Recent progress on micro-fine design of metal-organic frameworks: structure regulation and gas sorption/separation

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ABSTRACT: Metal-organic frameworks (MOFs) have emerged as an important/unique class of functional crystalline hybrid porous materials in the past two decades. Due to their modular structures and adjustable pore system, such distinctive materials have exhibited remarkable prospects in key applications pertaining to adsorption such as /separation area for gas storage, gas and liquid separations, and trace impurity removal. Evidently, gaining a better understanding of the structure-property relationship offers great potential for the enhancement of a given associated MOF property either by structural adjustments of a given MOF material via isorecticular chemistry or by the design and construction of new MOF structures via the practice of reticular chemistry. Correspondingly, the application of isorecticular chemistry paves the way for the micro-fine design and structure regulation of presented MOFs. Explicitly, the micro-fine tuning is mainly based on known MOF platforms, focusing on the modification and/or functionalization of a precise part of the MOF structure/pore system, and thus providing an effective approach to produce richer pore systems with enhanced performances from a limited

number of MOF platforms. Here, some latest progress about this field are highlighted by emphasizing the differences and connections between various methods. Finally, the challenges together with prospects are also discussed.

1. Introduction

Design, of which the definition from Oxford dictionary is “art or process of deciding how something will look, work, etc. by drawing plans, making models, etc.”, as an essential symbol of human civilization, from mega-structure in buildings to costume designing, penetrates everywhere in our daily lives. As indicated in the definition, the most important two points in the design are understanding “how something will look, work, etc.” and being able to “draw plans, make models, etc.” For the prior point, it requires in-depth research on the basic subjects related to it, such as physics to architectural design. As for the latter, it requires a lot of practice and experience accumulation. In scientific research, the design of new materials also follows the same rules. At first, the advent of a new material generally comes from occasional discovery. After appropriate understanding of the structure, synthesis method and mechanism, we can attain a certain degree of design and targeted synthesis. Promptly, with the ongoing maturity of design theory and synthesis methods, further development on the functionalization and applications will come along. From “discovery” to “design” to “development”, every leap through the stage has important scientific problems to be solved and among which, the micro-fine design is an essential part of any new materials, especially for microporous materials, in the process from design to development.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), are a new class of crystalline hybrid porous materials encompassing organic linkers and inorganic metal

moieties/clusters.^[1-9] Due to their excellent structural designability and tunable pore system, they have attracted extensive attention in academia and industry alike and explored in various key applications pertaining to gas storage/separation,^[10-16] catalysis,^[17-20] luminescence,^[21-23] biomedicine,^[24-27] proton conduction,^[28-30] etc. Different from other traditional porous materials (zeolites, activated carbons, etc.), the inherent diversity of MOFs is more suitable for on-demand targeted design; and the intrinsic hybrid feature comprised of inorganic and organic components enriches the prospect applications of MOFs. The assembly concepts based on novel secondary building units (SBUs) and different topologies enabled MOFs to flourish in the last two decades. Furthermore, the introduction of the molecular building block (MBB) and the supermolecular building block (SBB) approaches have led to the rational design of MOFs; and continuous progress in synthetic methods has also bestowed scientists control over these intricate self-assembly systems to some extent.^[31-33] With the gained understanding of the relationship between structure and properties, scientists recognized that in addition to the impact of different types of topology nets, the effect of micro-fine adjustments on structures is equally important for the MOF pore system engineering. In fact, during the very early days of MOF chemistry, scientists have realized the promise of adjusting the length of the ligand for the construction of isostructural frameworks in fine-tuning the resultant porosity and surface area, attesting to the birth of isorecticular chemistry.^[34] Correspondingly, open metal sites (OMSs) and Lewis base sites (LBSs) were also found to contribute to the adsorption of specific gases such as CO₂, prompting the functional design of MOFs as a hot research topic.^[35-39] In recent years, although major breakthroughs have been made in the high-level design of MOF structures, considering the current cost and difficulty for large deployment, scientists are still inclined to regulate the properties with limited resources by micro-fine design of the structural details.

Even if any research and modification of MOFs can be considered as “tiny” adjustments, the micro-fine design in this progress report is focused on the discussion of fine-tuning of the intrinsic constituents of the host MOF material, or regulation of limited parts, affecting the pore system environment while keeping the main structure topology unaltered. Therefore, regulation of properties based on discovering new structures as well as different topologies are beyond the scope of this article. The challenge of micro-fine design depends on how to use/deploy macro methods to realize the micro adjustment. Since “Chemical Self-Assembly” was listed as one of the 25 highlighted questions in basic scientific research by the Science journal, how to effectively control the self-assembly process is still a very challenging task.^[40] From the perspective of synthesis processes, we can divide the regulation methods into two parts: design before synthesis and regulation after crystallizing. The pre-synthesis design, as the name implies, is governed by the introduction of the functionality or a regulation of some specific structural parameters in the ligand or the inorganic SBU prior to the MOF synthesis.^[41, 42] However, complex self-assembly processes may also undergo huge diversities even the pre-synthesis design only alters a tiny part of the components. Post synthetic modification (PSM) is a widely studied regulatory approach. PSM is applied to modify MOFs using small chemical reagents after the structure is formed.^[43-45] It is to be noted that the PMS strategy relies heavily on the stability of the material itself, so there are significant limitations in the deployed reaction types for functionalization (organic reaction types, solvents, pH, etc.). Evidently, micro-fine design still faces great challenges.

In recent years, tremendous progress has been achieved in gas adsorption and separation for MOF materials, and a large number of excellent works and reviews have been reported.^[10-14, 46-53]

In this progress report, we will focus on the art of micro-fine design in MOF structures and their

influence on applications (mainly on gas sorption and separation), including micro-regulation of size effect, counter ions, functional groups, metal diversities and defects (Figure 1). We will not describe each part very comprehensively, but start from the holistic perspective of micro-fine design in recent years, taking some representative works related to the theme of this paper as examples to reveal the impact of different methods on structure and their associated gas adsorption and separation properties, as well as the relationship between them. Finally, we will provide an outlook based on prospect developments of micro-fine designed MOFs.

Figure 1. Schematic of micro-fine design in MOFs by micro-regulation of size effect, metal diversities, functional groups, counter ions and defects. Reproduced with permission.^[54] Copyright 2016, AAAS. Reproduced with permission.^[55] Copyright 2019, American Chemical Society. Reproduced with permission.^[56] Copyright 2017, American Chemical Society. Reproduced with permission.^[57] Copyright 2018, Cell press. Reproduced with permission.^[58] Copyright 2019, Springer Nature.

2. Micro-Regulation of Size Effect

The adjustable pore system is one of the most important features of MOFs. Although various methods have already been developed to achieve regulation of the pore size and surface area,

there is still a lack of systematic regulation approaches in the ultra-fine range (0.1 Å scale). As is known to all, many important industrial gas mixture components, such as C₂H₄/C₂H₆ and C₃H₆/C₃H₈, have extremely close molecular sizes and physical properties, so they are often very difficult to separate via adsorption and molecular sieving/exclusion.^[10, 11] In the past, most materials with excellent gas separation performance were based on special functional design or specific topology design, but could not provide a complete adjustable platform. It was not until the advent of several effective strategies as well as some outstanding MOFs platforms in recent years that make it possible to achieve micro-fine tuning of the pore size. In addition, the different factors in the structure restrict each other (e.g. counter ions, flexibility, etc.), which also makes the fine-tuning in size effect face huge challenges. Here, as two representative parts, the story of design, regulation, and application of fluorinated MOF platform and the recent progress in pore space partition (PSP) are selected to illustrate the micro-fine design for size effect.

2.1. Fine-tuning in Fluorinated MOF Platform

(SiF₆)²⁻ and other related fluorinated pillar based MOFs have generated a great interest recently and have shown potential for many applications, especially for gas sorption/separation.^[59-62] The platform is based on a simple **pcu** net, where four nitrogen-based ligands (pyrazine, bipyridine etc.) coordinate with transition metals (Zn, Cu, Ni, etc.) to form a two-dimensional (2D) square grid. The square grid is pillared by fluorinated pillars to form a three-dimensional (3D) framework.^[63, 64] Pyrazine based (SiF₆)²⁻ MOFs **SIFSIX-3-Zn**, **SIFSIX-3-Ni** and **SIFSIX-3-Cu** can be prepared using Zn, Ni or Cu precursors respectively, as shown in previous reports.^[65-70] All of the three structures are isostructural, with no significant structural differences between them. In such a case, no substantial difference in adsorption properties of the structures is expected as transition metal ions are fully coordinated and are not exposed to guest molecules for

intermolecular interactions/recognition. However, as metal is changed from Zn to Ni to Cu, the Metal-Nitrogen (pyrazine) distance decreases slightly as shown in Figure 2. This results in a slight compression of the square grid with a decrease in Metal-Metal distance from 7.141 Å to 7.015 Å to 6.919 Å as going from Zn to Ni to Cu. As a consequence, the pendent F...F distance in the channel decrease from 3.784(1) Å to 3.691(1) Å to 3.483(1) Å for Zn, Ni and Cu analogues respectively. This relatively small decrease in pendent F...F distance has a drastic impact on CO₂ heat of adsorption as well as CO₂ uptake at very low concentrations for these materials. This example demonstrates that when the distance between the two or more functional groups (F in this case) approaches the size of the guest molecule (CO₂ in this case) even nominal change in distance can have a drastic effect on the adsorption properties of the materials.

Figure 2. Micro-size regulation of fluorinated MOFs by metal ions and their CO₂ adsorption properties: (a) **SIFSIX-3-Zn**, (b) **SIFSIX-3-Ni**, (c) **SIFSIX-3-Cu** and (d) CO₂ adsorption curves at low pressure. Reproduced with permission.^[67] Copyright 2016, American Chemical Society.

These (SiF₆)²⁻ based MOFs have excellent carbon capture properties, **SIFSIX-3-Cu** has excellent CO₂ uptake even at atmospheric concentration (400 ppm). However these MOFs are found not stable to humidity and water; hence they could not be used for practical applications. To avert the issue of water stability, Eddaoudi and co-workers used (NbOF₅)²⁻, a stronger nucleophile than (SiF₆)²⁻ as a pillar to construct a stable isostructural framework.^[54, 67] The resultant

framework, **NbOFFIVE-1-Ni** (also known as **KAUST-7**) has excellent water stability. The relatively larger size of Nb compare to Si resulted in longer Nb-F distance than Si-F distance, making $(\text{NbOF}_5)^{2-}$ bulkier pillar compare to $(\text{SiF}_6)^{2-}$. As a result, although the square grid of **NbOFFIVE-1-Ni** and its $(\text{SiF}_6)^{2-}$ analogue **SIFSIX-3-Ni** has almost identical dimensions (7.030 Å and 7.015 Å respectively), pendent F...F distance decrease to 3.210(1) Å for **NbOFFIVE-1-Ni** compared to 3.691(1) Å for **SIFSIX-3-Ni** (Figure 3). The decreased F...F distance within the channel resulted in a drastic increase in CO_2 affinity for **NbOFFIVE-1-Ni**, making it one of the best physisorbent for CO_2 capture at the atmospheric concentration (400 ppm) as well as under humid flue gas conditions. In-situ single-crystal X-ray diffraction study of CO_2 loaded crystal of **NbOFFIVE-1-Ni** elucidated that $\text{C}^{\delta+}$ of CO_2 is surrounded by four $\text{F}^{\delta-}$ of four different pillars, with C...F distance less than the sum of Van der Waals radius, resulting in energetically highly stable arrangement of CO_2 in the framework. This example shows an additional degree of tunability in the fluorinated platform, where properties could be tuned by substitution of a pillar in addition to conventional metal substitution. Here, the use of strong nucleophilic and bulkier ligand $(\text{NbOF}_5)^{2-}$ resulted in a highly stable framework with very high CO_2 affinity in contrast to its $(\text{SiF}_6)^{2-}$ analogue.

Figure 3. Micro-size regulation of fluorinated MOFs by different pillars and their CO_2 adsorption properties: (a) **SIFSIX-3-Ni** by $(\text{SiF}_6)^{2-}$ and (b) **KAUST-7** by $(\text{NbOF}_5)^{2-}$; (c) drastic increase in CO_2 affinity of **KAUST-7**. Reproduced with permission.^[67] Copyright 2016, American Chemical Society.

Apart from $(\text{NbOF}_5)^{2-}$ pillar being bulkier than $(\text{SiF}_6)^{2-}$, $(\text{NbOF}_5)^{2-}$ is also longer pillar and forms stronger Ni-F bond compare to $(\text{SiF}_6)^{2-}$. As a result, the distance between two adjacent $(\text{NbOF}_5)^{2-}$ pillars is much shorter (4.000(1) Å) than that of two adjacent $(\text{SiF}_6)^{2-}$ pillars (4.586(1) Å). As a consequence, pyrazine moiety of the square grid also rotates little and forms F...H hydrogen bonds with the pillar. The rotation of pyrazine subsequently reduces the aperture of the channel gate formed by four pyrazine molecules compared to $(\text{SiF}_6)^{2-}$ analogue as shown in Figure 4. The reduced aperture of the channel gate resulted in a complete sieving of propane from propylene (Figure 5). It is to be noted that the propane/propylene separation is one of the highly challenging and industrially relevant separations.^[54]

Figure 4. Structural comparison of **SIFSIX-3-Ni** and **NbOFFIVE-1-Ni** demonstrates the rotation of pyrazine ring in **NbOFFIVE-1-Ni** resulting in smaller channel window aperture. Reproduced with permission.^[54] Copyright 2016, AAAS.

Figure 5. Complete sieving of propane from propylene by **NbOFFIVE-1-Ni** as demonstrated by (a) pure gas isotherms, (b) calorimetry and (c) dynamic mixed gas breakthrough experiments. Reproduced with permission.^[54] Copyright 2016, AAAS.

Further fine-tuning of the platform can be possible by substituting the central metal of the pillar to +3 oxidation state instead of +4 or +5 oxidation state as in the case of $(\text{SiF}_6)^{2-}$ and $(\text{NbOF}_5)^{2-}$ respectively. Using Al (III) and Fe (III) as central atom resulted in pillars $(\text{AlF}_5(\text{H}_2\text{O}))^{2-}$ and $(\text{FeF}_5(\text{H}_2\text{O}))^{2-}$ respectively with a coordinated water molecule.^[71] The coordinated water molecule can be removed to generate potential OMSs in the corresponding framework. The resultant frameworks, **AlFFIVE-1-Ni (KAUST-8)** and **FeFFIVE-1-Ni**, showed a very high water affinity (Figure 6). **AlFFIVE-1-Ni** have interesting dehydration/hydration chemistry; on dehydration, Al coordination geometry changes from octahedral to trigonal bipyramidal, which reverts back to octahedral coordination geometry upon rehydration. As a result, **AlFFIVE-1-Ni** has excellent dehydration properties at low water concentration, better than benchmark zeolites; at the same time, **AlFFIVE-1-Ni** can be regenerated by applying a fraction of energy required for regeneration of zeolites. **AlFFIVE-1-Ni** also has excellent water adsorption/desorption recyclability making it an attractive energy-efficient dehydrating agent (Figure 7). Interestingly, the size and shape of the **MFFIVE-1-Ni** channels also provided an excellent sieving effect in line with other isostructural materials, as a result, neither **AlFFIVE-1-Ni** nor **FeFFIVE-1-Ni**

showed adsorption of isobutane and isopropanol. This indicates that gases and vapours of equal or greater size than isobutane and isopropanol can be effectively dehydrated via full molecular sieving. **AIFFIVE**-1-Ni is further proven to be an excellent candidate for the removal of corrosive gases like $\text{H}_2\text{S}^{[72]}$ and $\text{SO}_2^{[73]}$ at very low concentrations.

Figure 6. Fine-tuning structure by using a pillar with a coordinated water molecule. Replacement of $(\text{NbOF}_5)^{2-}$ pillar with $(\text{AlF}_5(\text{H}_2\text{O}))^{2-}$ results in a structure with the potential OMSs. Reproduced with permission.^[71] Copyright 2017, AAAS.

Figure 7. Excellent hydrolytic stability and high water affinity of **AIFFFIVE-1-Ni** and **FeFFIVE-1-Ni** as demonstrated by (a) variable humidity PXRD, (b) water isotherms, (c) comparison of water uptake at low concentration and easy of regeneration of **AIFFFIVE-1-Ni** and **FeFFIVE-1-Ni** with other benchmark dehydrating agents and (d) water adsorption recyclability of **AIFFFIVE-1-Ni**. Reproduced with permission.^[71] Copyright 2017, AAAS.

2.2. Systematic Regulation with Pore Space Partition (PSP) Strategy

With regard to the design and synthesis of MOFs, the mixed SBUs strategy as well as mixed ligand strategy have always been two of the commonest methods to achieve regulation of structural complexity, stability and functionality.^[74-76] In some cases, if there are some independent components are embedded in the large cages or channels through coordination bonds or other interactions, the large cages or channels will be divided into several small parts. The concept of applying the suitable components to partition and regulate the cage space and pore size is regarded as PSP, or, as the definition from Prof. Feng's work, "PSP refers to the division of large cage or channel space into smaller segments with the aim to increase the density of binding sites and tune host-guest interactions."^[77]

Since this strategy was proposed, it has been successfully applied in stabilizing MOF structures and even creating new MOF materials that would otherwise not exist, as well as regulating the abilities in gas adsorption/separation, which has been fully proven thus we will not describe it in detail here.^[78-80] Moreover, due to the relative independence of pore-partition agents, this strategy provides us an excellent adjustable and functional platform, which highly extends the functionality and diversity of the parent materials.

Very recently, Feng and co-workers reported a series of functional MOFs constructed by applying PSP strategy to regulate the hexagonal channels of MIL-88/MOF-235-type MOFs.^[81] Moreover, additional variables regarding ligands and metal clusters have also been introduced, which resulted in nine heterometallic vanadium and titanium MOFs (Figure 8). The highest C₂H₆ uptake of this series reached 166.8 cm³/g ($Q_{st} = 21.9\text{-}30.4$ kJ/mol) which surpassed the benchmark made by peroxo-MOF-74-Fe (74.3 cm³/g). Although their C₂H₆/C₂H₄ separation abilities haven't reached the level of peroxo-MOF-74-Fe, their prominent thermal stability (can be stable to 450°C), excellent water stability, low regeneration energy, and remarkable structural tunability still proved the great advantage of PSP strategy in property regulation. While obviously, after successfully partitioning the channels, all the OMSs which can be beneficial for C₂H₄/C₂H₆ separation in the trinuclear clusters have been lost compared to the parent structure, but the channel complexity and structural stability are improved. Therefore, this kind of balance is still a key issue in the micro-fine design of structures.

Figure 8. (a) Representation of single crystal structure and three variables in MOFs construction by PSP strategy (BDC = terephthalate; DMBDC = 2,5-dimethylterephthalate; NDC = 1,4-naphthalenedicarboxylate; TPBz = 1,3,5-tri(4-pyridyl)-benzene, TPPy = 2,4,6-tris(4-pyridyl)pyridine, TPT = 2,4,6-tri(4-pyridyl)-1,3,5-triazine); (b) C₂H₆ and C₂H₄ adsorption of selected materials; (c) separation potential versus single-component C₂H₆ uptake compared to the selected reported materials (CPM-733: Co₂Vbdc- tpt; CPM-233: Mg₂V-bdc-tpt; CPM-223: Mg₂Ti-bdc-tpt; CPM-723: Co₂Ti-bdc-tpt). Reproduced with permission.^[81] Copyright 2020, American Chemical Society.

Another recent progress on applying PSP strategy to MOFs regulation was reported by Xiang and co-workers.^[82] In this work, the authors integrated the pillared-layer strategy with PSP strategy, and constructed a series of porous mm-MOFs (mm = multiclusters and multiligands). The assembled structure **FJU-6** contained three different ligands (H₃BTB = benzene-1,3,5-tribenzoate, HINA = isonicotinic acid, H₂BDC = 1,4-benzenedicarboxylate) and two kinds of metal clusters (9-connected [Co₃(μ₃-OH)N₃(COO)₆] and 12-connected [Co₆(μ₄-O)₂N₄(COO)₈]), forming a new (3,9,12)-connected llz topology (Figure 9). Furthermore, different ligands and clusters could be substituted by functionalized analogues systematically, resulting in a series of isostructural frameworks. As a result, seven isorecticular mm-MOFs exhibited as an adjustable pore system, their BET surface areas ranged from 731 to 1306 m²/g. In addition, the CO₂

sorption and $\text{C}_2\text{H}_2/\text{CO}_2$ separation abilities of these materials can be also fine-tuned with different functionalizations. The successful application of PSP strategy not only produces novel and stable MOF structures, but also endows the platform with the outstanding ability to regulate the channel system and achieve systematic functionalization.

Figure 9. Formation of the (3,9,12)-c Ilz topology of **FJU-6**. Reproduced with permission.^[82] Copyright 2020, American Chemical Society.

In general, the PSP strategy has shown its unique advantages in structure design, and the regulation of structural stabilities and gas adsorption/separation abilities. At the same time, its limitations are also very obvious, such as the restrictions on pore size for pore-partition agents, the huge loss of OMS and so on. Therefore, how to use the PSP strategy reasonably to achieve its greatest benefit still faces challenges.

3. Micro-Regulation of Counter Ions

Generally speaking, when the total charge of the metal ions and organic ligands in the framework are mismatching, it will result in ionic MOFs, thus additional positive (usually cationic organic amines) or negative counter ions are hosted in the pore system to maintain the framework's electrical neutrality. The important role of ionic MOFs raises from two facts. The first one is that different counter ions can direct the formation of MOF structures through the interaction with the frameworks, especially for some organic amine cations, which are also called structure-directing

agents (SDAs) and applied widely in designing zeolite-like metal-organic frameworks (ZMOFs).^[31] The second one is their ability to control and tune the performance towards catalysis, gas storage, proton conductivity, etc., due to the alterations in the pore system brought by different counter ions.

Due to their different sizes, regulating the counter ions in the pore channel, will also affect the porosity and surface area of the MOFs. For example, by replacing the dimethylamine cation with smaller Li^+ , the surface area of **usf**-ZMOF can be highly improved.^[83] Moreover, some counter ions may coordinate to the metal clusters, thus could reduce the density of OMSs. Therefore, while applying the regulation of counter ions, the influence on the porosity and OMSs should also be considered comprehensively to achieve the best balance between them. It is worth noting that the framework stability is still the biggest challenge when applying ion exchange as a PSM approach to alter the counter ions in the cage or channel of MOFs. Hence, the choice of the solvent and exchanged ions is a key problem that needs continuous exploration. Anyway, regulation of the counter ions in the pore system to achieve the micro-environment variation is one of the most important means to achieve micro-fine design.

3.1. Regulation of Anionic Ions

The cationic MOFs are usually balanced by the negative ions from metal salt present in the reaction system, such as NO_3^- , OH^- , SO_4^{2-} , SiF_6^{2-} , halide ions, etc. These counter ions can lie free in the pore channel through mutual effect with the framework, or weakly coordinate to the OMSs. Since the electrostatic field and polarizability of the pore environment are highly related to anion, fine-tuning of the counter ions is conducive to the related properties.

One such example was reported by Eddaoudi and co-workers.^[84] Based on rigid μ_3 -oxygen-centered trinuclear metal carboxylate clusters $[\text{M}_3\text{O}(\text{COO})_6]^+$ ($\text{M} = \text{In}^{3+}$, Fe^{3+}), five isorecticular

soc MOFs (Fe-**soc**-(NO₃, Cl), In-**soc**-MOF-(NO₃, Cl, Br) have been constructed (Figure 10). Among them, In-**soc**-MOF-Cl and In-**soc**-MOF-Br are the first trinuclear In-MBB comprised of different coordinated halide ions. Charged MOFs can be a perfect platform for systematic gas adsorption studies to check the influences on the H₂-MOF interactions from specific structural parameters. Low pressure H₂ adsorption showed that compound Fe-**soc**-MOF-NO₃ and Fe-**soc**-MOF-Cl could adsorb 2.62 and 2.53 wt% respectively at 77 K, with a Q_{st} value of 7.9 and 7.1 kJ/mol. Furthermore, In-**soc**-MOF-NO₃ also exhibited much higher H₂ sorption than In-**soc**-MOF-Cl and In-**soc**-MOF-Br with halide ions. The outcome shows that in fully activated **soc**-MOF system, the interaction between NO₃⁻ and H₂ is stronger than that of Cl⁻. However, different halogen ions on trinuclear inorganic MBB have little effect on the enhancement of H₂-MOF interaction.

Although the research on **soc**-MOF platform confirmed that halide ions do not have much influence on the adsorption of H₂, the differences in size and polarity of these unique anions have effect on other important aspects. In 2019, Liu and co-workers reported three isostructural cationic In-MOFs, InDCPN-X (H₃DCPN = 5-(3',5'-dicarboxylphenyl)nicotinic acid, X = Cl, Br, and I) based on dual SBUs which consist of different halogens as counter ions (Figure 10).^[55] The structure comprises a type of 18 Å 1D nanotubular channel which is constructed by the 3-connected mononuclear In-SBU. Different channels are further connected by 6-connected trinuclear In-SBU externally to form a 3D honeycomb framework with double-walled nanoscale channels. Three compounds exhibit different BET surface area (997, 875, and 726 m²/g, respectively) accorded with their different pore volumes reduced by halide ions of different radius. The precisely designed InDCPN-X series exhibited different pore performance, which exhibiting altered CO₂ sorption abilities (69, 50, and 42 cm³/g at 273 K, respectively). The

calculated Q_{st} were 30, 26, and 24 kJ/mol, respectively, which indicated adjustability of CO_2 affinity via different counter ions. Three compounds showed notable properties in cycloaddition of CO_2 , especially under relatively mild conditions, using large-sized epoxides for CO_2 fixation. Moreover, InDCPN-Cl shows high activity on substrates of different sizes, from the 89% yield of smallest propylene oxide ($4.2 \times 2.6 \text{ \AA}$) to 90% yield of cyclohexene oxide ($5.1 \times 3.9 \text{ \AA}$) and 88% yield of benzyl phenylglycidyl ether ($9.4 \times 4.3 \text{ \AA}$). The outcome showed that the order of influence of different counter halogen ions on catalytic activity was $\text{InDCPN-I} < \text{InDCPN-Br} < \text{InDCPN-Cl}$, which can be attributed to the increased affinity of I^- , Br^- and Cl^- with CO_2 .

Figure 10. Representation of the different counter ions (NO_3^- , Br^- , Cl^-) in (Fe or In)-soc-MOF and their H_2 sorption under 77K (upper); and halide ions (Cl^- , Br^- , I^-) decorated InDCPN MOFs and N_2 sorption (nether). Reproduced with permission.^[55, 84] Copyright 2016, American Chemical Society; copyright 2019, American Chemical Society.

3.2. Regulation of Cationic Ions

As is well known to all, under solvothermal conditions, commonly used organic solvents such as DMF, DMA, etc., easily undergo hydrolysis and subsequent decarbonylation into $\text{NH}_2\text{Me}^{2+}$ or $\text{NH}_2\text{Et}^{2+}$ cations, which will result in an anionic framework with organic amines counter ions. Therefore, by directly introducing other types of organic amine cations in the synthesis directly, they can serve as SDAs for the formation of the structure and guide to different topologies. At the same time, PSM approach can also be used for cationic ions exchange, such as smaller-sized cations (ie. Li^+) can be used to replace larger-sized organic amines, thereby improving the pore volume and surface area. In other words, the introduction of different cations during the synthesis process and PSM cation exchange after the lattice has formed, both are effective ways of regulating the pore properties.

As early as in 2009, Schroder and co-workers have reported an In(III) based anionic MOF in which kinetic trapping behavior is modulated by counter ions.^[85] In the case where the counter ion in its channel is piperazinium dications, H_2 adsorption shows a significant hysteretic phenomenon. When the cations are exchanged into Li^+ , the hysteresis disappeared, and the adsorption capacity and adsorption enthalpy both increased. Another example of tuning sorption properties via cation exchange was bio-MOF-1 ($\text{Zn}_8(\text{ad})_4(\text{BPDC})_6\text{O}\cdot 2\text{Me}_2\text{NH}_2$) reported by Rosi and co-workers.^[86] After cation exchange with tetramethylammonium, tetraethylammonium, and tetrabutylammonium cations they got three new analogues. Gas adsorption studies showed that although the surface area and pore volume are decreased due to the bigger counter ions, but the CO_2 sorption amount has significantly increased. The results showed that smaller pores could enhance the interactions between adsorbate and sorbent.

Host-guest interactions between anionic frameworks and cationic ions can also effectively influence the mechanical properties. In 2014, Cheetham and co-authors reported two analogue

MOFs with different cationic counter ions, $[\text{C}(\text{NH}_2)_3]^+$ and $[(\text{CH}_2)_3\text{NH}_2]^+$.^[87] Different counter ions formed completely different hydrogen bonding connections with framework, and the stronger cross-linking hydrogen bonding between $[\text{C}(\text{NH}_2)_3]^+$ and the MOF increased the Young's moduli and hardnesses, which are almost twice than another one, while the thermal expansion is much smaller.

Regulation of cationic ions could not only regulate the inherent properties of MOF itself, but also introduce the characteristics that MOF does not possess in this way. In 2019, Cheng and co-authors presented the first example of introducing chirality into an achiral MOFs through cation exchange.^[88] In this work, a chiral component N-benzylquininium chloride and another luminescent center Tb^{3+} have been assembled into an achiral luminescent anionic MOFs by PSM approach. This bifunctional material exhibits enantioselectivity luminescent sensing to the enantiomers, which can achieve high-efficiency corresponding to the Cinchonine and Cinchonidine epimers and amino alcohol enantiomers.

4. Micro-Regulation of Functional Groups

Functional modification of MOFs has always been one of its most outstanding features among all the porous materials. As early as in 2002, The IRMOF series has demonstrated the unparalleled extendibility of this type of material to the world.^[2] With further exploration, the relationship between property and structure has gradually become clear. Around 2009, Cohen and other researchers started using PSM approach to modify and improve the properties of MOF materials and made outstanding contributions.^[45] To this day, the functionalization of ligands, or the functionalization of OMSs, is still a key method to achieve function-oriented synthesis.

It is worth noting that functional modification can also affect the porosity and surface area. Generally speaking, in many aspects the prospect application of porous materials, the

performance is often positively related to the surface area. Therefore, even functional groups can theoretically contribute to some aspects, close attentions should also be paid to the negative effects caused by the decrease in porosity.

4.1. Regulation of Appended Functionalization

Without changing the overall structure, adding appended functional groups, such as amino groups, alkyl groups and so on, to the ligand or OMS is one of the most direct and effective ways to achieve functionalization.

Since the organic ligands usually possess available sites for functionalization on aromatic rings, functional groups with reasonable size and orientation can permit precise control of the pore environments. Several recent examples have excellently illustrated the impact of this strategy on MOFs. In 2019, Sun and co-workers reported a series of **fmj**-type MOFs **UMCM-151-X** with different functional groups ($X = -F, -Cl, -NH_2, -CH_3, \text{ and } -OCH_3$).^[89] The results showed that the electron-withdrawing groups $-F$ and $-Cl$ exhibit high sorption ability for C_2H_2 , whereas the electron-donating groups $-NH_2, -CH_3$ and $-OCH_3$ have high sorption ability for C_2H_4 . In 2017, Liu and co-workers exhibited a series of **fcu**-Zr-MOF **JLU-Liu34** to **36** with different functional groups ($-NO_2$ and $-NH_2$).^[90] As a result, although the functionalized **JLU-Liu35** and **JLU-Liu36** showed smaller pore size and lower surface areas compared with the parent material **JLU-Liu34**, the $-NH_2$ modified **JLU-Liu36** exhibits high CO_2 adsorption selectivity, which indicates that the introduction of amino groups can effectively enhance the affinity for CO_2 . Furthermore, the selectivity for CO_2/CH_4 and Q_{st} of the amino-functionalized **JLU-Liu36** were also significantly improved.

In 2010, Liu and co-workers proposed a novel strategy for constructing zeolite-like supramolecular assemblies (ZSAs) based on metal-organic squares (MOSs).^[91] Different isolated

MOSs connected by continuous hydrogen bonds, formed **ZSA-1** with **gis** topology and **ZSA-2** with **rho** topology. After further structural analysis of **ZSA-1**, it was found that the 2 position of H₃ImDC can be modified by functional groups, and therefore the pore system of **ZSA-1** can be precisely tuned. In 2017, Liu and Eddaoudi reported a series of functionalized **gis**-ZSA materials with alkyl groups (**ZSA-3-6** and **9**) and LBSs (**ZSA-7** and **8**) (Figure 11).^[56, 92] The modified ZSA materials maintain the same topology but the pore size can be tuned from smallest 3.7×8.2 Å (**ZSA-9**), to largest 13.0×8.7 Å (**ZSA-1**). The surface area can be precisely controlled from 767 to 1382 m²/g continuously. With LBSs modification, although the pore volumes of **ZSA-7** and **ZSA-8** have decreased to 0.42 and 0.44 cm³/g compared to parent **ZSA-1** (0.67 cm³/g), the volumetric CO₂ sorption abilities were enhanced to 261.4 cm³/cm³ and 259.1 cm³/cm³, which are much higher than **ZSA-1** (178.4 cm³/cm³). These outcomes were also the highest values among ZMOFs. Also, the modified **ZSA-7** exhibited very high CO₂/CH₄ selectivities (39.8 for CO₂/CH₄=0.5/0.5 at 298K, 1 bar) which surpass many reported materials.

Figure 11. (a) Representation of the synthetic strategy for the construction of MOS-Based ZSAs modified by series of functional groups (-methyl, -ethyl, -propyl, -amino, -hydroxymethyl); (b) different modified MOS; (c) different sizes of *gis* cages in the framework; (d) CPK model of functionalized ZSA materials. Reproduced with permission.^[56, 92] Copyright 2017, Royal Society of Chemistry; copyright 2017, American Chemical Society.

Reasonable modification on OMSs is also an effective way of micro-fine modification. Although in this case, some OMSs may be extinct, it is still worthwhile to make a choice according to the needs. A typical example of this contradiction was a post-synthetic functionalization of Mg-MOF-74 with tetraethylenepentamine (TEPA) reported by Hatton and co-authors.^[93] The successful modification and activation of TEPA-MOF kept the original framework unchanged. CO₂ adsorption amount of TEPA-MOF was as high as 26.9 wt % versus 23.4 wt % for the parent MOF. Moreover, compared to the saturated modified s-TEPA-MOF, retaining part of the OMS

could prevent the excess functionalization on the pore surface, the synergistic effect of Mg sites and TEPA was more conducive to the adsorption of CO₂. This work clearly exhibits that the degree of functionalization is particularly important.

Long and co-authors made a valuable contribution in this area. In 2017 and 2018, they reported a series of diamine-appended variants of MOF Mg₂(dobpdc) (dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) and found the different appended diamine could cause new adsorption mechanisms.^[94, 95] Later, in 2020, Long and co-authors reported a series of alcoholamine- and alkoxyalkylamine-functionalized MOF Mg₂(dobpdc).^[96] The modified materials were confirmed isorecticular to previous analogues by PXRD. The alcoholamine-appended Mg₂(dobpdc) variants exhibited step-shaped CO₂ adsorption via cooperative chain-forming mechanisms, and the calculated sorption capacity was 1 CO₂/2 alcoholamines. Solid-state NMR spectra and DFT calculations indicated that the enhancement of CO₂ adsorption could be attributed to the formation of carbamic acid or ammonium carbamate chains. These chains were stabilized by hydrogen bonding interactions in the channel.

4.2. Regulation of Heterocyclic Ligands

Heterocyclic ligands are an important class of organic ligands in constructing MOFs. Although some heterocycles have similar geometric configurations, due to the different number or different type of heteroatoms, they often show different chemical properties, which results in different pH or diverse interactions. The challenge of designing heterocyclic ligands is mainly on the difficulty of synthesizing organic ligand and the uncontrollable variations in MOF synthesis induced by the different pH or charges of the ligands, which should be particularly concerned when applying this method.

In 2008, Eddaoudi and co-workers reported an example of utilizing metal-organic polyhedra (MOP) as SBBs designed polyhedron-based metal-organic framework (PMOF), **rht**-MOF-1.^[97] However, such a Cu-paddlewheel and triangular $\text{Cu}_3\text{O}(\text{N}_4\text{CR})_3$ MBB based MOF was still in lack of enough stability, especially water stability. In order to explore the effect of inorganic MBB based on different heterofunctional ligands on the structural stability, Ma and co-workers replaced the tetrazole moiety of the ligand in **rht**-MOF-1 with 1,2,3-triazole or pyrazole, and obtained two new isorecticular **rht**-MOFs, named **rht**-MOF-tri and **rht**-MOF-pyr (Figure 12).^[98] Further water stability studies found that **rht**-MOF-1 based on tetrazolate decomposed after being immersed in water for less than 2 hours. However, **rht**-MOF-tri based on triazole salts can remain stable for 2 days. Even more, for **rht**-MOF-pyr based on pyrazolate, it can maintain its crystallinity even after soaking in water for 15 days. The reason for this phenomenon is the partial charges in the five-membered rings have changed due to different types of heterocycles. Compared to **rht**-MOF-1 in which the ligand has tetrazolate moiety, the 1,2,3-triazolate moiety and pyrazole moiety exhibit stronger electron density in the coordinated N atoms, which results in stronger Cu-N bonds in **rht**-MOF-tri and **rht**-MOF-pyr. This research shows that the regulation of heterocycles can effectively tune the stability of MOFs.

Figure 12. Illustration of (a) triangular $\text{Cu}_3\text{O}(\text{N}_4\text{CR})_3$ MBB in rht-MOF-1; (b) functional hexatopic carboxylate ligands; (c) triangular $\text{Cu}_3\text{O}(\text{N}_3\text{C}_2\text{R})_3$ MBB in rht-MOF-tri; (d) triangular $\text{Cu}_3\text{O}(\text{N}_2\text{C}_3\text{R})_3$ MBB rht-MOF-pyr.^[98] Copyright 2015, American Chemical Society.

Different heterofunctional ligands can also effectively regulate gas sorption and separation abilities. From 2015 to 2017, Liu and co-workers reported a series of Cu-MOP based PMOF (JLU-Liu20-22, JLU-Liu46 and 47) varies with different similar heterogeneous bent ligands and studied the relationship between CO_2 sorption and LBSs (Figure 13).^[99-101] JLU-Liu22 was constructed by C_2 -symmetric bent ligand H4tpta with an appropriate length of 7.5 Å and abundant in open metals sites. As a result, JLU-Liu22 exhibited high CO_2 uptake ($170 \text{ cm}^3/\text{g}$). Compared to JLU-Liu22, the later reported JLU-Liu20, 21, 46 and 47 were constructed by a similar type of ligands, however, with a replacement in the central benzene ring to 1,2,4-triazole and urea groups. As expected, LBSs functionalized PMOFs exhibited extraordinary CO_2 adsorption ability. The CO_2 uptake for JLU-Liu21 reached $210 \text{ cm}^3/\text{g}$ at 273 K, which was among the highest for porous MOFs. Grand canonical Monte Carlo simulation of JLU-Liu46

and **47** revealed the strong overlapping potentials between CO₂ and cages, which verify that the construction of MOFs with more OMSs and LBSs sites would significantly enhance the CO₂ adsorption.

Figure 13. Three different (3, 4)-c PMOFs (**JLU-Liu21**, **22** and **47**) with tunable CO₂ adsorption abilities constructed by Cu-paddlewheel MOP SBB and different ligand components. Reproduced with permission.^[99-101] Copyright 2015, Royal Society of Chemistry; copyright 2016, Royal Society of Chemistry; copyright 2017, American Chemical Society.

Change of carbon to hetero atom in otherwise similar ligand can change structural features of the MOFs, like control of interpenetration. For example, in the fluorinated MOF platform with (SiF₆)²⁻ and (TiF₆)²⁻ pillars, when Eddaoudi and co-workers used tetrazene based 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (dptz) as a ligand instead of 1,4-di(4-pyridyl)phenyl (dpp) or 3,6-di-4(4-pyridyl)-1,2,-diazine (dpdz), phenyl and diazine analogue of dptz respectively, doubly interpenetrated structure was obtained for dptz instead of non-interpenetrated structure observed for dpp and dpdz.^[102] The simulated interpenetrated structure for dpp and dpdz analogue suggested that structures have very close repulsive Hydrogen-Hydrogen contacts between central pheny/diazine ring and peripheral pyridyl ring as well as between two peripheral pyridyl rings of different interpenetrated networks as shown in Figure 14. On the contrary, the dptz analogue has

no repulsive Hydrogen-Hydrogen contacts between two interpenetrating frameworks; hence only dptz is able to form interpenetrated structure. The interpenetrated structure of dptz analogue has requisite arrangement of $(\text{TiF}_6)^{2-}$ pillar to create a confined environment in the channel with the right electrostatic to interact strongly with CO_2 that resulted in efficient packing of CO_2 inside the framework. Dptz- CuTiF_6 framework has excellent CO_2 uptake at flue gas concentration (10% CO_2) at 298 K with mild regeneration conditions. Moreover, interpenetration imparted the dptz- CuTiF_6 good moisture stability compared to its non-interpenetrated dpp and dpdz analogues.

Figure 14. Structural diagrams of (a) dptz- CuSiF_6 and (b) dpp- CuSiF_6 analyzing factors behind the formation of interpenetrated structures for dptz- CuSiF_6 and non-interpenetrated structure for dpp- CuSiF_6 . Repulsive Hydrogen-Hydrogen close contact restricts the formation of interpenetrated structure in the case of dpp- CuSiF_6 . Reproduced with permission.^[102] Copyright 2019, Cell press.

5. Micro-Regulation of Metal Diversity

As an essential component of MOF materials, the inorganic SBUs also have a huge impact on the physical and chemical properties of materials. On the one hand, due to the different outer

electron arrangements, the coordination geometry of different metals differs from each other. Even with similar topological networks, different metals may differ in their structural stability. On the other hand, different OMSs have always been a core point of concern in the application of MOF materials, and also an important method of structure regulation, which features the major advantage of MOFs compared to other porous materials, allowing precise regulation of the intrinsic characteristics of MOFs. Generally speaking, different metals can be used to construct analogues at the beginning of synthesis, but the attributes of metal ions sometimes hinder the construction of isorecticular structures. In this case, PSM is still the most effective method to achieve micro-fine tuning. It is worth noting that although the free cationic metal counter ions in the pore system can also provide OMSs, the PSM in this section refers specifically to the ion exchange in the SBUs. Additionally, because the valence of metals is often different, even for SBUs with the same structure, we need to pay close attention to the changes in counter ions caused by valence changes.

As stated above, the most direct way is using a different metals source during the synthesis to form MOF analogues. For example, in 2016, Dinca and co-authors reported a series of mesoporous MOFs M_2Cl_2BTDD (H_2BTDD = bis(1H-1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo-[1,4]dioxin; M = Mn, Co, Ni) with OMSs.^[103] Single crystal diffraction revealed that the three different analogues are 3D honeycomb networks and comprise 22 Å-wide hexagon mesopores. Isorecticular Mn, Co, and Ni materials showed near-record NH_3 sorption capacities of 15.47, 12.00, and 12.02 mmol/g, respectively, at STP. Further research showed that the adsorption amount of Mn-MOF at the lowest pressure point on the desorption curve was 9.35 mmol/g. It was calculated that 2.08 ammonia molecules were adsorbed corresponding to each exposed Mn

site, which is double the expected value. This may be due to the second coordination site open on the Mn atom by a structural rearrangement.

As early as in 2014, Gagliardi and co-workers have predicted that open V(II) site incorporated into a MOFs can effectively increase the enthalpy of N₂ sorption.^[104] However, some properties of V(II) make it difficult to construct a MOFs with OMSs. Very recently, Long and co-workers successfully realized a type of V(II)-BTDD MOF with the same network topology reported by Dinca mentioned above (Figure 15).^[105] Different from other OMSs reported in this same type of framework, exposed V(II) sites highly increased the affinity towards π -acidic gases via backbonding interactions. As a result, V(II)-BTDD shows a record N₂ sorption capacity reaching 1.9 mmol/g. Moreover, it also exhibited extraordinary selective N₂ adsorption ability towards CH₄ which reached 38 for N₂:CH₄=20:80 at 298K and 72 for N₂:CH₄=2:98 at 298K.

Figure 15. (a) Structural illustration of V₂Cl_{2.8}(btdd); (b) open V(II) sites; (c) structure of the organic linker H₂btdd; (d) N₂ and CH₄ adsorption at 298 K; (e) IAST selectivities calculated at 25, 35 and 45 °C for different N₂:CH₄ ratios at a total pressure of 1 bar; (f) cycling N₂ adsorption and desorption test. Reproduced with permission.^[105] Copyright 2020, Springer Nature.

As mentioned above, sometimes the attributes of different metals do not allow them to form MOF analogues directly. Thus, by using PSM to achieve cation exchange at SBUs, we can not only realize metal regulation by simple methods, but also control the doping ratio, and then precisely regulate the properties of MOFs. Since Dinca and co-workers reported a review about cation exchange in 2014, this area has attracted widespread attention.^[106]

As early as in 2013, Dinca and co-workers reported a series of substituted M-MOF-5 ($M = \text{Ti}^{3+}$ -, $\text{V}^{2+/3+}$ -, $\text{Cr}^{2+/3+}$ -, Mn^{2+} -, and Fe^{2+} -), which couldn't be synthesized through direct synthesis. Similar methods have been deployed nowadays.^[107] In 2020, Kaskel and co-workers presented an example of tuning flexibility and porosity of **DUT-47** by post cation exchange with Mn^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+} .^[108] Single crystal X-ray diffraction revealed that substituted **DUT-47** not only maintained the original structure, but also can afford unusual Mn–Mn and Cd–Cd paddle-wheel SBUs through this method. Gas adsorption results showed that Mn, Fe, Co, Zn, Cd substituted frameworks were relatively unstable compared to Ni and Cu exchanged ones. **DUT-47(Cu)** exhibited the highest porosity and prominent flexibility.

In 2019, Qiao and co-workers reported an example of the fine-tuning of metal species in Zn-MOF-74 through exchanging part of the Zn^{2+} in the structure with Ca^{2+} .^[109] To achieve the doped Ca/Zn-MOF-74, parent MOFs were immersed in CaCl_2/DMF solution. The outcome showed that the ratio of Ca/Zn can be effectively tuned by changing reaction temperature (from 20% to 68%). The PXRD of Ca/Zn-MOF-74 is slightly different compared to the original MOF-74 in which the 2θ value of 7.0° has shifted to 6.8° . This phenomenon can be attributed to the successful exchange of the smaller Ca^{2+} into the structure and also induce a slight increase in the BET surface area (688 to 758 m^2/g). Compared to the parent Zn-MOF-74, doped Ca/Zn-MOF-74 exhibited much higher catalysis activities in Knoevenagel condensation. The reaction of

benzaldehyde with malononitrile showed a very good yield of 88% under Ca/Zn-MOF-74, which was twice of the original Zn-MOF-74. Moreover, in comparison to another Ni doped analogue Ni/Zn-MOF-74, Ca/Zn-MOF-74 also shows a prominent increase in yield.

In 2020, Liu and co-workers reported a polyhedral MOF **JLU-Liu40-In** based on mononuclear and binuclear In(III) clusters with a nitrogen-rich tetracarboxylic acid ligand H₄TADIPA (H₄TADIPA = 5,5-(1H-1,2,4-triazole-3,5-diyl)diisophthalic acid).^[110] However, due to the fact that In(III) usually only forms mononuclear or trinuclear clusters, and In-paddlewheel is very rare, resulting in low surface area of **JLU-Liu40-In**. Through post-synthetic ion exchange, **JLU-Liu40-In/Cu** was obtained by successfully replacing the paddlewheel In (III) SBU with copper (II) ions without changing the mononuclear In(III). During the single-crystal to single-crystal (SC-SC) transformation process, the material still maintained a high degree of crystallinity. The successful substitution enhanced the resultant MOF thermal stability. The BET surface area can be tuned by the different substitution ratios (from 1083 to 1768 m²/g).

Eddaoudi and co-workers introduced the extension of the **soc**-MOF platform by using expanded ligand with requisite length-width ratio, [3,3'',5,5''-tetrakis(4-carboxyphenyl)-p-terphenyl (H₄TCPT)] instead of original azobenzene tetracarboxylic acid (H₄ABTC) to form a structure with **soc** topology. They successfully synthesized **soc**-MOF with larger pores using Fe trinuclear clusters; however resultant Fe-**soc**-MOF-1 has poor stability. As a result they prepared Al analogue, Al-**soc**-MOF-1, which is lighter and more stable than Fe analogue. Indeed, Al-**soc**-MOF-1 possesses a very high degree of porosity and it has one of the best compromises for gravimetric and volumetric storage of methane to date. Although Al-**soc**-MOF-1 has decent stability, however, it is unstable when exposed to high humidity for a long time. In order to gain further stability, Eddaoudi and co-worker exchanged Fe-**soc**-MOF-1 with Cr²⁺ post synthetically,

Cr^{2+} oxidized to Cr^{3+} while Fe^{3+} is reduced to Fe^{2+} during the exchange process to give Cr-**soc**-MOF-1 (Figure 16). The Cr-**soc**-MOF-1 has a high degree of hydrolytic stability due to the inert nature of Cr-O bond and it is stable in liquid water for a long period. Cr-**soc**-MOF-1 also has a high degree of porosity and can adsorb 200 wt% of water. The material also has a working capacity of more than 180 wt% between 25%-75% RH, humidity range important for indoor humidity control. In the above system based on **soc** topology, by changing metal ligand bonding strength, highly stable MOF from unstable MOF can be prepared while keeping the same structural features.^[57]

Figure 16. (a), (b) Formation of highly stable Cr-**soc**-MOF-1 with a high degree of porosity; (c) water isotherm of Cr-**soc**-MOF-1 demonstrating 200 wt% water uptake by the framework and (d) excellent recyclability and working capacity in the humidity range 25%-85% RH at 298 K. Reproduced with permission.^[57] Copyright 2019, Cell press.

6. Micro-Regulation of Defects

Defective MOFs is one of the most exciting crystal engineering studies in recent years. The continuous research of defects has unrestrained scientists from the category of “ideal crystals”, opening a new world for the adsorption and catalysis of MOF materials. When talking about defects, we would like to cite the definition from Kieslich’s work that “sites that locally break the regular periodic arrangement of atoms or ions of the crystalline parent framework because of missing or dislocated atoms or ions.”^[111] Therefore, introducing defect is an effective way to change the properties of MOF through micro-fine regulation without changing the overall long-range ordered structure. Since the milestone work reported by Goodwin and co-authors in 2014, scientists continue to study the defects in UiO-66, and then the understanding and application of defects have reached a new level.^[112]

As mentioned above, UiO-66 is one of the most studied MOF materials, in which the concentration of defects can be regulated by using different terminal monocarboxylic acids as modulators and exhibiting huge impacts on many aspects. In 2019, Jiang and co-authors conducted an experiment about the influence of defects in UiO-66-NH₂ on photo-catalysis.^[113] Forgan and co-authors explored the defect-controlled UiO-66 for anticancer drug delivery.^[114] Redox-active PdSx nanoparticles can be incorporated in the defected pores of UiO-66 thus exhibited unique semi-hydrogenation catalytic properties as reported by Wu and co-authors.^[115] However, although we can be aware of the existence of defects from many profiles, we still lack a visualized localization of it and cannot fully grasp the formation of defects at the molecular level. To reveal the truth of defects in UiO-66 which are either point defects or extended ones, Yu and Eddaoudi presented the true appearance of defects in UiO-66 for the first time by using a combination of low-dose transmission electron microscopy and electron crystallography.^[58] The results showed that ordered “missing linker” are coexisting with “missing cluster” defects which

are directly imaged with clearly high-resolution transmission electron microscopy (HRTEM) at sub-unit-cell resolution. Thus, with fine-tuning the defects, the authors further studied the catalytic properties which could be regulated by missing-linker defects and missing-cluster defects. The outcome showed that the defects of missing clusters have a greater influence on catalytic activity than those in missing linkers. Furthermore, they could also heal missing linker defects through ligand exchange method, which makes it possible to precisely regulate the defects in UiO-66 (Figure 17).

Figure 17. (a) Illustrations of various defective structures in UiO-66. Crystallographic structural models and corresponding topological representatives; (b) formate contents and BET surface areas of four UiO-66 samples as labelled; (c) catalytic performances of different UiO-66 samples in the isomerization of glucose to fructose. Reproduced with permission.^[58] Copyright 2019, Springer Nature.

Defects can also be used to effectively regulate the gas adsorption abilities. In 2015, Jiang and co-authors reported a defective sulfone-functionalized MOF **USTC-253** which was regulated by trifluoroacetic acid (TFA).^[116] The **USTC-253** with defects exhibited 167 % increased CO₂ adsorption ability compared to none defective **USTC-253** which can be attributed to the ligand-missing defects generated Lewis acidic exposed metal sites, which, together with the existed Brønsted acidity, highly improved the affinity to CO₂.

Eddaoudi and co-workers identified conditions to prepare Zr-fum-**fcu**-MOF (fum = fumarate) with varying amounts of defects by controlling the modulator ratio.^[117] The sample Zr-fum-100 has a minimum amount of defects and adsorb around 2.54 mmol/g n-butane and a negligible amount of isobutane from n-C₄H₁₀/iso-C₄H₁₀/N₂: 5/5/90 gas mixture during dynamic breakthrough experiments. On the contrary, Zr-fum-20 with a high degree of defects adsorbed both isobutane and butane and has poor separation performance. Zr-fum-100 has much higher butane uptake than previously reported rare earth based Tb-fum-**fcu**-MOF, mainly because of faster butane kinetics of the former. Hence the change of metal from Tb to Zr and regulation of defects resulted in better separation properties of butane and isobutane.

Although our understanding of defects has reached the level of visualization, and we have begun to use this crystallographic feature to adjust the properties of MOFs, there still lack a deeper understanding of defect control, and not all materials can be regulated by controlling defects. The secrets behind this “imperfect” phenomenon still need further research.

7. Conclusion and Outlook

The micro-fine design of MOFs has been demonstrated to be a very powerful method to achieve fine-tuning of structures and sorption/separation properties. Regulation of integral components or limited parts in the known MOF frameworks or modifiable MOFs platforms could enrich the

tunability and diversity of pore system in a limited number of MOFs. In this progress report, we have reviewed some recent progress in micro-fine designed MOFs and emphasized the importance of micro-regulation. Some successful platforms have been proposed, i.e., fluorinated MOFs (SIFSIX series, MOFFIVE series), ZSAs, PMOF, **soc**-MOF, etc., of which the influences have been discussed on the sorption/separation properties introduced by micro-fine tuning in detail. We have summarized the micro-regulation approaches based on five aspects including size effect, counter ions, functional groups, metal diversity and defects to outline the different methods that have been widely adopted. It is worth noting that intensive research on different micro-regulation approaches have revealed that isolated means of regulation are limited, and two or three strategies deployed together are more common. For example, to achieve micro-regulation of ZSA materials, the introduction of functional groups can also reduce the porosity and pore size, which may decrease the sorption amount but contribute to the separation abilities. Additionally, the whole story about fluorinated MOFs (SIFSIX series, MOFFIVE series) presented here emphasizes the huge impact on sorption/separation properties brought by tiny structure regulations.

Although any of the five aspects listed in this progress report can be a detailed review individually, understanding their common ground from the overall category helps us grasp the direction of the whole design. Not only that, as we mentioned above, different strategies often do not exist separately. Such as additional OMSs can be also introduced when we exchange the metal cations into the pore system at the same time; the pore size can be adjusted while performing functional modification of the ligands and affects the sieving ability. When micro-fine regulations are performed, we should consider them connectively and dynamically, cannot confine ourselves to a single detail and ignore the importance of the whole environment.

Nowadays, we still face huge challenges in micro-fine design of MOFs even if we have found so many ways to achieve micro regulation. One of the most important factors is the limited ability to control the self-assembly process, which leads to the lack of effective means to achieve targeted synthesis even if there are only micro-regulations in the design of structures. For example, even though MOFs with open V(II) sites have been theoretically predicted to have excellent N₂ adsorption behaviour in 2014, the isorecticular V(II)-BTDD has not been synthesized until recently.^[104, 105] At the same time, the relationship between structure and properties, especially the micro-mechanism of many applications, still lacks a deeper understanding, which results in the difficulty in on-demand micro-fine design. In addition, the tools for micro-fine regulation have not been developed enough. For example, when PSM is applied to achieve micro-regulation, the stability of the material is still the main limiting factor. More attentions should direct towards the exploration of effective and moderate micro-fine regulation methods to keep the fragile framework stable and meanwhile perform PSM, which will greatly promote the development of this field. Besides, it is still believed that with the continuous development of research and technology, one day, we will have complete control over this complex self-assembly process, and then the micro-fine design of MOFs will allow porous materials to enter a new era.

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Recent progress on micro-fine design of metal-organic frameworks: structure regulation and gas sorption/separation

Jiantang Li, Prashant M. Bhatt, Jiyang Li, Mohamed Eddaoudi* and Yunling Liu*

Keyword micro-fine design, metal-organic frameworks, fine-tuning structure, post-synthetic modification, functionalization

In this progress report, the application of micro-fine design in MOF structures and their influence on properties have been summarized in five aspects including size effect, counter ions, functional groups, metal diversities and defects. The differences and connections between each regulation methods have been discussed. Finally, current challenges and perspectives in micro-fine design are also presented.