RARE EARTH METAL-ORGANIC FRAMEWORK HYBRID MATERIALS FOR LUMINESCENCE RESPONSIVE CHEMICAL SENSORS

BING YAN
Rare Earth Metal-Organic Framework Hybrid Materials for Luminescence Responsive Chemical Sensors
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Rare earths (REs), as strategic resources of the 21st century, have played a great role in both industry and the economy. Due to the unique electronic structure and physiochemical properties of rare earth ions, their compounds are important active candidates in functional materials. In particular, rare earth ions display excellent optical behaviors, such as sharp emission spectra for high color purity, broad emission bands covering the ultraviolet (UV)-visible-near-infrared (NIR) region, a wide range of lifetimes from microseconds to the second level, high luminescence quantum efficiencies, and so forth, which makes them a huge treasury of luminescent materials. In recent years, REs have attracted much attention for their wide variety of applications in the fields of lighting devices (television and computer displays, optical fibers, optical amplifiers, and lasers) and biomedical analysis (medical diagnosis and cell imaging).

Metal-organic frameworks (MOFs, also known as porous coordination polymers, or PCPs) are an emerging class of porous molecular materials constructed from metal-containing nodes (also known as secondary building units (SBUs)) and organic linkers (bridging ligands). Due to their structural and functional tunability, the area of MOFs has become one of the fastest growing fields in chemistry. MOFs embody versatile functional applications in gas storage, purification, or separation; heterogeneous catalysis or photocatalysis; optic, electronic, or magnetic materials or devices; as well as biomedicines or biomages. Certainly, MOFs are employed as a platform for luminescent materials based on their intrinsic optical and photonic properties of metal ions and organic ligands, or guest species collaboratively assembled and/or encapsulated into their frameworks. The abundant luminescent responsive performance of MOFs provides their great potential in chemical sensing.

Rare earth metal-organic framework hybrid materials combine the virtues of both MOF materials and rare earth ions, which can create novel properties as well as functional and photofunctional applications. In particular, with rare earth ion functionalized MOF hybrid materials, luminescent RE$^{3+}$ ions are incorporated into MOF hosts with little content, and the characteristic emission of RE$^{3+}$ is obtained. This is identical to the traditional rare earth ion doped phosphors. Just like pure luminescent rare earth MOF materials, RE$^{3+}$ can produce an “antenna effect” and cause a pronounced increase in the luminescence intensity through the intramolecular energy transfer process from linkers to RE$^{3+}$. In addition, the relatively limited content of hybrid materials often allows the
existence of luminescence of original linkers or MOFs themselves if the functionalized amount of RE$^{3+}$ is controlled appropriately. This make it possible to exhibit multiple center luminescence for the same hybrid system and even realize luminescence color tuning or white luminescence integration. With regard to integrity, the pure rare earth MOF materials are considered in this book. Thus rare earth MOF hybrid materials encompass two main aspects: one is the pure rare earth MOFs, and the other is rare earth functionalized MOF hybrid materials.

This book consists of 6 parts, covered in 15 chapters. The first part (Chapters 1 and 2) is a general introduction to MOFs, rare earth MOFs, and rare earth functionalized MOF hybrid materials (Chapter 1); and rare earth luminescence, MOF luminescence, rare earth MOF luminescence, as well as luminescence response and chemical sensing (Chapter 2). The second part (Chapters 3, 4, and 5) gives an overview of the luminescent response mode and sensing mechanisms in rare earth metal-organic framework hybrid materials: single luminescent mode sensing (1D) (Chapter 3), dual luminescent mode (2D) for ratiometric sensing (Chapter 4), and luminescent responsive sensing mechanisms (Chapter 5). The third part (Chapters 6, 7, and 8) sheds light on rare earth metal-organic framework hybrid materials as luminescence response chemical sensors for typical ionic analytes, metal cations (I) (Chapter 6), (II) (Chapter 7), and anions (Chapter 8). The fourth part (Chapters 9, 10, and 11) focuses on rare earth metal-organic framework hybrid materials as luminescence response chemical sensors for molecules: general molecular chemicals (Chapter 9), special organic molecules (Chapter 10), and biomarkers (Chapter 11). The fifth part (Chapters 12, 13, and 14) involves rare earth metal-organic framework hybrid materials as luminescence response chemical sensors for other applications: including temperature and pH value (Chapter 12), logic gate operations (Chapter 13), and imaging applications (Chapter 14). The sixth part (Chapter 15) gives a summary and prospect for rare earth MOF hybrid materials as luminescence response chemical sensors.

Finally, I want to express my sincere gratitude to my PhD and master’s students, whose research work makes up the main content of this book. I also wish to show my appreciation to my colleagues, especially to the scholars in the research fields of rare earth metal-organic frameworks, which is an important component of this book. Many colleague scholars have provided valuable reviews of the relevant topics for the instruction and outline of this book. I hope that this book will provide readers with insights into the recent developments of rare earth metal-organic framework hybrid materials for luminescent responsive chemical sensing.

Bing Yan
Part I

Introduction for rare earth metal-organic frameworks hybrid materials
Chapter 1

Metal-organic frameworks (MOFs), rare earth MOFs, and rare earth functionalized MOF hybrid materials

1.1 Metal-organic frameworks (MOFs)

Metal-organic frameworks (abbreviated as MOFs and also known as porous coordination polymers (PCPs)) are a class of porous polymeric molecular materials, consisting of metal ion nodes connected together by organic bridging ligands (linkers) (Scheme in Fig. 1.1), which are a new development in the interdisciplinary field of coordination chemistry and functional materials [1–3]. Due to their structural and functional tunability, MOFs have become one of the fastest growing research fields in inorganic chemistry. The essence of MOFs chemistry is that the frameworks are assembled by linking molecular units of well-defined shapes by chemical bonds into periodic frameworks. An important component of reticular chemistry is the deconstruction of such structures into their underlying nets to facilitate designed synthesis of materials with targeted porosity, pore size, and functionality. The organic ligands of MOFs give them flexibility and diversity in their chemical structures and functions. The synthesis of MOFs has attracted extensive attention due to the possibility of obtaining a large variety of interesting structures for a range of applications related to porous materials [4–8]. The exploration of MOFs mainly involves four categories: (1) synthesis of metal-containing nodes or coordination bonds and linker design for MOFs; (2) postsynthetic modification (PSM) of MOFs; (3) MOF hybrids or composites; and (4) potential applications of MOFs.

1.1.1 Synthesis of metal-containing nodes or coordination bonds and linker design for MOFs

In MOFs structures, a node represents a particular environment (tetrahedra, octahedra, etc.) connected to a fixed number of related points, which depends on the geometry (tetrahedral = 4, octahedral = 6, cubic = 8). Their structures can then be represented mathematically as either a discrete (zero-dimensional—0D)
or an infinite (one-dimensional—1D), two-dimensional—2D), and three-dimensional—3D)) periodic arrangement as an extended representation of the nodes. Thus the topology of a net depends on the number of nodes in a particular structure. A simplified description of MOFs structure will be considered as a metal center or metal cluster of ions connected by an organic linker. To derive the vertex symbol and the correct topology for such structures, it is important to identify the nodes according to coordination chemistry principles [9].

To understand MOFs structures, the node and the net concept are used to describe the vertex symbols in some 2D and 3D systems. (1) **3D structures.** (a) **Uninodal structures** are based on only one type of node, which have 3 (triangular), 4 (square planar, tetrahedral), 5 (trigonal bipyramidal), 6 (octahedral), 8 (cubic), and other higher (10 or 12) connected nodes. (b) **Binodal structures** have two geometrically different nodes in a MOFs constitutes, formed using trigonal-tetrahedral; tetrahedral-square planar; tetrahedral-octahedral and tetrahedral-cubic nodes. (2) **2D structures.** MOFs with 2D layer structures can be described using nodal connectivity. (a) **Uninodal structures** contain 3 connected nodes, 4 connected nodes, 5 connected nodes, and 6 connected nodes, respectively. (b) **Binodal structures** in the context of the topology of MOFs based on common geometrical nodes are rare, although some topologies can be obtained based on trigonal-octahedral nodes. (3) **3D MOFs based on 2D layers.** The 3D MOFs with 2D network topologies are pillared by rigid linkers, which can have either a simple uninodal structure or a binodal structure within the layers using the organic ligands as the linker. Either the same ligand or a completely different organic linker can be used to arrive at the 3D structure. (4) **Zeolitic imidazolate frameworks (ZIFs).** Imidazole as the simple molecule has an ideal position between the nitrogen atoms in the structures, and behaves as a linker between the metal centers, addressing the concerns of charge neutrality. The most important topology based on the tetrahedral node is the diamond topology. These ZIF compounds have been extensively prepared for mimicking zeolite topologies [9–16].

On the other hand, the term MOFs originated from its secondary building units (SBUs) as clusters built entirely with covalent bonds [17–22].
The synthesis of SBUs can be used to direct the assembly of ordered frameworks with rigid organic linkers, which makes it highly possible to predict the chemistry of the yielded crystalline materials [17–30]. The orientation of organic linkers will result in the assembly of MOFs with predetermined structural topologies [23–30]. Generally, both SBUs (as connectors) and organic ligands (as linkers) combine to determine the final framework topology. (1) **Ditopic carboxylate linkers.** These linkers possess both ready accessibility and easily perceivable structures in combination with different SBUs: 4-connected paddlewheel clusters, 6-connected octahedral clusters, 6-connected trigonal-prismatic clusters, 12-connected clusters, and infinite chain clusters, respectively. (2) **Tritopic carboxylate linkers.** These linkers are related to different clusters: 4-connected paddlewheel clusters, 6-connected octahedral clusters, 6-connected trigonal-prismatic clusters, and multiple SBUs. (3) **Tetratopic carboxylate linkers.** These linkers appear to be very intriguing building units in MOFs constructions, especially those with tetrahedral geometry. Tetrahedral carboxylate linkers are related to different clusters: 8-connected cubical clusters, 4-connected square planar clusters, 8-connected hexagonal bipyramidal clusters, and nonregular tetrahedral carboxylate linkers. (4) **Hexatopic carboxylate linkers.** These linkers are related to 1,3-atedbenzenedicarboxylate units, 4,4'-azanediyldibenzoate units and 1,1''-terphenyl-4,4''-dicarboxylate units. (5) **Octatopic carboxylate linkers.** MOFs with these linkers are still rare, possibly due to the synthetic challenges in the linkers themselves, whose frameworks are based on linkers with long arms that tend to form interpenetrated structures. (6) **Mixed linkers.** They contain four types: ditopic-ditopic linear linkers, tritopic carboxylate-ditopic carboxylate linkers, carboxylate-pyridine linkers, and linkers coordinatively identical but with distinct shapes. (7) **Desymmetrized linkers.** (8) **Metallo-linkers.** These mainly involve four types with different donors: O and S donors, N and P donors, C donors, and mixed donor groups. (9) **N-heterocyclic linkers.** Organic linkers containing N donors, such as pyridine and azole derivatives, have achieved stable MOFs via N-metal coordination, including ditopic N-heterocyclic linkers and polytopic N-heterocyclic linkers [23].

### 1.1.2 Postsynthetic modification (PSM) of MOFs

Postsynthetic modifications (PSMs) are particularly attractive for use with MOFs materials for a variety of reasons. (I) The solvothermal reaction conditions to prepare most MOFs greatly limit the types of functional groups that can be functionalized by PSM. (II) The organic ligands in MOFs open the possibility of employing a wide range of organic transformations. (III) MOFs’ porous structures allow reagents to access the interior of the solids for their functionalization [31–44]. Thus various functions can be imparted to MOFs by incorporating different parts of the MOF structure, including metal ions/clusters, organic linkers, and empty spaces inside the cavities (Fig. 1.2, left). A variety
FIG. 1.2  Schematic depiction of functionalization (left) and PSM strategies (right) of MOFs: postsynthetic modification (PSM), postsynthetic deprotection (PSD), postsynthetic exchange (PSE), postsynthetic insertion (PSI), and postsynthetic polymerization (PSP). SBUs are represented as gold spheres, and ligand struts are represented by gray rods. (Reproduced with permission from S. A. A. Razavi, A. Morsali, Linker functionalized metal-organic frameworks. Coord. Chem. Rev. 399 (2019) 213023 and S. M. Cohen, The postsynthetic renaissance in porous solids. J. Am. Chem. Soc. 139 (2017) 2855–2863. Copyright 2019 Elsevier and 2014 American Chemical Society.)
of organic functional groups are functionalized to tune and optimize the host-guest chemistry of MOFs, which is a practical and rational strategy to improve MOF efficiency in different applications. Moreover, functionalization also has crucial influences on the structural properties of MOFs, such as crystallinity, porosity, flexibility, stability, and topology through induced structural changes and different types of secondary interactions. Subsequently, it is possible to synthesize functional MOFs and their hybrid materials using PSM [42].

(1) **Requirements for PSM.** MOFs require the following parameters: (a) Being sufficiently porous to allow access of all required reagents to the interior of the lattice. (b) Possessing an available functional group to undergo a chemical transformation. (c) Being stable to the reaction conditions. (d) Being stable to any byproducts produced by the reaction conditions. To date, the choices of both MOFs and reaction govern the scope of transformations that can be realized by PSM.

(2) **Types of PSM.** Broadly speaking, any change of the composition or structure of MOFs may be considered a form of PSM, such as the desolvation or activation of MOFs, the exchange of guest species from MOFs, the inclusion or encapsulation phenomena of being performed in a PSM manner, etc. In a narrow sense, however, it is important to define the different types of PSM to distinguish these chemical reactions from the previously mentioned routine handling and guest inclusion phenomena of MOFs. PSM of MOFs can be divided into three areas: (a) covalent PSM, (b) dative PSM (coordinate covalent PSM), and (c) postsynthetic deprotection (PSD) (Fig. 1.2, right). The type of chemical bond that is formed or broken during the PSM approach distinguishes each of these methods. It is important to note that these different PSM methods are not mutually exclusive, and perhaps utilize a combination of strategies to obtain materials of high complexity and functionality. In addition to achieving the desired chemical transformation, it is important that the MOFs cannot be destroyed under the reaction conditions. Indeed, PSM methods are intended to produce novel hybrid materials that retain the characteristic features of MOFs [36].

(1) **Covalent PSM.** This is defined as the use of a reagent to modify a component of the MOFs in a heterogeneous, postsynthetic manner to form a new covalent bond, whose target is generally the organic linker of the MOFs. Currently, covalent PSM is the most extensively investigated of the different PSM methods, and is proven to be a powerful and versatile method for introducing a broad range of chemical groups into MOFs. (2) **Dative PSM.** This type is defined as the use of a reagent that forms a dative bond with a component of the MOFs in a heterogeneous, postsynthetic manner. Not only can a ligand be added to the framework to coordinate to the SBU of the MOFs, but also a metal source can be added to the MOFs to bind to the organic linker of the MOFs, occurring through the formation of dative bonds. (3) **PSD.** This reaction is performed on the MOFs in a postsynthetic manner resulting in the cleavage of a chemical bond within an intact
framework. In principle, any kind of chemical bond can be broken during a PSD reaction to reveal a chemical functionality and produce materials with different properties. Within some highly stable MOFs, both the elimination and addition of multitopic linkers or metal ions are possible without destruction of the framework. (4) Postsynthetic metal exchange (PSME). Cation doping is also widely employed in nanocrystals to tune their properties. (5) Postsynthetic ligand exchange (PSLE). This represents the exchange of the key extending ligand of a framework by another similar ligand of different length or functional group, with the retention of the MOFs topology. (6) Postsynthetic elimination and installation (PSE&I). Some linkers constituting the framework can be eliminated with coordination changes in the metal cluster but preservation of the infinite framework connection. If the coordination site of the adjacent metal cluster matches well with an additional linker, PSI may succeed in creating a new MOFs with higher connection numbers. (7) Tandem PSM. This type is used in producing MOFs with multiple functionalities otherwise difficult or infeasible to acquire by direct synthetic methods. (i) Engineering porosity and pores by tandem PSM. Both increased and decreased porosity can be obtained depending on the size and spatial configuration of the modified groups, whose change in porosity is moderate and limited by the constant topology of the framework. (ii) Improving structural stability by tandem PSM. The direct introduction of target metal ions may be subjected to low exchange rate, uncompleted conversion, decomposition of the MOFs, and others. Based on the exchanging mechanism of different metal ions, tandem PSME is useful for improving structural stability. (iii) Modifying surface and interior by tandem PSM. Based on the reactivity and spatial effect within the confined channels, the traditional design of the reaction pathways provides a chance to engineer either the surface or the interior of MOFs (Fig. 1.2, right) [31–44].

1.1.3 MOFs hybrids or composites

In order to satisfy the practical applications of MOFs, it is desirable to further enhance their properties and create new functionalities. MOFs composites/hybrids are materials composed of one MOFs and one or more distinct constituent materials, including other MOFs, with properties noticeably different from those of the individual components. In composite or hybrid materials, the advantages of both MOFs (structural adaptivity and flexibility, high porosity with ordered crystalline pores) and various kinds of functions (optical, electrical, magnetic, and catalytic properties) can be combined effectively, accessing new physical and chemical properties along with enhanced performance that is not attainable with the individual components. Consequently, the remarkable features of composites or hybrids resulting from the synergistic combination of both MOFs and other active components make them suitable for a wide range of applications. To date, MOFs hybrids/composites have been made with versatile active species, including metal nanoparticles/nanorods (NPs/NRs), oxides, quantum dots (QDs), polyoxometalates (POMs), polymers, graphene,
carbon nanotubes (CNTs), dyes, biomolecules, and so on, resulting in performance unattainable by the individual constituents (Fig. 1.3). Moreover, these hybrids or composites offer the great advantage of flexible and optimum design, which is desirable to harness the useful properties through the incorporation of various kinds of functional materials into MOFs [45–65].

(1) **MOFs-metal or metal oxide NP composites.** Porous MOFs are thermally robust and have permanent nanoscale cavities or open channels that provide powerful confinement effects, which can be utilized as supports for metal NPs with controlled sizes inside the pores, thereby circumventing the common issue of NP aggregation and benefiting their utilization in applications. In addition, some attempts have been undertaken to integrate metal oxides (especially those with magnetic or semiconducting properties) and MOFs into core-shell nanostructures [45–53].

(2) **MOFs-silica composites.** There are currently two main types of MOFs-silica composites: (a) incorporating dispersed silica NPs within the pores/channels of MOFs or growth of a MOFs shell on a preformed silica sphere in MOFs precursor solutions (SiO\textsubscript{2}@MOFs); (b) using a silica shell as a surface coating or the mesoporous properties and processability of silica supports to promote the growth of microporous MOFs particles throughout the porous silica supports (MOFs@SiO\textsubscript{2}) [45,54].

(3) **MOFs-organic polymer composites.** Confined polymers at nanometer scales exhibit fascinating and unexpected properties different from those in the bulk state. MOFs-organic polymer composites formed from various combinations of MOFs and organic polymers can constitute a class of composite materials with combined properties [45,55].

(4) **MOFs-QDs composites.** The versatility of functional MOFs can be extended by introducing highly luminescent semiconductor QDs within the frameworks of MOFs. In QD@MOFs composites, QDs can be stabilized against photochemical degradation through the deposition of a nanometer MOFs shell, while retaining their valuable optical properties [45].

(5) **MOFs-POM composites.** The dispersion of POMs within MOFs prevents the POMs from conglomerating and deactivating. In such POM-based MOFs, the organic ligands substitute for the oxo groups of POMs to covalently link the metallic centers. What’s more, POMs can be encapsulated in the pores of MOFs through host-guest interactions to form POM@MOFs composites [45].

(6) **MOFs-carbon composites.** The exceptionally mechanical, electrical, and thermal properties of carbon materials (graphene and CNTs) commend them as valuable nanostructured fillers in MOF composites. Numerous MOFs-nanocarbon composites have been made with activated carbons, carbon monoliths, graphene oxide (GO), and CNTs, and have been intensively explored for diverse applications [45].

(7) **MOFs thin films on substrates.** The deposition of patterned thin films of MOFs on a substrate has paved the way for the nanotechnological applications of MOFs-based devices. Generally, two fabrication methods have been distinguished for the direct growth/deposition of MOFs thin films: (a) The substrate is added to a MOFs synthesis solution under ambient or solvothermal conditions, growing on the surface of the substrate and sometimes in solution at the same time. This growth leads to the formation of polycrystalline films where crystals are attached to the substrate surface in an intergrown and continuous fashion. (b) The layer-by-layer (LBL) method was developed for the facile preparation of MOFs thin films on the substrates and referred to as liquid phase epitaxy. This technique relies on the sequential deposition of monolayers of metal salts and organic linkers on a functionalized substrate. The LBL method permits the growth of smooth and homogeneous MOFs ultrathin films with diameters in the nanometer range, which achieve good control over the thickness, crystallographic orientation, and interpenetration of the MOFs multilayers [45,56–59].

(8) **MOFs@MOFs core-shell heterostructures.** The construction of multifunctional core-shell heterostructures involves two strategies. (a) Heteroepitaxial growth of a shell MOFs crystal on the external surface of another seed MOFs crystal could generate a composite crystal, in which the two coordination components are segregated into different regions of the crystal. This approach is based on a close crystal lattice match between the underlying MOFs substrate and the deposited MOFs. (b) PSM strategies include the selective reaction of the reactive residue of an organic linker and the controlled replacement of the framework metal ions or ligands, whose modification is selectively constrained to either the external surface or the internal core of the MOFs crystals [45].

(9) **MOFs-enzyme composites.** The tunable but uniform pore sizes and functionalizable pore walls of porous MOFs may make them appealing to accommodate enzymes for catalytic applications. Nevertheless, the micropore size of most MOFs precludes the entry of large-sized enzymes
and can result in only external surface attachment with low enzyme loading via adsorption and/or covalent bonding reaction [60–65].

(10) MOFs-other molecular species composites. Molecular materials such as organic dyes, organometallic compounds, metalloporphyrins, biomolecules, and other functional molecules can also be composed with MOFs for various applications. The use of MOFs as molecular encapsulators takes advantage of their powerful confinement effect to protect molecules from aggregation, heterogeneous distribution, and leaching. Impregnation procedures are mostly used to encapsulate these molecular materials. In addition, the self-assembly of MOFs in the presence of molecular moieties in the MOFs precursor solutions can lead to irreversible in-situ encapsulation [45].

1.1.4 Potential applications of MOFs

MOFs have unique properties as well as an extraordinary degree of variability for both the organic (ligands) and inorganic (metal ions or clusters) components of their structures, making them of interest for potential applications in practical fields (Fig. 1.4). With the input of industrial partners, some of these promising MOFs for important applications will soon be implemented in our daily lives [66–71].

1.1.4.1 MOFs for applications in adsorption, storage, and separation

First, in clean energy, MOFs are most significantly used as storage media for gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs [72–76]. MOFs have shown great application potential in various separations due to their tailored structures and functionalized pore surfaces, from CO$_2$ capture to natural gas purification, from air separation to harmful gas removal, from desulfurization to large-molecule inclusion, and from structural isomer separation to enantio-separations, in both gas-phase and liquid-phase systems. The precise tuning of MOFs material characteristics is expected to produce considerable improvements in sorbent performance, leading to reduced energy requirements for the capture process compared with current technologies. Meanwhile, the PSM availability of in-pore and outer-surface of MOFs is attractive for diverse analytical chemistry applications. MOFs have been either directly used or engineered to show excellent potential for use in air purification of toxic gases. Recently, MOFs have represented a new foreground for capturing various types of hazardous metal ion pollutants, including toxic and nuclear waste-related metal ions, which have harmful effects on human health and the environment [77–84].

MOFs are geometrically and crystallographically well-defined framework structures for the strength of coordination bonds, which are robust enough to allow the removal of the included guest species, resulting in permanent porosity. MOFs are ideal adsorbents for gas storage and separation due to their large surface areas, adjustable pore sizes, and controllable surface properties (Fig. 1.5). Currently, most of the research is focused on selective gas adsorption studies based on adsorption/desorption isotherm measurements of single gas components, which provide the predominant information for adsorbent screening. Practically, an adsorption-based process can afford molecular separation via diverse microscopic mechanisms: (i) thermodynamics (enthalpic)-driven, where the MOFs adsorbent expresses a relatively high affinity for a given molecule as a result of enhanced adsorbate/MOFs interactions, (ii) kinetics-driven, where the MOFs pore opening and its circumference constituents inflict a significant difference in the diffusivity of the adsorbate molecules, (iii) the combination thereof, (iv) conformational (entropic)-driven, where the MOFs pore size/shape permits a more efficient packing of the given molecule in a confined pore system, and (v) molecular sieving, where the MOFs pore aperture size/shape allows a full-size exclusion of a selected molecule. The key parameter in developing an efficient MOFs separation agent is the strong interplay between the size/shape of the targeted molecules and the structural features of the adsorbent. It needs to be pointed out that the (i) separation might require a dual effect conferred by a high degree of pore confinement and the presence of specific adsorption sites. Furtherly, it is more practical to consider a porous material displaying only one type of pore aperture to separate a specific molecule [76–85].