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REVIEW

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Coordination modulation: a way to improve the properties of metal-organic frameworks

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Metal–organic frameworks (MOFs) are highly valuable hybrid materials that have drawn significant research attention. One reason for such attractiveness is the designability of their important porosity features such as surface area, surface chemistry, pore shape, size, and size distribution. The coordination modulation method provides a useful way to further modify the porosity, size and shape of MOFs, whereby modulators act as guiding agents during the MOF synthesis. In this review, we discuss coordination modulation with various types of modulators, synthesis techniques, the action of modulators, as well as the effect of modulators on the properties of the modulated MOFs and their application.

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1. Introduction

Metal–organic frameworks (MOFs) are potentially porous coordination networks with metal nodes and bridging organic ligands, called linkers. It is essential to control the morphology and porosity of MOFs in order to advance their potential applications without altering the basic chemical framework structure. Various methods, such as microwave (MW) heating, ultrasonic (US) and surface active agent (surfactant)-assisted syntheses, and coordination modulation have been used to control MOF formation.^{1,2} The rate and direction of crystal growth can also be affected by modulators that may in turn change the crystallinity and phases of the MOFs.^{3–7}

Modulation is a popular and easy method for tuning MOFs by applying an auxiliary ligand named modulator. In 2009, Tsuruoka *et al.* were apparently the first to report a modulator effect in MOF synthesis.⁵ Traditionally, both inorganic and organic acids or bases have been used as modulators in MOF synthesis. This classical approach provides a solid foundation for MOF modulation. In addition, amino acids, which are characterized by both acidic and basic functionality, are proving to be versatile modulators,^{8,9} as are surfactants, polyoxometallates, and various guest molecules. These various species enable finely tuned MOF structures.

The crucial factor in modulating MOF formation is the interaction between the chosen modulators and the organic linkers or the inorganic metal centers. This interplay between the different modulators, organic components and metal ions is the cornerstone for precise control of MOF synthesis if the modulator has a coordinating group, similar to the linker of MOF, it can compete with the linker for coordination to the metal ion during the framework assembly. The presence of a coordinating modulator can affect the nucleation process and its kinetics. Further, the growth of the framework is influenced by this competition, leading to specific morphologies, crystal sizes, and porosity features. If the modulator is (in addition) an acid or base then it will also influence the pH of the reaction medium and, thus, the acid–base equilibrium of the linker if this is derived by deprotonation from its (carboxylic or azole) acid precursor.¹⁰

Several monodentate carboxylic acids have been reported in the literature as modulators such as formic acid (FA), acetic acid (AA), benzoic acid (BA), dodecanoic acid, or lauric acid.¹¹ The use of carboxylate or carboxylic acid modulators is frequent since multitopic carboxylate linkers are one of the main linker types in MOFs.^{5,12-14} Basic modulators include pyridine,¹⁵⁻¹⁷ sodium hydroxide,¹⁸ or ammonium hydroxide.¹⁹ The most commonly used surfactants are cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS) or sodium dodecyl sulfate SDS.²⁰⁻²²

Thus, modulating conditions may also be beneficial for the formation of specifically MOF nanoparticles.^{5,7,23-25} At the nanodimension, the diffusion path length is shorter, allowing guest molecules to enter the pores more quickly. Additionally, the larger outer surface area relative to the volume makes more active functional groups on the outside of the MOF particles accessible for interactions.^{7,23,26} Furthermore, modulation can lead to the formation of highly crystalline products due to the slowed growth rate of the crystal.^{1,27} In addition, modulators can facilitate the formation of clusters²⁸ and some topologies of the MOFs.²⁹

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Table 1 Examples for the effect of modulators

| Effect | Modulator ^a | Examples | Ref. |
|---------------|------------------------|---------------------------------------------|------|
| Crystal phase | BA | Zr-SXU-1, Zr-SXU-2, Zr-SXU-3 | 33 |
| | BA | MIL-101 (Cr), MIL-88B (Cr) | 34 |
| | TFA | NU-1000, NU-901 | 35 |
| Size | AA | MIL-101 (Cr) | 36 |
| | MNA | CuNDC | 37 |
| | NH_4OH | $Co_2(bim)_4$ | 38 |
| Morphology | CTAB | NMOF-1 | 25 |
| | AA, FA | MIL-88A (Fe) | 39 |
| Defects | Carboxylic acid | UiO-66 | 40 |
| | 1-HMIM | BIT-58 | 41 |
| Porosity | Citric acid | HKUST-1 | 42 |
| | FA, AA, DFA, TFA | UiO-66 | 43 |
| Surface area | AA | UiO-67 | 27 |
| | MeOH | MIL-88B (Fe) | 44 |
| Stability | TFA, AA | UiO-66 | 45 |
| Low | AA | UiO-66 | 46 |
| temperature | HCl | UiO-66 | 47 |
| | FA | DUT-67, UiO-66-NH ₂ , MOF-801 | 48 |

^{*a*} List of abbreviations (alphabetical order): AA = acetic acid, BA = benzoic acid, CTAB = cetyltrimethylammonium bromide, DFA = difluoroacetic acid, FA = formic acid, 1-HMIM = 1-methylimidazole, MNA = 6-methoxy-2-naphtholate, TFA = trifluoroacetic acid.

Despite lack of sufficient in-depth knowledge at the molecular level to understand the modulation mechanism, modulation allows the MOF properties to be changed and adapted or improved to potential applications.^{6,30–32} For example, MOF films with applications in catalysis and gas separation can be formed through the growth of crystal faces in certain directions.²³ In addition, by applying these modulation control techniques, we can gain a better understanding about the fundamentals of the framework assembly mechanism.²⁴

In this review, we aim to address the synthesis methods of modulated MOFs and the effect of modulation on their properties. Table 1 shows an introductory overview on the general effect of modulation on the properties of MOFs and this synthesis processes using various examples.

2. Types of modulators

2.1 Inorganic acids

Inorganic acids, such as aqueous HF or HCl, can directly shift the acid-base equilibrium of the organic linker acid to the protonated state. The deprotonation of the linker precursor acid to form the conjugated base anion is a requirement for the actual anionic linker coordination to the metal ions. Hence, an added acid will acid-base equilibrium of the linker to its acid form which consequently slows down the formation of the coordination network.^{24,49} Thereby, the crystallinity of the MOF can be improved. Further, the anions of inorganic acids, such as F^- , Cl^- , SO_4^{2-} , NO_3^- are also coordinating ligands to metal ions. Thereby, this anionic ligand can compete with the linker for coordination to the metal ion during the framework assembly. Using concentrated HCl as a protonation modulator is a wellstudied approach in the literature. It can increase the number of defective sites in UiO MOFs by replacing a linker with coordinating chloride ligands and by increasing the acidity of the reaction medium and the hydrolysis rate of the solution.¹⁰

In 2013, Katz *et al.* analyzed the effects of HCl as a modulator on the formation of UiO-66, UiO-67, and their functionalized derivatives such as UiO-66-NH₂. The results of this study showed that the use of HCl as a modulator resulted in obtaining phase-pure and reproducible results.⁴⁷

Fluoric acid, HF, has also been used for the synthesis of MOFs, including MIL-101(Cr),^{50,51} UiO-66,⁵² MIL-53 (ref. 53) and Al-MOFs.⁵⁴ These MOFs have sizes ranging from nano- to micrometers and regular morphologies. During the MOF synthesis, the fluorine anions can form strong metal-fluoride bonds with the metal centers, which then directly compete with the linkers used. The presence of HF modulator has been demonstrated to be effective in controlling morphology, size and volume of pores, and acidity of the reaction medium during the synthesis of MOFs.^{50,55,56}

In addition to the direct competition with the linkers, the anion of the inorganic acid modulator also contributes to charge balancing. This significantly influences the process of self-assembly of the MOF.⁵⁴

2.2 Inorganic bases

Inorganic basic modulators, with their alkaline properties, increase the solubility of the organic carboxylic acid precursors of the linkers by deprotonating the acid to the carboxylate anion. The increased solubility then leads to faster nucleation and the formation of smaller MOF crystallites. Additionally, basic modulators can form hydroxides or oxides with the metals involved, further accelerating the nucleation process. Ammonium hydroxide is a frequently employed base in MOF synthesis due to its effectiveness in enhancing linker solubility and facilitating nucleation, influencing the size and structure of the resulting MOF crystals.^{57–59} Abid *et al.* synthesized a series of UiO-66 MOFs with different concentrations of ammonium hydroxide as modulator. They were able to show that with increasing modulator concentration, the particle size decreased while the pore size increased.⁵⁷

2.3 Carboxylate modulators

The use of monocarboxylate modulators like formic acid, acetic acid, and benzoic acid is typical in the synthesis control of carboxylate MOFs.^{4,12-14} The metal–ligand coordination equilibrium between the monocarboxylate modulator and the oligocarboxylate linker affects the nucleation process, which is in turn connected to reaction kinetics.⁶⁰ Shearer *et al.* examined the impact of acetic acid (AA), formic acid (FA), difluoroacetic acid (DFA), and trifluoroacetic acid (TFA) at different concentrations on the synthesis of UiO-66 MOFs in terms of crystal-linity, surface area and defects. Their work revealed that all these modulators, also at different concentrations, exerted a beneficial influence on the formation of UiO-66.⁴³

The use of monocarboxylate modulators in their anionic form, *e.g.* sodium acetate, can also influence the deprotonation equilibrium of the oligocarboxylic acid linker precursor.^{1,49}

2.4 Amino acid modulators

Amino acids are appealing modulating agents due to their abundance and the wide variety of side chains in their structure, which can result in unique modulating properties. Diverse amino acids, such as proline, phenylalanine, and glycine, can be effective modulators for the synthesis of MOFs, especially Zr and Hf MOFs, ZIFs and the UiO-66 series. This can result in high-quality crystals with proper pore size and morphology, thereby increasing their application potential.^{9,61,62} Amino acids are divided into five categories based on side-chain polarity: aromatic, aliphatic non-polar, polar uncharged, positively charged, and negatively charged. Unlike inorganic acid modulators, amino acids have been employed to a lesser extent for the purpose of synthesizing MOFs in a controlled manner.

Liang *et al.* investigated the effect of 20 natural amino acids as modulators on the synthesis of ZIF-8 in an aqueous solution. It was observed that the size and morphology of the ZIF-8 particles depended on the chemical nature of the amino acids, especially in terms of their polarity. By increasing the hydrophobic property of non-polar amino acids, the morphology of ZIF-8 changed from spheroid and dodecahedron to rhombic and truncated cube, respectively. This change was accompanied by a decrease in particle size and an increase in the number of particles. The polar neutral amino acids exhibited a similar orientation. Small spheres of ZIF-8 were formed by the negatively charged amino acids. When a mixture of two different amino acids was used, two types of particle distributions were produced, relating to the MOFs synthesized by two different amino acids as modulators separately.⁶³

2.5 Amine modulators

Amine modulators can deprotonate the carboxyl acid linker precursor and also assume the role of competitive ligands in bonding with metal centers. Thus, through these two functions, they may modify the nucleation and crystal growth process. Cravillon *et al.* indicated that the presence of *n*-butylamine modulator during the synthesis of ZIF-8 led to the production of ZIF-8 nanocrystals. However, increasing the amount of *n*butylamine eventually did not result in smaller particles, as the amine then acted as a competing ligand with the imidazolate linker.²⁴

Lu *et al.* successfully synthesized NH_2 -MIL-53(Al) nanoplates using a urea modulator *via* a one-step hydrothermal method. This nanoplate was then employed as a fluorescent probe for the highly selective analysis of free chlorine in water.⁶⁴

Taddei *et al.*, studied the effect of substituting amine functional groups in benzoic acids on defect sites and electronic properties of MOF. The framework structure of the selected ABAs include 2-aminobenzoic acid (2-ABA), 3-aminobenzoic acid (3-ABA), 4-aminobenzoic acid (4-ABA), and 3,5-diaminobenzoic acid (3,5-DABA). Benzoic acid (BA) without amine substitution was also used to better evaluate the impact of amine groups on MOF performance. They confirmed that MOF band gaps can be influenced by defect engineering with the help of different aminobenzoic acids as modulators. These results demonstrate that the band gap can be modified by altering the position or number of amine groups in the aromatic ring. By using ABA modulators as species for defect engineering, a narrowing of the HOMO-LUMO gap will ensue.⁶⁵

2.6 Surfactant modulators

The main characteristic of surfactants is their amphiphilic behaviour based on the fact that they have both a polar head group and a long non-polar tail. The effect of surfactant modulators such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) on MOF structures depends upon the molecular interactions between the functional polar head groups of the surfactant and the surface of the growing MOF.66 They can either undergo adsorption onto crystal facets on the surface of MOF structure to favor one direction of growth, or function as capping agents to take control over particle size and morphology during the MOF formation process.67 The charge density of the surfactant head is critical for controlling the size and shape of MOFs. By using polyvinylpyrrolidone (PVP), Cai et al. showed that the structure of Fe-MIL-88B changes from hexagonal bipyramids to bipyramidal hexagonal prism as a function of the concentration of PVP, with a concomitant increase in particle size in one direction, from 1.8 to 5.4 nm. This type of morphology change occurred due to the preferential interaction of the pyrrolidone with the iron ions.68 Surfactants can be used to introduce mesopores in otherwise microporous MOFs during the synthesis.⁶⁹ The formation of micelles in solution by surfactants provides a template where the MOF can grow around. The mesopores are then surrounded by the walls of the micropore MOF. After the surfactant is removed through washing processes, mesopores remain in the MOF structure.23

Surfactant or surfactant/co-surfactant liquids form emulsions from hydrophilic and hydrophobic phases. The dispersed phases can be considered a large number of sites that facilitate chemical reactions, particularly towards nanomaterials.^{70,71} Using these microemulsions, it is possible to modulate the features of MOFs through parameters such as ratio of solvents and surfactants,⁷² additives,⁷⁰ and temperature.⁷³

2.7 Polyoxometallate modulators

Polyoxometalates (POMs) are inorganic anionic clusters and can act as structure-directing agents through hydrogen bonding, coordination interactions, and electrostatic interaction.⁷⁴ POMs may affect the coordination bonding between metal centers and organic ligands during the MOF synthesis. Therefore, they can control the nucleation and growth processes, which in turn affects the morphology and size of MOFs.⁷⁵ Wang *et al.* achieved the regular and uniform morphologies of octahedrons and hollow hierarchical spheres by using Keggin-type POMs (sodium phosphotungstate, abbreviated as NaPW) as a modulator in the synthesis of nano[Cu₃(BTC)₂]_n (BTC = benzene-1,3,5-tricarboxylate) (Fig. 1).⁷⁶



Fig. 1 Schematic representation of the synthesis of $[Cu_3(BTC)_2]_n$ nanoparticles modulated by POM and water. At the bottom, TEM/SEM images of the uniform $[Cu_3(BTC)_2]_n$ nanocrystals can be seen (scale bar is 200 nm).

In the report of Xu *et al.*, uniform hierarchical Fe/Co-BTC nanotubes were prepared using NaPW modulator, which exhibited appealing properties, such as increased specific area, large pores, and low density, leading to an increase in the number of active sites for desirable catalytic applications for the detoxification of sulfur compounds by O_2 .⁷⁷

2.8 Gas modulators

The field of gas modulation in MOFs remains relatively uncharted within the domain of MOF synthesis. In this methodology, distinct gases are intentionally introduced into the reaction autoclave under elevated pressures. A crucial prerequisite in this context is the specific interaction between the chosen gas and the metal species employed in the synthesis. This compatibility favors the interactions between the gas molecules and the metal atoms, facilitating and promoting the controlled formation of MOFs. In the example of Monteagudo-Olivan *et al.* the reaction time of MIL-88A(Fe) and MIL-53(Fe/Al)-Fa could be shortened with the aid of CO and O₂ gas at a pressure of 6 bar.⁷⁸

2.9 Large organic molecule modulators

Large organic molecule modulators comprise a category of molecules that exert a discernible influence on MOF formation due to their size and structural properties. These modulators span a broad spectrum, ranging from relatively small molecules such as caffeine to larger molecules such as rhodamine B or polyethylene glycol. In the case of caffeine, the effect of these modulators is shown by interactions with the organic linkers *via* hydrogen bonds.^{79,80} Among the largest representatives of this class are the porous polystyrenes. In this context, MOF formation is induced within the porous structure of the polystyrene framework itself. Following MOF formation, the polystyrene modulators are removed, leading to the formation of MOFs with different and tailored properties.⁸¹

In principle, when considering the influence of modulator molecules on MOF synthesis, it becomes important to account for the template effect. The template effect arises due to the size and structure of the modulator molecules, which can shape the resulting MOF structure. A notable example of this complex relationship is exemplified in the work of Liédana *et al.*, who investigated the role of caffeine in the synthesis of NH₂-MIL-88B(Fe). On one hand, it can be viewed as a template, on the other hand, the interaction of caffeine with the MOF and the resulting structure is also considered.⁸²

Such examples highlight the challenges in drawing a clear demarcation between the roles of modulators and templates in MOF synthesis. The transition between these roles can indeed be seamless, and it may vary depending on the specific modulator, the MOF system, and the concentration at which the modulator is employed.

3. Synthesis modification of MOFs by modulators

In hydrothermal MOF synthesis, multiphase products can be obtained which are difficult to separate, as MOFs cannot be recrystallized. Finding the optimal conditions to synthesize MOFs with high-quality crystallinity and desired properties is of interest in research.⁸³ Utilizing modulators, in addition to the structural metal and linker units, is another parameter that can be effective in the synthetic approaches.^{1,84} As mentioned previously, the nature of the modulators, their functional group, pK_a , and relative concentrations are factors to control the assembly of the MOF,^{85–87} either through intermediate modulator-metal coordination or modulator-linker interactions, such as hydrogen bonds.⁸⁸

Vakili *et al.* showed that the synthesis methods are effective in using the necessary amount of HCl modulator for the synthesis of UiO-67 crystals, and 135 and 65 equiv. of HCl are required in the microwave and solvothermal methods, respectively. By increasing the amount of modulator HCl for the synthesis of UiO-67, the amount of produced MOF also increased. This could be attributed to the presence of water in the HCl solution, which facilitates the hydrolysis of Zr salts and provides the required oxygen molecules for the formation of secondary building units (SBUs). This, in turn, accelerates the formation of UiO-67 (eqn (1)). In addition, increasing the concentration HCl as a modulator leads to an increase in the specific surface area of the MOF, albeit up to an optimal amount of the modulator.^{89,90}

$$6ZrCl_4 + 6H_2bpdc + 8H_2O \rightarrow Zr_6(O)_4(OH)_4(bpdc)_6 + 24HCl$$
(1)

The use of modulators can lead to the formation of a singlephase product, as well as improved crystallinity and reproducibility.^{91,92} For example, Shaikh *et al.* prepared several pure phases of Zr-MOFs (PCN-222, PCN-223, MOF-525) by adjusting the synthetic conditions, including the type and concentration of modulator and the acidity of the reaction medium. The modulators employed in the study were carboxylic acid species,

including trifluoroacetic acid, trichloroacetic acid, difluoroacetic acid, chloroacetic acid, formic acid, acetic acid, propionic acid, trimethylacetic acid, hexanoic acid (C6), decanoic acid (C10), myristic acid (C14), stearic acid (C18), pentafluorobenzoic acid, 2,6-difluorobenzoic acid, 4-nitrobenzoic acid, benzoic acid, and 4-methoxybenzoic acid.⁹³

If the modulator is incorporated into an initially formed MOF, *e.g.* as a labile terminal ligand at the metal ions, it could be removed to form open metal sites (coordinatively unsaturated sites).⁹⁴ Additionally, the modulator ligand can be post-synthetically replaced with another ligand to introduce a desired functional group.

The morphology, size, crystallinity, and uniformity of MOF particles can be altered by the use of modulators.⁹⁵ Uniformity and separated MOF particles are significant factors for numerous applications. Albuquerque and Herman used benzoic acid (BA) as a modulator during a microwave-assisted continuous flow synthesis at high temperature with a brief reaction time. Without the use of BA, this led to smaller agglomerated particles in the reagent. Using the optimum amount of modulator, particles with a uniform shape and increased crystallinity could be obtained.⁹⁶ In addition, the orientation of the crystal growth by modulators plays an influential role in the formation of high crystalline MOF films.⁹⁷

The synthesis of MOFs can be highly sensitive to reaction conditions such as temperature, concentration, and solvent. Interestingly, Zahn *et al.* reported that the MOF Zr-FMA could be synthesized in both water and *N*,*N*-dimethylformamide (DMF) solvent in the presence of FA modulator. As expected, the nucleation rate declined with increasing modulator concentration in water, while the reaction rate increased with increasing modulator concentration in DMF. This result is justified by the presence of a minuscule amount of water in commercial FA, which expedited the MOF-forming process in the organic solvent.⁹⁸

Liu *et al.* applied BA and trifluoroacetic acid (TFA) as modulators and a small amount of water to form the Fe-based porphyrinic MOF M-PMOF-3(Fe), which had not been previously obtained by other methods. Concurrent with modulator coordination, the water molecules increase the nucleation rate by hydrolysis of the metal salt.⁹⁹

The use of HNO3 as a modulator instead of HF in the synthesis of MIL-101(Cr) resulted in a yield of over 80%, with an average $S_{\text{BET}} > 3200 \text{ m}^2 \text{ g}^{-1}$ in repeated experiments in a smallscale laboratory synthesis. This is a significant improvement compared to the average yield of 50% observed in most published syntheses with and without HF. The large-scale synthesis of MIL-101(Cr) could use the finding of HNO3 addition, producing more than 100 g of the product with near 70% yield and a BET-surface area around 4000 m² g⁻¹. The modulator AA together with seeding could decrease the reaction temperature to as low as 160 °C, which is significantly lower than 220 °C typically used in published procedures with and without HF, while still maintaining a relatively good yield and BET surface area of the product.⁵⁰ Thus, it is possible to replace HF with other modulators in MOF synthesis, allowing for the synthesis to be conducted under more benign conditions and reducing the health risks associated with HF.100

With respect to surfactants and emulsions, often reverse microemulsions have been utilized for the synthesis of MOFs.¹⁰¹ Reverse emulsions are created when water droplets are dispersed in a hydrophobic organic solvent or oil. Microemulsions, in particular, are composed of dispersed droplets with radii ranging from 5–50 nm. In reverse microemulsions for MOF synthesis, two-micellar systems, containing either the metal salt or the organic linker, were mixed and the reaction was initiated through coalescence.¹⁰² The reaction temperature in the reverse microemulsion synthesis of MOFs was between 0 °C and 120 ° C.¹⁰³ To date, no reverse emulsion syntheses of MOFs have been carried out at temperatures higher than 180 °C.

On the other hand, an alternative approach has been explored in the literature, wherein surfactants assume the role of capping agents in MOF synthesis. In this context, the critical emphasis is not centered on the formation of micelles but rather on the direct interaction that transpires between the MOF surface and the surfactant molecules themselves.¹⁰⁴

A less conventional synthesis method for MOFs is dry gel conversion (DGC).⁹⁰ This method involves placing a small amount of the solvent at the bottom of the Teflon reactor and the starting materials on a porous support to physically separate the solvent and reactant mixture (Fig. 2). The ability to recover and reuse the solvent after the reaction and to use only one-sixth or less of the solvent volume compared to the solution synthesis on the same scale makes this process an economically and ecologically attractive option for industrial DGC application.⁹⁰

The importance of using modulators in the DGC method is highlighted. When BA is employed as a modulator in the synthesis of nano- to micro-sized Zr-based UiO-MOFs, the resulting product is more stable and of thick consistency. Without a modulator in the reaction system, much of the MOF is washed away through the pores with the solvent which loses its reusability. With BA or HCl as modulator in the DGC synthesis, the BET surface areas for UiO-66, UiO-66-NH₂, and UiO-67 were in good agreement with literature values, with yields up to 93%.⁹⁰

3.1 Post-synthetic modulator exchange

Post-synthetic procedures refer to follow-up reactions or treatments of the already formed MOF. In principle, the solvent



Fig. 2 Schematic representation of the reactor setup for DGC. Reproduced from ref. 90 with permission from The Royal Society of Chemistry, copyright 2017.

removal from the MOF pores upon activation is already a postsynthetic procedure.¹⁰⁵ Additionally, when MOFs have large enough pores to provide the access of reagents, generally metal clusters with labile coordination ligands and functional groups at the linker can be sites for a post-synthetic process.¹⁰⁶ Removing or exchanging a labile coordinating modulator ligand is a simple and inexpensive post-synthetic reaction.¹⁰⁷

Hu *et al.* used a post-synthetic exchange of modulator ligand to prepare chiral MOF-808 by replacing metal-coordinated formate with chiral ligands. It should be noted that the large size of the MOF-808 pores was essential for the successful exchange (Fig. 3).¹⁰⁸ However, the necessary porosity can also be provided by creating a defective MOF structure through coordination modulation.⁶⁵

Drache *et al.* enhanced the stability of the DUT-67 (a Zr-based MOF with 2,5-thiophenedicarboxylate linker) against water removal by increasing the hydrophobicity of the pore surfaces through the exchange of post-synthetic modulator ligands such as formate, acetate or propionate with fluorinated carboxylate ligands.¹⁰⁶

In another report by Drache *et al.*, the modulated DUT-67 was prepared by using formate modulator and modified postsynthetically by diluted acids including HCl or H_2SO_4 to enhance catalytic activity. The small size of DUT-67 crystals allowed anion exchange to be performed easily with a short treatment time and low concentration of the acidic solution. The exchange of the modulator with inorganic acids (for charge balance), resulted in the formation of DUT-67 with high crystallinity and porosity, hydrophilicity as well as increased acid strength, leading to high activity in the catalytic reactions.¹⁰⁹

Ardila-Suárez *et al.* synthesized a defective MOF-808 with the AA modulator, which had additional meso-pores in the structure.

The following post-synthesis treatment with sulfuric acid not only exchanged acetate with (hydrogen) sulfate on the Zr clusters, but also the benzene-1,3,5-tricarboxylate linkers were sulfonated, increasing the thermal stability and number of acidic sites of the Zr-MOF.⁹⁵

It is possible that interpenetration could lead to a reduction in the size of the pores and the available space; however, this is not always the case. The interpenetrated Zn-MOFs $[Zn_4OL_3]$.



Fig. 3 The structure of MOF-808 and the schematic representation of post-synthesis exchange of the formate modulator with chiral ligands towards MOF-808-His, MOF-808-Tar and MOF-808-Glu. Reproduced from ref. 108 with permission from The Royal Society of Chemistry, copyright 2020.



Fig. 4 (a) Section of interpenetrated NJU-Bai1 and (b) NJU-Bai2, (c) schematic representation of the small uniform pore size in NJU-Bai1 (d) and the large pore in NJU-Bai2 as the shifted framework in the presence of modulator $\$ -tyrosine. Reproduced from ref. 110 with permission from The Royal Society of Chemistry, copyright 2011.

guest (NJU-Bai1) and $[Zn_4OL_3DMF_2]$ ·guest (NJU-Bai2), $H_2L = 4,4'$ -(carbonylimino)dibenzoic acid, were synthesized by Duan *et al.* using the amino acid modulator L-tyrosine. The resulting compounds are interpenetrated MOFs with larger pores, demonstrating a high capacity to adsorb hydrogen gas. In addition, it has been shown that structural features can be controlled by altering the concentration of the modulator and the reaction temperature (Fig. 4).¹¹⁰

4. Action of modulators

4.1 Morphology and size of MOF crystallites

Altering the concentration, molar ratio, and acidic strength of modulators can affect the morphology and size of the MOF crystallites.²⁸ Frequently, a modification in morphology is also accompanied by an alteration in size; therefore, these two features are treated together here. Size-only changes are given in Section 4.2.

The mechanism of modulator function, which is in competition with the linker, was demonstrated by Tsuruoka *et al.* on the crystal growth direction of $[Cu_2(NDC)_2(DABCO)]$ (1,4-NDC = 1,4-naphthalenedicarboxylate; DABCO = 1,4-diazabicyclo[2.2.2] octane) when acetic acid (AA) was added as a modulator into the reaction medium. Crystal growth for DABCO–copper coordination occurs along the [001] direction, while 1,4-NDC–copper coordination happens along the [100] direction. Acetate and 1,4-NDC possess the same carboxylate functionality, which leads to their competition for coordination with copper. This competition results in the crystal growth more in the [001] direction.⁵

For Cu-MOF $[Cu_2(NDC)_2(DABCO)]$ (NDC = 1,4-naphthalene dicarboxylate), different morphologies have even been obtained by monocarboxylic acid or amine modulation for controlling

the selective growth of different crystalline facets of the MOF which gave rise to new morphologies (Fig. 5). These MOF nanocrystals exhibited enhanced crystallinity and gas absorption compared to the original MOF materials.¹¹¹

Brasil *et al.* reported a change of Tb³⁺-doped La-MOFs (with the linker 1,3-BDC) from micro-rods to flower-like small particle agglomerates by an increase in the concentration of the AA modulator.¹¹

Umemura *et al.* showed that in the synthesis of $[Cu_3(BTC)_2]_n$ (Cu–BTC, HKUST-1) crystals, where BTC = benzene-1,3,5tricarboxylatean, an increase in the concentrations of *n*-dodecanoic acid or lauric acid modulators led to morphology transformations from octahedron to cuboctahedron as well as a truncated cube and a cube. At a lauric acid/ligand ratio (*w*) of 50, the octahedral morphology still did not change. Further increasing this ratio then caused a morphology transition because of the thermodynamic stabilization of the growth face, giving rise to a cuboctahedron (*w* = 75), a truncated cube (*w* = 100), and a cube (*w* = 125).⁶

By changing the modulators in the synthesis of HKUST-1 to sodium formate or sodium acetate or triethylamine, additional morphologies can be obtained. This behavior was investigated by Wang *et al.* When sodium formate was introduced in various ratios, ranging from 1 to 5 equivalents relative to the linker, the HKUST-1 structure remained detectable by powder X-ray diffraction (PXRD) analysis. Already with the addition of one equivalent of sodium formate, a strong change in morphology from octahedral to platelet-like could be observed. This change in morphology can be attributed to the modulator's capping effect, which inhibits further growth. In comparison, triethylamine does not lead to capping, but favors faster nucleation by increasing the pH. Consequently, this led to a dramatic reduction in crystal size, shrinking from the range of $2.5-3 \,\mu$ m to 200– 250 nm as the concentration of triethylamine increased.¹¹²

Li *et al.* were able to synthesize an yttrium-based MOF by using yttrium nitrate and BTC. By using sodium acetate as a modulator, the size of the crystals could be greatly influenced from 5 μ m brick-like crystals to 0.5 μ m wide and 2 μ m long rods. This can be explained by the capping of the surface. These rods show a particularly good uptake of arsenate (Section 5.7).¹¹³



Fig. 5 Control of morphologies of $[Cu_2(NDC)_2(DABCO)]$ by modulators. Reproduced from ref. 111 with permission from the American Chemical Society, copyright 2012.

In the work of Han *et al.*, UiO-66 crystals were synthesized using hydrofluoric acid as the modulator (Fig. 6). The fluoride ion has two distinct functions: it balances the charge by coordination to Zr in oxygen defective sites, and it influences the direction of crystal growth through coordinative competition with the organic linkers. The resulting UiO morphologies then also differ in their gas uptake.⁵²

Chin *et al.*¹ found that the use of the modulator sodium acetate resulted in the formation of NH₂-MIL-53(Al) as nanorods, while the use of NaOH as modulator led to more isotropic growth and the production of smaller-sized particles, but no nanorods were formed anymore (Fig. 7). The stronger base (NaOH) increases the concentration of the deprotonated NH₂-BDC²⁻ linker, BDC = 1,4-benzenedicarboxylate. Increasing the molar ratio of AA to Al-salt from 0 to 30 during the synthesis of NH₂-MIL-53(Al) led to an increase in the length-to-width aspect ratio of the needles (Fig. 8); further increases in the ratio then caused the formation of large aggregates.¹

Li *et al.* conducted an investigation into the influence of 4-*n*butylbenzoic acid on the formation of 2D Cu(BDC) structures. Their findings revealed a correlation between the concentration of the modulator and the resulting structure. Increasing the modulator concentration from 1:1 (linker to modulator) to 1:10 resulted in the transformation of the initial nanosheet configuration into nanoflower. Further increasing the amount of modulator from a ratio of 1:20 eventually resulted in sheet structures.¹¹⁴

To exert control over the formation of MIL-125 morphology, Yang *et al.* introduced butyric acid as a modulator into the synthesis process. In the absence of a modulator, the typical circular platelets of MIL-125, featuring two {001} facets, were obtained. However, the introduction of butyric acid as a modulator induced the development of truncated octahedral structures, showcasing two {001} facets along with eight {101} facets (Fig. 9).¹¹⁵

This growth behavior highlights that butyric acid, as a modulator, exhibits a stronger interaction with the $\{101\}$ facet compared to the $\{001\}$ facet. Consequently, the growth of the



Fig. 6 Ar sorption isotherms of UiO-66 with different crystal sizes and morphologies. Reproduced from ref. 52 with permission from The Royal Society of Chemistry, copyright 2015.



Fig. 7 Transmission electron microscopy (TEM) images of (a) NH_2 -MIL-53(Al) nanorods (sodium acetate as modulator); (b) NH_2 -MIL-53(Al) nanoparticles (NaOH as modulator). Reproduced from ref. 1 with permission from The Royal Society of Chemistry, copyright 2012.



Fig. 8 Scanning electron microscopy (SEM) images of NH₂-MIL-53(Al) prepared by changing the molar ratio of AA to $Al(NO_3)_3 \cdot 9H_2O$: (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 (f) 60. All reactions were performed at 120 °C for 3 days in DMF. Reproduced from ref. 1 with permission from The Royal Society of Chemistry, copyright 2012.

{101} facets is decelerated, resulting in structural formation following the Bravais, Friedel, Donnay, and Harker (BFGH) law. This reduced growth rate also gives rise to smaller crystals in the modulated MIL-125. Interestingly, the different morphologies show different behavior with respect to their catalytic activity (see Section 5.1).¹¹⁵

Part of us illustrated the size- and morphology-controlled syntheses of $[Zn_2(OBA)_2(4\text{-BPDB})]_n \cdot 2(DMF)$ (TMU-4), $[Zn(OBA)(4\text{-BPDH})_{0.5}]_n \cdot 1.5(DMF)$ (TMU-5), and $[Zn(OBA)(4\text{-BPDH})_{0.5}]_n \cdot 1.5(DMF)$ (TMU-5), and



Fig. 9 SEM images of (a) MIL-125 and (b) MIL-125-TRO. Reproduced from ref. 115 with permission from The Royal Society of Chemistry, copyright 2020.

BPMB)_{0.5}]_{*n*}·1.5(DMF) (TMU-6), OBA = 4,4-oxybis(benzoate), 4-BPDB = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, by adjusting the concentration of the AA modulator together with temperature and reaction time. The formed rod and plate morphologies vary with these parameters, and by decreasing the concentration of the modulator at the same temperature and time, MOFs with uniform morphologies and smaller sizes can be produced (Fig. 10).⁶⁰

A nanorod morphology of $\{[Cu_2(BDC)_2(DABCO)] \cdot 2DMF \cdot 2H_2O\}$ was formed by using the modulator AA. Replacing BDC with BDC-NH₂ led to the formation of a nanotube morphology by the same modulator. This morphology change may be associated with the hydrogen bonding of acetate ions to the amino groups, thereby scavenging acetate and allowing the particles to grow in one-dimension. The results also indicate that at high concentrations of reactants, the modulator gradually loses its function to change the morphology.¹⁰⁰

Modulation is effective in forming kinetic or thermodynamic products. In the work of Bara *et al.*, the presence of a modulator (like acetic acid (AA), benzoic acid (BA), dichloroacetic acid (DCA), formic acid (FA), HCl, L-Proline (L-Pro), and trifluoroacetic acid (TFA)) facilitates the formation of the thermodynamic product of interpenetrated MIL-126(Fe) over noninterpenetrated MIL-88D(Fe) by slowing down the nucleation process such that the hydrogen bonds created between adjacent networks lead to the formation of the interpenetrated phase. In addition, they developed an effective synthetic approach for the



Fig. 10 Field-emission SEM (FE-SEM) images of TMU-5 samples prepared with different ratio (*r*) between AA and OBA: (a) r = 15, (b) r = 10, (c) r = 5, (d) r = 2, (inset is TEM image, scale 1500 nm) at T = 100 °C, 24 h. The concentration of OBA (c = 0.025 mol L⁻¹) is the same in all syntheses. Reproduced from ref. 60 with permission from the American Chemical Society, copyright 2015.



Fig. 11 SEM images of (a) octahedral o-NENU-3a without modulator and (b) cubic c-NENU-3a with a pTA/BTC mass ratio of 20. The morphology changes observed by changing the mass ratio pTA/BTCfrom 0 to 20 and the temperature from 50 to 80 °C for pTA/BTC of 20. Reproduced from ref. 117 with permission from the American Chemical Society, copyright 2015.

preparation of MOFs with high porosity, without inducing defectivity. This was achieved through the use of oxidation modulation (utilizing various oxidation states of the metal ions) and a modulator simultaneously, resulting in the formation of a new phase and desired properties for the synthesized MOF. The oxidation of Fe^{2+} to Fe^{3+} impedes the self-assembly process and thus, in this case, the thermodynamic product is produced. Considering that Fe^{2+} is a softer Lewis acid, it increases ligand lability and coordination reversibility, thus reducing defects and increasing crystallinity in MOF products.¹¹⁶

Liu et al. achieved a transformation in the morphology of the new MOF NENU-3a, a copper and phosphotungstic acid (HPW) based MOF, during its synthesis by employing p-toluic acid (*p*TA) as a modulator. In the absence of the modulator, the MOF displayed an octahedral morphology. With an increasing amount of *p*TA, the appearance of the $\{100\}$ facet became more prominent, while the {111} facet gradually diminished. This observation suggested that the modulator interacted more effectively with the {100} facet, particularly at temperatures below 50 °C. Further elevating the temperature to 80 °C resulted in a morphological transformation into spherical particles. This change occurred because the growth rates of the facets became nearly identical under these conditions (Fig. 11). Interestingly, the different morphologies show a different behavior in catalysis. A detailed investigation of these differences can be found in Section 5.1.117

Bagherzadeh *et al.* found that the absence or low concentrations of the modulators AA and FA in the synthesis of Fe-MIL-88A led to the formation of diamond-shaped particles with uniform size distribution and high crystallinity. Conversely, when high concentrations of the modulators were present, a spherical morphology with a rough surface was observed (Fig. 12). At high concentrations, the modulators acted as a structural unit and disrupted the assembly process such that the ligands could not be positioned properly.³⁹

Solvothermal synthesis of the MOF $[Cu_2(OBA)_2(-BPFB)] \cdot (DMF)_5$ (TMU-46), BPFB = N,N'-(1,4-phenylene)



Fig. 12 (a) Diamond-like Fe-MIL-88A crystal with perfect faceted morphology, (b) Fe-MIL-88A crystal with a more spherical morphology. Reproduced from ref. 39 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2018.



Fig. 13 FE-SEM images of nano-TMU-46 prepared by modulator (a) BA and (b) pyridine. Reproduced from ref. 118 with permission from the Elsevier B.V., copyright 2020.

diisonicotinamide, was performed in the presence of benzoic acid and pyridine modulators, resulting in the formation of nanorod and nanoplate morphologies, respectively (Fig. 13); these morphologies exhibited distinct sensing performance (*cf.* Section 5.8).¹¹⁸

Safari *et al.* investigated the influence of various amino acids as modulators in the synthesis of the alkaline earth based MOF BaBTC. They found that among the amino acids alanine, glutamine, histidine, aspartic acid and proline, only the use of proline as a modulator led to the formation of the desired MOF. However, this was accompanied by a change in the morphology of the MOF with increasing concentration of proline from initially rod-shaped to a sheet-like morphology.¹¹⁹

Carmona *et al.* demonstrated that modulation of [Al(OH)(SDC)] (SDC = 4,4'-stilbenedicarboxylate) with AA can have a profound impact on both the size and morphology of the resulting MOF. This phenomenon can be elucidated by the capping of aluminum centers within the MOF structure, which selectively promotes the growth of specific crystallographic facets and directions, thus influencing the final size and shape of the MOF material (Fig. 14). Increasing the modulator amount favored the formation of one-dimensional channel structures. These modulated compounds are applied in the storage of ALF794 (Section 5.6).¹²⁰

Rieter *et al.* used a microemulsion of water in surfactant to prepare nanorods of $[Gd(BDC)_{1.5}(H_2O)_2]$, BDC = 1,4-benzenedicarboxylate, which gave rise to nanoparticles under standard conditions. The morphology and size of the nanorods were



Fig. 14 Preparation of MOF with different features by coordination modulation. Reproduced from ref. 120 with permission from the American Chemical Society, copyright 2018.



Fig. 15 SEM images of $[Gd(BDC)_{1.5}(H_2O)_2]$ nanorods synthesized with w = 5 (left) and w = 10 (right) (w: water/surfactant molar ratio). Reproduced from ref. 121 with permission from the American Chemical Society, copyright 2006.

affected by the molar ratio of water to CTAB surfactant in the microemulsion of water/CTAB/isooctane/1-hexanol. When the molar ratio of water/surfactant (*w*) was 5 (concentration of Gd³⁺: 50 mM), the nanorods had a length of 100–125 nm and a diameter of 40 nm. When *w* increased to 10, the length of the nanorods increased to 1–2 μ m and the diameter to about 100 nm (Fig. 15).¹²¹

Yang *et al.* investigated the effect of different concentrations of the surfactant CTAB on the morphology of IRMOF-3. They found that without the presence of CTAB, cubic MOF crystals formed with six $\{100\}$ facets. The addition of CTAB first resulted in truncated cubes with small triangular faces corresponding to $\{111\}$ facets. As the concentration of CTAB increased, the morphology changed so that the $\{111\}$ facets grew while the $\{100\}$ facets became smaller and eventually



Fig. 16 SEM images of NMOF-1 synthesized by using various amounts of CTAB modulator; *w* is the molar ratio between CTAB and Eu(NO₃)₃·6H₂O. (a) NMOF-1 with morphology of rhombus-truncated bipyramid synthesized without CTAB. (b) NMOF-1 crystals with elongated micrometer (2–4 μ m) rod morphology prepared with CTAB at *w* = 30. (c) Elongated hexagonal nanorods (200–400 nm) synthesized with *w* = 20. (d) Hexagonal nanoplate morphology with *w* = 15. Reproduced from ref. 25 with permission from The Royal Society of Chemistry, copyright 2012.

disappeared, forming a perfect octahedron. This could be explained by the fact that the CTAB preferentially attaches to the $\{111\}$ facets. Thus, these surfaces can grow more slowly than the $\{100\}$ surfaces which then leads to the change in the morphology.¹⁰⁴

According to a report by Qian *et al.*, the rhombus-truncated bipyramidal morphology and μ m-size of $[Eu_2(FMA)_2(OX)(H_2-O)_4]\cdot 4H_2O$ (NMOF-1), where FMA = fumarate and OX = oxalate (Fig. 16a), can be changed to smaller micrometer plates with sizes below 2 μ m with different amounts of CTAB (Fig. 16b–d). Notably, the length of the rods or the length/width aspect ratio rises with increasing the amount of CTAB.²⁵

Sarawade *et al.* demonstrated that through different charge densities of the cationic surfactants $C_{16}H_{33}N(CH_3)_3^+$, $C_{16}H_{33}N(C_2H_5)_3^+$, and $C_{16}H_{33}N(C_3H_7)_3^+$ together with the Br anion, Cu-meso-MOF (give formula with ligand abbreviation) could be synthesized in an aqueous solution using as spheres with the higher charge density of the trimethyl and regular cubes with the lower charge density of the tripropyl ammonium surfactant.²¹

A Co-MOF (from BIPYEN and 2,6-H₂NDC), Cu-MOF (from H_3BTC), and In-MOF (H_3IMDC) were obtained with different morphologies by employing the three surfactants CTAB, sodium dodecyl sulfate (SDS), and pluronic triblock copolymer (P-123) For the Co-MOF, nanosheets/nanoplates, nanosheets and nanorod-like morphologies were obtained with CTAB, SDS and P123, respectively. For the In-MOF, a nanorod and for the Cu-MOF, a nanocube morphology was derived.²¹

4.2 Size only

In numerous reports, it has been verified that as the nucleation rate of MOFs increases, the particle size decreases. Hence, when



Fig. 17 Schematic illustration for the synthetic process of UiO-66 with Fe porphyrin as guest molecule in the presence of the fatty acid (FA) modulator. Reproduced from ref. 123 with permission from the Elsevier B.V., copyright 2023.

a modulator accelerates the rate of nucleation, *e.g.* through increased linker deprotonation, this leads to a particle size reduction. This is because more crystal seeds start to form and can only continue to grow until the solution is depleted of the starting materials. Conversely, a decrease in nucleation rate will give larger crystals Chem.^{7,23,24}

Li *et al.* indicated that the size of ZIF-7 can be controlled from 40 nm to 140 nm by changing the molar ratio of polyethyleneimine (PEI) and also the reaction time. Three samples of compounds were prepared as ZIF-7@PEI-1, ZIF-7@PEI-2, and ZIF-7@PEI-3 with 0.140 g, 0.140 g, and 0.360 g PEI and 5 h, 24 h, and 1 h reaction time, respectively. The particle size of samples 1 to 2, with the same values of the modulator PEI, was observed to rise with increasing reaction time, while the particle size increases with decreasing time from 24 h to 1 h as well as by increasing the amount of modulator PEI from 0.14 g to 0.36 g.¹²²

Sui *et al.* achieved the production of nano-sized UiO-66 crystals through the utilization of various fatty acids as modulators. The fatty acids thereby reduce the growth of UiO-66. Notably, they accomplished the encapsulation of Fe-porphyrin as a guest molecule within these nanostructures (Fig. 17). These nano UiO-66 crystals exhibit intriguing catalytic applications, which will be detailed in Section 5.1.¹²³

Diring *et al.* found that a high concentration of *n*-dodecanoic acid as a modulator for the preparation of $[Cu_3(BTC)_2]$ led to the formation of larger crystals in comparison to solvothermal techniques with no modulators.⁷

By increasing the amount of sodium acetate modulator in the synthesis of $[Dy(BTC)H_2O]$, the crystal sizes were reduced from micro- to nanometers.²³

In a study conducted by Pappas *et al.*, the impact of various monotopic modulators on the growth patterns of $Co_2(DOBDC)$ nanorods was systematically explored. In this investigation, six distinct modulators, all derived from salicylic acid and characterized by differing pK_a values, were employed. They were able to show that with increasing pK_a value, the size of the formed rods also increases. At the same time, it was shown that with smaller pK_a values, higher capping takes place. This capping, in turn, acted as a suppressive factor against further growth of the nanorods.¹²⁴

Guo *et al.* employed the organic base modulator triethyl amine (TEA) instead of sodium acetate in their attempt to synthesize $[Dy(BTC)H_2O]$, in which no MOF crystals were formed anymore.⁶⁶

In the synthesis of MIL-101(Cr) the MOF particle size can be reduced to the nanometer scale (<100 nm) with increasing AA modulator to Cr–bdc ratio of up to 17.5:1 which is attributed to effective suppression of frame extension. With an average diameter of about 90 nm, MIL-101(Cr) can be prepared reproducibly in gram-scale, with high BET-surface areas (3200–3500 m² g⁻¹) and fairly good yield (60–75%). Notably, at a slightly higher AA to Cr–bdc ratio of 20.4:1, the surface area, porosity, and yield are substantially reduced.³⁶

MIL-101(Cr) nanoparticles were obtained by microwave heating of the reaction between chromium nitrate and 1,4benzenedicarboxylic acid in heptane-in-water emulsions with the anionic surfactant sodium oleate as an emulsifier. The use of this emulsion with the phase inversion temperature (PIT) method offered the controlled nucleation and growth of nanoMIL-101 particles with an average size of less than 100 nm in 70 min, resulting in a high BET surface areas (2900 m² g⁻¹) and a yield of 45%.¹²⁵ Phase inversion refers here to the conversion of oil-in-water to water-in-oil emulsion, which is achieved by carrying out the reaction at a temperature at which the phase transition occurs.

Webber *et al.* developed a two-stage synthetic protocol for the synthesis of NU-1000 that demonstrates the action of a modulator. The modulator biphenyl-4-carboxylic acid (H₂BPCA) first reacts with the metal ions to form metal-modulator clusters of the same nuclearity as the metal nodes in the MOF. The molecular clusters then react with the linker molecules 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H₄TBAPy) to replace the modulator molecules. This competition of the carboxylate group for the metal coordination impedes the nucleation and growth of the MOF such that single crystals of NU-1000 were obtained. Based on this finding, by optimizing the reaction conditions and the amount of modulator used, they were able to produce NU-1000 crystals ranging in sizes from 300 nm to 9.3 mm.¹²⁶

The synthesis of ZIF-8 and ZIF-67 was conducted using an ionic liquid microemulsions (ILMEs), wherein an H₂O/TX-100/ BmimPF₆ mixture was applied to obtain a uniform particle size distribution. Additionally, the addition of ethanol to the reaction mixture was found to be essential in regulating the particle sizes of $[Cu_3(BTC)_2(H_2O)_3]$ (HKUST-1).⁷⁰

4.3 Crystal phase

Yang *et al.* observed MIL-101-Cr nanocrystal formation at low BA concentration.³⁴ However, when the concentration of the



Fig. 18 SEM images on the effect of benzoic-acid (BA) modulation in the reaction of chromium nitrate with benzene-1,4-dicarboxylic acid. (a) MIL-101(Cr) sample for low BA amounts (scale bar 500 nm), (b) MIL-88B(Cr) sample at high BA amounts (scale bar 3 μ m). Reproduced from ref. 34 with permission from The Royal Society of Chemistry, copyright 2019.



Fig. 19 Structure of (a) NU-1000, and (b) NU-901. Blue arrows indicate the angular or parallel orientations of the nodes in the frameworks. Reproduced from ref. 127 with permission from the American Chemical Society, copyright 2017.

modulator was increased under the same hydrothermal conditions, microparticulate MIL-88B(Cr) was formed (Fig. 18). This modulation enabled a new and efficient synthesis of MIL-88B(Cr).

The only structural difference between Zr-MOF polymorphs NU-1000 and NU-901 is in node orientation (Fig. 19). The angle between the Zr_6 nodes in NU-1000 is 120°, while NU-901 has all nodes parallel to each other. In the prevalent synthesis, NU-901 is formed with small pores. Webber *et al.* demonstrated that the modulator biphenyl-4-carboxylic acid favors the formation of the nodes with an angle of 120°, resulting in the production of the structure of NU-1000 with large pores when the modulator is replaced with the linker during the synthesis and framework growth (Fig. 19).¹²⁷

In an effort to separate the two phases of NU-1000 and NU-901, Islamoglu *et al.* employed TFA as a co-modulator together with BA during the synthesis process, thereby preventing the formation of the NU-901 phase. As depicted in Fig. 20, NU-1000 crystals synthesized without TFA resulted in crystals with "rough" surfaces in the center (Fig. 20a). On the other hand, NU-1000 crystals, when modulated by TFA, showed well-shaped hexagonal rods with smooth surfaces without the presence of the NU-901 phase (Fig. 20b).³⁵

In 2022 Gong *et al.* were able to prepare five new MOFs based on different [2,2]paracyclophane-based linkers. By exchanging AA with FA under the same synthesis conditions, two very different MOFs were synthesized, namely NU-405, which has a 3D structure and is connected with 12 linker molecules, and NU-700, which forms a 2D network structure with an unknown



Fig. 20 SEM images of (a) NU-1000 and (b) NU-1000-TFA crystals. Scale bars are 2 μ m. Reproduced from ref. 35 with permission from The Royal Society of Chemistry, copyright 2018.

9 linker structure. Three linker positions are occupied by FA. Furthermore, two more NU-MOFs, namely Nu-913 and NU-602 could be synthesized by simply exchanging the solvent DMF to DEF, using AA as modulator. This shows both the influence of the modulators on the formation of a particular crystal phase and the influence of the solvent on the crystal phase formation. NU-602 and NU-913 show interesting properties in the area of water sorption, discussed in Section 5.5.¹²⁸

The use of a very high amount of the modulator mercaptoacetic acid (HMAc) in the synthesis of UiO-66 caused the formation of the hexagonally close-packed (hcp) crystal structure instead of the face-centered cubic (fcc) packing, which is normally observed in the formation of UiO-66. By using 100 eq HMAc to metal in the synthesis, a functionalized hcp-UiO-66 containing the thiol HMAc modulator was produced for the first time.¹²⁹

Wang *et al.* demonstrated that varying the concentration of the BA modulator during the synthesis of Zr-MOFs induced the formation of three MOFs with distinct topologies as well as different pore sizes and structures. In this work, three Zr-MOFs (Zr-SXU-1, Zr-SXU-2, and Zr-SXU-3) were synthesized with the same ligands and metal clusters. The ligand used was tetratopic carboxylic 4,4',4'',4'''-(1,4-phenylenebis(pyridine-4,2,6-triyl))tetrabenzoic acid (H₄PBPTTBA) of 1 eq. concentration, and the modulator was BA with concentrations of 110, 150 and 140 eq., respectively. These Zr-MOFs exhibited different connectivity of the Zr clusters from 8 in Zr-SXU-3 to 10 in Zr-SXU-1 and 12 in Zr-SXU-2.³³

Hou *et al.* successfully synthesized five new thorium-based metal-organic frameworks (MOFs), namely NU-51 to NU-55, by employing the rigid tetratopic linker 1,3,5,7-adamantanete-tracarboxylic acid (H₄ATC) in combination with various carboxylic acids (FA, AA, TFA, BA). Notably, the choice of different modulators and their respective concentrations played a pivotal role in this synthesis process. For instance, NU-51 and NU-52 could be obtained using FA at varying concentrations, highlighting the sensitivity of MOF formation to both the type and concentration of the modulator.¹³⁰

4.4 Degree of crystallinity and defects

The degree of crystallinity is usually assessed only qualitatively by the width and sharpness of the reflexes in a powder X-ray diffractogram (PXRD). Thus, it is important to note that nanoparticles will also give broader reflexes.

MOFs based on metal ions with high oxidation states (Zr^{4+} , Cr^{3+} , Fe^{3+}), such as the Zr-MOFs UiO-66 and congeners possess high nucleation rates due to the strong bonds formed between the metal ions and the carboxylate-donor ligands. It has been shown that the presence of modulators is essential to produce UiO-MOFs with good crystallinity.²⁸

Schaate *et al.* demonstrated that in the ordinary synthesis of a Zr-MOF (UiO-66, UiO-67, UiO-68) in the absence of a modulator (BA or AA), only an amorphous phase or micro-sized aggregates of the products are obtained. They showed that modulation synthesis of UiO-67 with increasing equivalents of BA or AA resulted in PXRD patterns with sharper reflexes (Fig. 21).²⁷

Schaate *et al.* reported difficulty in reproducing the usual method of UiO-67 synthesis due to the formation of difficult-to-separate by-products with low crystallinity; however, in the presence of the modulator BA, the MOF nucleation process was slowed down, leading to UiO-67 products with higher crystallinity.¹³¹

Liu *et al.* added hydrophobic methyl groups in UiO-66 by using the linker 2,5-dimethylterephthalic acid to increase the hydrothermal stability in UiO-66-CH₃ films on a nickel support for the separation of N_2/CO_2 gases. It was found that the growth of UiO-66-CH₃ with an AA modulator enabled a facile secondary growth of the MOF on the support. Furthermore, the crystal growth can be controlled by tuning the modulator amount. For secondary crystal growth on the membrane, an optimal amount of acetic acid modulator is required to ensure that the membrane surface remains porous when using lower amounts of acetic acid.¹³²

The engineering of defects in MOFs is an effective way for tuning the pore features, including the formation of open metal sites, alteration of the surface chemistry, modification of the properties, and improvement of applications in fields such as catalysis and gas storage. Ren et al. reviewed formation and detection methods and application details of structural defects of MOFs.^{46,133,134} There are two types of defects: missing linker defects and missing metal cluster defects. When the linkers are replaced with terminal modulator ligands, missing linker defects occur.85,135 Modulators create missing linker defects by competing with the linkers in coordination to the metal center during the framework formation.⁸⁵ Subsequently, post-synthetic elimination or replacement of the bound modulator can be performed (see Section 3.1).¹³⁶ To create an open metal site, modulator species are often removed from the structure by heating to a certain temperature.¹³⁷ Defect control can be an effective way to adjust the properties of MOFs for



Fig. 21 Powder X-ray diffraction (PXRD) patterns of UiO-66 (a) and UiO-67 (b) synthesized with different proportions of BA modulator towards $ZrCl_4$. The same feature was obtained with AA as modulator. Reproduced from ref. 27 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2011.

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Fig. 22 (a) N₂ isotherms for MOFs synthesized with 30 equiv. (black), 40 equiv. (red), 50 equiv. (blue), 60 equiv. (orange), 70 equiv. (green) of AA (b) N₂ isotherms for MOFs synthesized with 10 equiv. (black), 15 equiv. (red), 20 equiv. (blue), 25 equiv. (orange), 30 equiv. (green) of BA. Reproduced from ref. 135 with permission from the American Chemical Society, copyright 2017.

applications.¹³⁸ In the work of Epley *et al.*, the role of modulators including AA, FA and BA was investigated in the defect nature of UiO-AZB (AZB = 4,4'-azobenzenedicarboxylate). Generally, the highest surface area was obtained with AA modulator. Some testings of BET analysis were applied to evaluate the batch alteration of modulators over the concentration range. The results indicated that changes in the modulator concentrations and/or acidity formed more defects, which can be advantageous for applications such as gas adsorption (Fig. 22).¹³⁵

Butova *et al.* employed the BA modulator in the synthesis of UiO-66-NDC. By altering the ratio of modulator to linker, the reaction kinetics are altered, resulting in the formation of crystals of different sizes. Additionally, the specific surface area changes through the formation of defects in the framework. A higher ratio of modulator to ligand resulted in larger crystal sizes and greater surface areas; however, this also caused a decrease in the thermal stability because of the formation of defects in the MOF structure.¹³⁸

Olsbye *et al.* used BA as a modulator to produce a highly crystalline UiO-67 structure with varying degrees of defects. A crystalline and defect-free MOF was produced at a minimal amount of DMF and an optimized ratio of BA (Fig. 23 $C-3_{BA}$), while increasing the BA concentration to 15 equivalents resulted in no MOF formation. Defective MOFs were created at high-



Fig. 23 SEM images of UiO-67 samples formed under concentrated (C- x_{BA} , where x = 0, 3, 6, 9, and 15 equivalent BA : Zr ratio) and diluted synthesis conditions (D- x_{BA} , where x = 0, 3, 6, 9, and 18 equivalent) (BA as a modulator, concentrated and diluted mean Zr : DMF ratios of 1 : 50 for C and 1 : 300 for D). Adapted from ref. 139 with permission from the American Chemical Society, copyright 2019.



Fig. 24 Types of reversible reactions during the modulated synthesis of UiO-67. Reproduced from ref. 139 with permission from the American Chemical Society, copyright 2019.

dilution conditions (Fig. 23 $D-3_{BA}$ to $D-18_{BA}$). Moreover, figures $D-6_{BA}$ to $D-18_{BA}$ show that with increasing ratio of BA, both shape and size of the crystals could be optimized. At diluted conditions, the crystallization process is affected in two additional ways: first, the hydrolysis of DMF produces formate and H⁺ ions; the latter reduce the solubility of the linker molecules (H₂BDCA) by affecting the equilibrium reactions and second; the formate ions act as an additional modulator to further compete for the coordination bond between the linkers and metal centers (Fig. 24).¹³⁹

In UiO-66 monocarboxylic acid modulators, such as difluoroacetic acid, allowed for an increase in the density of defects which resulted in increased surface area and pore volume compared with "defect-free" UiO-66. The extent of defects was observed to increase in proportion to the modulator amount.⁴³ Cai *et al.* used alkyl carboxylic acid modulators for the formation of meso- to macropore structural defects in UiO-66 (Fig. 25a–c). The diameter of the pore defect could be



Fig. 25 Schematic representation of the synthesis of hierarchically porous UiO-66 with adjustable porosity by carboxylic acid modulators with different alkyl chain lengths. Steps (a)–(c) show the effect mechanism of alkyl carboxylic acid modulator in creating structural defects. The process of increasing size of the defect pores with the increase in the length of the alkyl chain of the modulator can be observed in the parts (d)–(f). Reproduced from ref. 40 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2017.

increased with the alkyl chain length of the modulator and its concentration (Fig. 25d–f). By using an excess amount of the modulator and sub-stoichiometric amounts of the BDC linker, some coordination sites were occupied by the modulators. The large open pore defects were then formed as a result of the elimination of the modulator. These hierarchically porous UiO-66 MOFs (HP-UiO-66) were then tested in various applications (see Section 5).⁴⁰

Bueken *et al.* synthesized a Zr-MOF by using the linker squaric acid (H_2 SQA) which is therfore called ZrSQU. It has the smallest unit cell in the family of UiO-MOFs. Based on the crystal structure no porosity is expected. By using FA or AA as modulators, various defects could be incorporated into the structure. Depending on the modulator, 9.5 wt% acetate or 17.1 wt% formate ions were detected in the structure. By using the modulators, a sieve character could be incorporated into the structure, which will be discussed in more detail in Section 5.2.⁸⁵

Chen *et al.* synthesized a new Ce-MOF called BIT-58, which exhibits excellent chemical and thermal stability. Hierarchical porous Ce-MOF (nano-BIT-58) could be synthesized by utilizing nitrogenous heterocyclic modulators, such as 1-methylimidazole (1-HMIM). The meso-pore volume in nano-BIT-58 significantly increased, approximately seven times more than native BIT-58, due to structural defects and led to an increase in acidic sites, including unsaturated open metal sites, allowing for easier mass transfer and exhibiting more catalytically active sites than BIT-58. Section 5.1 presents the catalytic properties in more detail.⁴¹

In synthesizing HKUST-1 films, Muller *et al.* used water as a modulator to control the amount of defects. Water slowed down and thereby controlled the coordinative bonding of the linkers to the metal centers by solvation. HKUST-1 films were obtained by stepwise growth with the coating method. Different amounts of water between 0 and 30% in solutions of water and ethanol were selected. The results demonstrated that the water content in the synthetic solutions has a great effect on the crystallinity of MOF thin films. The highest crystallinity and the least defect were gained for about 10% water in ethanolic synthesis solutions. A low-density of defects in these HKUST-1 films is ideal for application in semi-conductors.¹⁴⁰

4.5 Surface area and porosity

The porosity control of MOFs is important for a variety of applications, such as magnetic,¹⁴¹ catalytic,¹⁴² adsorptive,¹⁴³ and chemical sensing purposes.¹⁴⁴ Most MOFs are microporous materials. Micropores (diameter <2 nm) engage in more effective interactions with the adsorbate and provide high surface areas. Yet micropores are not suitable for the adsorption of large molecules and also kinetically limit the diffusion of small molecules. In addition, their uptake capacity cannot be increased by factors such as increasing pressure. Mesopores (2 to 50 nm diameter) facilitates the diffusion of molecules and offer increased diffusion kinetics. Consequently, MOFs with both meso- and microporosity as hierarchical porous (HP-) MOFs can be provided, allowing for the utilization of the

benefits of both types of pores. Many synthesis methods have been suggested and applied for the design of hierarchical pore structures, including the ligand-extension method, surfactant templating, and ionic liquids as well as modulators.

With respect to the formation process, these mesopores differ from defects. Defect are created through missing linkers or metal units, best known for UiO-66, where linkers can be replaced, for example, by modulators.⁴⁰ Templates such as surfactants, on the other hand, form micelles in solution which serve as a site where the MOF can grow around.²³

For example, Dissegna *et al.* synthesized UiO-66 structures using a series of monocarboxylic acid modulators. Through N_2 measurements, they demonstrated that the surface area of UiO-66 increased in response to increased modulator concentrations and enhanced acid strength. In addition, using water sorption measurements, their studies illuminated the changes in hydrophilicity and Lewis acidity that occur when different modulators are used. TFA as a modulator showed the strongest change in both cases.¹⁴⁵

Prasetya *et al.* showed that, in addition to the conventional solvothermal synthesis with DMF, a more environmentally friendly "green" reaction approach also led to the desired MOF structure. In this alternative approach, water was used as solvent and various amounts of FA as modulator. After a reaction time of 24 hours at room temperature, MOF-801 was detected for all "green" approaches. It was found that the surface area of the synthesized MOFs decreased with increasing concentration of FA. Nevertheless, the resulting MOFs exhibited good adsorption capabilities for diclofenac from aqueous solutions (Section 5.7).¹⁴⁶



Fig. 26 Suggested mechanism for the synthesis of HP-MIL-101(Cr) with AA modulator. (a) Substitution of acetate with the terephthalate ligand. (b) Nanofusion of crystal nuclei. (c) Representation of micro-particle-phase formation by increasing AA concentration at high temperature (scale bar is 1 μ m). Reproduced from ref. 147 with permission from the Science China Press and Springer-Verlag GmbH Germany, part of Springer Nature, copyright 2020.

Hierarchical MIL-101(Cr) was obtained using high concentrations of AA as modulator under hydrothermal conditions. Moreover, by providing a particle size decrease due to growth limiting, the modulator caused the formation of an aggregated microparticle-phase with macropores (>50 nm), giving rise to a hierarchical micro-meso-macro-porous material which featured pores with \sim 3, 20–60, and 800–1000 nm sizes. The possible mechanism for the formation of HP-MIL-101(Cr) is presented in Fig. 26.¹⁴⁷

An increase in both surface area and pore size was achieved in several shaped forms of MIL-101(Cr) prepared by using and increasing FA modulator to Cr ratio. The increasing porosity was tested for hydrogen adsorption (Fig. 27).¹⁴⁸

UiO-67 with no modulator displayed a low surface area of only 270 m² g⁻¹, while UiO-67 prepared with 30 equivalents of AA or BA modulator possessed high surface areas of 2400 and 3000 m² g⁻¹, respectively.²⁷

Kim et al. adopted an acetic acid-modulated strategy for the synthesis of HKUST-1. Through this approach, they deliberately introduced defects into the MOF structure. This deliberate defect incorporation led to the formation of a HP-MOF with a significantly enhanced surface area. Specifically, the surface area increased from 1787 $m^2 g^{-1}$ to 2396 $m^2 g^{-1}$. This substantial enhancement in surface area rendered the HP-MOF highly attractive for gas adsorption and storage applications (Section 5.2).149 In addition to the use of monocarboxylic acids, polyprotonic acids can also be used as modulator. Liu et al. employed citric acid for the preparation of HP-HKUST-1, $[Cu_3(BTC)_2(H_2O)_3]$, with a pore size distribution in the range of 30-100 nm. Citric acid equivalent to less than 20% of the BTC linker was added to the reaction mixture. Despite the strong interaction of chelating citrate with Cu²⁺, a hierarchical porous HKUST-1 was formed, which enabled HKUST-1 to be a host for the phosphomolybdic acid hydrate (HPMo) cluster, thereby constructing the composite HPMo@HP-HKUST-1 with excellent catalytic activity (see Section 5.1).42



Fig. 27 H_2 sorption isotherms at 77 K for activated MIL-101(Cr) samples prepared with 0, 50 and 100 Fa/Cr equivalents. Reproduced from ref. 148 with permission from the Hydrogen Energy Publications, LLC. Published by Elsevier Ltd, copyright 2014.

One promising approach to modulation is the use of large organic molecules as modulator. Gau et al. introduced a modulator-based technique to prepare HP-MOF with pore size distributions in the range of 1 nm, 1.3 nm, 1.4 nm, 2 nm, 3.8 nm, and 10.5 nm, using RhB (Rhodamine B) as a modulator for the construction of a RhB@Al-MOF, where Al-MOF = amino-MIL-53. In the first step, RhB is weakly coordinated to Al³⁺ ions through the interaction of its -COOH group with Al³⁺. Upon the addition of the linkers H₂BDC-NH₂ to the reaction mixture, the MOF formation begins. RhB with its approximate dimensions of $16 \times 10 \times 6 \text{ Å}^3$ is larger than the channel cross-section in amino-MIL-53. Thus, the incorporation of the RhB molecules in the growing Al-MOF creates meso-pores in the framework. These meso-pores are created as the MOF grows around the templating guest molecules. The amount of mesoporous cavities created in RhB@Al-MOF depends directly on the RhB concentration. The presence of meso- and micro-pores in the HP-MOF framework makes MOF an interesting material for the uptake of various guest molecules (see Section 5 for applications).150

The work of Jin *et al.* also dealt with the modulation of MOFs with the aid of Rhodamine B. MIL-125-NH₂ was successfully transformed into a HP-MOF with the assistance of RhB (Fig. 28). Their investigations elucidated the mechanistic details of this modulation process, revealing that RhB coordinates with the Ti_8O_8 clusters formed during the MOF synthesis. In addition, the steric properties of RhB resulted in both missing linker and missing cluster defects within the MOF structure. Subsequently, RhB can be selectively removed from the MOF through washing and photodegradation processes, leaving behind a pure HP-MOF structure. This resulting HP-MOF exhibits intriguing properties, particularly in the realm of catalysis (detailed in Section 5.1). Furthermore, the study highlights that similar structural effects can also be achieved using the dye Eosin Y.⁸⁰

In addition to using large organic molecules, whole organic scaffolds can also act as modulators. In their work, Li *et al.* show that porous styrene scaffolds can be used as structure-directing modulators in the synthesis of ZIF-8. Thus, after removal of the polystyrene, an increased porosity can be achieved.⁸¹

Surfactants, as another distinct group of large organic modulators, play a crucial role in MOF synthesis. They can engage with MOF formation through two primary mechanisms: micelle formation and direct interactions. He *et al.* employed the coordination competition between the BDC linker and the surfactant modulator lauric acid to generate mesopores in MOF-5.¹⁵¹ The surfactant 4-(dodecyloxy)benzoic acid was found by Choi *et al.* to act as both a coordinating modulator ligand and templating agent (porogen) to form mesopores in MOF-5 with its alkyl chain.¹⁵² Because of framework interpenetration, it is challenging to otherwise produce MOFs with permanent meso-porosity.¹⁵³

The surfactant modulators CTAB, SDS, and pluronic triblock copolymer (P-123), increased the porosity in Co-MOF (from BIPYEN and 2,6-H₂NDC), Cu-MOF (from H₃BTC), and In-MOF (from H₃IMDC). In the presence of surfactants, the specific surface area in Cu-MOF increased by about two times (from 200 cm³ g⁻¹ to 400 cm³ g⁻¹).²¹

To synthesize meso- $[Cu_3(BTC)_2(H_2O)_3]$, Qiu *et al.* used the surfactant CTAB, and adjusted the pore size from 4 to 31 nm by changing the Cu²⁺: H₃BTC: CTAB: TMB molar ratio from 1: 0.556: 0.15: 0 to 1: 0.956: 0.30: 0.15 (TMB = 1,3,5-trime-thylbenzene acts as an auxiliary agent to inflate the CTAB micelles).¹⁵⁴

Peng *et al.* used the *N*-ethyl perfluorooctylsulfonamide surfactant as a directing agent for the crystal growth and template for the creation of the meso-porous $[Cu_3(BTC)_2(H_2O)_3]$ simultaneously. The surfactant concentrations determined the MOF morphologies and high surfactant concentration led to the formation of more meso-pores (Fig. 29).¹⁵⁵

When the construction of mesoporous MOFs with surfactants does not work, Li *et al.* suggested to use ligands containing both weak and strong sites. Therefore, MOF walls are formed by bonding between metal-ion and active sites surrounding the meso-cavities. Weak sites cause surfactants to overcome lattice stability and form meso-spaces by the electrostatic interaction or the hydrogen bonding with MOF walls.¹⁵⁶

In addition to the previously mentioned modulators, simple solvents like methanol or ethanol can also serve as modulators.



Microporous MIL-125-NH₂

Fig. 28 Rhodamine B as a modulator in the synthesis of MIL-125-NH₂. Reproduced from ref. 80 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2023.



Fig. 29 Schematic representation for preparing meso-porous $[Cu_3(-BTC)_2(H_2O)_3]$ nanoplates in surfactant-IL solutions at (a) low, (b) medium and (c) high surfactant concentrations. Reproduced from ref. 155 with permission from The Royal Society of Chemistry, copyright 2012.

An example of the use of alcohol as a modulator is demonstrated in the work of Wang *et al.* in the synthesis of MIL-88B. By varying the quantities of methanol used during synthesis, they were able to optimize the porosity of MIL-88B. The surface area of the MOF increased significantly from 28 m² g⁻¹ to 177 m² g⁻¹. In this context, methanol binds to the iron centers, leading to defects in the MOF structure. Interestingly, this defective MIL-88B structure exhibits excellent properties in the realm of sensing, which will be discussed in greater detail in Section 5.8.⁴⁴

5. Application of modulated MOFs

Traditional MOFs often feature pores with dimensions smaller than 2 nm, which can impose limitations on their potential applications. These constraints can hinder the accommodation, separation, or transport of substrates within or through the MOF structure. Additionally, accessing catalytic or sensory active sites within such small pores can be challenging. In contrast, modulated MOFs, which exhibit various effects such as missing linkers defects, missing cluster defects, or other modulated properties, broaden the range of potential applications significantly. These modulated MOFs offer greater versatility and open up new possibilities in various fields by overcoming the limitations associated with traditional MOFs.

5.1 Catalysis

The catalytic performance of nano-sized MOF TMU-5 was studied by part of our us. Conventional synthesis without the presence of modulator led to the production of the MOF with undefined bulk morphology. Uniform and defined nanorod and nanoplate morphologies of this MOF were obtained through modulated synthesis with AA as modulator, which showed better catalytic activity in Knoevenagel condensation reaction due to high specific surface area and ease of substrate mass transfer in the structure. A comparison of the catalytic activity of modulated TMU-5 and original unmodulated TMU-5 can be seen in Fig. 30. The nanorod and nanoplate morphologies exhibited the highest yields.⁶⁰



Fig. 30 Yield (%) vs. time (h) for Knoevenagel condensation reaction of benzaldehyde with malononitrile catalysed by bulk, nanorod, nanoplate, and microrod morphologies of TMU-5.

The work of Chen *et al.* also addresses the catalytic activity of nano-BIT-58 with respect to the Knoevenagel condensation reaction (Section 4.4). Here, Ce^{3+} centers act as Lewis acid catalysts. Due to the modulation with 1-HMIM, a hierarchical pore structure could be formed and a large number of free metal sites generated. This led to an increased catalytic effect compared to the non-modulated MOF BIT-58. A further advantage of the modulation becomes clear when larger molecules are used in the catalysis. For example, Chen *et al.* showed that the condensation of 9-anthraldehyde with malononitrile exhibited a 14-fold improvement in conversion efficiency.⁴¹

HP-MOF-5 nanosheets, hierarchical-pores (HPs), were prepared by He *et al.* with the aid of the modulator lauric acid as the substrate for the immobilization of Pd nanoparticles. Due to the high capacity of HP-MOF-5 for gas adsorption, Pd showed high-yield catalytic performance in the reduction of nitroarene by hydrogen which is a significant industrial reduction reaction.¹⁵¹

In the report of Jiang *et al.*, the influence of HCl modulator on the photocatalytic activity of MIL-53 was examined. HCl was able to generate more active sites for surface adsorption and catalysis. The photocatalytic activity was determined by the decomposition of tetracycline using visible light in aqueous solutions. The photocatalytic activity of MIL-53 with HCl modulator increased up to 1.5 times compared to unmodulated MIL-53. On the basis of recycling tests, it could be shown that the catalyst still shows good activity even after several cycles, which indicates good stability.¹⁵⁷

Ly *et al.* used TFA modulators to enhance the catalytic hydrolysis of peptide bonds by UiO-66 through the formation of a defective missing-linker structure in the MOF. The catalytic activity was assessed by examining the cleavage of the peptide bond within the Gly–Gly molecule. The TFA-modulated UiO-66 showed a similar catalytic reaction rate as UiO-66-NH₂/NO₂. However, as expected, the UiO-66-NO₂/NH₂ MOFs demonstrated a higher adsorption capacity compared to the original UiO-66 structure due to the ability to form hydrogen bonds with peptide molecules. This result indicated a rise in active sites, including acidic centers, in the defective UiO-66.¹⁵⁸

Dissegna *et al.* established a correlation between modulators and the presence of active Lewis acid centers by water sorption measurements. These Lewis acid centers are central to catalytic processes. To assess catalytic activity, they employed the cyanosilylation of benzaldehyde as a benchmark reaction. In this context, they observed that TFA-modulated UiO-66 exhibited significantly enhanced catalytic activity compared to unmodulated UiO-66. This result led to the conclusion that modulation introduces a greater number of defects, consequently increasing the availability of free metal sites. Notably, the UiO-66 catalyst employed exhibited robust stability, allowing for recyclability in catalytic processes.¹⁴⁵

HP-UiO-66, synthesized by Cai *et al.* through the application of monocarboxylic acids of varying chain lengths as modulators, possessed high porosity that rendered it applicable across diverse fields. In catalysis, HP-UiO-66 demonstrated its efficacy in the [3 + 3] cycloaddition of 1,3-cyclohexanedione and various α , β -unsaturated aldehydes. The combination of its large pores



Fig. 31 Catalytic [3 + 3] cycloaddition reaction using Uio-66 and HP-UiO-66. Reproduced from ref. 40 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2017.

and available open metal sites enhanced its catalytic performance, as demonstrated in several examples. While nonmodulated UiO-66 and HP-UiO-66 showed nearly identical conversions for small substrates, HP-UiO-66 showed a distinct advantage for larger substrates due to its easier accessibility (Fig. 31).⁴⁰

In their catalytic application research, Sui *et al.* employed a variety of fatty acids as modulators to synthesize nano-sized crystals of UiO-66. Within these nanostructures, they encapsulated Fe porphyrin (with Fe³⁺) and the presence of hydrophobic fatty acids within the MOF generated catalytic properties reminiscent of enzymes. This system catalyzed the oxidation of CH₄ to CH₃OH (Fig. 32). The hydrophobic modulators played a dual role by regulating both the electronic states of the active Fe nuclei in the structure and the concentration of reactive oxygen species, in this case H₂O₂. Experimental data from both neat UiO-66 and mixtures of Fe-porphyrin with UiO-66 indicated either no conversion or extremely low conversion (2.9%). However, the most remarkable outcome was achieved with



Fig. 32 Catalytic performance of Fe porphyrin with different modulator for CH_4 oxidation. Reproduced from ref. 123 with permission from the Elsevier B.V., copyright 2023.

tetradecanoic acid (C_{14}) as the modulator, yielding a substantial conversion of 42.9%. This underscores the critical role played by the modulator, which emulates the hydrophobic pocket found in enzymes and proves to be indispensable for the catalytic reaction.¹²³

By using citric acid, Liu et al. were able to synthesize a HP-HUKST 1 MOF. This modulation process introduced defects, resulting in pores within the MOF capable of accommodating molecules such as phosphomolybdic acid hydrate cluster (HPMo), which possesses dimensions of approximately 10.5 \times 10.5×7.4 Å. This guest molecule could be effectively stabilized within the MOF, making it suitable for applications in heterogeneous catalysis. As an illustrative example, they conducted the ring opening of styrene oxide with methanol. The composite's stability was substantiated through XRD measurements before and after the reaction, confirming its robust performance. Remarkably, the composite exhibited a high conversion of 99.6% achieved within just 20 minutes. This marked a significant improvement over the conversion observed for non-modulated HKUST-1 with HPMo, highlighting the catalytic efficiency of the modulated composite.42

By controlling the specific facet expansion in the phosphotungstic acid (HPW)-containing Cu-MOF NENU-3a, it could be grown in octahedral and cubic crystals, the latter with the modulator pTA. The catalytic activity was first tested with acetic acid and methanol. For small molecules, it could be shown that the esterification for both morphologies exhibit a high conversion. By increasing the alcohol or the carboxylic acid chain length, the activity of the octahedral crystals decreased strongly while the activity of the cubic crystals remained almost the same. The cubic morphology of Cu-MOF NENU-3a enabled a catalytic conversion of fatty acids (C12-C22) to biodiesel of 90%, whereas the octahedral crystals only achieved a conversion of 22%. In contrast to esterification reactions with acetic acid, which can occur both on the surface and within the pores of the MOF due to the small AA molecule size, the fatty acids employed in the study were unable to penetrate into the MOF pores. This observation suggested that the catalytic process in this context primarily takes place on the surface, and it is particularly favored by the presence of the {100} facet. The {100} facet facilitates the interaction of fatty acids with both the Lewis acid sites (free copper sites) and the Brønsted acid sites (HPW sites), promoting more efficient catalysis. Consequently, the cubic morphology, which exhibits a pronounced 100 facet, proves to be more advantageous for this specific catalytic process.¹¹⁷

Part of us investigated the catalytic properties of a zinc-based MOF using combinations of two different modulators. In one approach, mandelic acid was used as the sole modulator, while in three alternative approaches, mixtures of mandelic acid were used in combination with propanoic acid (Zn.Mand(PRA)), mercaptopropanoic acid (Zn.Mand(MPA)), and lauric acid (Zn.Mand(LA)) as modulator. We chose the enantioselective ring opening of styrene oxide with methanol as the benchmark reaction. From a mechanistic point of view, it can be deduced that catalysis occurs both through open metal sites within the MOF and through the Brønsted acidity of the modulators. This process involves the coordination and protonation of styrene

oxide by the respective MOF. Remarkably, the introduction of a second modulator at the same concentration resulted in a significant increase in conversion ($48\% \nu s$. 98%). In comparison, unmodulated Zn-BDC only achieved a conversion of 21%. The most exceptional result was obtained when ethanol was used instead of methanol. In this case, Zn. Mand(MPA) achieved a complete conversion with a selectivity of 98% and an enantiomeric excess (ee) of 97% for the *S*-enantiomer.¹⁵⁹

Yang *et al.* reported the modification of MIL-125 MOF by butyric acid as modulator to increase the catalytic activity of the MOF for oxidative desulfurization reaction of sulfur compounds. To investigate the catalytic performance of these different morphologies, dibenzothiophene (DBT) and 4,6dimethyldibenzothiophene (4,6-DMDBT) in *n*-heptane, along with H₂O₂, were employed as example reactions. MIL-125 with {101} facets in greater abundance than pristine MIL-125 with predominant {001} facets displayed a better catalytic performance. The significantly higher turnover frequency (TOF) observed for 4,6-DMDBT in the presence of MIL-125 with {101} facets can be attributed to an increased number of available Ti sites. This enables the rapid formation of the necessary Tihydroperoxo species when reacting with H₂O₂, thus accelerating the overall reaction rate.¹¹⁵

Utilizing rhodamine B as a modulator, Jin *et al.* successfully synthesized HP-MIL-125-NH₂. Subsequent removal of the modulator resulted in pronounced porosity within the MOF structure and increased formation of open metal sites. This enhanced porosity facilitated the uptake of toluene. The unique feature of this modified MOF lies in its photocatalytic properties, particularly in its ability to decompose toluene under the influence of atmospheric oxygen. The excitation of the MOF linker initiates an electron transfer from the BDClinker to the MOF cluster. This electron transfer process subsequently reduces an oxygen molecule to generate a superoxide anion radical. These highly reactive O_2^- radicals, in conjunction with the electron hole at the BDC-linker, function as potent agents for the oxidative transformation of toluene into CO_2 (Fig. 33).⁸⁰

5.2 Gas sorption

The native Zr-MOF ZrSQA is not permeable to hydrogen and nitrogen gas; however, using the modulators AA and FA, Bueken *et al.* were able to synthesise the ZrSQU MOF with a type II isotherm, which is indicative of a non-porous material and a type I isotherm, with an uptake of 40 cm³ g⁻¹, for N₂ adsorption and an increased H₂ uptake (Fig. 34) which is explained by the formation of defects in the frameworks.⁸⁵

Choi et al. reported that defected MOF-5, wich was formed by using surfactant 4-(dodecyloxy)benzoic acid as a modulator, to have a significantly higher adsorption capacity for CO₂ compared to original MOF-5. The increased adsorption of CO₂ was demonstrated by two different methods. First, by adsorption measurements, where the isotherm in the lowpressure micropore region was similar to that of nonmodulated MOF-5. However, with increasing pressure, the modulated MOF showed a significant increase in CO₂ uptake. This trend indicated that the modulated MOF-5 effectively adsorbed CO₂ in its mesoporous and macroporous regions, unlike the non-modulated MOF-5. Second, the enhanced CO₂ adsorption was confirmed by synchrotron measurements.152 Wu et al. reported that the introduction of defects into UiO-66 via the modulator acetic acid resulted in a porosity increase of up to 150%. This led to an enhanced adsorption of N₂, CH₄, and especially CO₂ gases. The -OH groups coordinated to Zr in UiO-66 have a significant impact on the adsorption of CO₂.¹³⁷

Through the utilization of AA as a modulating agent, Kim *et al.* successfully synthesized a modified version of the HKUST-1, denoted as HP-HKUST-1 (Section 4.5). Remarkably, this material exhibited a 13% increase in methane storage



Fig. 33 Scheme for HP-MIL-125, synthesized with rhodamine B as modulator, and its photocatalytic degradation of toluene. Reproduced from ref. 80 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2023.

Fig. 34 N₂ (blue) and H₂ (red) adsorption isotherms measured at 77 K on ZrSQU_A (square, AA modulator) and ZrSQU_F (circle, FA modulator) outgassed at 10^{-4} bar at 373 K for 4 h. Reproduced from ref. 85 with permission from The Royal Society of Chemistry, copyright 2014.



Fig. 35 (a) Increasing modulator hemilability. (b) Hypothesized modulator dynamics upon CO_2 adsorption. Reproduced from ref. 160 with permission from the American Chemical Society, copyright 2023.

capacity at a pressure of 65 bar and a 16% augmentation in deliverable capacity across the pressure range from 65 bar down to 5 bar when compared to its unmodified counterpart, HKUST-1.¹⁴⁹

The behavior of zirconium-based MOFs with respect to CO_2 uptake was reexamined in 2023 by Rayder *et al.* from the perspective of dynamic interactions. For this purpose, MOF-808 was investigated with different modulators. Up to then, it was assumed that it is a static internal porous surface that interacts with gases such as CO_2 at their uptake. Through various investigations, Rayder *et al.* were able to show that it is a dynamic adsorption, depending on the modulator which was used as a capping agent and the resulting coverage of the open metal sides. The electron density at the carboxylate oxygen atoms is of particular importance as it influences the hemilability of the modulator and thus the access to the Zr center for the adsorbed CO_2 (Fig. 35).¹⁶⁰

Thur *et al.* used modulators in the MOF-808 structure to enhance the uptake of CO_2 molecules. They incorporated a series of fluorinated carboxylic acid modulators as the CO_2 -philic portions in the MOF-808 structure in place of the linkers. These MOFs were employed for CO_2/CH_4 separation and showed a much better performance compared to the native MOF-808.¹⁶¹

5.3 Separation

Slater *et al.* synthesized the defective MOF $[Zn_2(BDC)(L-lac)(DMF)]$ (ZnBLD), using propanoic acid as a modulator and indicated that the enantioselective ability was increased in the enantiomeric excess for 1-phenylethanol of 35% compared to the non-defective MOF. The enhanced enantioselectivity was ascribed to size-matchable molecules with the pore size of the



Fig. 36 Sulfur capacity of CuBDC with different concentration of AA modulator. Reproduced from ref. 163 with permission from the Elsevier B.V., copyright 2023.

defective MOF. 1-Phenylethanol exhibited a superior response to enantiomeric separation compared to 2-butanol and pantolactone due to its molecules providing a better size-matching with the pores of the MOF.¹⁶²

Zhang et al. conducted a study showcasing the significant impact of modulating CuBDC with AA on the desulfurization of gasoline. In their model fuel, they employed n-pentyl mercaptan for the reference reaction. The results of their study showed that an increased amount of the modulator followed by hot ethanol treatment resulted in an enhanced removal of the sulfur compound. This observation suggests an increased incidence of structural defects within the MOF. In addition, the study highlighted the critical role played by the oxidation state of free copper atoms. Zhang et al. demonstrated that the use of ethanol served to reduce copper from the 2+ to the 1+ oxidation state, which, notably, exhibits a heightened affinity for sulfur. As a result of modulation and subsequent reduction of the MOF, the total sulfur uptake capacity was substantially enhanced, achieving an impressive increase of 104.5% in comparison to non-modulated CuBDC (Fig. 36).163

5.4 Mechanical stability

MOFs with high mechanical stability are of great importance for industrial applications. Zr-MOFs often show a good mechanical stability due to several strong Zr–O bonds in their framework. Voorde *et al.* indicated that crystal defects can play an essential role in the mechanical stability of UiO-66 without altering its porosity. They used mono-coordinating modulators with different acidic property including trifluoroacetic acid, chloroacetic acid, and acetic acid. The mechanical stability of the modulated UiO-66 (physical stability under ball-milling) increases as the modulator pK_a decreases, due to electron withdrawing effect that strengthens the Zr–O bonds and increases the positive partial charge of the Zr⁴⁺ centers.^{45,137}



Fig. 37 Stability upon water uptake of (a) NU-913-AA and (b) Nu-913-TFA over three cycles. Black, blue, and yellow isotherms represent first, second, and third cycle, respectively. Reproduced from ref. 128 with permission from the American Chemical Society, copyright 2023.

5.5 Water sorption

Controlled adsorption and release of water by porous materials is widely used in fields such as water absorption from air,¹⁶⁴ dehumidification and thermal batteries.

Considering that zirconium-based MOFs are stable in water and easily recovered, they are suitable candidates for absorbing and releasing water. On the other hand, the synthesis of most crystals of zirconium MOFs is possible only in the presence of the modulator. Yaghi *et al.* showed that zirconium MOFs prepared with the modulating agents including formic acid or acetic acid are ideal materials for adsorption and release of water from the air.¹⁶⁵

As mentioned in Section 4.3, the work of Gong *et al.* showed that different MOFs could be synthesized under the same conditions by changing the modulator. Furthermore, by changing the modulator from AA to TFA in the synthesis of Nu-913, an increased stability of the scaffold towards water sorption could be achieved due to the higher hydrophobicity introduced by the TFA modulator. The water uptake of AA and TFA Nu-913 was in the same range (0.88 g g^{-1} for AA and 0.85 g g^{-1} for TFA), showing that even over several cycles the uptake of the TFA-modulated MOF remained the same, while the uptake of the AA-modulated MOF decreased dramatically with the third cycle (Fig. 37).¹²⁸

An investigation by Teo *et al.* highlighted the influence of modulation with varying quantities of FA on the water sorption behavior of Al-Fum. Their findings revealed that the most favorable outcome was achieved when 10 mL of FA were employed as the modulating agent. Under this condition, the water uptake capacity exhibited a noteworthy increase of 12.5% compared to the non-modulated Al-Fum.¹⁶⁶

5.6 Storage of reactive gases

Storage and release of carbon monoxide (CO) at low concentrations have important therapeutic uses. The size and morphology of MOFs have an effective role in the loading of carbon monoxide containing and releasing molecules, known as CORMs. Carmona *et al.* showed that the MOF [Al(OH)(SDC)] (SDC = 4,4'-stilbenedicarboxylate) can be a suitable carrier for CORMs with controlled release of carbon monoxide in the physiological environment. The AA-modulated MOF was successfully loaded with the light-active photoCORM ALF794. Notably, this loading process could only be achieved with the modulated MOF, as the non-modulated MOF underwent decomposition during the loading procedure. Upon exposure to light, a gradual release of CO from the composite material was observed. It is worth noting that the release from the composite was marginally less efficient compared to the neat photoCORM, which may be attributed to the hindrance of CO release imposed by the MOF structure. Nevertheless, the composite still exhibited a substantial release, with approximately 35% of the loaded CO being released under the given conditions. In comparison, the neat photoCORM displayed a photo release efficiency of approximately 42%.¹²⁰

Zhang *et al.* successfully improved the adsorption of sulfurcontaining compounds in MOF-199 by using BA as a modulator. H_2S and dimethyl sulfide at different concentrations were used as test adsorbates. The results consistently showed that all modulated MOFs exhibited a better uptake of H_2S and dimethyl sulfide compared to the non-modulated MOF-199. The reason for using the modulator was the formation of structural defects in the MOF-199 lattice. These defects resulted in open copper sites that were more accessible for the interaction with sulfurcontaining compounds. In addition, these defects facilitated the transport of H_2S and dimethyl sulfide through the MOF, which promoted enhanced uptake. The best value for the modulated MOF-199 was 20% higher than that of the nonmodulated MOF for both adsorbates.¹⁶⁷

Walton *et al.* used cyanoacetic acid as a modulator in the synthesis of UiO-66 in addition to AA, TFA, and acrylic acid. The reason for selecting these modulators was their ability to interact with SO₂ and consequently enhance its uptake. The results of their study showed that all modulated MOFs exhibited better SO₂ adsorption than their non-modulated counterparts. Moreover, the concentration of the modulator was found to be a crucial factor for SO₂ uptake. The strongest interaction, and consequently the highest uptake, was obtained when cyanoacetic acid was used as modulator at a ratio of 18:1 between modulator and linker. However, it should be noted that the crucial factor for SO₂ uptake is not the choice of modulator alone, but also the interaction between the modulator, the linker and the adsorbed SO₂ molecules within the MOF structure.¹⁶⁸

Maddock *et al.* studied the uptake and storage of radioactive iodine with HP-UiO-66 modulated with FA. Using thermogravimetric measurements, they demonstrated that the modulated HP-UiO-66 had almost twice the uptake capacity for radioactive iodine compared to the unmodulated HP-UiO-66 (2.25 g g⁻¹ vs. 1.17 g g⁻¹).¹⁶⁹

5.7 Water decontamination

Contamination of drinking water by heavy metals or organic compounds such as benzene is a significant threat for the human health in many areas of the world.¹⁷⁰

Prabhu *et al.* indicated that the surface charge of the MOF Zr-FMA can be controlled by the help of the modulator BA by affecting the colloid stability of the MOF. The resulting defectfree MOF showed a considerable enhancement in the



Fig. 38 The effect of temperature (A), pH (B) and the presence of various salts (C) on the diclofenac adsorption performance of d-MOF-801(35) and MOF-801. Reproduced from ref. 146 with permission from the Elsevier B.V., copyright 2022.

adsorption capacity of $\rm AsO_4{}^{3-}$ and $\rm AsO_3{}^{3-}$ ions from water that is attributed to the positive surface of the MOF.^{171}

Li et al. demonstrated that the modulated vttrium MOF-76 showed better uptake of arsenate than the non-modulated MOF-76 under basic conditions. The high uptake was favored by the open metal sites formed during modulation. Uptake occurred in a basic environment (pH: 9-11) due to the formation of a Y-O-As bond. Furthermore, it was shown that ligand exchange in the MOF could also positively affect the uptake. Treating the MOF with HCl led to reactivation, and recycling tests achieved good uptake of arsenate even after several cycles.113 Further, part of us synthesized Zr-based functionalized UiO-66 with a modulated synthesis for the removal of Ag(1) from wastewater.129 By using the modifier mercaptoacetic acid (HMAc), an easy and economical way of incorporating a thiol group into the MOF was found. Despite the increasing amount of sulfur groups, the BET surface area of standard UiO-66 was maintained. The inclusion of ligands containing free thiol groups resulted in increased Ag⁺ uptake when compared to the unfunctionalized (non-thiol) form. MOF-801 synthesized by Prasetya et al. showed good uptake of diclofenac from aqueous solutions, with the best results obtained with the lowest amount of FA as modulator. It should be mentioned that for all defective MOFs here, water was used as solvent and the reaction was carried out at room temperature. The modulated MOF d-MOF-801(35) showed a nearly four times higher uptake compared to non-modulated MOF-801, synthesised in DMF. Particularly noteworthy was the consistently high uptake under different temperature and pH conditions as well as in the presence of salts (Fig. 38). Recycling experiments showed a constant high uptake over several cycles.146

Assaad *et al.* synthesized UiO-66 in the presence of the modulators AA and TFA. The defects in the modulated Zr-MOFs provided avenues for entering arsenate ions into MOF to bind with the metal clusters. Therefore, modulated UiO-66 exhibited greater effective adsorption in comparison to the non-modulated one. UiO-66-36TFA (with a modulator ratio of 36 equivalents) presented the most defective sample and

possessed the highest adsorption efficiency of 200 mg g $^{-1}$ compared to 89.3 mg g $^{-1}$ for unmodulated UiO-66.172

Li *et al.* were able to show that both the missing linker and the missing cluster approach for defective UiO-66 structures resulted in a higher uptake of selenium(vi) oxoanions. For the missing linker structure, HCl was used as a modulator, whereas for the missing cluster structure, TFA was employed. An uptake almost twice as high as that of the non-modulated MOF was achieved. The selenium(vi) oxoanions used bind to the open metal sites of the Zr clusters.¹⁷³

Generally, MOFs consisting of defective structure facilitate the transfer of mass in the framework, which is important for catalysis and sensing applications.¹⁷⁴

5.8 Sensing

The morphologies of the MOF $[Cu_2(OBA)_2(BPFB)] \cdot (DMF)_5$ (TMU-46) could be controlled by the benzoic acid and pyridine modulators as nanorods and nanoplates, respectively. The sensing experiments for trinitrophenol (TNP) and trinitrotoluene (TNT) showed that the plate morphology exhibits a better sensor performance (Fig. 39).¹¹⁸

Methanol was used as a modulating agent in the synthesis of MIL-88B-Fe, which is described in detail by Wang *et al.* in Section 4.5. This modified MIL-88B-Fe material exhibited exceptional sensitivity to hydrogen sulfide (H_2S), primarily due to the enhanced presence of open iron sites. Moreover, this modified material exhibited a remarkable long-term stability of more than 31 days. It also exhibited an impressive recovery time of only 88.5 seconds. When MIL-88B-was modulated with 20% methanol (referred to as MIL-88B-20%), the response to H_2S was ten times higher than the non-modulated MIL-88B (Fig. 40).⁴⁴

Li *et al.* used the HCl modulator, to form the defective MOF HCleNH₂-UiO-66 NPs which could be coated with a significant amount of iron nanoparticles due to its increased defects. The peroxidase-like activity of FeeHCleNH₂-UiO-66 NPs was found to be highly effective even at low concentrations of substrates, suggesting its potential application for detecting H₂O₂ in cancer cells.¹⁷⁵



Fig. 39 Comparison of the fluorescence intensity of the rod and plate morphology of TMU-46 for TNT and TNP sensing. Reproduced from ref. 118 with permission from the Elsevier B.V., copyright 2020.

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Fig. 40 (a) Selectivity tests of MIL-88B-20% and (b) sensitivity as a function of modulator amount. Reproduced from ref. 44 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2023.

6. Conclusion and outlook

Coordination modulation is an easy and effective way for controlling the MOF properties. MOFs with high crystallinity, pure phases, good reproducibility, high porosity, desired morphology, and size can be produced by the coordination modulation method. Stability of the MOFs is one of the most important features not only for widespread applications, but also for easy pore engineering by creating defects in the MOFs. This is because the amount of defects is limited in the unstable MOFs due to the possibility of their structure collapsing. On the other hand, the existence of the modulators is necessary to synthesize some stable MOFs, such as zirconium-based MOFs, with suitable crystallinity. In addition, the post-synthesis process with the help of modulators can be conducted easily in mild conditions. The size and morphology characteristics of the MOFs are directly related to the type and quality of their application. For example, for catalytic applications and adsorption, both the shape and size of the MOFs should be optimized to maximize the mass transfer and adsorption capacity of the material. Self-assembly of MOFs can be controlled by using coordination modulators, paving the way for the preparation of MOFs with greater potential applications.

Generally, it appears that a suitable coordination modulator is a functional molecule with a weaker coordination bond affinity so that it can have a favorable performance to guide the self-assembly path towards the formation of MOF with the expected characteristics in terms of shape and size. In other words, in this case, the modulator can only intervene in the kinetic process of MOF synthesis and control the nucleation process without changing the chemical structure of MOF. On the other hand, the chemical nature and size of the modulator is the factor that determines the final properties of MOF, for example, MOF with a larger pore size can be synthesized by choosing a modulator with a long molecular chain size.

The synthesis of new modulators, to produce MOFs with various characteristics or the production of new MOFs whose crystal phase synthesis is not possible, can be the subject of researchers' research in the future. The effective steps can be taken in the design of the modulation procedure by using of computational chemistry, for example, by designing a suitable modulator, the growth of certain crystal faces of MOF can be controlled to produce nanoplates, nanosheets and other widely used morphologies.

Abbreviations

| AA | Acetic acid |
|------------------------|--------------------------------------------------------------------------|
| AZB | 4,4'-Azobenzenedicarboxylate |
| 4-BPDB | 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene |
| 4-BPDH | 2,5-Bis(4-pyridyl)-3,4-diaza-2,4-hexadiene |
| 4-BPMB | N^1, N^4 -Bis((pyridine-4-yl)methylene)benzene-1,4- |
| | diamine |
| BA | Benzoic acid |
| BBTA | 1 <i>H</i> ,5 <i>H</i> -Benzo(1,2- <i>d</i> :4,5- <i>d</i> ')bistriazole |
| BDC | 1,4-Benzenedicarboxylate |
| BET | Brunauer–Emmett–Teller |
| BHC | The conjugate acid is also called mellitic acid |
| BIPYEN | Trans-1,2-bis(4-pyridyl)ethylene |
| BPFB | <i>N</i> , <i>N</i> '-(1,4-phenylene)diisonicotinamide |
| BTC | Benzene-1,3,5-tricarboxylate |
| СТАВ | Cetyltrimethylammonium bromide |
| DABCO | 1,4-Diazabicyclo[2.2.2]octane |
| DCA | Dichloroacetic acid |
| DGC | Dry gel conversion |
| DMF | <i>N</i> , <i>N</i> -dimethylformamide |
| FA | Formic acid |
| fcc | Face-centered cubic |
| FE-SEM | Field-emission scanning electron microscopy |
| FMA | Fumarate |
| Glu | Glutamate |
| H_2BDCA | Biphenyl-4-carboxylic acid |
| H_4 TBAPy | 1,3,6,8-Tetrakis(<i>p</i> -benzoic acid)pyrene |
| hcp | Hexagonal close packed |
| H ₃ IMDC | 4,5-Imidazoledicarboxylic acid |
| 1-HMIM | 1-Methylimidazole |
| His | l-Histidine |
| HMAc | Mercaptoacetic acid |
| HP-MOF | Hierarchical-porous MOF |
| ILME | Ionic liquid microemulsion |
| L-Pro | l-Proline |
| MNA | 6-Methoxy-2-naphtholate |
| MW | Microwave |
| NDC | Naphthalenedicarboxylate |
| NMOF | NanoMOF |
| NMR | Nuclear magnetic resonance |
| OBA | 4,4-Oxybis(benzoate) |
| ORR | Oxygen reduction reaction |
| OX | Oxalate |
| P-123 | Pluronic triblock copolymer |
| H ₄ PBPTTBA | 4,4',4'',4'''-(1,4-Phenylenebis(pyridine-4,2,6 triyl)) |
| | tetrabenzoic acid |
| PEI | Polyethyleneimine |
| <i>р</i> ТА | <i>p</i> -Toluic acid |
| PVP | Poly(vinylpyrrolidone) |
| PXRD | Powder X-ray diffraction |
| KNB | Rnodamine B |
| SDBS | Sodium dodecylbenzenesulfonate |
| SDS | Sodium dodecyl sulfate |
| SEM | Scanning electron microscopy |

Squaric acid $(C_4O_4H_2)$

| - | · · · · | |
|--------------------------------------------------------------------------------|----------------------------------------|--|
| Tar | Tartrate | |
| TCPP | Mesotetrakis(4-carboxyphenyl)porphyrin | |
| TEA | Triethyl amine | |
| TEM | Transmission electron microscopy | |
| TFA | Trifluoroacetic acid | |
| TMB | 1,3,5-Trimethylbenzene | |
| TNP | Trinitrophenol | |
| TNT | Trinitrotoluene | |
| TRO | Truncated octahedron | |
| US | Ultrasonic | |
| Conflicts of interest There are no conflicts of interest to declare. | | |
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H₂SQA

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