Substitution Reaction in Metal-Organic Frameworks and Metal-Organic Polyhedra

Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-01-2014-000033.R1
Article Type:	Review Article
Date Submitted by the Author:	01-Apr-2014
Complete List of Authors:	Han, Yi; Beijing University Of Technology, Department of Chemistry and Chemical Engineering Li, Jian-Rong; Beijing University Of Technology, Department of Chemistry and Chemical Engineering Xie, Ya-Bo; Beijing University Of Technology, Department of Chemistry and Chemical Engineering Guo, Guangsheng; Beijing University Of Technology, Department of Chemistry and Chemical Engineering

Substitution Reaction in Metal-Organic Frameworks and Metal-Organic Polyhedra

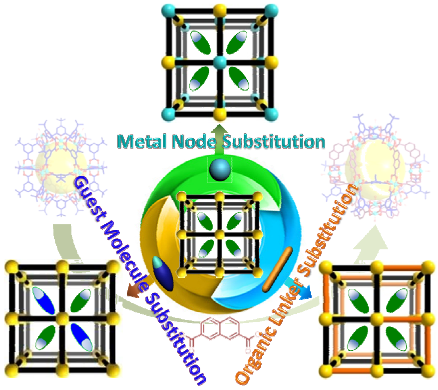
Yi Han, Jian-Rong Li*, Yabo Xie, and Guangsheng Guo*

Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, P. R. China.

*Corresponding author. E-mail: jrli@bjut.edu.cn; guogs@bjut.edu.cn

To ***Chem. Soc. Rev.***

Table of Content



This review summarizes the advances in the study of substitution reaction in metal-organic frameworks (MOFs) and metal-organic polyhedra (MOPs).

Abstract

Substitution reaction, as one of the most powerful and efficient chemical reactions has been widely used in various syntheses, including those for the design and preparation of functional molecules or materials. In past decade, a class of newly-developed inorganic-organic hybrid materials, namely metal-organic materials (MOMs) has generated a rapid development. MOMs are composed of metal-containing nodes connected by organic linkers through strong chemical bonds, and can be divided into metal-organic frameworks (MOFs) and metal-organic polygons/polyhedra (MOPs) with infinite and discrete structural feature, respectively. Recent research has showed that the substitution reaction can be used as a new strategy in the synthesis and modification of MOFs and MOPs, particularly for pre-designed ones with desired structures and functions, which are usually difficult to be accessed by a direct one-pot self-assembly synthetic approach. This review highlights the implementation of the substitution reaction in MOFs and MOPs. Examples of substitution reactions happened at metal ions, organic ligands, and free guest molecules of MOFs and MOPs are listed and analyzed, respectively. The change or modification in the structures and/or properties of these materials induced by the substitutions, as well as associated reaction nature are discussed, concluding that the substitution reaction is really feasible and powerful in synthesizing and tailoring MOMs.

1. Introduction

Solid-state materials chemically including inorganic,[1-3] organic,[4, 5] and inorganic-organic hybrid species[6,7] play an important role in every aspect of daily life and industrial manufacture. Recent decade, as a novel class of inorganic-organic hybrid materials, metal-organic materials (MOMs)[8-11] have generated a rapid development due to their diverse and easily tailored structures and associated properties, as well as potential applications[12,13] such as in gas storage,[14,15] separation,[16-20] catalysis,[21-23] chemical sensing,[24-26] drug delivery.[27-29] MOMs are composed of metal ions or clusters connected by organic ligands through strong chemical bonds. This derivative greatly extended the research field of solid-state chemistry and materials science. Two main branches can be derived from MOMs based on their structural features: infinite networked metal-organic frameworks (MOFs) and discrete molecular coordination assemblies,[10,30] while the latter in this review primarily refers metal-organic polygons/polyhedra (MOPs). As mentioned above, MOFs and MOPs are mainly made up of metal-based nodes and bridging organic linkers in their host skeletons, however they are also usually accompanied by guest molecules of coordinated or free species.

So far, the generally used method for the synthesis of MOFs and MOPs is based on the direct reaction of metal ions and organic ligands in a specific solvent system[31] (or solid state in a few cases[32]), typically a self-assembly reaction process. This traditional synthetic route is quite convenient and dominant, but limited to some extent. Normally, metal ions own variational coordination geometries in different coordination cases, for example, Cu^{2+} ion can adopt octahedral, square pyramidal, square-planar, or trigonal bi-pyramidal configurations and Zn^{2+} prefers octahedral or tetrahedral one. Similarly, organic ligands such as carboxylic species possess varieties of coordination models under different reaction/coordination conditions. Furthermore, the coordination or combination of given metal ions and organic ligands can also be affected by some other factors, including reaction temperature, reactant concentration, used solvents, template, and so on,[33-38] thereby resulting in distinct outcomes. That means, it is difficult to find a suitable reaction condition to control the outcome of such a self-assembly process in some cases, particularly in using a new type of ligand to synthesize MOPs or MOFs. However, it should clarify that even so, we do not unswear the easy control and modification of MOFs and MOPs in the synthesis, which emphasizes mostly the outcomes from the reaction between metal ions and ligands under a given/optimized synthetic conditions.[39,40]

Alternately, the substitution reaction, as the one of the most powerful and efficient chemical reactions has been widely used in inorganic and organic chemistry, particularly for designing and preparing functional molecules.[41-43] A straightforward definition of the substitution reaction is that any atom or group in a molecule is replaced by other similar composition in the reagent. The overall substitution reaction refers R-L + A → R-A + L, where R-L and A are reaction substrate and attacking reagent, R-A and L represent substituted product and leaving group, respectively. Recent research has indeed showed that the substitution reaction can be used as a new strategy for the synthesis and modification of MOFs and MOPs, particularly for pre-designed ones with desired structures and functions, when a direct self-assembly approach is not able to give the expected product.[44-47] In this context, the substitution reaction usually takes place via a two-phase process in terms of three cases: (1) two kinds of solid MOMs are mixed together and suspended in a specific solvent (sometimes do not need a solvent) for a period of time to achieve the reaction, known as a solid-solid substitution process; (2) one solid MOM is soaked in a solution containing attacking metal ions, organic ligands, or guest molecules to get substituted MOM, known as a solid-liquid substitution process, being extensively adopted in MOFs; (3) a soluble MOP reacts with new organic ligands or metal ions in given solvents to get new MOPs or MOFs, known as a liquid-liquid substitution process.

Because of the simple operation and mild reaction condition, the substitution reaction has been increasingly identifying as a new synthetic strategy towards arriving at expected and desired MOMs. In such a substitution process the parent MOM can be regarded as template to fabricate a new MOM, which greatly enhances the controllability of the resulting MOM in both its structure and property. In addition, with the control of reactant concentration and/or reaction time, different substitution degrees can be easily achieved to get partially or completely substituted products. Particularly, the partially substituted product is thus multi-components, which usually presents unique multi-functionalities. Furthermore, when several reactants are used, more complicated multi-components substituted MOMs might also be obtained, which would present interesting multi-functionalities.

Whatever partial or complete substitution, these reactions usually involve the cleavage and re-generation of coordination bonds between metal ions and organic ligands. The partial substitution of a framework often maintains its original network skeleton, while a complete substitution can lead to the structural transformation accompanied by the change of coordination environment, framework dimensionality, and structural interpenetration. Besides structural modifications, the performances of the final materials in properties and functions can be improved through the substitutions. For examples, the substitution at central metal ion can make parent inert material catalytically more active, magnetic property modified, or gas storage/separation capacity changed; the substitution at organic ligand can desirably tune pore size or surface functionality; and the substitution at free guest molecule can finely modulate fluorescent performance and molecule sorption. In this context, the substitution reaction has indeed been proposed to be an ideal and feasible approach for the synthesis and property modifications of solid materials.

The substitutions of metal ions and/or ligands in the network skeletons of MOMs were firstly observed in less chemically stable materials where metal-ligand coordination bonds were comparatively labile, but recently those were also observed in some highly robust systems.[48-51] The mechanism involved in the reactions is obviously important. Cohen and co-workers demonstrated that central metal ion or organic bridging ligand substitution in MOFs should be an absolute substitution process due to the reversible nature of the coordination bond, suggesting that the substitution was almost widespread in MOMs.[48] Even so, it should be pointed out that the substitution in some highly stable MOMs is quite difficult due to the strong bonds between metal ions and organic ligands. For example, MIL-101 (Cr)[52] is a chemically stable MOF, and attempts to exchange the metal ion or organic ligand in it failed.[48]

In some cases, before and after substitutions, the samples of MOMs are still crystalline, particularly for MOFs; single-crystal X-ray diffraction (SXRD) and powder X-ray diffraction (PXRD) are thus principal methods in characterizing the resulting substituted materials. In addition, aerosol time-of-flight mass spectroscopy (ATOFMS) has also been applied to analyze the chemical composition of microcrystalline particles of substituted MOFs in this topic. Other characterization methods such as ^{1}H NMR, UV-Vis, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDS), and time-dependent DFT calculations can also be used in these related studies.

Clearly, substitution reaction is a promising and feasible approach in the design and preparation of novel MOMs that may be difficult to be accessed by other synthetic methods. Although several excellent reviews in the topics of metal exchange/transmetalation,[44-45] sequential self-assembly,[46] solid-state reactivity,[47,53] single-crystal to single-crystal (SC-SC) transformation,[54,55] and post-synthetic modification (PSM) in MOFs[56-59] have recently appeared, a review for the summing-up and understanding of the substitution reactions in MOMs is still lacking. Herein, we attempt to collect and comment reported examples from our and others' works to contribute a review article in this new topic of substitution reaction happened in MOFs and MOPs. The discussions are organized in following three aspects: substitution at metal ion, substitution at organic ligand, and substitution at free guest molecule.

2. Substitution at metal ion

Single metal ions as the inorganic moieties predominated in the early stage of MOMs development. Subsequently, an important evolution was of using metal clusters, usually called secondary building units (SBUs) to generate porous MOMs, which could enhance the robustness and structural controllability of resulting materials.[39,60-62] The metal containing entities as the essential parts of MOMs mainly include central metal ions/clusters and metal ions within some metalolligands. Moreover, coordinated guest molecules on metal moieties can also be replaced by other chemical entities, thus we classify these three types of related substitutions in the same class, as the substitution at metal ion.

2.1. Central metal ion substitution

Since a MOM is essentially the metal salt of a base (such as pyridine-based ligand) or a conjugate base of a weak acid (such as carboxylate ligand), the substitution of original metal ion in the backbone of a MOF or MOP by other metal ions, remaining the framework integrality, should be feasible based on an acid-base displacement reaction. Central metal ion substitution (or called central metal exchange,[63-64] transmetalation,[44-45] or postsynthetic cation exchange,[48] in some cases) has indeed undergone a rapid development in the last few years, and become a feasible method for the functional modification of MOFs. By introducing suitable metal ions into well-defined structures, central metal ion substitution enables the rational design and control of physical and chemical properties of the resulting materials. Some examples have demonstrated the complete or partial substitution of metal centers in MOFs performed under mild conditions, and accompanied by the change of related properties.

Long and co-workers have reported one of the earliest examples of metal ion substitution in MOFs.[65] They presented the central metal substitution in the MOF, $\{Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2\}_n$, (BTT = 1,3,5-benzenetristetrazolate) with a sod network topology, in which chloride-centered square-planar $[Mn_4Cl]^{7+}$ units are linked by BTT^{3-} ligands to form an anionic three-dimensional (3D) framework, while charge is balanced by Mn^{2+} solvates.[66] As shown in Fig. 1, the substitution of Mn^{2+} ions in both the framework backbones and/or the cations with selected monovalent and divalent ions including Li^+, Cu^+, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} resulted in the formation of series of isostructural MOFs with different colors. Inductively coupled plasma-atomic absorption (ICP-AA) measurements demonstrated that along with the expected substitution of extra-framework Mn^{2+} ions, the adsorption of metal halides took place in the Fe^{2+} or Co^{2+} solution, to form $\{Fe_3[(Mn_4Cl)_3(BTT)_8]_2{\cdot}FeCl_2\}_n$ and $\{Co_3[(Mn_4Cl)_3(BTT)_8]_2{\cdot}1.7CoCl_2\}_n$, respectively. However, for the Cu^{2+} or Zn^{2+} substitution, a significant degree of intra-framework Mn^{2+} ions substitution also occurred simultaneously, to form $\{Cu_3[(Cu_{2.9}Mn_{1.1}Cl)_3(BTT)_8]_2{\cdot}2CuCl_2\}_n$ and $\{Zn_3[(Zn_{0.7}Mn_{3.3}Cl)_3(BTT)_8]_2{\cdot}2ZnCl_2\}_n$, respectively. For the replacement in this MOF with monovalent ions, only partial substitution of extra-framework Mn^{2+} ions was observed for Li^+ to give $\{Li_{3.2}Mn_{1.4}[(Mn_4Cl)_3(BTT)_8]_2{\cdot}0.4LiCl\}_n$, and almost negligible substitution for Cu^+ ion performed. These results demonstrated that the substitution in this system was metal ion dependent. Subsequent H_2 sorption experiments revealed the variation of adsorption enthalpies among these metal-substituted MOFs, indicating a dependence of the H_2 binding strength on the nature of the metal ions. It was found that Fe^{2+} and Co^{2+} ions substituted MOFs exhibited stronger H_2 binding than the parent material, with the Co^{2+} one having the highest initial adsorption enthalpy of 10.5 kJ/mol.

Similarly, Hou and co-workers also confirmed that the central metal ion substitution took place along with metal ion sorption when immersing a series of ferrocenyl carboxylate MOFs samples into the aqueous solution of target metal ions.[67-69] Interestingly, it was found that central metal ion substitution happened in single crystals, whereas the MOFs crystals grinded into powder performed the metal ion sorption. And, the metal ion sorption mainly occurred in a dilute solution system, while both the substitution and sorption dominated in a concentrated solution. Moreover, they also found that the substitution rate of metal ions was rapider in low-dimensional structure MOFs than those in high-dimensional ones, likely owing to high steric hindrance in the latter.

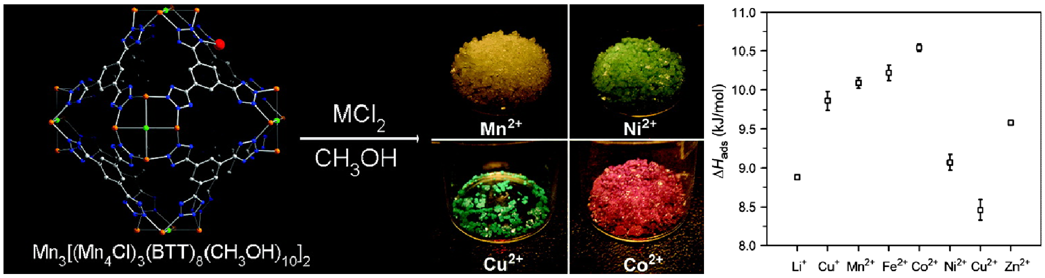


Fig. 1 The substitution of Mn^{2+} ions in $\{Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2\}_n$ with selected metal ions results in the formation of the isostructural substituted materials (left). The enthalpies of H_2 adsorption in the original and substituted MOFs (right). Reprinted with permission from ref. 65. Copyright 2007 American Chemical Society.

Not only in MOF, but also they observed the central metal ion substitution in a MOP, $[Cu_8L_{16}]$ (HL = 4′-[4-methyl-6-(1-methyl-1*H*-benzimidazolyl-2-group)-2-*n*-propyl-1*H*-benzimidazolyl methyl), which has a double-helical wheel structure (Fig. 2).[70] In the structure the central Cu^{2+} ion has a slightly distorted quadrilateral coordination geometry, which gives more room to accept incoming metal ions, thereby helping to the observed substitution. By immersing the crystals of this MOP into an aqueous solution of Zn^{2+} or Co^{2+} ions for 5 days, the partially substituted crystals of $[Zn_{1.6}Cu_{6.4}L_{16}]$ and $[Co_{1.2}Cu_{6.8}L_{16}]$ were harvested, respectively. SXRD and PXRD analyses confirmed the occurrence of the reactions, and showed the process in both cases was a SC-SC transformation induced by the central metal ion substitution. Furthermore, they also demonstrated that the central metal ion substitution reaction was indeed relative with the coordination ability of the incoming metal ions towards the organic ligands. When the coordination ability of the incoming metal ions was close to that of the original metal ion, the substitution performed and the resulting products preserved the original structure. It was also found that these MOPs materials with different substituted metal ions presented different antitumor properties and H_2

uptake capacities.

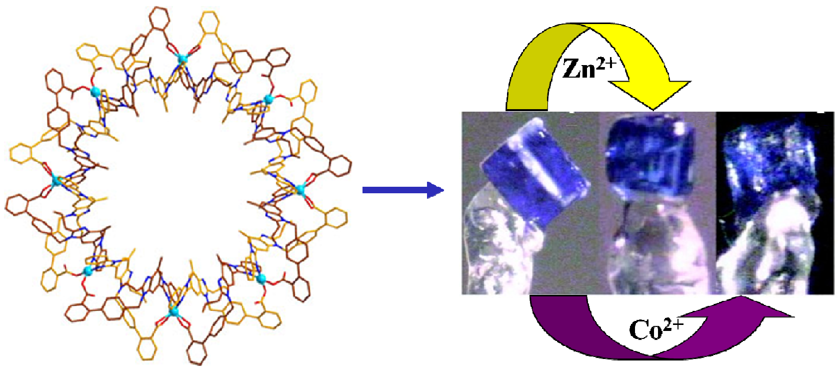


Fig. 2 Double-helical octanuclear wheel structure of [Cu_8L_{16}] (left). Single crystal photos of [Cu_8L_{16}], Zn^{2+}-, and Co^{2+}-substituted analogues (right). Reprinted with permission from ref. 70. Copyright 2008 American Chemical Society.

Another example of the central metal ion substitution was reported by Zhao and co-workers.[71] They achieved the substitution of Zn^{2+} by Cu^{2+} ion in a 3D structural MOF, $[Zn_2(L)(DMF)_3]_n$ (NTU-101-Zn; L = 5,5'-(1*H*-1,2,3-triazole-1,4-diyl)-diisophthalate, DMF = N,N-dimethylformamide) (Fig. 3). In this MOF, there exist two crystallographically independent Zn^{2+} ions with one coordinating with three DMF molecules, which maybe make it easily accessible and replaceable by other metal ions. The crystals of NTU-101-Zn were soaked in a DMF solution of $Cu(NO_3)_2$ for two weeks, the original colorless crystals gradually turned into green-blue ones (NTU-101-Cu) while maintaining their original shapes and sizes, thereby the same framework structure as confirmed by PXRD. Inductively coupled plasma (ICP) analysis indicated that approximately 80% of Zn^{2+} ions were substituted by the Cu^{2+} ions in this process, and no significant increase with the extension of the reaction time. They also demonstrated that the substitution process was irreversible, by putting NTU-101-Cu into a concentrated DMF solution of $Zn(NO_3)_2$ in a long period of time. This result suggested that the framework of NTU-101-Cu was more stable than that of NTU-101-Zn, which was also confirmed by subsequent gas adsorption experiments. It was found that the activated NTU-101-Cu exhibited a N_2 adsorption uptake of 526 cm^3g^{-1} at 1 atm and a higher adsorption selectivity towards CO_2 over N_2 and CH_4, whereas the framework of NTU-101-Zn collapsed upon the sample activation as evidenced by PXRD, resulting in poor gas adsorption capacities towards both N_2 and CO_2.

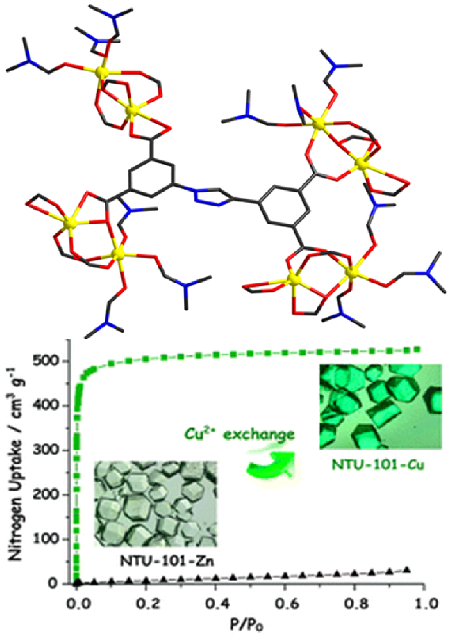


Fig. 3 Crystal structure of NTU-101-Zn showing coordination environments of organic ligands and metal ions (top). Color change along with the metal ion substitution and N_2 sorption isotherms of activated NTU-101-Zn and NTU-101-Cu at 77 K (bottom). Reprinted with permission from ref. 71. Copyright 2012 The Royal Society of Chemistry.

Similarly, Cheng and co-workers reported the substitution of Zn^{2+} ion by Cu^{2+}, Co^{2+}, and Ni^{2+} ions in MOF $\{[Zn_7(L)_3(H_2O)_7]\cdot[Zn_5(L)_3(H_2O)_5]\}_n$ (L = *N*-phenyl-*N'*-phenyl bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxdiimide tetracarboxylate), which was built by interpenetrated cationic $[Zn_7(L)_3(H_2O)_7]$ (MOF-A^+) and anionic $[Zn_5(L)_3(H_2O)_5]$ (MOF-B^-) networks.[72] The crystals of this MOF were immersed in a methanol solution of Cu^{2+}, Co^{2+}, or Ni^{2+} ions over one week to achieve the metal ion substitution. It was found that approximately 87% of the Zn^{2+} was substituted by Cu^{2+} ions, while no Co^{2+} or Ni^{2+} ions was detected in the resulting respective material. PXRD confirmed that the resulting Cu-substituted MOF was isostructural with the original one. The authors attributed the substitution only subjecting to Cu^{2+} to the fact that Cu^{2+} and Zn^{2+} ions has a close ion diameter and similar coordination geometry or feature.

The examples discussed above all performed a partial substitution of central metal ions. The authors did not explore why not a complete substitution happened in the target samples, or the exact location of the substituted metal ions in a MOF with multiple crystallographically independent central metal sites. These information would be very useful in elucidating the involved mechanism in these substitution reactions. In this context, Dincă and co-workers proposed that a kinetic barrier induced by the preferential coordination geometries of metal ions indeed dominated the partial or complete substitution.[73] They initiated the study of the substitution of Zn^{2+} ions with Ni^{2+} ions in the Zn_4O cluster of $[Zn_4O(BDC)_3]_n$ (MOF-5; BDC = 1,4-benzenedicarboxylate) (Fig. 4a-b).[60] Soaking colorless crystals of MOF-5 in a saturated DMF solution of $Ni(NO_3)_2$ for 1 year, a Zn:Ni ratio of 3:1 in the $[M_4O]^{6+}$ cluster of the resulting yellow crystals was achieved. This limited content of Ni^{2+} in the final material was consistent with those observed in the earlier reported Co-, and Ni-doping MOF-5 materials synthesized by a direct reaction of different Zn:Ni/Co ratio (up to 1:6) metal salts with the ligand.[74,75] In terms of such a fact that Ni^{2+} ion prefers an octahedral coordination in oxygen ligand field, the authors attributed this observed phenomenon to that an octahedral coordinated Ni^{2+} ion distorted the parent Zn_4O core and the framework lattice, which prevented the incorporation of additional Ni^{2+} ions due to the presence of a large kinetic barrier. In addition, thermogravimetric analysis (TGA) confirmed that two DMF molecules coordinated to each Ni^{2+} center in the substituted structure. Heating the Ni-substituted MOF-5 led to a color change from yellow to blue-purple, implying that a pseudo-tetrahedral Ni^{2+} ion might be generated. N_2 absorption analysis indicated this blue Ni-MOF-5 material had a N_2 uptake of 825 cm^3 at 1 atm and 77 K and a BET surface area of 3300 (100) m^2g^{-1} very close to those for MOF-5 parent. In a following work, this group prepared redox-active Ti^{3+}-, $V^{2+/3+}$-, $Cr^{2+/3+}$-, Mn^{2+}-, and Fe^{2+}-substituted MOF-5 materials by soaking MOF-5 crystals in a concentrated DMF solution of $TiCl_3{\cdot}3THF$, $VCl_2(pyridine)_4$, $VCl_3{\cdot}3THF$, $CrCl_2$, $CrCl_3{\cdot}3THF$, $MnCl_2$, or $Fe(BF_4)_2{\cdot}6H_2O$ for one week, respectively (Fig. 4c).[76] Unlike Ni-MOF-5, this series substituted MOF-5 materials can not be obtained by a direct solvothermal reaction from the starting reactants of $Zn(NO_3)_2$ mixed with the corresponding metal ion sources. Importantly, it was found that the substitution rates of metal ions in these cases were much faster than that observed in Ni^{2+} ion case, and the substitution degrees seemed to be kinetically controlled by the stability constant of each substituting metal ion. Furthermore, all these MOF-5 substituents were highly porous with BET surface areas ranging from 2393 m^2/g to 2700 m^2/g, but being lower than that of Ni-MOF-5 (3300 m^2/g). This was attributed to a partial disruption and introduction of defects in the MOF lattice by the rapid substitution, by authors.

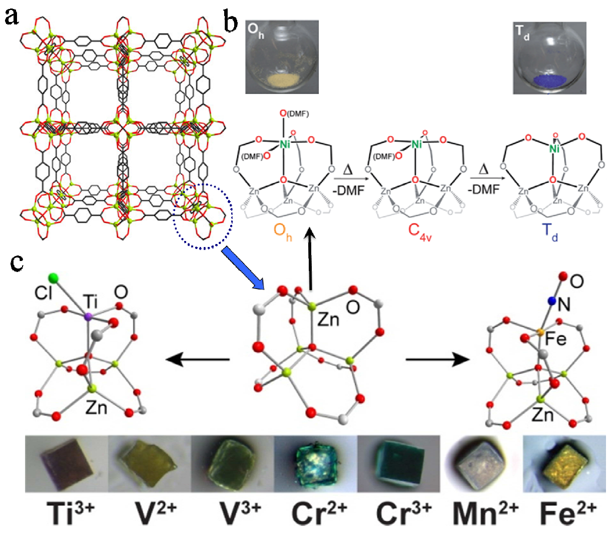


Fig. 4 (a) Crystal structure of MOF-5. (b) Color change accompanied by the sequential loss of DMF molecules from $(DMF)_2NiZn_3O(COO)_6$ cluster. (c) The $MZn_3O(COO)_6$ cluster featuring Ti^{3+} and Fe^{2+} substitutions and crystal photos of all metal-substituted MOF-5 analogues. Reprinted with permission from refs. 73 and 76. Copyright 2012 The Royal Society of Chemistry and 2013 American Chemical Society.

On the other hand, Dincă and co-workers demonstrated that multi-wavelength anomalous dispersion (MAD) was a powerful technique to determine the locations of substituted metal ions in MOFs with more than one crystallographically independent metal site.[77] By treating colorless crystals of MOF $\{Mn_3[(Mn_4Cl)_3(BTT)_8]_2\}_n$ (MnMnBTT) with concentrated solution of Fe^{2+}, Zn^{2+}, or Cu^{2+} ions in MeOH for 7 days, followed by heating under dynamic vacuum for 12 hours at 150 ^{o}C, they obtained FeMnBTT, CuMnBTT, and ZnMnBTT materials, respectively. The MAD analyses demonstrated that only the extra-framework Mn^{2+} ions were substituted. It was also found that upon the removal of solvent molecules dissociative metal ions in the original or substituted frameworks migrated to bind the tetrazolyl N atoms of the ligands, simultaneously free water molecules inside the cavities also bound to these metal ions.

Similar partial substitution controlled by the preferential coordination of metal ions was also observed in MOF $[Zn_5Cl_4(BTDD)_3]_n$ (MFU-4*l*; H_2BTDD = bis(1*H*-1,2,3-triazolo-[4,5-*b*],[4′,5′-*i*])dibenzo-[1,4]-dioxin)[78] reported by Volkmer and co-workers.[79] There are two crystallographically independent Zn^{2+} ions in the MOF structures: one is octahedral and the other is tetrahedral. It was found that heating

MFU-4*l* in a DMF solution of Co^{2+} ions led to the replacement of only tetrahedral Zn^{2+} centers, whereas the octahedral ones remained intact. Interestingly, an attempt for the Co^{2+} substitution in a similar structure MOF $\{[Zn_5Cl_4(BBTA)_3]\cdot 3DMF\}_n$ (MFU-4; H_2BBTA = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d′*)bistriazole)[80] was unsuccessful probably due to the diffusion limitation from small pores in this MOF structure.[79] Therefore, the presence of larger pores in the MOF seems to be the prerequisite for the metal ion substitution in this system. In addition, the metal ion substitution in MFU-4*l* has introduced unsaturated tetrahedral Co^{2+} centers into the resulting material, which efficaciously enhanced its catalytic activity towards CO oxidation.

It is clear that apart from the coordination bond features, the coordination geometries of metal ions, steric hindrance, kinetic barrier, and pore sizes of MOFs also play key roles in deciding the degrees of central metal ion substitutions, as demonstrated by above examples of partial substitutions. To achieve a high degree or complete substitution, all these factors should be considered. One straightforward strategy is to use MOFs with large pores and substituted metal ions having similar properties.

Kim and co-workers reported the complete substitution of central metal ions in the MOF $\{Cd_{1.5}[H_3O]_3[(Cd_4O)_3(HETT)_8]\cdot 6H_2O\}_n$ (HETT = 5,5′,10,10′,15,15′-hexaethayltruxene-2,7,12-tricarboxylate) (Fig. 5 top).[81] When crystals of this MOF were immersed in an aqueous solution of Pb^{2+} ions, almost 98% of Cd^{2+} ions from the framework were replaced by Pb^{2+} ions within 2 hours and a complete substitution was targeted in 2 days, as confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), to give the Pb^{2+}-substituted MOF. The authors also confirmed that the exchange process was reversible, but the reverse process took a longer time. The ICP-AES analysis showed that about 50% Pb^{2+} were replaced by Cd^{2+} in 1 day, and the exchange completed in almost 3 weeks. This complete reversible substitution was also a SC-SC transformation process, as evidenced by SXRD analysis. Furthermore, Cd^{2+} ions in this MOF could also be completely substituted by lanthanide ions such as Nd^{3+} and Dy^{3+} in a longer time of 12 days. It was also noted that the syntheses of the two Ln-MOFs were indeed quite difficult by using a direct reaction from lanthanide ions and H_3HETT ligand. SXRD analysis of the Dy-MOF revealed a hydroxyl-bridged square planar $\{Dy_4(\mu_4\text{-}OH)\}^{11+}$ instead of $\{Cd_4(\mu_4\text{-}O)\}^{6+}$ unit in its structure, but the original framework topology was still preserved.

Shortly afterwards, another complete and reversible metal ion substitution was demonstrated in a similar structure MOF $\{Mn[H_3O][(Mn_4Cl)_3(HMTT)_8]\}_n$ (POST-65; HMTT = 5,5′,10,10′,15,15′-hexameth-yltruxene- 2,7,12-tricarboxylate) by the same group (Fig. 5 bottom).[82] Soaking the POST-65 in DMF solutions of MCl_2 (M = Fe^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+}) for 12 days led to the formation of POST-65(Fe/Co/Ni/Cu) with preserved framework structures, which were indeed difficult of access by the direct reaction between respective metal salt and the ligand. It was also confirmed that POST-65(Fe) had a different SBU of $\{Fe_4OH\}^{11+}$ from that in the parent and other substituted MOF-65, going with by the observation of Fe^{3+} rather than Fe^{2+} in it. In addition, H_2 adsorption and magnetization measurements demonstrated the metal-specific properties of these POST-65 MOFs. Different from these, a complete but irreversible central metal ion substitution by Co^{2+} and Ni^{2+} ions in $\{Cd_3[(Cd_4Cl)_3(BTT)_8]_2\}_n$ was observed by Liao and co-workers.[83] Gas adsorption studies showed that resulting two substituted products exhibited larger adsorption capacities than that of parent one.

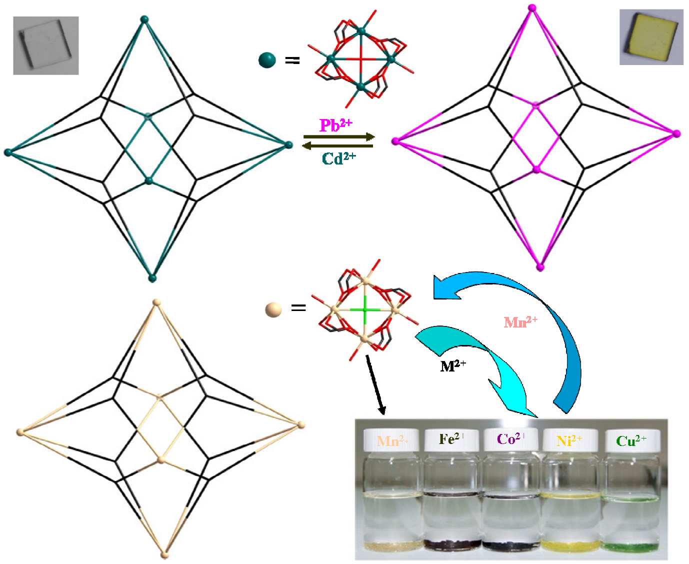


Fig. 5 Reversible and complete central metal ion substitution in the $[Cd_4O]^{6+}$ unit of $\{Cd_{1.5}[H_3O]_3[(Cd_4O)_3(HETT)_8]\cdot 6H_2O\}_n$ (top). Syntheses of POST-65-M (M = Fe^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+}) through the metal ion substitution in $\{Mn[H_3O][(Mn_4Cl)_3(HMTT)_8]\}_n$ (POST-65) and the reversible return (bottom). Reprinted with permission from ref. 81 and 82. Copyright 2009 American Chemical Society and 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Similarly, Zou and co-workers tested the possibility of complete metal ion substitution in paddle-wheel SBU-based MOFs systems.[84] In a mesoporous MOF $\{[Zn_6(BTB)_4(BIPY)_3]\cdot(S)_x\}_n$ (SUMOF-1-Zn; H_3BTB = 4,4′,4″-benzene-1,3,5-triylbenzoic acid; BIPY = 4,4′-bipyridine; S = solvent molecules), it was found that the Zn^{2+} ions in the paddle-wheel SBUs could be substituted by other transition metal ions including Co^{2+}, Ni^{2+}, and Cu^{2+} via a SC-SC transformation. The kinetics studies monitored by ICP-AES showed that 50% of the Zn^{2+} ions were replaced by Cu^{2+} ions within 1 hour, 95% within 3 days, and almost complete substitution (99%) was achieved in 3 months. But, those could only be partially exchanged by Co^{2+} and Ni^{2+} ions with a lower substitution ratio of 38% and 35%, respectively in even 3 months. It was also interesting that only 38% of Cu^{2+} ions in SUMOF-1-Cu could be exchanged by Zn^{2+} ions even after 3 months, whereas metal ions in the Co^{2+} and Ni^{2+}-based MOFs could be completely substituted by Zn^{2+} ions within only 7 days. The relative stabilities of the dinuclear paddle-wheel $[M_2(O_2C\text{-}R)_4]$ can thus be deduced in an order of Co ≈ Ni < Zn < Cu, which is consistent with the Irving-Williams series.[85] Achieving a complete central metal ion substitution of other Zn-paddle-wheel based MOFs by Cu^{2+} has also reported by Zhou's[86] and Suh's[87] groups, respectively. In Zhou's work, the resulting Cu-substituted MOF exhibited an increased stability and enhanced adsorption ability towards N_2, H_2, CO_2, and CH_4. The authors attributed the increased stability to the Cu^{2+} ion having a decreased distorted square pyramidal configuration in the paddle-wheel cluster, as opposed to the Zn^{2+} ion. In addition, it was found that the Cd^{2+} ions in $\{[Cd_6(BPT)_4Cl_4(H_2O)_4]\cdot[C_{44}H_{36}N_8CdCl]\cdot[H_3O]\cdot(S)\}_n$ (porph@MOM-10; BPT = biphenyl-3,4′,5-tricarboxylate) could be completely substituted by Mn^{2+} ions, but only partially replaced by Cu^{2+} ions.[88] The authors attributed this observed results to the lability of the high-spin d^{10} and d^9 metal ions and the relative inertness of low-spin d^5 Mn^{2+} ion in this system. The resulting porph@MOM-Mn and -Cu materials were permanently porous and exhibited catalytic activity in the epoxidation of trans-stilbene by *t*-BuOOH.

On the other hand, it was considered that central metal ion substitution usually went forward from the surface to the core in a MOF crystal. It means that MOFs with different substitution degrees can be isolated by the control of the reaction time, leading to some unique core-shell MOF crystals. Lah and co-workers reported the observation of the substitution progress in crystals of MOFs, $[M_6(BTB)_4(BIPY)_3]_n$

(ITHD(M); M = Zn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+}) as shown in Fig. 6.[89] The central metal ions substitution experiments were performed by soaking crystals of ITHD(M) MOF in DMF solutions of variant metal nitrates. Because it would take time for the metal ions diffusing from the surface to the core in a crystal, a rapider rate was observed at the beginning of the substitution. Thus, both thermodynamically controlled complete substitution and kinetically controlled core-shell hetero-structures were finally achieved by controlling the soaking time. Meanwhile, these core-shell crystals could also be prepared by using an epitaxial growth technique as shown in Fig. 6. Similar situations have been observed in $[Zn_3(BTC)_2(H_2O)_2]_n$ (Zn-HKUST-1; BTC = 1,3,5-benzenetricarboxylate) and $[Zn_{24}L_8(H_2O)_{12}]_n$ (PMOF-2; H_6L = 1,2,3-tris(3,5-dicarboxylphenylethynyl)benzene).[90] Except for the formation of core-shell structures/crystals, this work also demonstrated that solvents had a significant effect on the kinetics of the central metal ion substitution: much faster exchange in MeOH solution of Cu^{2+} ion than that in DMF. In addition, only partial Zn^{2+} ions in Zn-HKUST-1 could be substituted by Cu^{2+} even after 3 months, whereas PMOF-2 underwent a complete substitution in just 3 days. The authors attributed this difference to the much more flexibility of the ligand L than that of BTC. These findings not only demonstrate that the solvent selection is important for the metal ion substitution which is usually controlled by kinetics, but also clarify possible factors triggering a thermodynamically controlled complete substitution, including the size, shape, and property of the linkers and the framework structures.

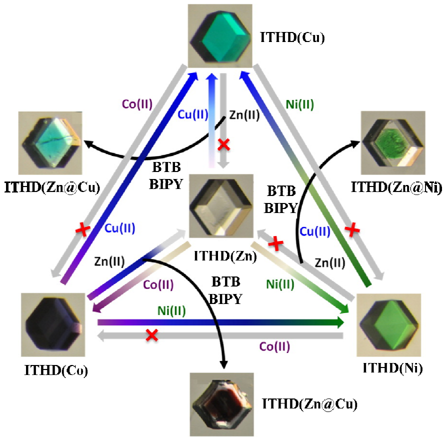


Fig. 6 Schematic representation of central metal ion substitutions and epitaxial growth of core-shell crystals of $[M_6(BTB)_4(BIPY)_3]_n$ (ITHD(M); M = Zn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+}). Reprinted with permission from ref. 89. Copyright 2012 American Chemical Society.

In above-mentioned examples, the central metal ion substitutions were observed in some MOFs with low water and thermal stability, however practical applications would require MOFs possess high stability. Fortunately, water and thermal stable MOFs, such as MIL series,[52, 91-93] UiO series,[94] and ZIFs[95-97] have also been explored for their central metal ion substitution. Cohen and co-workers studied the metal ion exchange[48] between MOFs $[Al(OH)(BDC\text{-}Br)]_n$ (MIL-53-Br(Al))[98] and $[Fe(OH)(BDC\text{-}Br)]_n$ (MIL-53-Br(Fe)).[99] As shown in Fig. 7-left, both MOFs were mixed in solid state and then soaked in water for 5 days at 85 °C. PXRD confirmed that the framework structures of the two MOFs did not change. Aerosol time-of-flight mass spectrometry (ATOFMS) spectra of the resulting solid mixture showed that about 40% of crystalline particles contained both Al and Fe ions. It was also detected that the particle sizes did not change, which ruled out the simple mechanical aggregation of the two MOFs. Both characterizations thus suggested the formation of MIL-53-Br(Al/Fe) MOF. They also studied the metal ion substitution in another stable MOF $[Zr_6O_4(OH)_4(BDC)_6]_n$ (UiO-66(Zr)) (Fig. 7-right).[94] After soaking UiO-66(Zr) in the DMF solution of Ti^{4+} salt, such as $TiCp_2Cl_2$, $TiCl_4(THF)_2$, or $TiBr_4$ (Cp = η^5-cyclopentadienyl, THF = tetrahydrofuran) for 5 days at 85 °C, it was found that Zr^{4+} ions in the MOF were partially replaced by Ti^{4+} ions, and the Ti-exchange degree was dependent on the used metal sources. $TiBr_4$ showed the lowest exchange level, whereas $TiCl_4(THF)_4$ presented the best with about 38% of metal ions being substituted in the whole sample. Similar experiment was performed with $HfCl_4$, but only a modest amount of Hf^{4+} ions of about 20% were introduced into the UiO-66 MOF even at an enhanced reaction temperature. It should be pointed out that Ti^{4+} is receiving increasing attention due to its low toxicity, good redox activity, high photocatalytic property, and lower density in constructing MOFs. However, because of the facile hydrolysis of Ti^{4+} ion, the synthesis of Ti-MOFs is quite challenged with very rare examples being reported so far.[100,101] As demonstrated by this work, the metal ion substitution method would thus be feasible and powerful in the preparation of Ti-based MOFs.

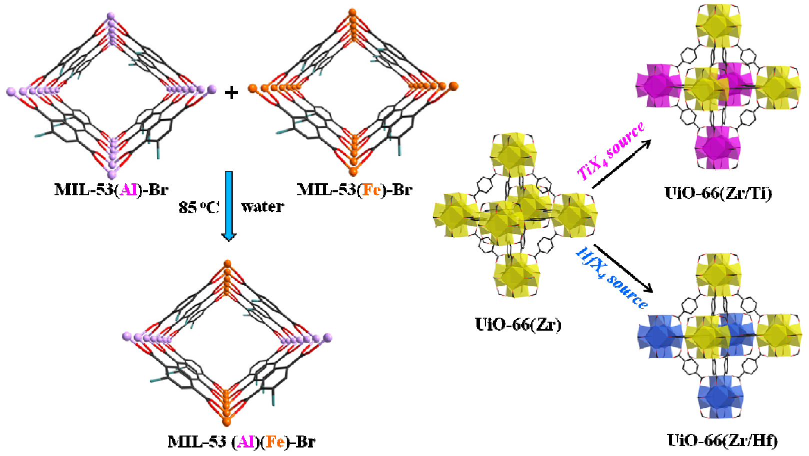


Fig. 7 Central metal ion substitutions in $[M(OH)(BDC\text{-}Br)]_n$ (MIL-53 series; M = Al^{3+} or Fe^{3+}) (left)[48] and $[M_6O_4(OH)_4(BDC)_6]_n$ (UiO-66 series; M = Zr^{4+}, Ti^{4+} or Hf^{4+}) (right).[94]

ZIFs, mostly based on Zn^{2+} or Co^{2+} ions and combined by inorganic zeotype topologies and organic functionalities, are another subclass of highly stable MOFs. Cohen and co-workers also studied the central metal ion substitution in these MOFs.[49] When activated $[Zn(DCIM)_2]_n$ (ZIF-71; DCIM = 4,5-dichloroimidazole)[102] or $[Zn(MeIM)_2]_n$ (ZIF-8; MeIM = 2-methylimidazolate)[97] was incubated in a MeOH solution of $Mn(ACAC)_2$ (ACAC = acetylacetonate) at 55 °C for 24 hours. X-ray fluorescence spectroscopy (XRF) analysis indicated that about 12% and 10% of the Zn^{2+} ions in them were replaced by Mn^{2+} ions, respectively. Subsequently, exposing ZIF-71(Zn/Mn) into a 3 molar excess of $Zn(ACAC)_2$ solution in MeOH resulted in almost all of Mn^{2+} ions being exchanged back to Zn^{2+}. These results showed that the central metal ion substitution was indeed a general phenomenon in even very robust MOFs, and the crystallinity and porosity of them could perfectly be inherited in the substitution process. It was also noteworthy that several above-mentioned cases underwent partial substitutions but not complete ones, which might be attributed to the strong coordination bonds in these stable MOFs.

As discussed above, in most cases the central metal ion substitution enabled the resulting MOFs to inherit their original framework integrity including the SBUs and the whole structural topologies. However, Zaworotko and co-workers showed that Cd^{2+} ions in $\{[Cd_4(BPT)_4][Cd(C_{44}H_{36}N_8)(S)]\cdot[S]\}_n$, (P11) could be completely but irreversibly replaced by Cu^{2+} ions when immersing its crystals in a MeOH solution of $Cu(NO_3)_2$ for 10 days, to form a new MOF of

$\{[Cu_8(X)_4(BPT)_4(S)_8](NO_3)_4\cdot[Cu(C_{44}H_{36}N_8)S]\cdot[S]\}_n$ (P11-Cu) (Fig. 8).[103] SXRD analysis of P11-Cu revealed a new SBU in its structure and a 20% unit cell volume expansion from 3779.3(2) in P11 to 4133.0(5) Å^3. Importantly, P11-Cu afforded a larger pore size and a higher surface area of 1406 m^2/g than that of 997 m^2/g for P11. In addition, a stepwise substitution mechanism was proposed in this work. Because the overall linkage geometry of the SBU in P11-Cu is similar to that in P11, the network topologies of P11-Cu and P11 are indeed identical.

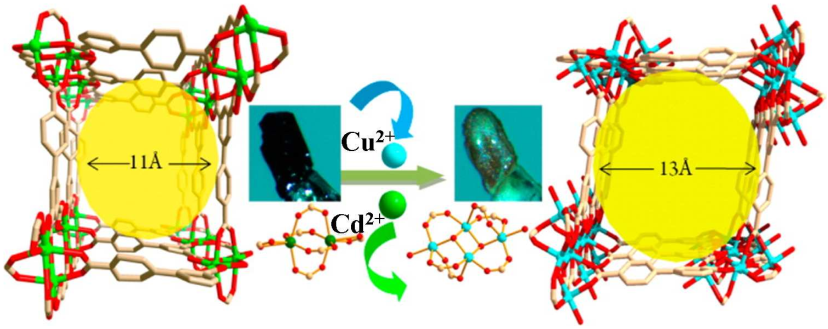


Fig. 8 Schematic representation of the central metal ion substitution in $\{[Cd_4(BPT)_4]$-$[Cd(C_{44}H_{36}N_8)(S)]\cdot[S]\}_n$ to form $\{[Cu_8(X)_4(BPT)_4(S)_8](NO_3)_4\cdot[Cu(C_{44}H_{36}N_8)S]\cdot[S]\}_n$, accompanied by the generation of tetranuclear Cu^{2+} SBUs from dinuclear Cd^{2+} ones and the modification of pore sizes. Reprinted with permission from ref. 103. Copyright 2013 American Chemical Society.

2.2. Metal ion substitution within metalolligand

Using metalloligands as building blocks has become a new approach for the construction of functional MOMs.[104] Compared with the central metal ions that usually locate in an environment with larger steric hindrance from ligands, the metal ions in some metalloligands are more open, which is very useful in catalysis and adsorption-based applications.[105-108] For example, in molecule catalysis the metal center within a metalloligand can easily interact with the substrate to perform a high activity. Metal ion substitution within the metalloligand is thus a powerful tool in tuning related properties of MOMs.

A typical metalloligand is metalloporphyrin, which is quite interesting due to its good catalytic activity and molecule bonding ability.[109-112] It has been confirmed that some divalent cations in the core of porphyrin moiety could be easily replaced by others in metalloporphyrins.[113] In MOFs systems, Ma and co-workers studied the substitution of core metal ion in metalloporphyrin ligand of a MOF called MMPF-5, $\{[Cd_{11}(TDCPP)_3][H_3O]_8\cdot(DMSO)_{36}\cdot(H_2O)_{11}\}_n$ ($H_8TDCPP\text{-}H_2$ = tetrakis(3,5-dicarboxyphenyl)porphine; DMSO = dimethyl sulfoxide), which was constructed by Cd^{2+}-metalated tetrakis(3,5-dicarboxyphenyl)porphine (TDCPP-Cd) moieties and triangular $Cd(CO_2)_3$ SBUs.[114,115] Immersing MMPF-5 crystals in a DMSO solution of $Co(NO_3)_2$ at 85 °C for 2 days afforded the Co^{2+}-exchanged MMPF-5(Co). UV/Vis spectroscopy studies revealed the complete exchange of Cd^{2+} ions by Co^{2+} ions in the metalloporphyrin ligands. Interestingly, the Cd^{2+} ions in the SBUs of the framework remained intact, possibly due to their strong coordination with O atoms of carboxylate groups. The metal ion substitution in this case is thus selective, preferring to those in the metalloporphyrin ligands. Other metal ions including Cu^{2+}, Mn^{3+}, Ni^{2+}, and Zn^{2+} have also been checked for the substitution, to easily get the relative analogies. It is interesting that MMPF-5(Co) showed a much more efficient catalytic activity and high selectivity for the epoxidation of trans-stilbene, compared with the parent MMPF-5. In addition, Zhou,[116] Yaghi,[117] and Ma's[118] groups simultaneously but respectively presented the metalation within free binding porphyrin-based MOF struts of $\{Zr_6O_4(OH)_4(TCPP\text{-}H_2)_3\}_n$ and $\{Zr_6O_8(H_2O)_8(TCPP\text{-}H_2)_2\}_n$ ($H_4TCPP\text{-}H_2$ = meso-tetrakis(4-carboxyphenyl)porphyrin). Both MOFs were reacted with Fe^{3+} or Cu^{2+} salts in solution to yield the related metalated MOFs with preserved high surface area and chemical stability, respectively. In Zhou and Ma's work, they also demonstrated that $\{Zr_6O_8(H_2O)_8(Fe\text{-}TCPP)_2\}_n$ had a good biomimetic catalytic activity in the oxidation of pyrogallol, 3,3,5,5-tetramethylbenzidine, and *o*-phenylenediamine, respectively.

The foregoing examples reveal that in most cases the metal ion substitutions in MOMs are related with the bonding stability of the parent and daughter frameworks. That is, the reaction equilibrium in the substitution finally tends to the formation of a more stable phase. Usually, a reversible substitution is always able to occur between the MOFs (such as Zn-MOFs versus Co-MOFs, or Zn-MOFs versus Ni-MOFs) with similar stability features. Furthermore, we find that most metal ions in the nodes of MOFs can be irreversibly replaced by Cu^{2+} ions, suggesting the high stability of the Cu-based MOMs probably due to the stabilization efficiency from the Jahn-Teller effect of Cu^{2+}. In addition, above-mentioned examples have also demonstrated that either a complete or partial substitution is determined by the preferential coordination of the metal ion, pore size of the MOF, and framework flexibility. On the other hand, the substitution reaction rate tends to be widely varied, ranging from a few hours to even one year. The faster substitution rate is often observed at the beginning of the reaction process, because the diffusion of the metal ions always goes from the surface to the internal in a MOF crystal. Furthermore, the solvent selection also plays a key role in this respect. For example, methanol is recognized as a more effective solvent than DMF, which can be attributed to such a fact that methanol usually forms a relatively small solvation shell around the metal ions in solvent, allowing their faster diffusion and interaction with the framework metal ions. Anyway, all these assumptions are deduced from limited experimental observations; further efforts are required to clarify the substantial mechanisms.

2.3. Coordinated guest molecule substitution

Coordinated guest molecules in metal ions of MOMs include neutral small molecules and courter ions which usually come from solvents, templates, and metal sources used in their syntheses. These guest molecules play important roles in the formation of MOMs, such as for finishing the required coordination geometry of the central metal ion to sustain the framework structure, or for balancing the charge of the whole molecule. In some cases, the coordination bonds between metal ions and guest molecules are slightly labile so that coordinated guest molecules can be easily substituted or removed without destroying the backbone of the MOMs. A lot of examples can be documented, with respect to the removal or the substitution of coordinated guest molecules in MOFs, to modify their properties.[47,53]

For example, Tasiopoulos and co-workers reported the substitution of coordinated DMF molecules by a series of guest solvent molecules of MeOH, EtOH, acetone, THF, and pyridine via a SC-SC transformation in the MOF $[Nd_2(CIP)_2(DMF)_{2.8}(H_2O)_{1.2}]_n$ (H_3CIP = 5-(4-carboxybenzylideneamino)isophthalic acid).[119] Another interesting example was the functionalization of Zr-based MOF $[Zr_6(\mu_3\text{-}OH)_8(OH)_8(TBAPY)_2]_n$ (NU-1000; H_4TBAPY = 1,3,6,8-tetrakis(p-benzoic acid)pyrene) through the coordinated anions substitution, reported by Hupp and co-workers.[120] NU-1000 possesses an octahedral Zr6 cluster capped by eight μ_3-OH and eight terminal –OH entities. In this work, these terminal –OH groups were substituted by a series of fluoroalkyl carboxylate ligands with different chain lengths, when the MOF reacting with their acids in DMF at 60 °C for 18~24 hours. Finally, these modified MOFs showed enhanced CO_2 capture capacities and systematically increased adsorption enthalpies (Q_{st}) with increasing chain length of perfluoroalkanes.[121] Whereafter, the authors in the same group continued their research in this topic by the incorporation of some carboxylate-derived functional entities (isonicotinate, 4-aminobenzoate, and 4-ethynybenzoate) into NU-1000 in a similar procedure. Chemical reactions such as click chemistry, imine condensation, and pyridine quaternization were then used to modify the functionalities of these materials.[122]

An alternative approach in the substitution manipulation of coordinated guest molecules or counter ions in MOMs is to firstly remove these coordinated entities to leave unsaturated metal sites, where are then grafted by other functional molecules. Both generating open metal sites and adding special functional groups can efficaciously modify the pore properties, such as for enhancing catalytic activities and gas binding capacities of the resulting MOMs.[123-129] As a typical example, $\{[Cr_3(F,OH)(H_2O)_2O(BDC)_3]\cdot m(H_2BDC)\cdot nH_2O\}_n$ (MIL-101)[52] has been widely explored in this context. The removal of coordinated water molecules in MIL-101 could be achieved through the thermal treatment of the as-synthesized sample under vacuum, to get the dehydrated MIL-101. With this method, Kim and co-workers successfully grafted chiral functional groups into MIL-101 to get $\{[Cr_3O(L_1)_{1.8}(H_2O)_{0.2}F(BDC)_3]\cdot 0.15(H_2BDC)\cdot H_2O\}_n$ (CMIL-1) and $\{[Cr_3O(L_2)_{1.75}(H_2O)_{0.25}F(BDC)_3]\cdot 0.15(H_2BDC)\cdot H_2O\}_n$ (CMIL-2) through treating the dehydrated MIL-101 with the pre-designed chiral ligands (*S*)-*N*-(pyridin-3-yl)-pyrrolidine-2-carboxamide (L_1) and (*S*)-*N*-(pyridin-4-yl)-pyrrolidine-2-carboxamide (L_2), respectively.[130] It was found that these CMIL materials had good catalytic activities in asymmetric aldol reactions between aromatic aldehydes and ketones, with a high enantioselectivity. Similarly, Chang and co-workers demonstrated that ethylenediamine (ED) and diethylenetriamine (DETA) could be grafted into this MOF to give amine-grafted MIL-101, which finally exhibited high catalytic activities in the Knoevenagel condensation reaction.[131]

Using similar method, Long and co-workers modified a new MOF, $\{Mg_2(DOBPDC)(DEF)_2\}_n$ (DOBPDC = 4,4′-dioxido-3,3′-biphenyldicarboxylate; DEF = *N,N′*-diethylformamide) to get a functionalized MOF material with excellent CO_2 capture ability.[132] As illuminated in Fig. 9, coordinated DEF molecules in this MOF were firstly removed through heating the sample and then *N*,*N′*-

dimethylethylenediamine (mmen) was grafted to afford $\{Mg_2(DOBPDC)(mmen)_{1.6}(H_2O)_{0.4}\}_n$ (mmen-Mg_2(DOBPDC)). As expected, this material displayed an exceptional capacity for CO_2 adsorption at low pressures, taking up 2.0 mmol/g (8.1 wt %) at 0.39 mbar and 25 °C, and 3.14 mmol/g (12.1 wt %) at 0.15 bar and 40 °C. Interestingly, upon the exposure in air white crystalline powder of $\{Mg_2(DOBPDC)(DEF)_2\}_n$ turned blue and lost crystallinity, implying the collapse of its framework. The mmen-Mg_2(DOBPDC) however was stable in air, even staying for 1 week. A very similar study can be found in Long's another report based on an air- and water-stable MOF, $\{H_3[(Cu_4Cl)_3(BTTri)_8(DMF)_{12}]\cdot 7DMF\cdot 76H_2O\}_n$ (Cu-BTTri-DMF; H_3BTTri = 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene). The desolvated framework of Cu-BTTri, featuring open Cu^{2+} coordination sites, could incorporate ED to afford a functionalized MOF with greatly enhanced affinity and selectivity towards CO_2.[133] It should be pointed out that the introduction of alkylamines into the pores of MOFs is a powerful approach to make the materials have a high CO_2 adsorption and separation capacity, one of keys in the CO_2 capture with MOFs. However, the direct preparation of MOFs with alkylamine groups is highly challenged due to the difficulty in the synthesis of related ligands, as well as their MOFs. The substitution strategy discussed here is thus attractive and feasible, with a bright future in this topic.

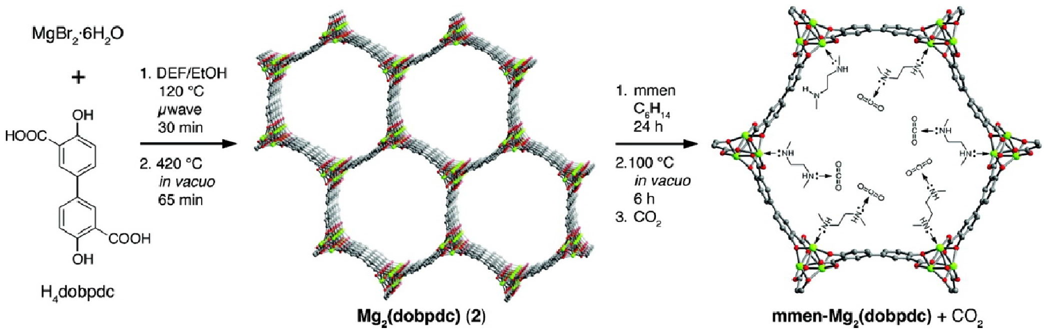


Fig. 9 Stepwise synthesis of amine-appended mmen-Mg_2(DOBPDC) MOF, as well as its bonding with CO_2 molecules. Reprinted with permission from ref. 132. Copyright 2012 American Chemical Society.

Furthermore, as a special example, the substitution of labile solvents by multi-topic organic linkers has been performed to modify the pore size and shape of a MOF, thereby tuning its gas adsorption properties.[134] In this work, Suh and co-workers firstly prepared MOF $\{[Zn_2(TCPBDA)(H_2O)_2]\cdot 30DMF\cdot 6H_2O\}_n$ (SNU-30; TCPBDA

= *N,N,N′,N′*-tetrakis(4-carboxyphenyl)biphenyl-4,4′-diamine). Soaking the yellow crystals of SNU-30 in a DMF solution of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (BPTA) at 80 ºC for 3 hours led to the substitution of each two coordinated water molecules in SNU-30 by a BPTA ligand, resulting in red crystals of $\{[Zn_2(TCPBDA)(BPTA)]\cdot 23DMF\cdot 4H_2O\}_n$ (SNU-31) via a SC-SC transformation (Fig. 10). In SNU-31, original channels in SNU-30 were divided by BPTA linkers. It was demonstrated that the desolvated solid of SNU-30 was able to absorb all N_2, O_2, H_2, CO_2, and CH_4 gases, whereas desolvated SNU-31 exhibited the selective adsorption of CO_2 over N_2, O_2, H_2, and CH_4. Furthermore, SNU-31 could reversibly liberate BPTA linkers when being immersed in fresh DEF, through the substitution of BPTA ligands by DEF molecules.

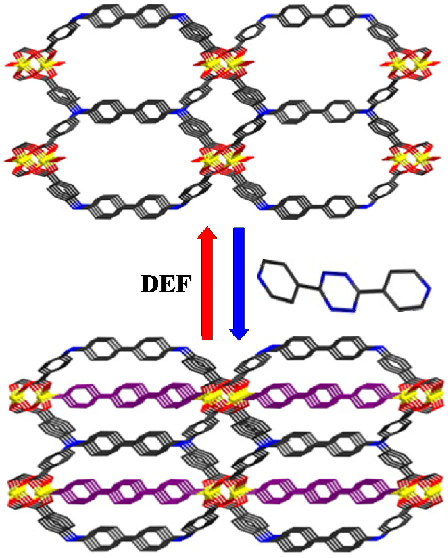


Fig. 10 Reversible substitution of coordinated guest molecules by organic linker 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (BPTA) in $\{[Zn_2(TCPBDA)(H_2O)_2]\cdot 30DMF\cdot 6H_2O\}_n$ to get $\{[Zn_2(TCPBDA)(BPTA)]\cdot 23DMF\cdot 4H_2O\}_n$, and vise versa.[134]

In addition, the substitution of the guest solvents or counter ions by multi-topic organic linkers can also lead to the formations of distinct MOFs, in some cases with an enhanced dimension in structures.[46,47] For example, Kitagawa and co-workers reported the transformation of a two-dimensional (2D) layer MOF $[Cu(TFBDC)(MeOH)]_n$ (TFBDC = tetrafluorobenzene-1,4-dicarboxylate) into a 3D MOF $[Cu(TFBDC)(DABCO)_{0.5}]_n$ via the substitution of coordinated MeOH molecules in the former by a ditopic organic linker 1,4-diazabicyclo[2.2.2]octane

(DABCO).[135] Much more interesting that Chen and co-workers demonstrated that a 3D pillared-layer MOF $\{[Zn_2(BDC)_2(DABCO)]\cdot 4DMF\cdot 0.5H_2O\}_n$ could be firstly transferred into a 2D layer MOF $\{[Zn_2(BDC)_2(H_2O)_2]\cdot DMF\}_n$ in air via a SC-SC transformation through the substitution of DABCO ligands by water molecules.[136] And then, this process can be reversed by the substitution of these water molecules in the 2D structure by the DABCO ligands. Similarly, Vittal and co-workers showed that a 2D sheet-like $[Cd(\mu\text{-BPE})(\mu\text{-Br})_2]_n$ (BPE = 4,4′-bipyridylethylene) could be generated through the substitution of coordinated guest molecules and anions in a one-dimensional (1D) chain $[Cd(CH_3CO_2)_2(\mu\text{-BPE})(H_2O)]_n$[137] by bridging Br^- anions.[138]

Along this line, a new stepwise synthetic approach has been developed for the construction of MOP-based MOFs starting from molecular MOPs acting as reactants.[139-143] This synthesis involves a substitution process of the coordinated guest molecules or anions in MOPs by judiciously selected bridging organic ligands. As the first example in this context, Zhou and co-workers firstly designed and synthesized a soluble and robust MOP $[Cu_2(CDC)_2(DMA)(EtOH)]_6$ (CDC = 9-*H*-carbazole-3,6-dicarboxylate; DMA = *N*,*N*′-dimethylacetamide) with an octahedral cage structure, in which all six external Cu^{2+} sites in the vertices of the octahedral cage were occupied by coordinated DMA molecules.[142] As shown in Fig. 11, $[Cu_2(CDC)_2(DMA)(EtOH)]_6$ underwent a solvent substitution reaction to yield $[Cu_2(CDC)_2(DEF)(EtOH)]_6$. Further substitution of the coordinated DEF molecules by BIPY was achieved by treating the MOP and BIPY in DEF/EtOH to obtain a 2-fold interpenetrated 3D structural MOF $\{[Cu_4(CDC)_4(BIPY)(H_2O)_2]_3\}_n$ with an augmented pcu-a topology. It should be pointed out that MOFs are usually synthesized through a “one-pot” self-assemble approach from all reaction components. The structures of resulting products are however unpredictable and difficult to be controlled in some cases, particularly for some MOFs with complicated hierarchical structures, such as the MOP-based MOFs. Clearly, this substitution approach takes a stepwise construction procedure, which can greatly enhance the design and controllability of resulting MOFs, being widely accessible in the MOFs synthesis. Furthermore, in this work based on the substitution of the BIPY by pyridine the MOF was returned back to the MOP when the former dissolved in a 4:1 DEF/pyridine solvent mixture. This is the first example that a reversible interconversion between MOP and MOF achieved, just through the substitution reaction between coordinated guest molecules and bridging ligands. The pyridine-coordinated MOP could also be obtained through the guest substitution of DEF-coordinated one in solution. Similar substitution of coordinated solvent molecules that led to a stepwise assembly of MOF via a MOP intermediate has also been subsequently reported by Su and co-workers,[143] where a 12-connected network $\{[Cu_{24}(5\text{-}NH_2\text{-}m\mathrm{BDC})_{24}(BIPY)_6(H_2O)_{12}]\cdot 72DMA\}_n$ with a fcu topology was synthesized using a pre-designed MOP precursor of $Cu_{24}(5\text{-}NH_2\text{-}m\mathrm{BDC})_{24}(DMF)_{12}(H_2O)_{12}\cdot 32DMF\cdot 6EtOH\cdot 12H_2O$.[144]

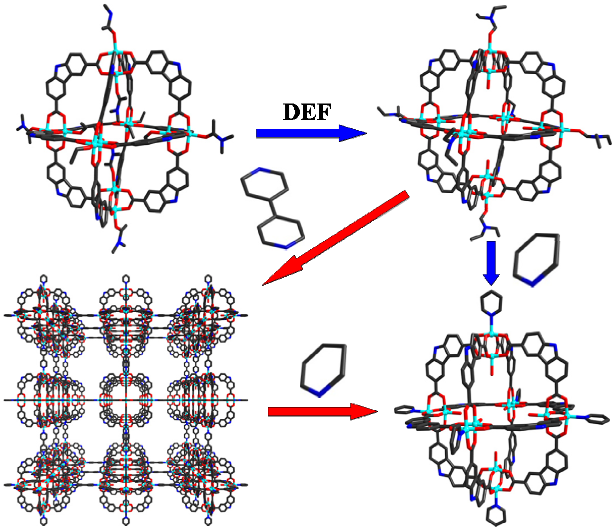


Fig. 11 The transformation between MOPs $[Cu_2(CDC)_2(S)]_6$ (S = DMA, DEF, or pyridine) and a MOF $\{[Cu_4(CDC)_4(BIPY)(H_2O)_2]_3\}_n$ induced by the substitution reaction between coordinated solvent molecules and bridging ligands.[142]

Besides neutral guest moieties, coordinated anions in some molecular assembles can also be substituted by bridging organic ligands to form MOFs. For examples, Wang and co-workers firstly synthesized a pentanuclear tetrahedral compound, $Zn_5(BTZ)_6(NO_3)_4(H_2O)$ (BTZ = benzotriazolate), in which each Zn^{2+} ion in four vertices carried a NO_3^- ion. These coordinated NO_3^- anions were then substituted by several linear carboxylate ligands to extend these molecular clusters to form MOFs (Fig. 12).[145] Experimentally, the reaction of this compound with a series of dicarboxylate ligands of BDC, NH_2-BDC, and 4,4′-biphenyldicarboxylate (BPBC) in DMA gave rise to three 3D structural MOFs $\{[Zn_5(BTZ)_6(BDC)_2(H_2O)_2]\cdot 7DMA\}_n$, $\{[Zn_5(BTZ)_6(NH_2\text{-}BDC)_2(H_2O)_2]\cdot 7DMA\}_n$, and

$\{[Zn_5(BTZ)_6(BPDC)_2(H_2O)_2]_{1.5}\cdot 10DMA\}_n$, respectively, all having a dia topological network. Furthermore, Xu and co-workers used similar pentanuclear $Zn_5(BTZ)_6(X)_4(H_2O)$ ($X = NO_3^-$ or Cl^-) precursors to synthesize series of isostructural MOFs also having a dia topology, through the substitution of the coordinated NO_3^- or Cl^- anions by pre-designed tetratopic ligands.[146] Similarly, Zaworotko and co-workers also confirmed a two step assembly of MOFs from a pre-designed trigonal-prismatic molecular compound $[Cr_3(\mu_3\text{-}O)(ISONIC)_6](NO_3)$ (ISONIC = pyridine-4-carboxylate).[147-149]

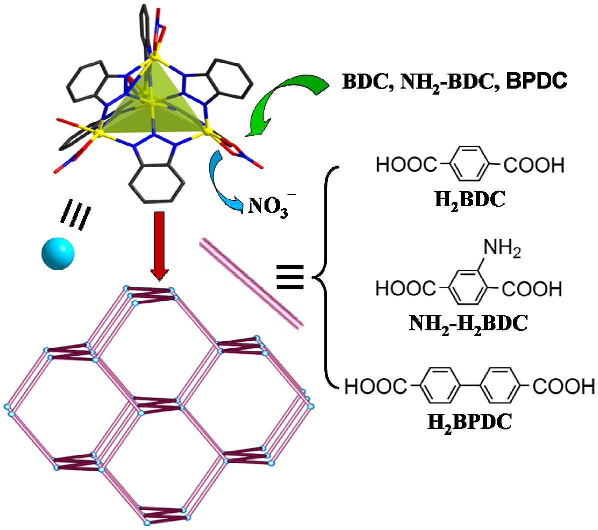


Fig. 12 Substitution of coordinated NO_3^- anions in $Zn_5(BTZ)_6(NO_3)_4(H_2O)$ by dicarboxylate linkers to form serials of MOFs $\{[Zn_5(BTZ)_6(L)_2(H_2O)_2]\cdot nDMA\}_n$ (L = BDC, NH_2-BDC, or BPBC) with a dia net structure.[145]

Apart from using additional reactants, substitution reaction can also happen in a MOF crystal itself. Such a substitution usually leads to the rearrangement and change of the MOF structure, along with bond breaking and re-generating. In most cases, the resulting new compound phases are amorphous, being difficult to determine their structures. However, in some examples, after the substitutions the samples remain crystalline, which allows the further analysis of their structures by SXRD or PXRD and the exploration of the associated transformation processes. These coordinated guest substitution induced SC-SC transformations have attracted intense interest in crystal engineering and coordination polymers fields. Readers interested in those can refer to several excellent reviews for details.[47,53,54] Herein, we just listed a few examples to clarify the importance of the substitution reaction in this context.

As a typical example, Rosseinsky and co-workers demonstrated that the MOF $\{[Co_2(BIPY)_3(SO_4)_2(H_2O)_2]\cdot(BIPY)\cdot CH_3OH\}_n$ could undergo a reversible substitution of coordinated water molecules by guest BIPY and methanol molecules in its structure.[150] As shown in Fig. 13, in the structure of this MOF uncoordinated BIPY ligands are H-bonded to the coordinated water molecules, and lattice MeOH molecules H-bonded to SO_4^{2-} anions. It was found that pink single crystals of the MOF were heated at 95 °C to give purple crystals of a new MOF $[Co_2(BIPY)_4(SO_4)_2(CH_3OH)]_n$, where lattice MeOH and BIPY molecules replaced the coordinated water molecules in $\{[Co_2(BIPY)_3(SO_4)_2(H_2O)_2]\cdot(BIPY)\cdot CH_3OH\}_n$. This structural transformation was found to be reversible. In air, atmospheric water could replace the coordinated BIPY and MeOH molecules at room temperature to afford the rehydrated phase. It should be pointed out that this is also an uncommon example, where low-boiling MeOH does not escape from the crystals upon heating, whereas substitutes coordinated water molecules to form a new MOF phase.

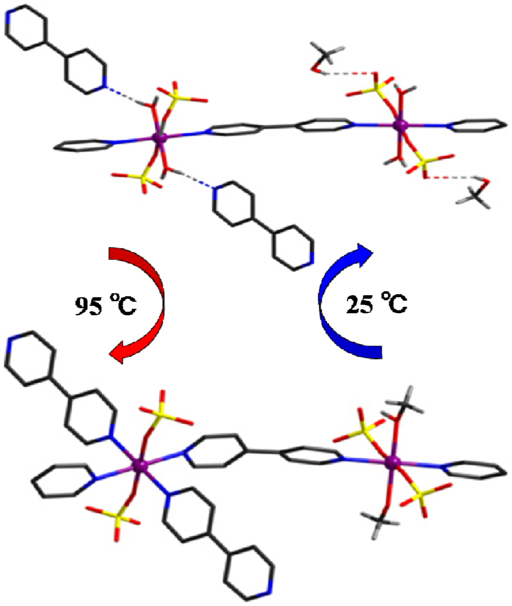


Fig. 13 Reversible substitution of coordinated water molecules in $\{[Co_2(BIPY)_3(SO_4)_2(H_2O)_2]\cdot(BIPY)\cdot CH_3OH\}_n$ by lattice BIPY and MeOH guest molecules.[150]

In addition, Chen and co-workers also demonstrated an irreversible SC-SC transformation from a 0D structure compound to a 2D MOF based the guest molecule substitution reaction.[151] They firstly synthesized a discrete compound Co_2(8-QOAC)$_2$(N_3)$_2$(H_2O)$_2$ (8-QOAC = quinoline-8-oxy-acetate) in which each Co^{2+} center was coordinated by one tridentate 8-QOAC, two azido, and one water molecule. When the single crystals of this compound were heated at 150 °C, a new phase of MOF [Co_2(8-QOAC)$_2$(N_3)$_2$]$_n$ was generated. SXRD analysis revealed that the dinuclear unit in the resulting MOF was similar to that in the starting compound. However, each water molecule in the former was substituted by a carboxy O atom from a neighboring dinuclear unit, thus each dinuclear entity was connected to four neighboring ones by the anti-anti carboxylate bridges to form a 2D layer MOF. This transformation led a drastic magnetic property change from short range coupling to long-range spin-canting antiferromagnetic ordering of the two materials.

As discussed above, a variety of examples of substitutions at metal ions of MOMs were documented. The substitution at metal ion clearly provided a feasible approach to modify or tune not only structures but also associated properties of MOMs, as well as a new strategy to hierarchically synthesize MOFs, for example via MOPs intermediates. Particularly, the modifications in properties such as catalysis, magnetism, and gas absorption triggered by the structural transformations can be finally used in designing advanced functional materials for practical applications.

3. Substitution at organic ligand

Besides that at metal ion, the substitution reaction at organic ligand was also explored and led to plenty of new structures and properties of MOMs, as well as the development of new synthesis strategy for them. Organic ligands used in MOM construction are various and almost countless, and more and more new ligands have been designing and synthesizing in virtue of powerful organic synthesis for the construction of MOMs.[152-154] Most popularly used ligands are those with carboxylate, N-donor, or both of them acting as coordination groups. In this section, we discuss: the exchange or replacement of organic bridging ligands which directly coordinate to metal ions to sustain the frameworks of MOMs and the chemical modifications of organic ligands in MOMs without disturbing coordination bonds and framework structures. The former usually leads to new structures and associated properties but the latter mostly modifies the related properties of parent materials.

3.1 Organic bridging ligand substitution

Although the structures and pore properties of MOFs or the shapes and sizes of MOPs can be designed in a "one-pot" assembly of pre-designed metal-containing nodes and carefully selected organic bridging ligands, and this direct route also appears to be convenient,[11,62,155] it remains difficult to find suitable reaction conditions in some cases. Alternative, organic ligand substitution,[156-158] also known as solvent-assisted linker exchange (SALE)[50] or postsynthetic ligand exchange (ligand-based PSE),[48] has been approved as a feasible strategy to tune the formations, structures, and properties of MOMs with improved functions. This method indeed has been widely used in discrete coordination complexes[159] or organometallic species.[160-164] Like the substitution at metal ion, all three kinds of two-phase substitutions of solid-solid, solid-liquid, and liquid-liquid (only for soluble MOPs) have also been observed in the organic bridging ligand substitution of MOMs. Furthermore, in some cases, partial substitution happened and allowed to access mixed-ligand species, which are however difficult to achieve by means of a direct synthetic approach.

For example, Choe and co-workers observed a series of SC-SC transformations of MOFs induced by the organic bridging ligand substitutions (Fig. 14).[165] They firstly synthesized two parent MOFs $[Zn_2(ZnTCPP)(DPNI)]_n$ (PPF-18) and $[Zn_2(ZnTCPP)(DPNI)_{1.5}]_n$ (PPF-20) (DPNI = *N,N′*-di-4-pyridylnaphthalenetetracarboxydiimide). The former has a 2D bilayer structure of porphyrin paddle-wheel layers, whereas the latter is a 3D pillared-layer framework, in both of which the 2D porphyrin paddle-wheel layers are coordinately connected by DPNI ligands on the axial Zn^{2+} sites of the paddle-wheel entities.[166] When the crystals of PPF-18 were immersed in a DEF/EtOH solution of BIPY, the DPNI ligands were replaced by the BIPY, resulting in another 2D layer MOF $[Zn_2(ZnTCPP)(BIPY)]_n$ (PPF-27). PPF-27 was confirmed to be inaccessible as a single phase via a one-step synthesis approach. When excess BIPY (>2 equiv) were used, additional BIPY linkers coordinated to the paddle-wheel Zn^{2+} sites between the bilayers, resulting in a 3D MOF $[Zn_2(ZnTCPP)(BIPY)_{1.5}]$ (PPF-4).[167,168] The similar situation was also observed in PPF-20, and a substitution procedure in the case of PPF-18 gave the single phase material of PPF-4. Another example of organic bridging ligand substitution in a 3D pillared-layer structure was reported by Hupp and co-workers based on the MOF $\{Zn_2(H_2\text{-}TCPP)(M^2\text{-}L)\}_n$ (ZnM^2-RPM; L = 5,15-dipyridyl-10,20-

bis(pentafluorophenyl)porphyrin),[169] where dipyridyl-porphyrin-Zn(II) (Zn-DIPY) struts could be replaced by M^2-DIPY ($M^2 = 2H^+$, Al^{3+}, and Sn^{4+}).[170] Subsequent catalysis experiment based on the ring-opening of styrene epoxide through reacting with trimethylsilylazide (a reaction known to be catalyzed by Lewis acid) indicated that Zn2H- and ZnSn-RPM did not have a catalytic activity, whereas ZnAl-RPM proved significantly catalytic capacity due to its comparatively strong Lewis acidity.

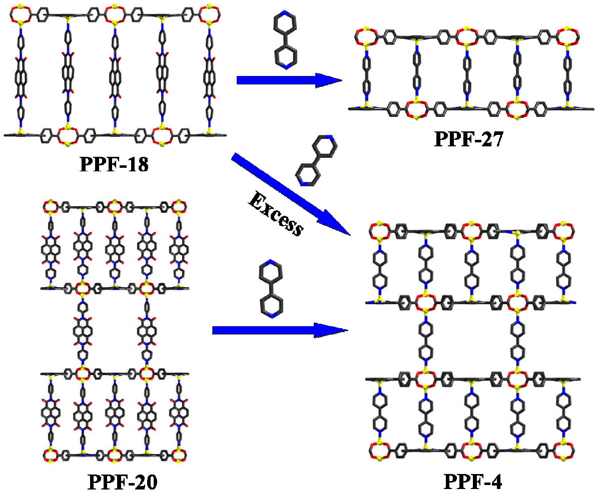


Fig. 14 Schematic representation of bridging organic ligand substitutions in MOFs $[Zn_2(ZnTCPP)(DPNI)]_n$ (PPF-18) and $[Zn_2(ZnTCPP)(DPNI)_{1.5}]_n$ (PPF-20) to form $[Zn_2(ZnTCPP)(BIPY)]_n$ (PPF-27) and $[Zn_2(ZnTCPP)(BIPY)_{1.5}]$ (PPF-4).[165]

Apart from the neutral organic bridging ligands, negatively charged carboxylate ligands can also be substituted in some MOFs. Rosi and co-workers reported the synthesis of three isoreticular analogues of $\{[Me_2NH_2]_4[Zn_8(AD)_4(BPDC)_6O_2]\cdot 49DMF\cdot 31H_2O\}_n$ (Bio-MOF-100; AD = adenine[171]): Bio-MOF-101, -102, and -103 through using a stepwise dicarboxylic ligand substitution procedure, where shorter ligands were replaced by longer ones via a SC-SC transformation (Fig. 15).[172] Bio-MOF-100 has a 3D structure being composted of $[Zn_8(AD)_4O_2]^{8+}$ clusters periodically linked by BPDC ligands. It was found that Bio-MOF-101 with 2,6-naphthalenedicarboxylate (NDC) linkers could be obtained via a direct synthesis procedure, however, the analogues with organic linkers longer than BPDC were unable to get at this stage. The organic bridging ligand substitution was thus used herein for accessing more porous analogues of bio-MOF-100 with the longer linkers. The conversion between bio-MOF-101 and bio-MOF-100 was achieved by soaking bio-MOF-101 in a BPDC/DMF/NMP solution (NMP = N-methylpyrolidinone). The resulting crystals were transparent and slightly cracked. ^{1}H NMR spectra revealed that only adenine and BPDC linkers without NDC existed in the product, indicating a complete substitution of ligand NDC by BPDC. Similarly, bio-MOF-102 could be obtained by using the same procedure of substituting BPDC in bio-MOF-100 with the longer azobenzene-4,4′-dicarboxylate (ABDC) ligand. And, soaking crystals of Bio-MOF-102 in much longer 2′-amino-1,1′:4,1″-terphenyl-4,4″-dicarboxylate (NH_2-TPDC) ligand solution yielded light orange crystals of bio-MOF-103, even if complete substitution was not achieved in this transformation. Interestingly, the volume changes of the crystals in these stepwise ligand substitutions have also been directly observed.

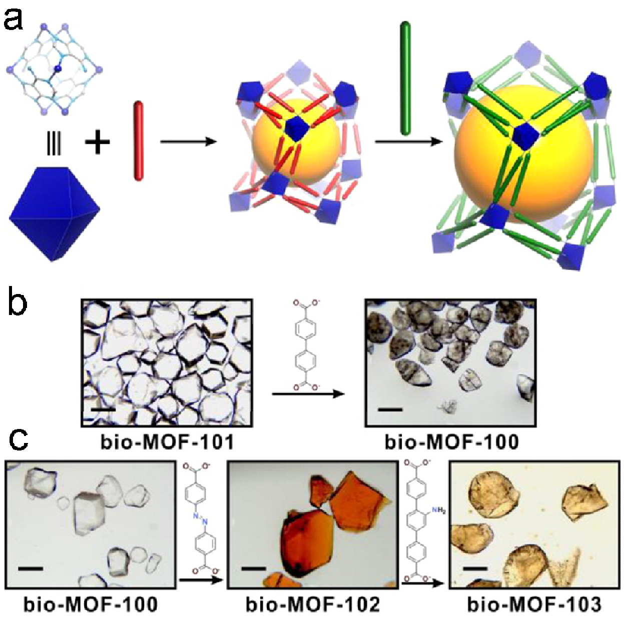


Fig. 15 (a) Scheme representing the pore expansion strategy. (b) bio-MOF-101 was converted to bio-MOF-100 via the ligand exchange of BPDC. (c) BPDC in bio-MOF-100 was substituted by ABDC to yield bio-MOF-102; thereafter ABDC in bio-MOF-102 was substituted by NH_2-TPDC to yield bio-MOF-103. Reprinted with permission from ref. 172. Copyright 2013 American Chemical Society.

On the other hand, a partial organic ligand substitution can lead to the immobilization of functional molecules on the surface of a regular MOF crystal. Kitagawa and co-workers performed such a study based on two MOFs,

$[Zn_2(BDC)_2(DABCO)]_n$ (**F1**) and $[Zn_2(NDC)_2(DABCO)]_n$ (**F2**).[173] Where their crystal surfaces were functionalized by the fluorescent dye molecule of mono-carboxylic boron dipyrromethene (BODIPY).[174] Immersing single crystals of **F1** or **F2** in a dehydrated DMF solution of BODIPY dye resulted in their coloration due to the substitution of dicarboxylate ligands BDC and NDC by BODIPY on the crystal surface. As illustrated in Fig. 16, in **F1** and **F2**, only four faces of their rectangular prismatic crystals exposed carboxylate entities, therefore only these faces were dyed during the substitution process. They also explored the colorization of $[Cu_3(BTC)_2(H_2O)_3]_n$ (HKUST-1) crystals by a similar procedure.[175] HKUST-1 crystal is octahedral with all faces exposing carboxylate sites. As expected, all the faces were covered by a monolayer of the fluorescent dye after the substitution reaction. These surface-modified MOF crystals were then detected by using confocal laser scanning microscopy (CLSM) to present attractive images as shown in Fig. 16. These results demonstrated a stepwise method of using the regular structure to facilitate the immobilization of functional molecules onto MOF particles.

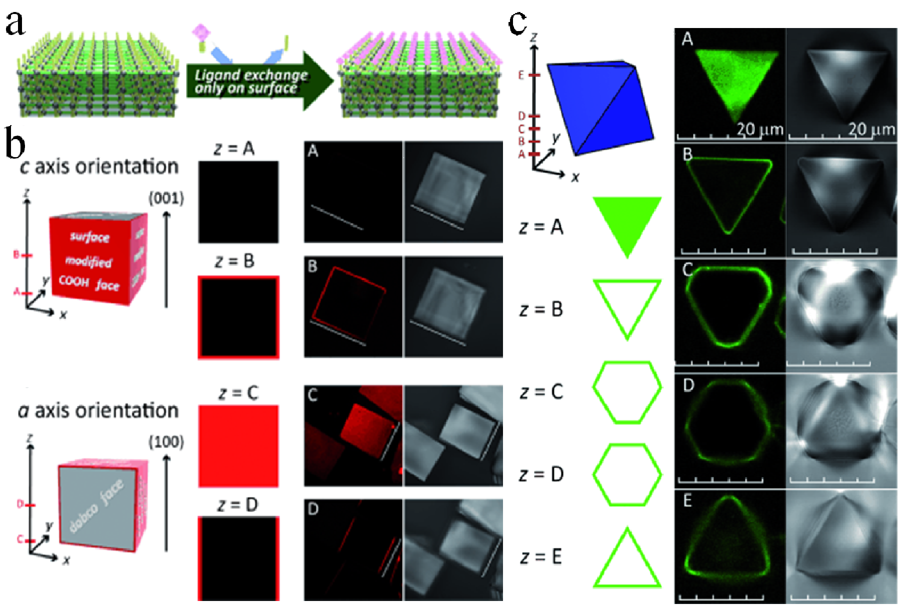


Fig. 16 (a) Schematic representation of ligand substitution on the crystal surface. (b) and (c) Representations of surface-modified crystals (left), CLSM images (middle) and transmission images (right) of BODIPY functionalized **F2** and HKUST-1 crystals, respectively. Reprinted with permission from ref. 174. Copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Like those observed in metal center substitution, organic ligand substitution can also take place in some comparably stable/robust MOFs, such as ZIFs, UiO, and MIL series. Hupp and co-workers reported the first example of solvent-assisted linker exchange (SALE) in ZIFs.[50] A cadmium-based ZIF, $[Cd(EIM)_2]_n$ (CdIF-4; EIM = 2-ethylimidazolate[176]) was chosen as the parent framework, which has a rho topology and large apertures. To perform the organic ligand exchange, CdIF-4 crystals were immersed in a DMF solution of 2-nitroimidazole (HNIM) at 100 ºC. After 48 hours, it was found that all of EIM ligands in CdIF-4 were replaced by NIM ligands to give $[Cd(NIM)_2]_n$ (CdIF-9[176]), and the crystals maintained their original shapes. PXRD also confirmed the integrity of the original rho framework. The resulting CdIF-9 possessed one of the highest surface areas among reported ZIFs. Similar complete substitution was also achieved when using 2-methylimidazole (HMIM) to substitute EIM under similar conditions, giving $[Cd(MIM)_2]_n$ (SALEM-1) with again preserved rho topological structure. Further studies revealed that the exposure of SALEM-1 into a DMF solution of excess HEIM or HNIM could also lead to the formation of CdIF-4 and CdIF-9, respectively. However, the reversible conversion from CdIF-9 to CdIF-4 and SALEM-1 was inacceptable under similar conditions. Another example of organic bridging ligand substitution in ZIFs was subsequently reported by Cohen and co-workers.[49] They examined the ligand exchange in dichloro-substituted Zn^{2+}-based ZIF-71[102] through exposing its crystals into a MeOH solution of 4-bromo-1*H*-imidazole at 55 °C for 5 days. It was found that in the process, 30% of the ZIF-71 was transformed after the substitution reaction.

Cohen and co-workers also explored the organic ligand substitution in UiO-66 and MIL series.[48,51] In the UiO-66 system it was found that the substitution reaction could perform through a reaction between one MOF and another one both in solid state (a solid-solid process) (Fig. 17). In this work, UiO-66-NH_2 and UiO-66-Br were firstly synthesized by using the ligand 2-amino-1,4-benzenedicarboxylate (NH_2-BDC) and 2-bromo-1,4-benzenedicarboxylate (Br-BDC), respectively.[177] Then, a mixture of UiO-66-NH_2 and UiO-66-Br particles were suspended in water for 5 days at room temperature, ATOFMS analysis of the resulting sample indicated that more than 50% UiO-66-X particles underwent a ligand exchange. At an elevated reaction temperature of 85 ºC it was confirmed that nearly all of the particles took the exchange. It was also found that the ligand exchange rate in this system strongly correlated with the used solvents, with water being highest followed by DMF, methanol, and chloroform. In addition, a solid-liquid ligand exchange was also explored in this system. UiO-66-Br was suspended in an aqueous solution of NH_2-BDC for 5 days to get UiO-66-NH_2(Br), where the ligand exchange ratios were found to be temperature dependent. For example, at room temperature about 9% of Br-BDC was replaced by NH_2-BDC, but at 85 ºC, the substitution ratio was about 76%. Following the same procedure, it was also confirmed that 2-azido-1,4-benzenedicarboxylate (N_3-BDC), 2-hydroxy-1,4-benzendicarboxylate (OH-BDC), and 2,5-dihydroxy-1,4-benzenedicarboxylate (2,5-$(OH)_2$-BDC) could partially substitute BDC in UiO-66 under similar conditions, with the retention of the crystalline samples in all cases.

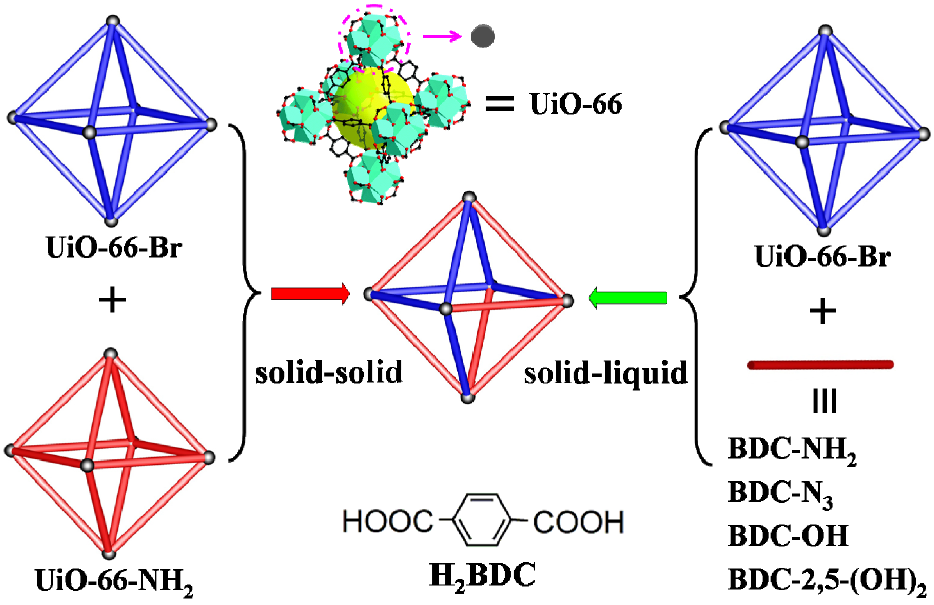


Fig. 17 Schematic representation of solid-solid or solid-liquid ligand substitutions in UiO-66 series.[177]

Similarly, the same group also studied the solid-solid substitution reaction in MIL series. To do this for MIL-53(Al)-NH_2[178] and MIL-53(Al)-Br,[98] the two MOFs were mixed together and suspended in water at 85 °C for 5 days. ATOFMS analysis showed that approximately 56% of the resulting materials contained both ligands, implying ligand exchange occurred between more than half of each MOF particles. For the MIL-68(In) system, two types of solids of MIL-68(In)-NH_2 and MIL-68(In)-Br[92] were mixed together and incubated in DMF at 55 °C for 5 days to get an about

42% of particles that contained both Br- and NH_2-containing ligands. However, attempts to examine MIL-101(Cr)[52] with respect to the ligand substitution failed, probably due to the high kinetic inertness of the Cr^{3+} ions in the MOF. The foregoing results demonstrated that despite structural robustness, ligand substitutions could still readily carry out on some stable and inert MOFs through a solid-solid or a solid-solution substitution reaction process.

Besides those achieved in MOFs, ligand substitution can also happen in MOPs to get new members, which sometimes are difficult to access by a direction reaction of metal ions and organic ligands.[179-183] Zhou and co-workers for the first time extended the ligand substitution into the interconversion between MOPs. An "organic-bridging-ligand-substitution" synthetic strategy was developed to prepare and isolate series of novel MOPs with various compositions, pore sizes and shapes, and functionalities.[182] As shown in Fig. 18, three soluble MOPs $[Cu_{24}(5\text{-t-Bu-1,3-BDC})_{24}(S)_{24}]$ (**1**), $[Cu_{24}(5\text{-OH-1,3-BDC})_{24}(S)_{24}]$ (**2**), and $Na_6H_{18}[Cu_{24}(5\text{-}SO_3\text{-1,3-BDC})_{24}(S)_{24}]$ (**3**) were firstly prepared by the substitution reaction between $Cu_2(OAc)_4{\cdot}2H_2O$ and three dicarboxylic ligands. Reaction of these soluble MOPs with several new ligands in solution gave other MOPs of **6**~**9**. Particularly, MOPs **4** and **5** with mixed ligands have been obtained through a partial ligand substitution in this system, which were quite difficult to achieve through a direct self-assemble reaction between the two types of ligands and the metal ions. Finally, a monocarboxylic ligand terminated the formation of MOPs again based on the ligand substitution reaction to give a simple dinuclear compound **10**. This work has opened up a new way for accessing novel MOPs through the bridging ligand substitution reaction. In principle, by judiciously selecting a suitable solvent system, this method can be applied in the preparation of many novel MOPs, and even MOFs as discussed above. This general approach is also useful in constructing and isolating other complex metal-organic supramolecular architectures.

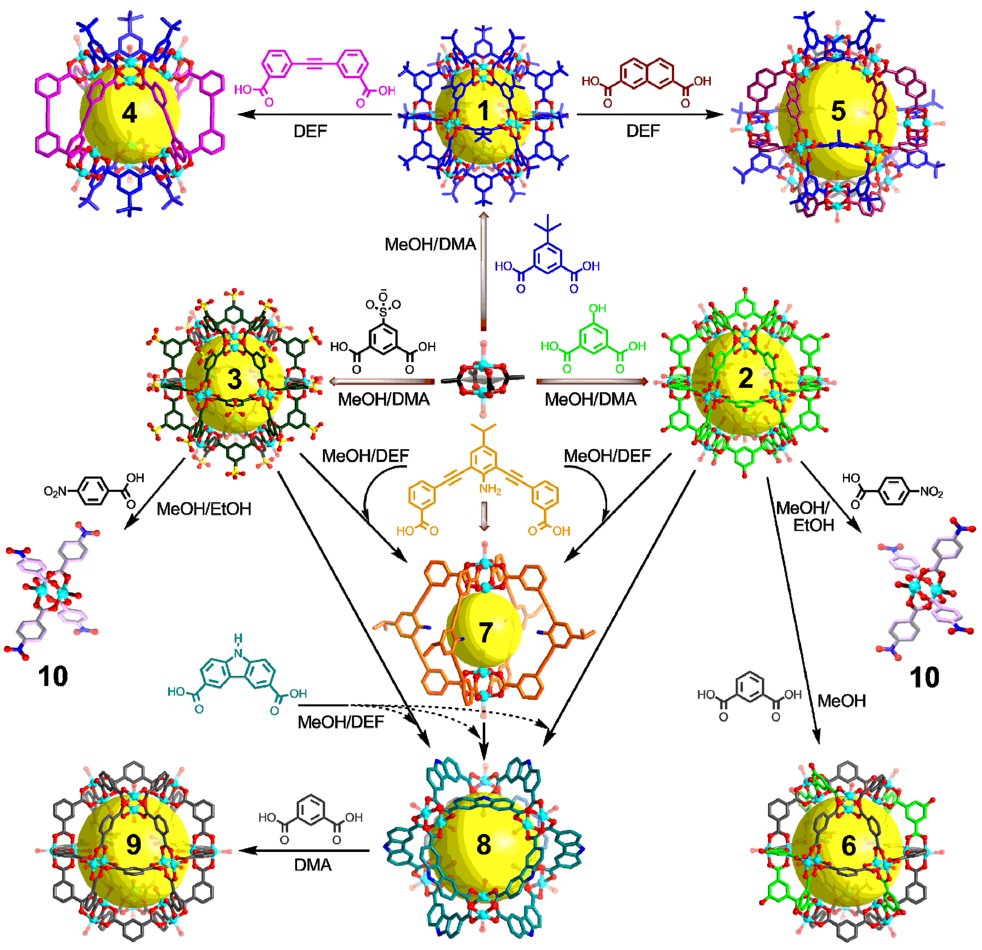


Fig. 18 Schematic representation of the synthesis of MOPs **1**-**3** and their transformation to MOPs **4**-**9** and compound **10**, all based on the ligand substitution reaction. Reprinted with permission from ref. 182. Copyright 2010 Nature Publishing Group.

Similar example of bridging ligand substitution in MOPs was also reported by Stang and co-workers.[183] In their work, the observed structural transformation achieved by the substitution can be divided into two situations: a ligand in the initial MOP is replaced by another ligand with similar linkage mode and the same number of binding sites to give rise a new MOP with the same shape but different composition; and the incorporation of a new ligand with different shape and numbers of binding sites leads to a drastic change in the size and shape of resulting new MOPs. As shown in Fig. 19, these transformations started from a two-component [6+4] MOP (**3**). Experimentally, an acetone solution of **3** was added into an aqueous solution of tricarboxylate ligand **4**, giving the modified three-component MOP **5**, which is structurally similar to **3**. When using several bicarboxylate ligands (**6**, **8**, **10**, and **12**) to react with **3** again in water/acetone obtained MOPs **7**, **9**, **11**, and **13** with different shapes. Organic bridging ligand substitution in these MOPs thus resulted in series of new members with not only different compositions but also distinct sizes and geometric shapes, being also quite interesting in supramolecular self-assembly of complex systems.

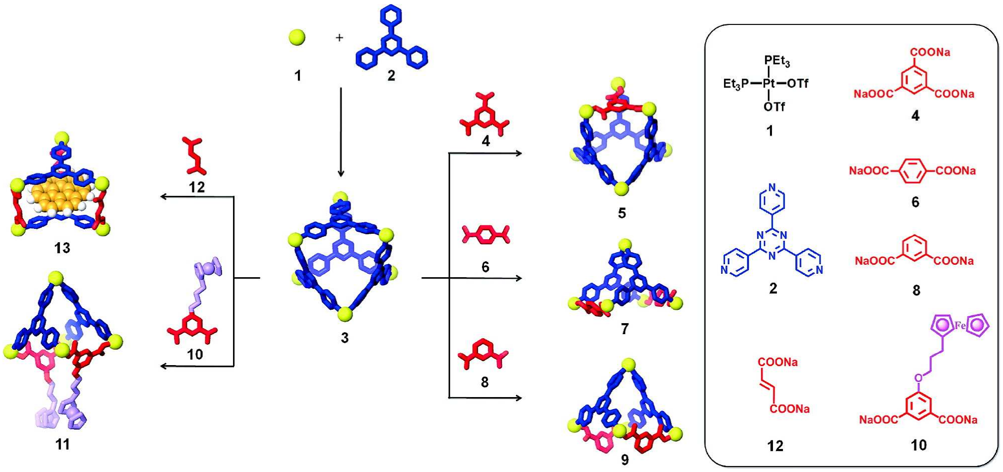


Fig. 19 Schematic representation of component substitution, structural modifications, and functional evolution induced by the ligand substitution in a MOP **3**. Reprinted with permission from ref. 183. Copyright 2011 American Chemical Society.

It should be pointed out that the substitutions happened at metal ions or organic bridging ligands in MOFs and MOPs can be essentially attributed to the reversible nature of the coordination bonds between metal ions and organic ligands in these materials. In this way, a mechanism can be speculated: when such a substitution reaction happened, the cleavage of partial chemical bonds in the original framework produces an intermediate state with lattice defects to meet foreign components to finally come into more stable substituted state, which promotes the accomplishment of the reaction process. This process also allows the access to novel products (mixed metal ions or mixed organic ligands in one lattice) that may be thermodynamically unfavorable in the transformation process, as discussed above.

3.2. Chemical modification in organic ligand

Another powerful and versatile method to chemically modify the properties of MOMs is of adding functional groups on organic ligands, without destroying original framework skeleton.[177,178,184-186] Chemical modification initially recognized by

Robson[187] and recently carried forward by Cohen and others has been widely used in functionalizing MOFs by the rational introduction of new entities into parent structures, mainly manipulated on organic ligands.[56,188] Several excellent reviews/book chapters in the topic of post-modification (synthesis) of MOFs cover most of works in this aspect,[56-59,188,189] here we only list some selective examples to emphasize the substitution reactions happened in organic ligands (covalent modification), as well as the loading of metal ions onto open organic coordination sites (coordination modification) to functionalize MOMs.

Among the examples of chemically covalent modification of MOMs, amine-tagged MOFs such as those with NH_2-BDC ligand have been extensively explored in this context. Several such MOFs have been used as platforms to graft various functional groups such as aldehydes, isocyanates, anhydrides, and sulfonates.[190-192] For example, Yaghi and co-workers showed the ring-opening covalent modifications in $[Zn_4O(NH_2\text{-BDC})_3]_n$ (IRMOF-3)[184] with 1,3-propane sultone or 2-methylaziridine could give functional products without decaying the crystallinity and porosity of the original MOF.[193] In the case of using 1,3-propane sultone, the resulting MOF encapsulated free sulfonate groups within its pores, while the modification with 2-methylaziridine produced free alkylamine groups in the pores. The introduction of these functional groups thus greatly changed the pore properties of resulting MOFs. Similar ring-opening covalent modifications have also been achieved with cyclic anhydrides acting as graft reagents in Cohen and co-workers' work.[194,195] Alternately, click chemistry typically referring to the 1,3-dipolar cycloaddition between an azide and an alkyne[196] has also been used in the covalent ligand modification of MOFs.[197-199] The first example was reported by Sada and co-workers on the MOF $[Zn_4O(N_3)_3]_n$ (N_3-MOF-16; H_2N_3 = 2',5'-bis(azidomethyl)-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid).[200] The click reactions of the azide groups in the MOF with various alkynes were successfully performed, without leading any decomposition of the original MOF network. Similarly, Zhou and co-workers also reported the click modifications of pore properties in Zr^{4+}-based MOFs with azide functionalized terphenyl-4,4″-dicarboxylate (TPDCR) ligands.[201] In this work, two MOFs, $\{Zr_3O_2(OH)_2(\text{TPDCR})_3\}_n$ (PCN-58, R = $2CH_2N_3$; PCN-59, R = $4CH_2N_3$) were firstly synthesized and used to be clicked by various alkynes with different functional groups (Fig. 20). After the click modifications, the resulting materials showed similar PXRD patterns to those of PCN-

58 and PCN-59, respectively, indicating the retention of the framework structures. With these modifications various functional groups were thus grafted into the MOFs pores, which led to tuned CO_2 selective adsorption ability over N_2 of these modified materials.

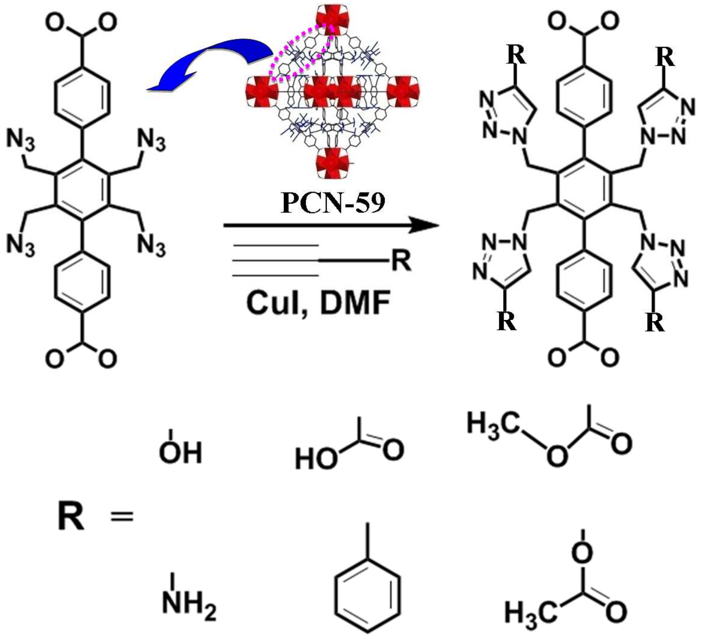


Fig. 20 Schematic representation of grafting various functional groups onto the pore walls of $\{Zr_3O_2(OH)_2(TPDCR)_3\}_n$ [R = $4CH_2N_3$ (PCN-59)] via the click reactions on ligands.[201]

Besides covalent modification, the coordination modification of ligands in MOFs was also explored. For example, Lin and co-workers reported such a study in homochiral MOF $\{[Cd_3Cl_6L_3]\cdot 4DMF\cdot 6MeOH\cdot 3H_2O\}_n$ constructed by a bipyridine ligand, (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine (L) containing additional orthogonal chiral 2,2′-dihydroxy coordination groups.[202] Treatment of this MOF with $Ti(O^iPr)_4$ gave the modified MOF material, in which $Ti(O^iPr)_2$ entities were coordinated to the binaphthol sites of the L ligand. This material was then used as a catalyst in the addition of $ZnEt_2$ to aromatic aldehydes, to afford chiral secondary alcohols at up to 93% enantiomeric excess (*ee*). It was also found that only one-third of the binaphthol sites in ligands were modified with $Ti(O^iPr)_4$, typically a partial coordination modification. Subsequent efforts in the same group produced a series of chiral MOFs with functionalized pores, realized again by using the similar coordination modification of ligands.[203] These modified

MOFs also proved high activities in the asymmetric catalysis of above-mentioned reactions. It was also demonstrated that the enantioselectivities of these reactions could be varied by tuning the pore sizes of these MOFs, from adding different functional entities.

Another typical example of ligand coordination modification in MOFs was reported by Long and co-workers.[204] In this study, a MOF [Al(OH)(BYPDC)]$_n$ (MOF-253) was constructed through the coordination of Al(OH) chains with the carboxylate groups of ligand 2,2'-bipyridine-5,5'-dicarboxylate (BYPDC), leaving free chelating sites of 2,2'-bipyridine suitable for the metal coordination modification. The 2,2'-bipyridine sites in MOF-253 were then coordinated by Cu^{2+} or Pd^{2+} ions, experimentally through soaking MOF-253 in an acetonitrile solutions of $Cu(BF_4)_2$ or $PdCl_2$, to obtain the functionalized materials (Fig. 21). It was found that in both cases, more than 90% and 80% of the BYPDC ligands were metalated by Cu^{2+} and Pd^{2+} ions, respectively. Significantly, an enhanced selectivity in binding CO_2 over N_2 under typical flue gas conditions was observed in the Cu-modified MOF-253. This material is thus potentially useful in carbon capture. It could also be speculated that the Pd^{2+}-modified one should be a good candidate for the application in catalysis, but related reports were not documented up to date.

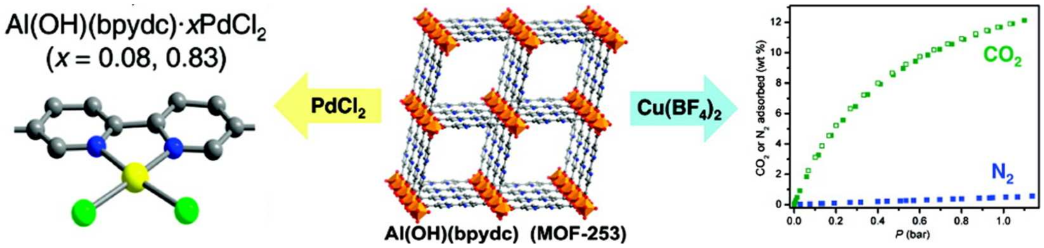


Fig. 21 Schematic representation of coordination modification in [Al(OH)(BYPDC)]$_n$ (MOF-253) with $PdCl_2$ (left). An enhanced selectivity for binding CO_2 over N_2 observed in the Cu-modified MOF-253 (right). Reprinted with permission from ref. 204. Copyright 2010 American Chemical Society.

Clearly, the chemical modification in organic ligand has been growing a hot topic in the functionalization of MOFs. Numerous chemical reactions have been explored in this aspect, generally included in the covalent modification. The resulting new functional materials are usually difficult to be synthesized by a direct reaction between related functionalized ligands and metal ions. This is because a slight modification in ligand could lead to the formation of distinct MOFs even if under similar synthesis conditions. To achieve these modifications, a careful selection of reaction type, reactant, and reaction condition is thus quite important. Overall, chemical modification in organic ligands has indeed paved the way for the production of novel MOFs with unprecedented structural complexity and a broad range of properties and functions.

4. Substitution at free guest molecule

As porous materials, studying host-guest chemistry in them is one of the most promising applications of MOFs and MOPs.[205-209] Free guest molecules in the cavities of such materials are not so free, but usually involved in several types of interactions such as H-bonding, $\pi\cdots\pi$ stacking, or weak interactions with metal sites or ligands. Host-guest chemistry including guest inclusions, exchanges, and separations induced by the substitution of guest molecules has indeed been investigated in MOFs and MOPs. In this regard, these materials are potentially useful, such as in molecule sensing, inclusions and recognitions, separations, and even acting as molecular reactors for specific reactions performed inside their pores. Particularly, in some cases the guest substitution takes place in a material that still remains crystallinity, the exact nature of interactions between the host and guest can thus be studied in detail by SXRD to give important information. Guest molecules in MOFs and MOPs can be neutral, cationic, and anionic, which are separately discussed with respect to their associated substitutions in the following sections. It should be pointed out that a large number of examples treating the host-guest chemistry in MOPs or supramolecular cages have been reported, and summarized in several reviews.[210-214] A discussion of only those on MOFs and triggered functional modifications by guest substitutions is given herein.

4.1. Neutral guest molecule substitution

Neutral solvent molecule exchange or substitution is universally existed in MOFs and MOPs research, hence we do not give a detailed discussion herein. For example, in empting a MOF as-synthesized in high-boiling point solvents (such as DMF, DMA, DEF, or DMSO), usually these solvent molecules are firstly exchanged by low-boiling point ones, so that the sample can be desolvated at a lower temperature to avoid the collapse of the framework at high temperature. Apart from small solvent guests, large organic molecules can also be introduced into pores of MOFs or MOPs via the guest substitution, to perform interesting phenomena of host-guest chemistry or endow with unique properties of the host frameworks and/or the guest molecules.

For examples, Fujita and co-workers reported the guest molecule substitution in a 3D MOF $[(ZnI_2)_3(TPT)_2]\cdot5.5(\text{nitrobenzene})\}_n$ (TPT = 2,4,6-tris(4-pyridyl)triazine).[215] It was found that the nitrobenzene molecules in the MOF pores can be substituted by some large organic molecules including triphenylene, anthracene, and perylene. SXRD analysis revealed an efficient stacking between the included planar guest molecules and the ligands of the MOF skeleton. The crystals of the inclusion complexes also presented a drastic color change because of the strong donor-acceptor interactions between the electron-deficient ligand and electron-rich guests.[216] Another example reported by the same group is the guest substitution in a MOF $\{[(Co(SCN)_2)_3(TPT)_4]_n\cdot x(G)\}_n$ (G = guest molecules) with $Co_6(TPT)_4$ MOP cages acting as molecular building units (Fig. 22).[217] Treatment with a saturated toluene solution of tetrathiafulvalene (TTF) resulted in the color change of the MOF crystals from orange to black. SXRD analysis revealed that four TTF molecules were encapsulated in each $Co_6(TPT)_4$ cage chamber in the MOF framework. Similarly, the $(TTF)_4\cdot Pd_6(TPT)_4$ could also be obtained by suspending excess TTF in an aqueous solution of discrete $Pd_6(TPT)_4$ MOP cage[218] based on again the guest exchange. Further studies demonstrated that both the MOF and the MOP could also reversibly

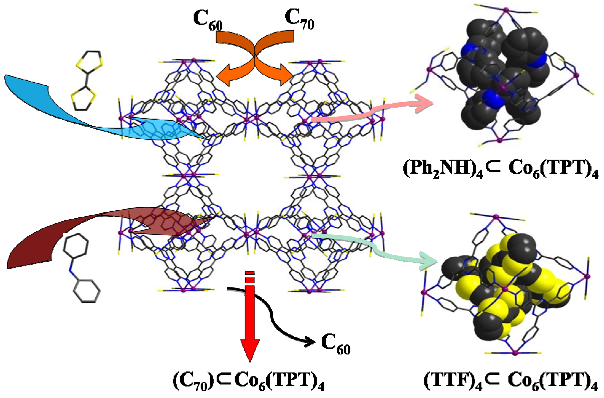


Fig. 22 Schematic representation of the guest molecule encapsulations and separations in $\{[(Co(SCN)_2)_3(TPT)_4]_n\cdot x(G)\}_n$ based on the guest substitutions.[217]

upload and release diphenylamine (Ph_2NH), C_{60}, and C_{70} molecules in toluene. It was found that this MOF was able to take about 35 wt% C_{60} and 34 wt% C_{70} in their saturated toluene solutions, respectively. Interestingly, when the crystals of the MOF were immersed in a fullerene mixture, C_{70} was preferentially absorbed over C_{60}. On the basis of these results, Fujita group developed a general method for the crystallographically structural analysis of non-crystalline guests on a nanogram to microgram scale through loading them into the pores of a crystalline and structurally well-determined MOF host framework.[219]

In the guest substitution, some MOFs showed a selective uptake of incoming guests as mentioned above, which is highly desirable for their application in the separation or purification of molecule mixture. As another example, Dong and co-workers reported a 3D MOF $\{[Cd(ClO_4)_2(L)_2]\cdot 2CH_2Cl_2\}_n$ (L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole), which showed a selective uptake ability towards different small organic molecules.[220,221] It was found that when exposure in air, the desolvated MOF $[Cd(ClO_4)_2(L)_2]_n$ (removing CH_2Cl_2) converted into a hydrate phase $\{[Cd(ClO_4)_2(L)_2]\cdot H_2O\}_n$, which could be used as a robust host for the reversible uptake and separation of benzene and its methyl- and halide-substituted derivatives via a SC-SC transformation.[220] Furthermore, this MOF also presented the ability in the encapsulation and separation of aromatic guest molecules with reactive function groups.[221] As shown in Fig. 23, when the crystals of the hydrated MOF were exposed in 2-furaldehyde, 3-furaldehyde, 2-thiophenaldehyde, 3-thiophenaldehyde, *o*-toluidine, *m*-toluidine, *p*-toluidine, or aniline vapor at 50 ºC for 4 days, respectively, SXRD analysis indicated that all original water molecules in the pores were substituted by these corresponding organic guests. It was also found that these guest molecules were stabilized in the MOF channels through hydrogen bonding interactions with the host framework and ClO_4^- anions. In addition, it was confirmed that this MOF was capable of discerning and completely separating several functionalized aromatic isomers in both vapor and liquid phases, including 2-furaldehyde *vs* 3-furaldehyde, 2-thiophenaldehyde *vs* 3-thiophenaldehyde, and *o*-toluidine *vs* *m*-toluidine *vs* *p*-toluidine, under mild conditions.

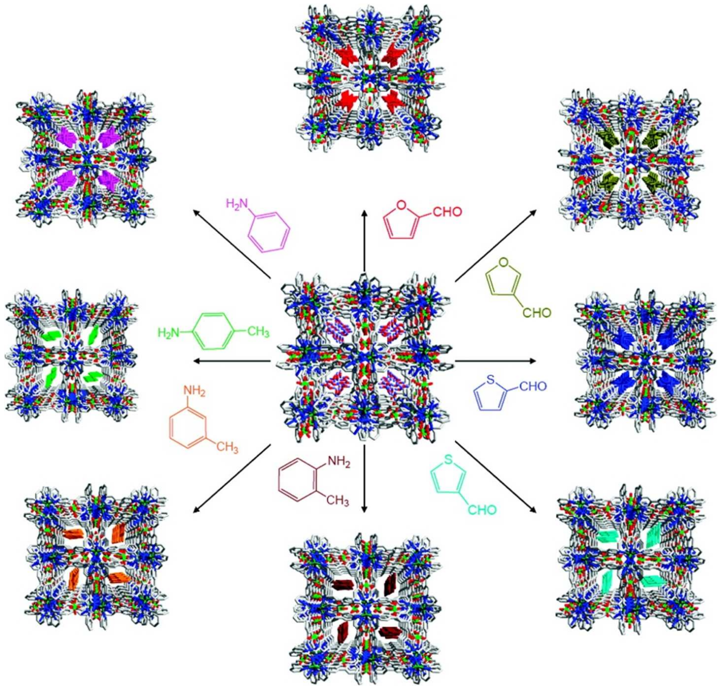


Fig. 23 Schematic representation of molecule encapsulations in $\{[Cd(ClO_4)_2(L)_2]\cdot H_2O\}_n$ based on the guest molecule substitutions. Reprinted with permission from ref. 221. Copyright 2010 American Chemical Society.

In addition, structural transformations triggered by the guest molecule substitution have been observed in flexible/soft MOFs.[222] The first example in this context was reported by Lin and co-workers on a 1D compound $\{[CdL_2(ClO_4)_2]\cdot 11EtOH\cdot 6H_2O\}_n$ (L = (S)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(4-vinylpyridine)). The original crystals lost its crystallinity upon the removal of guest molecules as confirmed by PXRD. However, the crystallinity was restored when exposing the resulting amorphous material in a solvent vapor. More importantly, the compound remained all through crystalline but exhibited SC-SC transformations along with the formations of different structures, during several guest solvent substitution processes.[223] Vittal and co-workers reported another structural transformation example in a 3D MOF $\{[Zn_2(BPEB)(OBC)_2]\cdot 2DMF\cdot H_2O\}_n$ (BPEB = 1,4-bis[2-(4-pyridyl)ethenyl]benzene, H_2OBC = 4,4′-oxybisbenzoic acid) triggered by the guest exchange.[224] It was found that this MOF could converted into $\{[Zn_2(BPEB)(OBC)_2]\cdot 2H_2O\}_n$ in MeOH via the solvent exchange, accompanied by the transformation from *trans-cis-trans* to *trans-trans-trans* conformation of the BPEB ligand. And, the reversible conversion could be achieved by soaking

$\{[Zn_2(BPEB)(OBC)_2]\cdot 2H_2O\}_n$ in DMF solvent.

On the other hand, some flexible MOFs also showed unique and interesting guest-induced structural transformation features, such as a “breathing” effect.[225] In these cases, the flexible frameworks were able to optimize their pore sizes and shapes in accordance with the incoming guest molecules. For example, Walton and co-workers observed a “breathing” effect in $\{Fe(OH,F)(BDC)\cdot H_2O\}_n$ (MIL-53(Fe),H_2O), which was induced by the substitution of water molecules in the framework pores by a variety of organic molecules including methanol, acetonitrile, lutidine, pyridine, and *m*-xylene.[226] Interestingly, it was found that pyridine has led to a small increase in unit cell volume of the MOF, whereas lutidine gave the largest swelling. Particularly, a dramatic stepwise expansion-contraction of the framework was observed in the presence of different amounts of the guest molecules in each case.

4.2. Cationic guest molecule substitution

Cation substitution has also been explored in some MOFs with anionic framework skeletons. For example, Rosi and co-workers have showed potential applications of a MOF $\{[Me_2NH_2]_2[Zn_8(AD)_4(BPDC)_6O]\cdot 8DMF\cdot 11H_2O\}_n$ (bio-MOF-1) in terms of its cation substitutions, in drug delivery,[227] CO_2 separation,[228] and ion-dependent luminescence[229] (Fig. 24). The bio-MOF-1 has an anionic framework skeleton, with dimethylammonium (DMAM) counter cations residing in its pores. When the crystals of bio-MOF-1 were soaked in an antiarrythmia drug-procainamide HCl solution for 15 days, a complete procainamide-loaded material $\{[procainamideH^+]_{3.5}[Zn_8(AD)_4(BPDC)_6O]\cdot 1.5Cl\cdot 16.5H_2O\}_n$ was obtained. Further studies showed the release of the procainamide could be achieved by putting the inclusion sample in phosphate-buffered saline (PBS) buffer (pH = 7.4). On the other hand, based on the cation exchange, the pore properties of bio-MOF-1 could be modified to give different gas adsorption performances of the resulting materials. It was confirmed that the incorporation of tetramethylammonium (TMAM), tetraethylammonium (TEAM), and tetrabutylammonium (TBAM) via the guest exchange with DMAM into the pores of this MOF, respectively resulted in a systematical decrease of the pore volume and surface area, but an enhanced CO_2 uptake of resulting materials compared with bio-MOF-1. This result demonstrated that small pores in MOFs might be better for preferentially adsorbing CO_2 molecules. In addition, bio-MOF-1 has also been used to encapsulate Ln^{3+} ions through the cation substitution, to give series of luminescent MOFs. Experimentally, Ln^{3+}@bio-MOF-1 materials were obtained via the substitution of DMAM with Tb^{3+}, Sm^{3+}, Eu^{3+}, or Yb^{3+} through soaking bio-MOF-1 crystals into DMF solutions of the corresponding lanthanide nitrate salts. The DMF molecules in the pores were then washed with water. It was found that despite the strong quenching effect of the water molecules located in their pores, these Ln^{3+}@bio-MOF-1 materials emitted distinctive colors: Eu^{3+}, red; Tb^{3+}, green; Sm^{3+}, orange-pink, when excited with a 365 nm light. The bio-MOF-1 can thus be used as a sensing material to identify different lanthanide ions.

Furthermore, Ma and co-workers also developed a "two-step" approach to encapsulate larger metal(II) phthalocyanine molecules into bio-MOF-1.[230] In the first step, metal ions were introduced into the MOF pores through the cationic substitution. And then, in the second step the metal functionalized molecules were generated in the pores by the *de novo* assembly of the metal ions and coming-in small molecule reactant (of synthesizing phthalocyanine). This work demonstrated a new strategy to encapsulate large metal-functionalized guest molecules into MOFs for various applications.

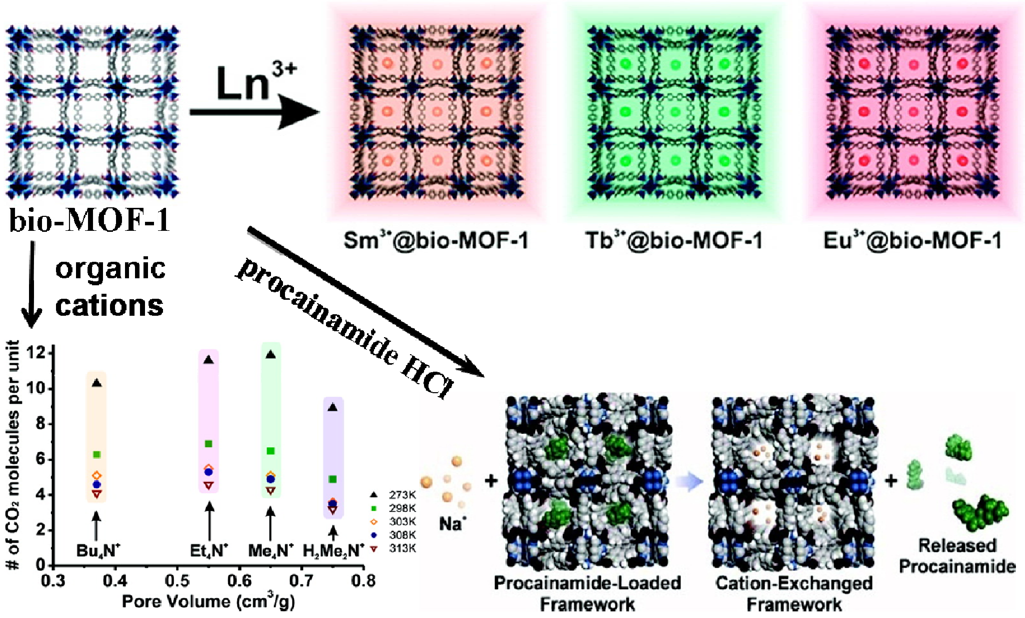


Fig. 24 Schematic representation of applications of $\{[Me_2NH_2]_2[Zn_8(AD)_4(BPDC)_6O]\cdot 8DMF\cdot 11H_2O\}_n$ (bio-MOF-1) in drug delivery, CO_2 absorption, and lanthanide ions sensing, all based on the cation substitutions. Reprinted with permission from ref. 227-229. Copyright 2009, 2010 and 2011 American Chemical Society.

Apart from luminescence, tuned nonlinear optical responses have been observed in MOFs based on the cation substitutions. The MOF $\{[DMAM]_3[In_3(BTB)_4]\cdot 12DMF\cdot 22H_2O\}_n$ (ZJU-28) reported by Chen and co-workers, did not present a second order nonlinear optical response.[231] The substitution of DMAM in this MOF with different hemicyanine chromophore of (4-(4-(diphenylamino)styryl)-1-methylpyridinium (DPASM), 1-butyl-4-(4-(diphenylamino)styryl) pyridinium (DPASB), 4-(4-(diphenylamino)styryl)-1-nonylpyridinium (DPASN), or 4-(4-(diphenylamino)styryl)-1-dodecylpyridinium (DPASD) containing different lengths of alkylchains in DMF solution resulted in the nonlinear optical respondent MOF materials: ZJU-28⊂DPASM, ZJU-28⊂DPASB, ZJU-28⊂DPASN, and ZJU-28⊂DPASD, respectively (Fig. 25). Second harmonic generation (SHG) measurements indicated that the longer the terminal alkylchain of the chromophore guest ion, the stronger the SHG intensity of the resulting MOF material. This observation was explained as that the included chromophore guest ions with longer alkyl chains might get the maximum match with the 1D channels of the MOF, thus enhanced their interactions with the host framework to give stronger SHG intensity. In addition, the luminescent properties of these materials also changed after the cation substitutions. For instance, when excited at 365 nm, ZJU-28 displayed a blue light emission at 414 nm, whereas ZJU-28⊂DPASD showed a red emission at 634 nm. Whereafter, through the cationic guest exchange, a very unique MOF material for lasing application has been realized, by the same group.[232] The confinement of pyridinium hemicyanine dye 4-[p-(dimethylamino)styryl]-1-methylpyridinium (DMASM) within the anionic bio-MOF-1 to produce bio-MOF-1⊂DMASM composite. This material exhibited two-photon fluorescence on account of the large absorption cross-section and the enhanced luminescent efficiency of the encapsulated DMASM. More importantly, the MOF composit crystal can serve as a Fabry-Perot resonance cavity to give rise to two-photon-pumped lasing around 640 nm when pumped with a 1064-nm pulse laser.

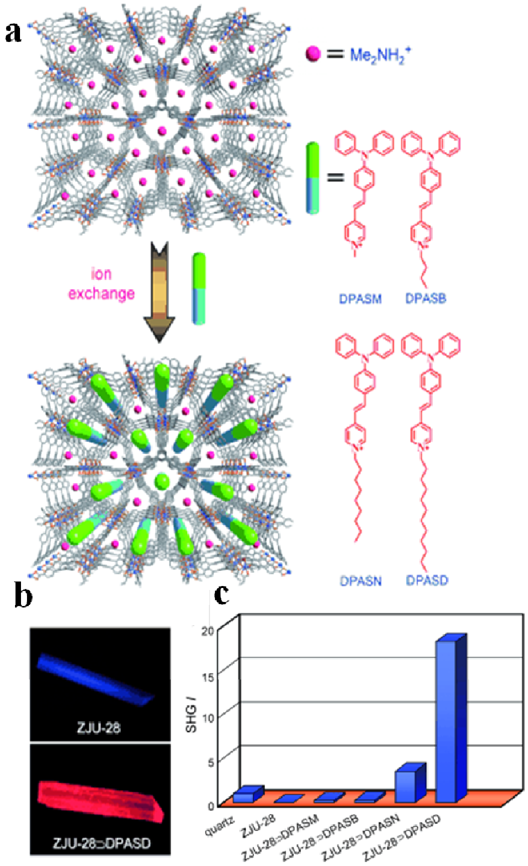


Fig. 25 (a) Schematic representation of the incorporation of pyridinium hemicyanine chromophores into $\{[DMAM]_3[In_3(BTB)_4]\cdot 12DMF\cdot 22H_2O\}_n$ (ZJU-28) via cation substitutions. (b) Fluorescent microscope images of ZJU-28 and ZJU-28DPASD illuminated with 365 nm UV light. (c) Comparison of the SHG intensities of α-quartz, ZJU-28, and the chromophore-substituted ZJU-28. Reprinted with permission from ref. 231. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The cation substitution has been also proved to be a powerful method of tuning gas adsorption properties of MOFs, such as in H_2 storage.[233-235] Li^+-doped MOFs have received considerable attention due to the involved strong Li^+---H_2 interaction, thereby their high H_2 storage ability. In several reported examples, Li^+ ions were introduced into pores of MOFs through the cation substitution to get materials with enhanced H_2 adsorption ability.[236-240] For instance, Schröder and co-workers reported the Li^+ exchange in $\{[H_2PPZ][In_2(L^1)_2]\cdot 3.5DMF\cdot 5H_2O\}_n$ (NOTT-200; L^1 = 1,1',4',1'',4'',1'''-quaterphenyl-3,5,3''',5'''-tetracarboxylate, PPZ = piperazine), which has a 2-fold interpenetrated anionic framework containing three interlinked channels (A, B, and C) as illustrated in Fig. 26.[241] In the structure, H_2PPZ^{2+} cations are fully ordered and located in the centre of channel B. The crystals of NOTT-200 were immersed in a saturated solution of LiCl in water/acetone at room temperature to give the expected Li$^+$-exchanged MOF, $\{Li_{1.5}[H_3O]_{0.5}[In_2(L)_2]\cdot 11H_2O\}_n$ (NOTT-201). It was found that in NOTT-201 the Li$^+$ ions located in the channel C and were tetrahedrally coordinated by two water molecules and two O atoms from carboxylate groups of the L^1 ligands. After removal of the coordinated water molecules, the Li$^+$ sites were exposed to give the material with a greatly enhanced H_2 adsorption ability. Before and after the cation exchange, both MOFs indeed performed different gas adsorption behaviors: NOTT-200 showed a significant kinetic hysteresis for N_2 and H_2 adsorptions, whereas NOTT-201 exhibited not only no hysteresis but a higher isosteric heat of adsorption towards H_2.

The same group also reported similar examples based on another two isostructural MOFs $\{[(DMAM)(H_3O)][In_2(L^2)_2]_3\cdot 4DMF\cdot 5H_2O\}_n$ (NOTT-206-solv, L^2 = 5,5'-(9,10-dihydrophenanthrene-2,7-diyl)diisophthalate) and $\{[H_2PPZ][In_2(L^3)_2]\cdot 4DMF\cdot 5.5H_2O\}_n$ (NOTT-208-solv, L^3 = 1,1',4',1'',4'',1'''-quinquephenyl-3,5,3''',5'''-tetracarboxylate), in which organic cations were replaced by Li$^+$ ions to yield corresponding Li$^+$-containing MOFs $\{Li_{1.2}[H_3O]_{0.8}[In_2(L^2)_2]\cdot 14H_2O\}_n$ (NOTT-207-solv) and $\{Li_{1.4}[H_3O]_{0.6}[In_2(L^3)_2]\cdot 4acetone\cdot 11H_2O\}_n$ (NOTT-209-solv).[242] After the substitution, a remarkable enhancement in H_2 storage capacity with the increased isosteric heat of adsorption was achieved in each case.

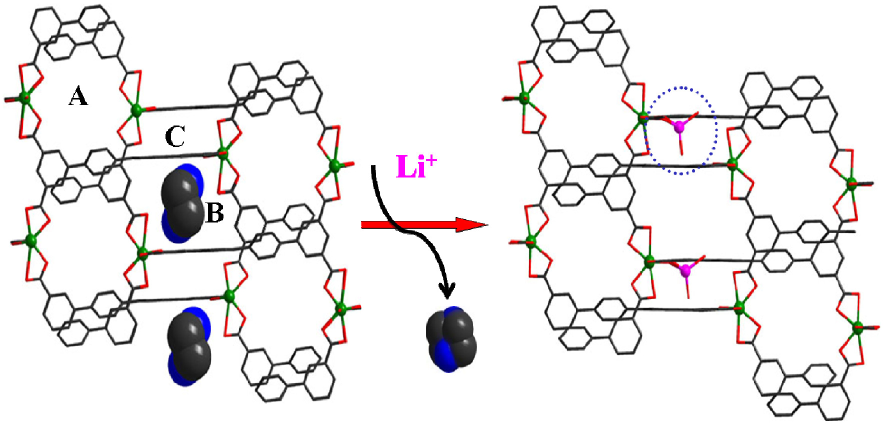


Fig. 26 Schematic representation of the substitution of H_2PPZ^{2+} cations in $\{[H_2PPZ][In_2(L^1)_2]\cdot 3.5DMF\cdot 5H_2O\}_n$ (NOTT-201) by Li$^+$ ions to form $\{Li_{1.5}[H_3O]_{0.5}[In_2(L)_2]\cdot 11H_2O\}_n$ (NOTT-201).[241]

Another interesting example was the observation of the coordination of incoming metal ions after the cation substitution to give a new MOF, a transformation from an anionic framework MOF to a neutral bimetallic one, reported by Thallapally and co-workers.[243] It was demonstrated that immersing the crystals of anionic framework MOF $\{[DMAM]_2[Mn_3(L)_2]\cdot 9DMF\}_n$ (H_4L = tetrakis[4-(carboxyphenyl)oxamethyl]-methane acid) in a DMF solution of $M(NO_3)_2$ (M = Co, Ni, or Cu) produced the corresponding neutral heterobimetallic MOFs via a SC-SC transformation process (Fig. 27). Where, DMAM cations in the parent MOF were substituted by metal ions. Different from most of observed guest molecule substitutions, these transformations were accompanied by the breakage and the regeneration of coordination bonds, being quite interesting in MOF chemistry. It was also found that Co^{2+} and Ni^{2+} ions could be selectively taken up over Li^+ and Na^+ ions by this MOF based on the cation substitution. This MOF is thus potentially useful for the removal of heavy metal ions from some complex solution systems.

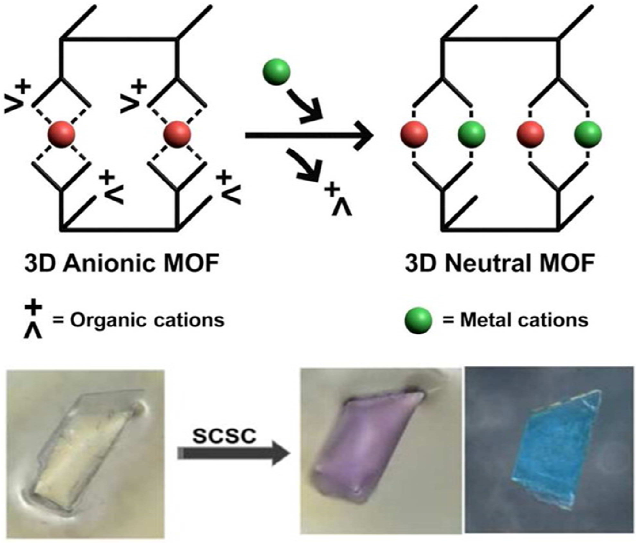


Fig. 27 Schematic representation of the cation substitution of organic DMAM by M^{2+} ions in anionic $\{[DMAM]_2[Mn_3(L)_2]\cdot 9DMF\}_n$ to afford a neutral MOF (top). Photographs of a crystal before and after the cationic guest exchange in the MOF (bottom). Reprinted with permission from ref. 243. Copyright 2012 American Chemical Society.

4.3. Anionic guest molecule substitution

Similar to the cation substitution, anion substitution has also been observed, and explored in MOFs and MOPs for tuning their properties.[244,245] When using a neutral organic ligand to coordinate with metal ions, the resulting MOFs usually have a cationic framework with un-coordinated anions balancing the charge. In the early state of MOFs development, a lot of these MOFs were synthesized, where the free anions can be substituted by others. Some examples have been reported, mostly for exploring the potential applications of these MOFs such as in pollution removal and molecule adsorption.[246]

For example, Oliver and co-workers studied the anion exchange in two cationic framework MOFs $\{Ag_2(BIPY)_2(EDS)\}_n$ (SLUG-21; EDS = 1,2-ethanedisulfonate)[247] and $\{Cu_2(BIPY)_2(EDS)\}_n$ (SLUG-22),[248] in which the Cu^+- or Ag^+-BIPY chains were held together via π⋯π stacking to form cationic layers. EDS anions located between the layers and formed weak coordination interactions with Cu^+ or Ag^+ ions. It was found that immersing SLUG-21 crystals in an aqueous solution of $NaNO_3$ at room temperature produced complete NO_3^--exchanged product $[Ag(BIPY)_2(NO_3)]_n$ (SLUG-21-NO_3[249]), and the substitution process was reversible under similar conditions. In addition to the NO_3^- substitution, SLUG-21 also showed a reversible substitution towards ClO_4^-, but irreversible towards MnO_4^-. Similarly, SLUG-22 exhibited the same anion exchange properties with NO_3^- and ClO_4^-. Furthermore, a selective anion exchange of MnO_4^- over NO_3^- was also observed in SLUG-21. It was found that MnO_4^- could preferably substitute EDS and formed stronger interactions with the SLUG-21 cationic framework than NO_3^-, which explained the observed irreversible exchange in the MnO_4^- case. The preferable substitution was also observed for ClO_4^- over NO_3^-, and ReO_4^- over NO_3^- and CO_3^{2-}.[250] The same group also reported the anion substitution in another MOF $\{[Pb_2F_2][EDS]\}_n$ (SLUG-6) consisting of cationic $[Pb_2F_2]^{2+}$ layers pillared by EDS anions (Fig. 28).[251] It was found that the immersion of SLUG-6 crystals in an aqueous solution of excess disodium succinate under ambient conditions gave crystalline $\{[Pb_2F_2][succinate]\}_n$ (SLUG-32). In situ optical microscopy analysis indicated that SLUG-6 underwent a solvent-mediated anion exchange, probably a dissolution and recrystallization process. Similarly, longer dicarboxylate ligands, glutarate and sebacate have also been confirmed to be able to substitute EDS in SLUG-6 to produce new MOFs with a similar structure.[252]

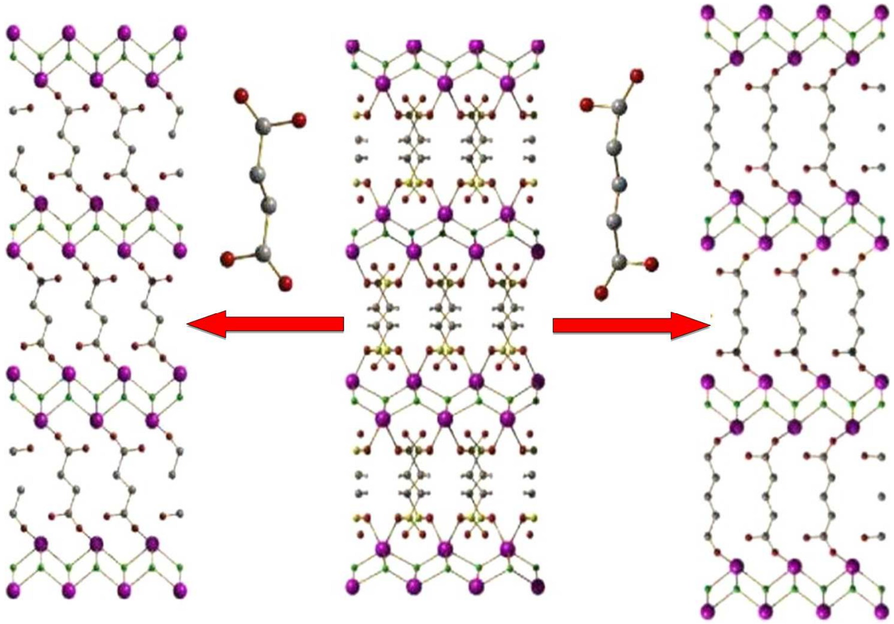


Fig. 28 Schematic representation of the guest anion substitutions in $\{[Pb_2F_2][EDS]\}_n$ (SLUG-6) to form new MOFs. Reprinted with permission from ref. 252. Copyright 2012 American Chemical Society.

Another example of anion exchange was reported by Wang and co-workers on the MOF $\{[Ag_2(BTR)_2]\cdot 2ClO_4\cdot 3H_2O\}_n$ (BTR = 4,4′-bis(1,2,4-triazole)) with 1D channels, which were filled by ClO_4^- anions.[253] Immersing colorless crystals of this MOF into an aqueous solution of $K_2Cr_2O_7$ produced the orange yellow crystals of $Cr_2O_7^{2-}$ loaded MOF. SXRD analysis indicated that ClO_4^- anions in the parent MOF were completely exchanged by $Cr_2O_7^{2-}$ ions and the cationic framework was still intact. It was also found that this MOF presented a high substitution selectivity towards $Cr_2O_7^{2-}$ over NO_3^-, $CF_3SO_3^-$, and BF_4^- ions, probably due to the stronger interactions of $Cr_2O_7^{2-}$ with the cationic framework than other anions. Interestingly, a bluish violet luminescence of $\{[Ag_2(BTR)_2]\cdot 2ClO_4\}_n$ was quenched upon the $Cr_2O_7^{2-}$ exchange. It should be pointed out that a lot of pollutants occurred in anionic form, such as MnO_4^-, ClO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, salicylate, carbamazepine, clofibrate, and ibuprofen. Above-mentioned examples showed that MOFs with a cationic framework were potential applicable in the pollutant removal, even if only very limited MOFs were explored to date in this aspect.

Based on the anion substitution some MOFs could also exhibit sensing responses towards given anions. For example, Kitagawa and co-workers reported the selective anion substitution in a 3D flexible MOF $\{[Ni(BPE)_2(N(CN)_2)]\cdot N(CN)_2\cdot 5H_2O\}_n$ (BPE = 1,2-bis(4-pyridyl)ethane, $N(CN)_2^-$ = dicyanamide), which can identify N_3^- ion in terms of its color change.[254] When crystals of this MOF were immersed in an aqueous solution of excess NaN_3 for 1 day, a color change of the crystals from violet to light green was observed. Following characterizations confirmed that free $N(CN)_2^-$ anions in the MOF was completely substituted by N_3^- ions to give $\{[Ni(BPE)_2(N(CN)_2)]\cdot N_3\cdot 5H_2O)\}_n$. However, other anions including NCO^-, NO_3^-, BF_4^-, ClO_4^-, and PF_6^- were not able to substitute $N(CN)_2^-$, showing the selectivity of this MOF towards different substituted anions. Interestingly, due to the decreased size of N_3^- compared with $N(CN)_2^-$ anion, the N_3^- substitution led to a slight breath of the structure and an increase in its channel size, thereby an enhanced CO_2 uptake of this MOF. In addition, the structural transformation triggered by the anion substitution in MOFs has been also observed. For example, Hou and co-workers presented a SC-SC transformation from $\{[Cu_6(TTTMB)_8(OH)_4(H_2O)_6]\cdot 8(NO_3)\}_n$ to $\{[Cu_6(TTTMB)_8I_3]\cdot 9I\}_n$ (TTTMB = 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene) achieved by the replacement of guest NO_3^- anions in the former with I^-.[255] Where, the coordination geometry of Cu^{2+} ions in the two MOFs changed from octahedral to square-planar, accompanied by a visible color change of the crystals from light blue to dark blue.

Another colorimetric anion sensing was achieved in the MOF $\{[CuL_2(H_2O)_{0.5})](NO_3)_2\cdot 3.25(CH_2Cl_2)\cdot(CH_3OH)\cdot 0.5H_2O\}_n$ (L = 4,4'-(9,9-dibutyl-9*H*-fluorene-2,7-diyl)dipyridine) reported by Dong and co-workers.[256] As shown in Fig. 29, it was found that immersing the crystals of the MOF in an aqueous solution of NaF, NaCl, KBr, KI, KSCN, or NaN_3, respectively resulted in a detectable color change of them. Different anions gave different colors of resulting materials: green for Cl^-, dark green for Br^-, deep brown for I^-, blackish green for SCN^-, and tan for N_3^-. However, no color change was observed for F^-. In addition, this MOF was confirmed to be able to separate Cl^-/Br^-, Br^-/I^-, and SCN^-/N_3^- anions under ambient conditions based on their selective substitutions.

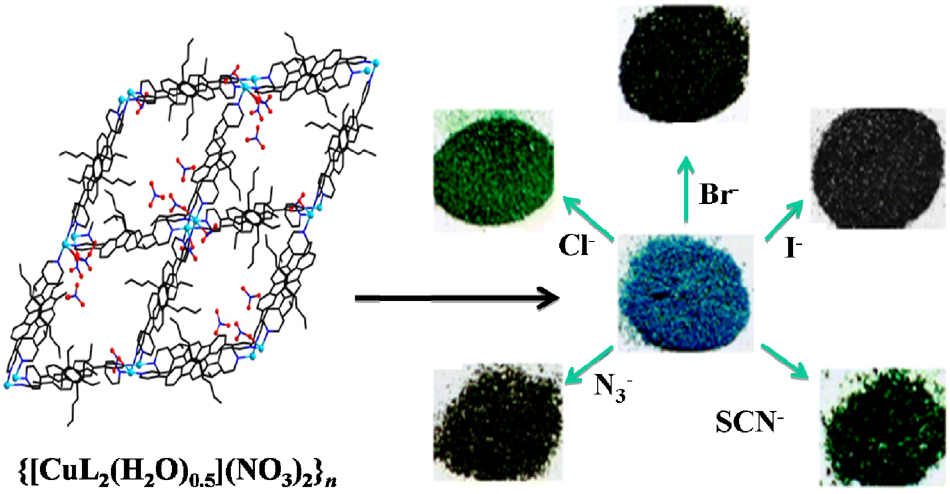


Fig. 29 Crystal structure and color changes of $\{[CuL_2(H_2O)_{0.5})](NO_3)_2{\cdot}3.25(CH_2Cl_2){\text{-}}{\cdot}(CH_3OH){\cdot}0.5H_2O\}_n$ resulted from anion substitutions. Reprinted with permission from ref. 256. Copyright 2012 The Royal Society of Chemistry.

It is clear that free guest molecules are usually stabilized in the cavities of MOMs via weak interactions. Compared with relatively strong coordination bonds, such weak interactions make guest molecules much easier to be substituted. And simultaneously, the substitution can also lead to some responses of the host framework towards the incoming guest molecules due to these weak interactions, to give unique phenomena, which are useful in several fields such as chemical sensing and reorganization. Thus, a lot of new structures or new properties of MOFs and MOPs can be achieved by the guest substitution strategy. In addition, we speculate that a lot of other new effects and/or applications are accessible in this context with the effort of further exploration in the future.

5. Conclusions and outlook

Metal-organic materials (MOMs) including MOFs and MOPs are a class of newly developed multifunctional materials with a wide range of potential applications. The synthesis and functional modifications of these materials are crucial for their applications. Compared with efforts on the exploitation of suitable synthetic methods/conditions based on usually used “one-pot” self-assembly strategy for preparing functional MOMs, the study of substitution reactions in MOMs for their preparations, modifications, and transformations is still at the early stage, despite some examples being reported as discussed in this review.

Different from the traditional synthetic method, the preparation of MOMs via the substitution reaction at metal ion or organic ligand is mainly based on a process starting from a pre-designed framework template, which could lead to a desired functional structure that may be difficult to access through a direct construction strategy. A lot of examples have demonstrated that the substitution reaction is universal in MOMs even very “inert” ones. The substitution strategy is thus powerful and widely accessible in the synthesis and modification of MOMs. The happening of the substitution reaction suggests the dynamic feature of MOMs, which can be attributed to the nature of the coordination bond involved in all MOMs; that is “lability and reversibility”. Furthermore, the substitution/exchange of guest molecules can greatly enrich the MOMs chemistry, as well as host-guest chemistry. Consequently, the substitution reaction in MOMs has a great potential and big space for further exploration.

However, reported examples in this topic mainly treated the structural transformations and associated property/function modifications induced by the substitution reactions, mostly from experimental observations. An in-depth exploration on the mechanism, particularly on reaction rate, selectivity, and the relationship between structural transformations and resulting properties needs to be carried out in the future, not only from experimental investigations but also from theoretical calculations based on molecular simulations. We are looking forward to a bright future for the substitution reaction application in MOFs and MOPs.

Acknowledgements

We thank the financial support from Natural Science Foundation of China (No. 21271015, 21322601) and Beijing Municipal Natural Science Foundation (No. 2132013).

Biographies

Yi Han

Yi Han obtained his Ph.D. degree in 2013 from Zhengzhou University in the research field of small molecule sensing. Then, he joined Prof. Jian-Rong Li's group as a postdoctoral research associate at Beijing University of Technology. His recent research focuses on the design, synthesis, and application of new porous materials.

Jian-Rong Li

Jian-Rong "Jeff" Li obtained his Ph.D. in 2005 from Nankai University. Until 2007, he was an assistant professor at the same University. In 2004, he was also a research assistant at Hong Kong University of Science & Technology. From 2008 to 2009, he has been a postdoctoral research associate, first at Miami University and later at Texas A&M University; from 2010 he has been an assistant research scientist at the same university. Since 2011, he has been a full professor at Beijing University of Technology. His research interest focuses on new porous materials for energy and environmental science.

Yabo Xie

Yabo Xie obtained his Ph.D. in 2004 from Nankai University. From 1991 to 2001, he has been a lectuer at Hebei Normal University. From 2005, he has been an assistant professor, and then associate professor at Beijing University of Technology. His research interest focuses on the design, synthesis, and property exploration of coordination polymers, and crystal engineering.

Guangsheng Guo

Guangsheng Guo obtained his Ph.D. from Beijing University of Chemical Technology. From 1986 to 2009, he has been an assistant professor, associate professor, and professor at the same university. In 1995, he was also a visiting scholar at the Chinese University of Hong Kong, where he conducted profound research in the field of Higher Education. From 2010, he has been a full professor at Beijing University of Technology. His research interest focuses on the preparation and application of nano-functional materials and applied laser-chemistry, as well as higher education management.

References

1. R. Xu, W. Pang, J. Yu, Q. Huo and J. Chen, *Chemistry of Zeolites and Related Porous Materials Synthesis and Structure*, Wiley, Singapore, 2007.
2. D. W. Beck, *Zeolite Molecular Sieves*, John Wiley & Sons, New York, 1974.
3. S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of Zeolite Science and Technology*, Marcel Dekker, Inc., New York, 2003.
4. F. Schuth, K. S. W. Sing and J. Weitkamp, *Handbook of Porous Solids*, Wiley-VCH, New York, 2002.
5. S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548-568.
6. A. Lee, S. Dubinsky, E. Tumarkin, M. Moulin, A. A. Beharry and E. Kumacheva, *Adv. Funct. Mater.*, 2011, **21**, 1959-1969.
7. G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.
8. H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673-674.
9. J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213-1214.
10. T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev*, 2013, **113**, 734-777.
11. R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev*, 2011, **111**, 6810-6918.
12. H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013,

341, 1230444.

13. C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222-13234.
14. T. A. Makal, J.-R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761-7779.
15. M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782-835.
16. D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058-6082.
17. J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
18. J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
19. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781.
20. Z. Zhang, Y. Zhao, Q. Gong, Z. Li and J. Li, *Chem. Commun.*, 2013, **49**, 653-661.
21. L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248-1256.
22. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
23. M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196-1231.
24. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
25. B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.,* 2010, **43**, 1115-1124.
26. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
27. P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232-1268.
28. J. Della Rocca, D. Liu and W. Lin, *Acc. Chem. Res.*, 2011, **44**, 957-968.
29. Z. Ma and B. Moulton, *Cood. Chem. Rev.*, 2011, **255**, 1623-1641.
30. J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400-1417.
31. N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933-969.
32. D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans*, 2006, 1249-1263.

33. C.-P. Li and M. Du, *Chem. Commun.*, 2011, **47**, 5958-5972.

34. S. S. Nagarkar, A. K. Chaudhari and S. K. Ghosh, *Cryst. Growth. Des.*, 2012, **12**, 572-576.

35. P. Mahata, M. Prabu and S. Natarajan, *Inorg. Chem.*, 2008, **47**, 8451-8463.

36. N. A. Khan, J. W. Jun and S. H. Jhung, *Eur. J. Inorg. Chem.*, 2010, **2010**, 1043-1048.

37. I. A. Riddell, Y. R. Hristova, J. K. Clegg, C. S. Wood, B. Breiner and J. R. Nitschke, *J. Am. Chem. Soc.*, 2013, **135**, 2723-2733.

38. Z. Zhang, L. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 928-933.

39. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.

40. D. J. Tranchemontagne, Z. Ni, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2008, **47**, 5136-5147.

41. J. B. Rivest and P. K. Jain, *Chem. Soc. Rev.*, 2013, **42**, 89-96.

42. R. J. Puddephatt, *Chem. Soc. Rev.*, 2008, **37**, 2012-2027.

43. D. T. Richens, *Chem. Rev.*, 2005, **105**, 1961-2002.

44. M. Lalonde, W. Bury, O. Karagiaridi, Z. Brown, J. T. Hupp and O. K. Farha, *J. Mater. Chem. A*, 2013, **1**, 5453-5468.

45. M. E. Carnes, M. S. Collins and D. W. Johnson, *Chem. Soc. Rev.*, 2014, **43**, 1825-1834.

46. B. J. Burnett and W. Choe, *Dalton Trans*, 2012, **41**, 3889-3894.

47. G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755-1775.

48. M. Kim, J. F. Cahill, H. Fei, K. A. Prather and S. M. Cohen, *J. Am. Chem. Soc.*, 2012, **134**, 18082-18088.

49. H. Fei, J. F. Cahill, K. A. Prather and S. M. Cohen, *Inorg. Chem.*, 2013, **52**, 4011-4016.

50. O. Karagiaridi, W. Bury, A. A. Sarjeant, C. L. Stern, O. K. Farha and J. T. Hupp, *Chem. Sci.*, 2012, **3**, 3256-3260.

51. M. Kim, J. F. Cahill, Y. Su, K. A. Prather and S. M. Cohen, *Chem. Sci.*, 2012, **3**, 126-130.

52. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and

I. Margiolaki, *Science*, 2005, **309**, 2040-2042.

53. J. J. Vittal, *Cood. Chem. Rev.*, 2007, **251**, 1781-1795.
54. S. Neogi, S. Sen and P. K. Bharadwaj, *CrystEngComm*, 2013, **15**, 9239-9248.
55. G. J. Halder and C. J. Kepert, *Aust. J. Chem.*, 2006, **59**, 597-604.
56. S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970-1000.
57. S. M. Cohen, *Chem. Sci.*, 2010, **1**, 32-36.
58. Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315-1329.
59. K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498-519.
60. H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276-279.
61. M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675-702.
62. D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257-1283.
63. Y. Han, N. F. Chilton, M. Li, C. Huang, H. Xu, H. Hou, B. Moubaraki, S. K. Langley, S. R. Batten, Y. Fan and K. S. Murray, *Chem. Eur. J.*, 2013, **19**, 6321-6328.
64. G. Mukherjee and K. Biradha, *Chem. Commun.*, 2012, **48**, 4293-4295.
65. M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172-11176.
66. M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876-16883.
67. L. Mi, H. Hou, Z. Song, H. Han and Y. Fan, *Chem. Eur. J.*, 2008, **14**, 1814-1821.
68. L. Mi, H. Hou, Z. Song, H. Han, H. Xu, Y. Fan and S.-W. Ng, *Cryst. Growth. Des.*, 2007, **7**, 2553-2561.
69. J. Li, L. Li, H. Hou and Y. Fan, *Cryst. Growth. Des.*, 2009, **9**, 4504-4513.
70. J.-A. Zhao, L. Mi, J. Hu, H. Hou and Y. Fan, *J. Am. Chem. Soc.*, 2008, **130**, 15222-15223.
71. X.-J. Wang, P.-Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li and Y. Zhao, *Chem. Commun.*, 2012, **48**, 10286-10288.
72. Z.-J. Zhang, W. Shi, Z. Niu, H.-H. Li, B. Zhao, P. Cheng, D.-Z. Liao and S.-P. Yan, *Chem. Commun.*, 2011, **47**, 6425-6427.

73. C. K. Brozek and M. Dincă, *Chem. Sci.*, 2012, **3**, 2110-2113.

74. H. Li, W. Shi, K. Zhao, H. Li, Y. Bing and P. Cheng, *Inorg. Chem.*, 2012, **51**, 9200-9207.

75. J. A. Botas, G. Calleja, M. Sanchez-Sanchez and M. G. Orcajo, *Langmuir*, 2010, **26**, 5300-5303.

76. C. K. Brozek and M. Dincă, *J. Am. Chem. Soc.*, 2013, **135**, 12886-12891.

77. C. K. Brozek, A. F. Cozzolino, S. J. Teat, Y.-S. Chen and M. Dincă, *Chem. Mater.*, 2013, **25**, 2998-3002.

78. D. Denysenko, M. Grzywa, M. Tonigold, B. Streppel, I. Krkljus, M. Hirscher, E. Mugnaioli, U. Kolb, J. Hanss and D. Volkmer, *Chem. Eur. J.*, 2011, **17**, 1837-1848.

79. D. Denysenko, T. Werner, M. Grzywa, A. Puls, V. Hagen, G. Eickerling, J. Jelic, K. Reuter and D. Volkmer, *Chem. Commun*., 2012, **48**, 1236-1238.

80. S. Biswas, M. Grzywa, H. P. Nayek, S. Dehnen, I. Senkovska, S. Kaskel and D. Volkmer, *Dalton Trans*, 2009, 6487-6495.

81. S. Das, H. Kim and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814-3815.

82. Y. Kim, S. Das, S. Bhattacharya, S. Hong, M. G. Kim, M. Yoon, S. Natarajan and K. Kim, *Chem. Eur. J.*, 2012, **18**, 16642-16648.

83. J.-H. Liao, W.-T. Chen, C.-S. Tsai and C.-C. Wang, *CrystEngComm*, 2013, **15**, 3377-3384.

84. Q. Yao, J. Sun, K. Li, J. Su, M. V. Peskov and X. Zou, *Dalton Trans*, 2012, **41**, 3953-3955.

85. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192-3210.

86. Z. Wei, W. Lu, H.-L. Jiang and H.-C. Zhou, *Inorg. Chem.*, 2013, **52**, 1164-1166.

87. T. K. Prasad, D. H. Hong and M. P. Suh, *Chem. Eur. J.*, 2010, **16**, 14043-14050.

88. Z. Zhang, L. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 924-927.

89. X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon and M. S. Lah, *Chem. Mater.*, 2012, **24**, 3065-3073.

90. X. Song, S. Jeong, D. Kim and M. S. Lah, *CrystEngComm*, 2012, **14**, 5753.

91. G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surble, J. Dutour and I. Margiolaki, *Angew. Chem. Int. Ed.*, 2004, **43**, 6296-6301.

92. C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Férey, M. Haouas, F. Taulelle, N. Audebrand and M. Latroche, *Inorg. Chem.*, 2008, **47**, 11892-11901.

93. K. Barthelet, J. Marrot, G. Férey and D. Riou, *Chem. Commun.*, 2004, 520-521.

94. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.

95. H. Hayashi, A. P. Cote, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nat. Mater.*, 2007, **6**, 501-506.

96. J.-P. Zhang, Y.-B. Zhang, J.-B. Lin and X.-M. Chen, *Chem. Rev.*, 2012, **112**, 1001-1033.

97. K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186-10191.

98. S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50**, 9518-9526.

99. T. Devic, P. Horcajada, C. Serre, F. Salles, G. Maurin, B. Moulin, D. Heurtaux, G. Clet, A. Vimont, J.-M. Grenèche, B. L. Ouay, F. Moreau, E. Magnier, Y. Filinchuk, J. Marrot, J.-C. Lavalley, M. Daturi and G. Férey, *J. Am. Chem. Soc.*, 2009, **132**, 1127-1136.

100. M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 10857-10859.

101. C. H. Hendon, D. Tiana, M. Fontecave, C. Sanchez, L. D'Arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks and A. Walsh, *J. Am. Chem. Soc.*, 2013, **135**, 10942-10945.

102. R. P. Lively, M. E. Dose, J. A. Thompson, B. A. McCool, R. R. Chance and W. J. Koros, *Chem. Commun.*, 2011, **47**, 8667-8669.

103. Z. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2013, **135**, 5982-5985.

104. G. Kumar and R. Gupta, *Chem. Soc. Rev.*, 2013, **42**, 9403-9453.

105. J. M. Falkowski, C. Wang, S. Liu and W. Lin, *Angew. Chem. Int. Ed.*, 2011, **50**, 8674-8678.

106. Z. Xie, L. Ma, K. E. deKrafft, A. Jin and W. Lin, *J. Am. Chem. Soc.*, 2009, **132**, 922-923.

107. R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-i. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684-2687.

108. B. Chen, X. Zhao, A. Putkham, K. Hong, E. B. Lobkovsky, E. J. Hurtado, A. J. Fletcher and K. M. Thomas, *J. Am. Chem. Soc.*, 2008, **130**, 6411-6423.

109. X.-S. Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y.-S. Chen, X.-P. Zhang and S. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 16322-16325.

110. X.-L. Yang, M.-H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 10638-10645.

111. D. Feng, H.-L. Jiang, Y.-P. Chen, Z.-Y. Gu, Z. Wei and H.-C. Zhou, *Inorg. Chem.*, 2013, **52**, 12661-12667.

112. D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105-17110.

113. P. Hambright, In *The Porphyrin Handbook*; K. M. Kadish, K. M. Smith, R. Guilard, Eds.; Academic Press: New York, 2000.

114. X.-S. Wang, M. Chrzanowski, L. Wojtas, Y.-S. Chen and S. Ma, *Chem. Eur. J.*, 2013, **19**, 3297-3301.

115. X.-S. Wang, M. Chrzanowski, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko and S. Ma, *Chem. Sci.*, 2012, **3**, 2823-2827.

116. D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10307-10310.

117. W. Morris, B. Volosskiy, S. Demir, F. Gandara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443-6445.

118. Y. Chen, T. Hoang and S. Ma, *Inorg. Chem.*, 2012, **51**, 12600-12602.

119. M. J. Manos, E. J. Kyprianidou, G. S. Papaefstathiou and A. J. Tasiopoulos, *Inorg. Chem.*, 2012, **51**, 6308-6314.

120. J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 10294-10297.

121. P. Deria, J. E. Mondloch, E. Tylianakis, P. Ghosh, W. Bury, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2013, **135**, 16801-16804.

122. P. Deria, W. Bury, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2014, **50**,

1965-1968.

123. A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Commun.*, 2012, **48**, 11275-11288.

124. E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606-1610.

125. J. G. Vitillo, L. Regli, S. Chavan, G. Ricchiardi, G. Spoto, P. D. C. Dietzel, S. Bordiga and A. Zecchina, *J. Am. Chem. Soc.*, 2008, **130**, 8386-8396.

126. Q. Yang and C. Zhong, *J. Phys. Chem. B*, 2005, **110**, 655-658.

127. B. Supronowicz, A. Mavrandonakis and T. Heine, *J. Phys. Chem. C*, 2013, **117**, 14570-14578.

128. J. J. Gutiérrez-Sevillano, J. M. Vicent-Luna, D. Dubbeldam and S. Calero, *J. Phys. Chem. C*, 2013, **117**, 11357-11366.

129. M. J. Ingleson, R. Heck, J. A. Gould and M. J. Rosseinsky, *Inorg. Chem.*, 2009, **48**, 9986-9988.

130. M. Banerjee, S. Das, M. Yoon, H. J. Choi, M. H. Hyun, S. M. Park, G. Seo and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 7524-7525.

131. Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem. Int. Ed.*, 2008, **47**, 4144-4148.

132. T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 7056-7065.

133. A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784-8786.

134. H. J. Park, Y. E. Cheon and M. P. Suh, *Chem. Eur. J.*, 2010, **16**, 11662-11669.

135. R. Kitaura, F. Iwahori, R. Matsuda, S. Kitagawa, Y. Kubota, M. Takata and T. C. Kobayashi, *Inorg. Chem.*, 2004, **43**, 6522-6524.

136. Z. Chen, S. Xiang, D. Zhao and B. Chen, *Cryst. Growth. Des.*, 2009, **9**, 5293-5296.

137. M. Nagarathinam and J. J. Vittal, *Chem. Commun.*, 2008, **44**, 438-440.

138. M. Nagarathinam, A. Chanthapally, S. H. Lapidus, P. W. Stephens and J. J. Vittal, *Chem. Commun.*, 2012, **48**, 2585-2587.

139. A. Mallick, B. Garai, D. D. Diaz and R. Banerjee, *Angew. Chem. Int. Ed.*, 2013, **52**, 13755-13759.

140. M. J. Zaworotko, *Nat. Chem.*, 2009, **1**, 267-268.

141. T.-F. Liu, Y.-P. Chen, A. A. Yakovenko and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 17358-17361.

142. J.-R. Li, D. J. Timmons and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368-6369.

143. H.-N. Wang, X. Meng, G.-S. Yang, X.-L. Wang, K.-Z. Shao, Z.-M. Su and C.-G. Wang, *Chem. Commun.*, 2011, **47**, 7128-7130.

144. H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 11650-11661.

145. X.-L. Wang, C. Qin, S.-X. Wu, K.-Z. Shao, Y.-Q. Lan, S. Wang, D.-X. Zhu, Z.-M. Su and E.-B. Wang, *Angew. Chem. Int. Ed.*, 2009, **48**, 5291-5295.

146. Y.-Q. Lan, S.-L. Li, H.-L. Jiang and Q. Xu, *Chem. Eur. J.*, 2012, **18**, 8076-8083.

147. A. Schoedel, L. Wojtas, S. P. Kelley, R. D. Rogers, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 2011, **50**, 11421-11424.

148. A. Schoedel, A. J. Cairns, Y. Belmabkhout, L. Wojtas, M. Mohamed, Z. Zhang, D. M. Proserpio, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 2013, **52**, 2902-2905.

149. A. Schoedel, W. Boyette, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2013, **135**, 14016-14019.

150. D. Bradshaw, J. E. Warren and M. J. Rosseinsky, *Science*, 2007, **315**, 977-980.

151. X.-N. Cheng, W.-X. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 15738-15739.

152. Y.-B. He, Z.-Y. Guo, S.-C. Xiang, Z.-J. Zhang, W. Zhou, F. R. Fronczek, S. Parkin, S. T. Hyde, M. O'Keeffe and B. Chen, *Inorg. Chem.*, 2013, **52**, 11580-11584.

153. D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res.*, 2010, **44**, 123-133.

154. F. A. Paz, J. Klinowski, S. M. Vilela, J. P. Tome, J. A. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088-1110.

155. M. M. Smulders, I. A. Riddell, C. Browne and J. R. Nitschke, *Chem. Soc. Rev.*, 2013, **42**, 1728-1754.

156. S. Jeong, D. Kim, X. Song, M. Choi, N. Park and M. S. Lah, *Chem. Mater.*,

2013, **25**, 1047-1054.

157. S. Jeong, D. Kim, S. Shin, M. D. Moon, S. J. Cho and M. S. Lah, *Chem. Mater.*, 2014, **26**, 1711-1719.

158. W. Bury, D. Fairen-Jimenez, M. B. Lalonde, R. Q. Snurr, O. K. Farha and J. T. Hupp, *Chem. Mater.*, 2013, **25**, 739-744.

159. R. Bagai and G. Christou, *Chem. Soc. Rev.*, 2009, **38**, 1011-1026.

160. M. M. Smulders, A. Jimenez and J. R. Nitschke, *Angew. Chem. Int. Ed.*, 2012, **51**, 6681-6685.

161. J. R. Nitschke, *Acc. Chem. Res.*, 2006, **40**, 103-112.

162. Y.-R. Zheng and P. J. Stang, *J. Am. Chem. Soc.*, 2009, **131**, 3487-3489.

163. Y.-R. Zheng, Z. Zhao, M. Wang, K. Ghosh, J. B. Pollock, T. R. Cook and P. J. Stang, *J. Am. Chem. Soc.*, 2010, **132**, 16873-16882.

164. W. Meng, T. K. Ronson, J. K. Clegg and J. R. Nitschke, *Angew. Chem. Int. Ed.*, 2013, **52**, 1017-1021.

165. B. J. Burnett, P. M. Barron, C. Hu and W. Choe, *J. Am. Chem. Soc.*, 2011, **133**, 9984-9987.

166. H. Chung, P. M. Barron, R. W. Novotny, H.-T. Son, C. Hu and W. Choe, *Cryst. Growth. Des.*, 2009, **9**, 3327-3332.

167. E.-Y. Choi, P. M. Barron, R. W. Novotny, H.-T. Son, C. Hu and W. Choe, *Inorg. Chem.*, 2008, **48**, 426-428.

168. E.-Y. Choi, C. A. Wray, C. Hu and W. Choe, *CrystEngComm*, 2009, **11**, 553-555.

169. O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 5652-5655.

170. S. Takaishi, E. J. DeMarco, M. J. Pellin, O. K. Farha and J. T. Hupp, *Chem. Sci.*, 2013, **4**, 1509-1513.

171. J. An, O. K. Farha, J. T. Hupp, E. Pohl, J. I. Yeh and N. L. Rosi, *Nat. Commun.*, 2012, **3**, 604-609.

172. T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 11688-11691.

173. H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem. Eur. J.*, 2005, **11**, 3521-3529.

174. M. Kondo, S. Furukawa, K. Hirai and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2010, **49**, 5327-5330.

175. S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.

176. Y.-Q. Tian, S.-Y. Yao, D. Gu, K.-H. Cui, D.-W. Guo, G. Zhang, Z.-X. Chen and D.-Y. Zhao, *Chem. Eur. J.*, 2010, **16**, 1137-1141.

177. S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700-7702.

178. T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. r. Senker, G. Férey and N. Stock, *Inorg. Chem.*, 2009, **48**, 3057-3064.

179. X.-P. Zhou, Y. Wu and D. Li, *J. Am. Chem. Soc.*, 2013, **135**, 16062−16065.

180. W. Lu, D. Yuan, A. Yakovenko and H.-C. Zhou, *Chem. Commun.*, 2011, **47**, 4968-4970.

181. S. Sato, Y. Ishido and M. Fujita, *J. Am. Chem. Soc.*, 2009, **131**, 6064-6065.

182. J.-R. Li and H.-C. Zhou, *Nat. Chem.*, 2010, **2**, 893-898.

183. Y.-R. Zheng, W.-J. Lan, M. Wang, T. R. Cook and P. J. Stang, *J. Am. Chem. Soc.*, 2011, **133**, 17045-17055.

184. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472.

185. H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, **327**, 846-850.

186. Z. Zhang, W. -Y. Gao, L. Wojtas, S. Ma, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 2012, **51**, 9330-9334.

187. B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546-1554.

188. A. D. Burrows, *CrystEngComm*, 2011, **13**, 3623-3642.

189. A. D. Burrows, *Post-synthetic Modification of MOFs*, Chaper 3 of *Metal Organic Frameworks as Heterogeneous Catalysts*, RSC, UK, 2013.

190. M. J. Ingleson, J. P. Barrio, J. B. Guilbaud, Y. Z. Khimyak and M. J. Rosseinsky, *Chem. Commun.*, 2008, 2680-2682.

191. E. Dugan, Z. Wang, M. Okamura, A. Medina and S. M. Cohen, *Chem. Commun.*, 2008, 3366-3368.

192. Z. Wang and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2008, **47**, 4699-4702.

193. D. Britt, C. Lee, F. J. Uribe-Romo, H. Furukawa and O. M. Yaghi, *Inorg.*

Chem., 2010, **49**, 6387-6389.

194. S. J. Garibay, Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2009, **48**, 7341-7349.

195. S. J. Garibay, Z. Wang and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 8086-8091.

196. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004-2021.

197. T. Gadzikwa, G. Lu, C. L. Stern, S. R. Wilson, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 5493-5495.

198. T. Gadzikwa, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2009, **131**, 13613-13615.

199. M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel and D. Farrusseng, *J. Am. Chem. Soc.*, 2010, **132**, 4518-4519.

200. Y. Goto, H. Sato, S. Shinkai and K. Sada, *J. Am. Chem. Soc.*, 2008, **130**, 14354-14355.

201. H.-L. Jiang, D. Feng, T.-F. Liu, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 14690-14693.

202. C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940-8941.

203. L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838-846.

204. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382-14384.

205. M. Kawano and M. Fujita, *Cood. Chem. Rev.*, 2007, **251**, 2592-2605.

206. T. Kawamichi, T. Haneda, M. Kawano and M. Fujita, *Nature*, 2009, **461**, 633-635.

207. J. Marti-Rujas, N. Islam, D. Hashizume, F. Izumi, M. Fujita, H. J. Song, H. C. Choi and M. Kawano, *Angew. Chem. Int. Ed.*, 2011, **50**, 6105-6108.

208. T. K. Ronson, S. Zarra, S. P. Black and J. R. Nitschke, *Chem. Commun.*, 2013, **49**, 2476-2490.

209. Y.-B. Dong, Q. Zhang, L.-L. Liu, J.-P. Ma, B. Tang and R.-Q. Huang, *J. Am. Chem. Soc.*, 2007, **129**, 1514-1515.

210. Y. Inokuma, M. Kawano and M. Fujita, *Nat. Chem.*, 2011, **3**, 349-358.

211. M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem. Int. Ed.*, 2009,

48, 3418-3438.

212. D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2004, **38**, 349-358.
213. S. J. Dalgarno, N. P. Power and J. L. Atwood, *Cood. Chem. Rev.*, 2008, **252**, 825-841.
214. M. D. Pluth and K. N. Raymond, *Chem. Soc. Rev.*, 2007, **36**, 161-171.
215. K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **114**, 3542-3545.
216. O. Ohmori, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 16292-16293.
217. Y. Inokuma, T. Arai and M. Fujita, *Nat. Chem.*, 2010, **2**, 780-783.
218. M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469-471.
219. Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature*, 2013, **495**, 461-466.
220. Q.-K. Liu, J.-P. Ma and Y.-B. Dong, *Chem. Eur. J.*, 2009, **15**, 10364-10368.
221. Q.-K. Liu, J.-P. Ma and Y.-B. Dong, *J. Am. Chem. Soc.*, 2010, **132**, 7005-7017.
222. S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem*., 2009, **1**, 695-704.
223. C.-D. Wu and W. Lin, *Angew. Chem. Int. Ed.*, 2005, **44**, 1958-1961.
224. I. H. Park, S. S. Lee and J. J. Vittal, *Chem. Eur. J.*, 2013, **19**, 2695-2702.
225. G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 1380-1399.
226. F. Millange, C. Serre, N. Guillou, G. Férey and R. I. Walton, *Angew. Chem. Int. Ed.*, 2008, **47**, 4100-4105.
227. J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **131**, 8376-8377.
228. J. An and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 5578-5579.
229. J. An, C. M. Shade, D. A. Chengelis-Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 1220-1223.
230. B. Li, Y. Zhang, D. Ma, T. Ma, Z. Shi and S. Ma, *J. Am. Chem. Soc.*, 2014, **136**, 1202-1205.
231. J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen and G. Qian, *Angew. Chem. Int. Ed.*, 2012, **51**, 10542-10545.
232. J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen and G. Qian, *Nat. Commun.*,

2013, **4**, 2719-2725.

233. Y. Liu, V. Kravtsov and M. Eddaoudi, *Angew. Chem. Int. Ed.*, 2008, **47**, 8446-8449.

234. P. He, H. Liu, Y. Li, Z. Lei, S. Huang, P. Wang and H. Tian, *Mol. Simul.*, 2012, **38**, 72-83.

235. G. Calleja, J. A. Botas, M. Sánchez-Sánchez and M. G. Orcajo, *Int. J. Hydrogen. Energy.*, 2010, **35**, 9916-9923.

236. A. Blomqvist, C. M. Araujo, P. Srepusharawoot and R. Ahuja, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 20173-20176.

237. D. Himsl, D. Wallacher and M. Hartmann, *Angew. Chem. Int. Ed.*, 2009, **48**, 4639-4642.

238. K. L. Mulfort, O. K. Farha, C. L. Stern, A. A. Sarjeant and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 3866-3868.

239. S. S. Han and W. A. Goddard, *J. Am. Chem. Soc.*, 2007, **129**, 8422-8423.

240. P. Dalach, H. Frost, R. Q. Snurr and D. E. Ellis, *J. Phys. Chem. C*, 2008, **112**, 9278-9284.

241. S. Yang, X. Lin, A. J. Blake, G. S. Walker, P. Hubberstey, N. R. Champness and M. Schröder, *Nat. Chem.*, 2009, **1**, 487-493.

242. S. Yang, G. S. Martin, J. J. Titman, A. J. Blake, D. R. Allan, N. R. Champness and M. Schröder, *Inorg. Chem.*, 2011, **50**, 9374-9384.

243. J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno and P. K. Thallapally, *J. Am. Chem. Soc.*, 2012, **134**, 9581-9584.

244. Q.-K. Liu, J.-P. Ma and Y.-B. Dong, *Chem. Commun.*, 2011, **47**, 7185-7187.

245. R. Custelcean, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C3CS60371G.

246. S. R. Oliver, *Chem. Soc. Rev.*, 2009, **38**, 1868-1881.

247. H. Fei, L. Paw U, D. L. Rogow, M. R. Bresler, Y. A. Abdollahian and S. R. J. Oliver, *Chem. Mater.*, 2010, **22**, 2027-2032.

248. H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202-7209.

249. O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295-296.

250. H. Fei, M. R. Bresler and S. R. Oliver, *J. Am. Chem. Soc.*, 2011, **133**, 11110-11113.

251. D. L. Rogow, G. Zapeda, C. H. Swanson, X. Fan, A. G. Oliver and S. R. J. Oliver, *Chem. Mater.*, 2007, **19**, 4658-4662.

252. H. Fei, C. H. Pham and S. R. Oliver, *J. Am. Chem. Soc.*, 2012, **134**, 10729-10732.

253. X. Li, H. Xu, F. Kong and R. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 13769-13773.

254. T. K. Maji, R. Matsuda and S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142-148.

255. J. Fu, H. Li, Y. Mu, H. Hou and Y. Fan, *Chem. Commun.*, 2011, **47**, 5271-5273.

256. J.-P. Ma, Y. Yu and Y.-B. Dong, *Chem. Commun.*, 2012, **48**, 2946-2948.