenomenon of acid generation by condensation of specific compounds was utilized to achieve simultaneous etching of ZIF-67 during the encapsulation process, which is conducive to the improvement of the flame retardancy and synthesis efficiency for the prepared fillers.

As a porous material, MOFs can adsorb smoke particles and toxic gases generated during polymer combustion. However, MOFs as flame retardants often face the problem of insufficient char formation capacity. The loading of functional fillers is an effective strategy to solve this problem. The effective loading of guests can be realized by preparing carriers with hierarchical porous or hollow structures.

This research group constructed bird's nest-like hierarchical porous nanocages with effective loading of triphenyl phosphate up to 35.8 wt%, and the prepared polyurea composites showed good durability in terms of flame retardant properties. In addition, designing MOFs with open nanostructures can improve their smoke particle trapping ability. Toxic gases and smoke particles are more easily captured by MOFs through physical and chemical adsorption.

The easy functionalization of MOFs also creates convenient conditions for grafting target molecules. The main methods include the substitution reaction between amino-functionalized MOFs and flame retardants containing phosphorus-chlorine bonds; the addition reaction between double-bond functionalized MOFs and flame retardants containing phosphorus-hydrogen bonds; and the salt formation reaction between amino-functionalized MOFs and flame retardants containing phosphate ester bonds.

Flame retardants derived from MOFs have outstanding flame retardant advantages, and improving the flame retardancy of MOFs through coordination bond cleavage as well as expanding their functional applications is one of the effective means.

"In this work, we systematically summarize and outline the direct or indirect breaking of coordination bonds based on conformational relationships and further functionalization to construct highly efficient MOFs flame retardants, as well as the future prospects and challenges

faced. It is also hoped that this work will quickly guide researchers through the field and inspire their next studies," said Professor Pan.

**More information:** Kunpeng Song et al, Coordination bond cleavage of metal–organic frameworks and application to flame-retardant polymeric materials, *Industrial Chemistry & Materials* (2023). [DOI: 10.1039/D3IM00110E](https://doi.org/10.1039/D3IM00110E)

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