Recent advance in porous polyoxometalate-based metal-organic framework materials

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Graphical Abstract

Recent advance in porous polyoxometalate-based metal-organic framework materials

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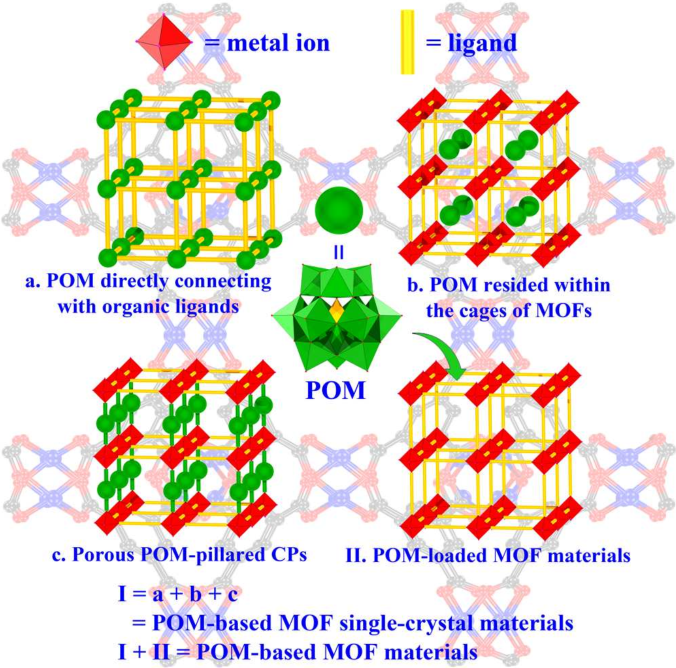
POM-based MOF materials, which take the advantages of both POMs and MOFs, have received increasing attention, and much effort has been devoted to their preparation and relevant applications over the past decades. In this review, we present the recent development of porous POM-based MOF materials for the first time, including their classification, synthesis strategies and applications, especially in the field of catalysis.



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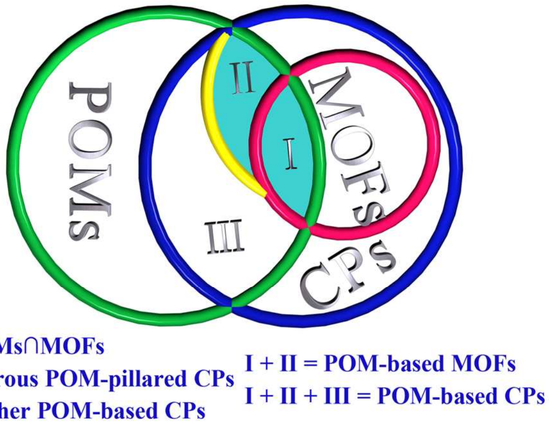
Polyoxometalates (POMs)-based metal-organic framework (MOF) materials contain POM units and generally generate MOF materials with open networks. POM-based MOF materials, which utilize the advantages of both POMs and MOFs, have received increasing attention, and much effort has been devoted to their preparation and relevant applications over the past decades. They have good prospects in catalysis owing to the electronic and physical properties of POMs that are tunable by varying constituent elements. In this review, we present recent development of porous POM-based MOF materials, including their classification, synthesis strategies, and applications, especially in the field of catalysis.

1. Introduction

Polyoxometalates (POMs) are a subset of metal oxides that represent a tremendous range of inorganic clusters with an unmatched range of physical and chemical properties and the ability to generate dynamic structures that can range in size from nano- to micrometer scale.[1,2] On the one hand, POMs can undergo reversible multielectron redox transformations without any significant structural alteration under rather mild conditions, which makes them attractive for diverse applications. On the other hand, POM anions represent a well-defined library of inorganic building blocks with Lewis and Brønsted acidity that can be utilized as efficient solid-acid catalysts for a series of organic reactions. Furthermore, their properties such as solubility, redox potential, and acidity can be finely-tuned by varying constituent elements. In early 1990s, Pope and Müller published a Review highlighted these key features and sparkled rapid expansion in this field.[3] The vast growth was also well-documented in *Chemical Reviews* organized by Hill[4] and *Chemical Society Reviews* organized by Cronin and Müller,[5] which spans a comprehensive range of possibilities offered by POMs.

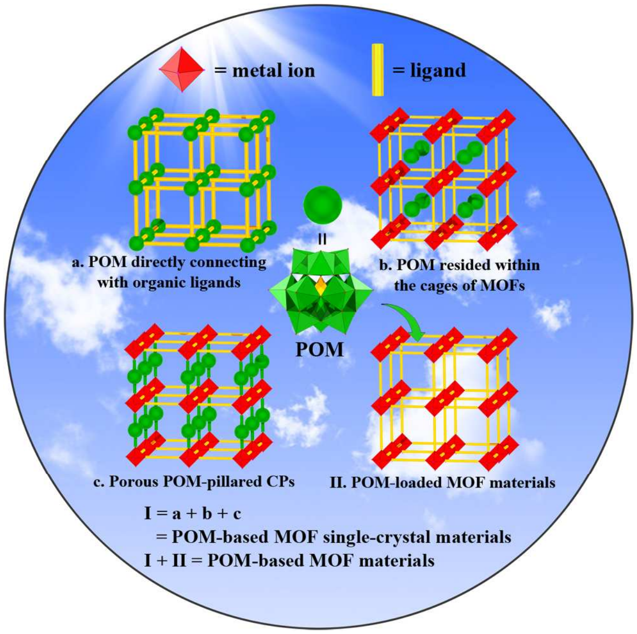
Coordination polymers (CPs) are assemblies of metal ions (or metal clusters) and organic ligands linked through coordination bonds.[6] Once POMs were introduced into the CP system, a research field of POM-based inorganic-organic hybrid materials began to flourish (Scheme 1). Metal-organic frameworks (MOFs), a new class of crystalline porous CP materials with open frameworks, act as unique and outstanding candidates as carriers based on their high surface areas and permanent porosity.[7,8] In this context, POM-based MOFs materials jumped into the researchers' eyes. Overall, POM-based MOF materials normally contain POM units and thus generate MOF materials with open network structures. Because POMs are either directly part of the frameworks of MOFs or encapsulated within the cavities of MOFs, we called this kind of materials as a POM-based MOF material. Thus, such materials can combine the advantages of both POMs and MOFs. Up to now, there are some reviews have been published covered by some special topics upon POM and MOF sciences with their rapid developments,[9-12] but there is no review upon the development of POM-based MOF materials. As a result, it is imperative to make a summarization on the recent progress of POM-based MOF materials, especially such materials with porosity, including their design, syntheses and applications.

Scheme 1 Schematic view of the research field between POMs and MOFs



The topic of this review focuses on the recent progress of porous POM-based MOF materials. In the first section, the strategies employed for the preparation of POM-based MOF materials were described. Then, we divided POM-based MOF materials into two parts: POM-based MOF single-crystal materials and POM-loaded MOF materials (Scheme 2). The typical examples have been presented in the following two sections. There are three kinds of POM-based MOF single-crystal materials: (i) d/f-block metal ions-modified POM units directly connecting with organic ligands, (ii) POM anions resided within the cages of MOFs as templates, and (iii) porous inorganic-organic materials with POMs anions as pillars. As some POM-based CP single-crystal materials are not porous cases, so they cannot cover all the refined branches. According to the synthetic pathways of POM-loaded MOF materials, it can be achieved by three methods: (i) synthesis of MOF in the presence of POM, (ii) synthesis of POM inside the cages of formed MOF, and (iii) impregnation of MOF with a POM solution. Finally, we summarize some of the current issues and challenges that need to be addressed to work towards POM-based MOF materials and look ahead to possible emerging application areas. Our aim is to demonstrate the recent developments, discussion and challenges related to the applications of porous POM-based MOF materials, especially in the area of catalysis.

Scheme 2 The schematic view of POM-based MOF materials.



2. Synthesis

The investigation on POM-based MOF materials sprung up rapidly, thanks to the quick development of characterization techniques. In this set of materials, POMs are either part of the frameworks or are encapsulated within the cavities of MOFs. Self-assembly has proven to be a powerful method for synthesizing POM-based materials, but the mechanism is often masked by the common one-pot procedure. Additionally, such self-assembly process is highly dependent upon the reaction conditions (such as, concentration/type of metal oxide anion and heteroatom, pH, ionic strength, reducing agent, ligands, reaction temperature and so on), often to such a degree that total control is never easily achieved. Therefore, the preparation of POM-based MOF materials is one of the most challenging issues in synthetic chemistry. Generally, the synthetic methods reported for POM-based MOF materials can be classified into two groups: (i) direct synthesis for POM-based MOF single-crystal materials and (ii) post-synthetic modification of POM-loaded MOF materials.

2.1 Syntheses of POM-based MOF single-crystal materials

POM-based MOF single-crystal materials are often prepared by POM precursors, metal ions and organic ligands via conventional aqueous solution method or hydro/solvo/iono-thermal methods.

In conventional synthesis, the operations are easily conducted and most of the reactions have relatively good reproducibility.[13-16] For instance, Wang and co-workers prepared two 3D chiral POM-based frameworks utilizing enantiopure proline ligands, copper cations, and Keggin-type $[BW_{12}O_{40}]^{5-}$ anions as precursors.[13] However, the use of water or organic solvents (e.g. acetonitrile, methanol, and pyridine) would limit the reaction temperature. Though POM anions like to dissolve and then crystallize in water medium, inorganic-organic hybrid POM-based materials are not easy to form crystalline phases under conventional conditions owing to the poor solubility of organic ligands.

Therefore, hydrothermal (solvothermal) method has been adapted to the preparation of various metastable or intermediate POM species after they were well established for the synthesis of zeolites. This method, typically carried out under autogenous pressure in a sealed container, exploring the self-assembly of the products from soluble precursors. The reduced viscosity and the increased ionicity of the solvents under the conditions enhance the diffusion of the reactants and improve their solubility. A great number of POM-based compounds have been prepared by hydrothermal technique.[17-21] However, most of these materials were synthesized at higher temperature (usually above 140 °C), which always suffer from the formation of interpenetrating and is not conducive to the formation of porous materials. In addition, the cavities of resulting porous materials always occupied by water molecules, which is difficult to remove owing to the stronger hydrogen bonding between water molecules and frameworks. Moreover, a few groups studied the preparation of POM-based compounds by solvothermal approach.[22] It is not easy to prepare POM-based materials in organic systems, perhaps resulting from that the POM ions prefer to crystallize in water phase. It may be a challenge topic to obtain POM-based MOF compounds in an organic or mixed solvent media in the future. Additionally, it is relatively easy to generate porous POM-based materials by employing bulky organic cations as templates. It might be an important topic to synthesize porous POM-based materials using big organic molecules as solvents in the future work. However, there are some intrinsic shortcomings accompanied this method: the general reproducibility of the reactions requires perfect control of reaction parameters, and still limited reaction temperature because of safety concerns.

Researchers have focused on developing new synthetic approaches, because of the increasing interest in the applications and various challenges associated with the traditional synthesis methods. Morris et al. introduced ionothermal synthesis—a relatively new and effective method for preparing crystalline solids using ionic liquids (ILs) instead of water or organic solvents as reaction medium.[23,24] As ILs are simply composed of ions, the enthalpy of vaporization is significantly higher than that of water or organic solvents. So, Wang et al., Pakhomova et al., and others have extended this method for the synthesis of POMs.[25-30] The intrinsic value of this synthetic approach lies in the ability to offer an environmentally friendly and effective alternative to prepare porous POM-based MOF materials. Furthermore, the use of bulky IL cations could be a key point for the buildup of macroporous crystalline solids.

ILs have a number of additional properties, such as high chemical and thermal stability, a wide liquid range, and low toxicity, which make them ideal solvents for organic and inorganic synthesis and become the key motivation to be considered as green alternatives to volatile organic solvents.[31] The future of ionothermal synthesis is exciting and promising, and a better understanding of the principles that underpin the assembly mechanisms of POMs should result in their designed construction.

2.2 Synthesis of POM-loaded MOF materials

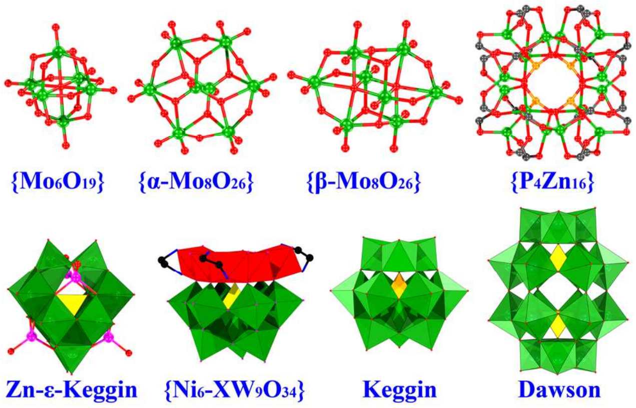
On the other hand, supporting POM in the host framework of a MOF obtained as POM-loaded MOF materials offers several advantages and has recently attracted tremendous attention. POM-loaded MOF materials can be achieved by different synthetic methods: (i) synthesis of MOF in the presence of POM, (ii) synthesis of POM inside the cages of formed MOF, and (iii) impregnation of MOF with a POM solution. Among the three methods, the promising strategy is the one-pot encapsulation of POMs into the pores of MOFs from aqueous or organic solutions (such as acetonitrile) at room temperature.[32,33] In addition, POM incorporated MOF thin films through grown on metallic substrates in various solvents at ambient conditions was performed by Martens and co-workers.[34] Furthermore, microwave synthesis was also investigated in order to obtain POM-loaded MOF materials.[35,36]

3. Porous POM-based MOF materials and their applications

3.1 POM-based MOF single-crystal materials and their applications

In this section, the POM-based MOF single-crystal materials with multidimensional open networks were introduced. They are composed of POM units and metal-organic fragments. That is to say, they mainly contain three components: POM anions (Scheme 3), organic ligands (Scheme 4) and metal ions. Here, we will present the POM-based MOF single-crystal materials as the following four aspects: (i) d/f-block metal ions-modified POM units directly connecting with organic ligands, (ii) POM anions resided within the cages of MOFs as templates; (iii) porous inorganic-organic materials with POMs anions as pillars, and (iv) nanoscale POM-based MOF crystalline materials.

Scheme 3 The POM units employed to construct POM-based MOF materials in the literatures.



Scheme 4 The organic ligands employed to construct POM-based MOF materials in the literatures.

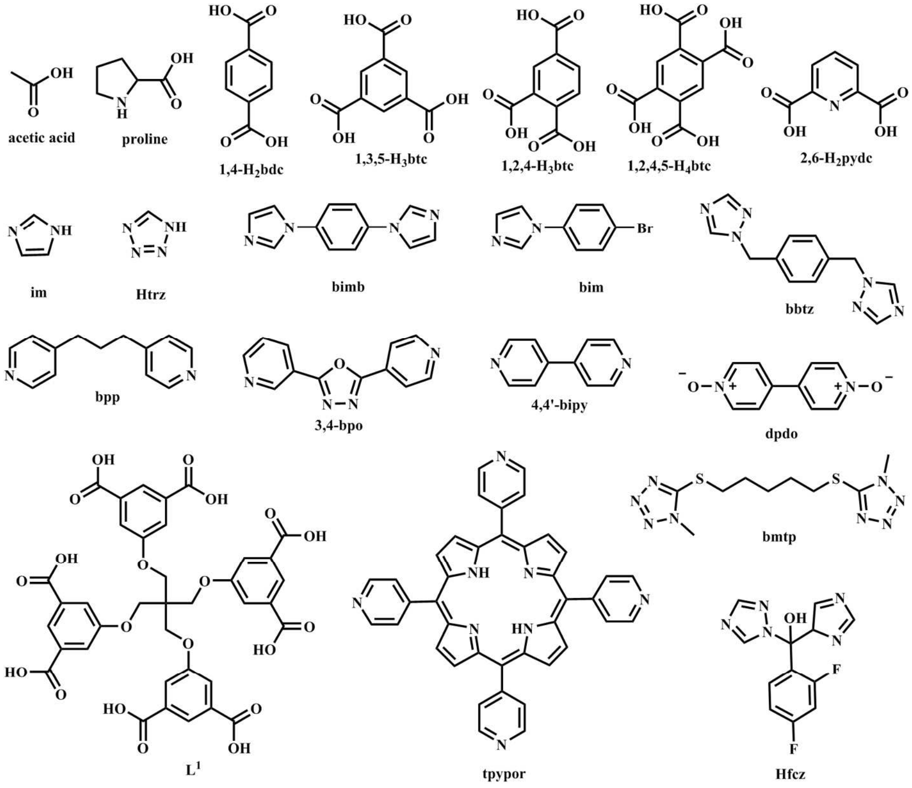


Table 1 Summary of MOF compounds with POMs units directly connecting with organic ligands

No.	Compounds	Space group	Topology	POM units	Organic linkers	Dimensionality	Ref.
1	$(TMA)_2[Mo_{22}O_{52}(OH)_{18}\{La(H_2O)_4\}_2\{La(CH_3CO_2)_2\}_4]\cdot 8H_2O$	*Cmca*	sql	$\{Mo_{22}O_{70}\}$	acetic acid	2D	48
2	$Na(4,4'\text{-bipy})[\varepsilon\text{-}PMo_{12}O_{40}Zn_4(H_2O)_2(4,4'\text{-bipy})_3]\cdot 10H_2O$	$P2_1/m$	6-connected	$\{PMo_{12}O_{40}Zn_4\}$	4,4'-bipy	2D	49
3	$[\varepsilon\text{-}PMo_{12}O_{35}(OH)_5\{La(H_2O)_3\}_4(1,3,5\text{-btc})_2]\cdot 44H_2O$	$P2_12_12$	rtl	$\{PMo_{12}O_{40}La_4\}$	1,3,5-H_3btc	3D	49
4	$[\varepsilon\text{-}PMo_{12}O_{37}(OH)_3\{La(H_2O)_4\}_4(1,2,4,5\text{-btc})]\cdot 24H_2O$	*P*-1	PtS	$\{PMo_{12}O_{40}La_4\}$	1,2,4,5-H_4btc	3D	49
5	$[CH_3NH_3][4,4'\text{-}H_2bipy][Zn_4(4,4'\text{-}H_2bipy)_3(H_2O)_2Mo^{V}_8Mo^{VI}_4O_{36}(PO_4)]\cdot 4H_2O$	$P2_1/c$	6-connected	$\{PMo_{12}O_{40}Zn_4\}$	4,4'-bipy	2D	50
6	$[GeMo^{V}_8Mo^{VI}_4O_{36}(\mu_2\text{-}OH)_4\{Ni(pda)\}_2\{Ni(pda)(4,4'\text{-bipy})_{0.5}\}\{Ni(pda)(4,4'\text{-bipy})\}]_n\cdot 7nH_2O$	*P*-1	sql	$\{GeMo_{12}O_{40}Ni_4\}$	4,4'-bipy	2D	51
7	$(TBA)_3[PMo^{V}_8Mo^{VI}_4O_{36}(OH)_4Zn_4(1,4\text{-bdc})_2]\cdot 2H_2O$	*C*2/*c*	crs	$\{PMo_{12}O_{40}Zn_4\}$	1,4-H_2bdc	3D	52
8	$(TBA)[PMo^{V}_8Mo^{VI}_4O_{37}(OH)_3Zn_4(im)(Him)]$	*Pbca*	sql	$\{PMo_{12}O_{40}Zn_4\}$	imidazole	2D	53
9	$(TBA)_3[PMo^{V}_8Mo^{VI}_4O_{36}(OH)_4Zn_4][1,3,5\text{-btc}]_{4/3}\cdot 6H_2O$	*I*222	ofp	$\{PMo_{12}O_{40}Zn_4\}$	1,3,5-H_3btc	3D	54
10	$(TBA)_3[PMo^{V}_8Mo^{VI}_4O_{37}(OH)_3Zn_4][1,3,5\text{-btc}]$	*Pnnm*	ins	$\{PMo_{12}O_{40}Zn_4\}$	1,3,5-H_3btc	3D	54
11	$(TBA)_3[PMo^{V}_8Mo^{VI}_4O_{37}(OH)_3Zn_4][1,3,5\text{-btc}]\cdot 8H_2O$	*Pmma*	sql	$\{PMo_{12}O_{40}Zn_4\}$	1,3,5-H_3btc	2D	54
12	$(TBA)_3\{PMo^{V}_8Mo^{VI}_4O_{36}(OH)_4Zn_4\}[1,4\text{-bdc}]_2$	$Pna2_1$	sql	$\{PMo_{12}O_{40}Zn_4\}$	1,4-H_2bdc	2D	55
13	$(TPA)_3\{PMo^{V}_8Mo^{VI}_4O_{37}(OH)_3Zn_4\}[1,3,5\text{-btc}]$	*Pcab*	sql	$\{PMo_{12}O_{40}Zn_4\}$	1,3,5-H_3btc	2D	55
14	$\{[Ni_6(OH)_3(H_2O)(en)_3(PW_9O_{34})][Ni_6(OH)_3(H_2O)_4(en)_3(PW_9O_{34})](1,4\text{-bdc})_{1.5}\}[Ni(en)(H_2O)_4]\cdot H_2O$	*P*-1	hcb	$\{\mathbf{Ni_6PW_9}\}$	1,4-H_2bdc	2D	57
15	$\{[Ni_6(OH)_3(en)_3(PW_9O_{34})](1,3,5\text{-Hbtc})\}[Ni(en)(H_2O)_3)]\cdot 2H_2O$	*Pbcm*	sql	$\{\mathbf{Ni_6PW_9}\}$	1,3,5-H_3btc	2D	57
16	$\{[\{Ni_6(OH)_3(H_2O)_5(PW_9O_{34})\}(1,2,4\text{-Hbtc})]\}\cdot H_2enMe\cdot 5H_2O$	$P4_1$	(3,5)-connected	$\{\mathbf{Ni_6PW_9}\}$	1,2,4-H_3btc	3D	57
17	$[Zn_{16}(HPO_3)_4]\mathbf{L}^{\mathbf{1}}_3$	*F*-43*c*	ddy/ftw	$\{P_4Zn_{16}\}$	$\mathbf{L^1}$	3D	63

$TMA^+ = NMe_4^+$; $TBA^+ = N(n\text{-}Bu)_4^+$; $TPA^+ = N(n\text{-}Pr)_4^+$; pda = 1,2-propanediamine; 1,2,4,5-H_4btc = 1,2,4,5-benzenetetracarboxylic acid; 1,2,4-H_3btc = 1,2,4-benzene tricarboxylate.

3.1.1 d/f-block metal ions-modified POM units directly connecting with organic ligands

POM clusters consist of metal ions and oxo ligands. Organic moieties can be grafted via addenda organometallic compounds on lacunary POM clusters.[37,38] For instance, the reaction of Keggin- and Dawson-based lacunary clusters with organotin, organogermanium and organosilicon compounds results in the formation of stable covalent bonds between POMs and organic moieties.[39,40] Anderson and Dawson clusters with formula of $[P_2W_{15}V_3O_{62}]^{9-}$ can be modified with trisalkoxo ligands by substituting the oxo ligands with alkoxo moieties.[41-43] Moreover, the organoimido derivatives of Lindqvist clusters were vigorously investigated after the establishment of DCC (DCC = N,N′-dicyclohexylcarbodiimide) protocol.[44-46] However, most of the POM-organic materials obtained by these methods were discrete or 1D chain. How to prepare POM-based MOF single-crystal materials by the covalent functionalization of POM clusters with organic linkers? Some POM chemists devoted their efforts to investigating this topic and obtained a series of excellent results.

Sécheresse and co-workers isolated the first ε-Keggin ion with a central phosphorous atom stabilized by four $\{La(H_2O)_4\}^{3+}$ capping groups at room temperature in 2002.[47] The crystallization of ε-Keggin ion in concentrated chloride solutions has indicated that the water molecules bound to the La^{3+} ions are labile and can be substituted by chloride ions. This result provides the possibility for functionalization of the ε-Keggin ion capped by four La^{3+} ions (La-ε-Keggin) by reaction with various organic ligands. Then, glutarate and squarate acids were employed to isolate two 1D chains built from alternating La-ε-Keggin ions and organic ligands connected through La−O links, which confirmed this inference.[48] Later, they used 1,3,5-benzene tricarboxylate (noted as 1,3,5-H_3btc) as organic linker to extend ε-Keggin units and isolated two 3D La-ε-Keggin MOFs under standard bench conditions and a 2D Zn-ε-Keggin MOF by hydrothermal method (Table 1).[49] Besides the experimental results, they also simulated two phases constructed from the connection of a hypothetical ε-Keggin capped by pentacoordinate transition metal Zn^{2+} ions by a rigid 1,4-benzene dicarboxylate (noted as 1,4-H_2bdc), in order to demonstrate the potentiality of Zn-ε-Keggin for the design of organic-inorganic hybrid materials with large pores. In addition, more examples of the ε-Keggin ions capped by four Zn^{2+} and Ni^{2+} cations have been generated *in situ* by hydrothermal synthesis.[50,51] The Keggin entity has the general formula with $\{\varepsilon\text{-}PMo^{V}_8Mo^{VI}_4O_{40-x}(OH)_xM_4\}$ ($M = Zn^{II}, Ni^{II}, La^{III}$; $x = 0 – 5$). The overall charge of the ε-Keggin unit mainly depends on the number of protonated oxo bridging ligands, which may vary from 0 to 5. Rodriguez-Albelo and co-workers performed a study on the targeted design and simulation of 21 zeolitic MOFs based on benzenedicarboxylate as the linker and Zn-ε-Keggin as building units as the node.[52] Among these structures, the cristobalite-like one was predicted to be the most stable structure. This prediction has been validated by the targeted synthesis of the first experimental structure, which was strikingly found to possess the cristobalite topology, with three interpenetrated networks. Furthermore, they selected 40 hypothetical polymorphs including dense minerals and zeotypes built from Zn-ε-Keggin and imidazole (noted as im) to compute their relative stabilities.[53] The isolation of imidazole-based MOF is an encouraging step towards the synthesis of a new family of POM-based MOF compounds. Moreover, the triangular trimesate acid was employed as linkers to modify tetrahedral Zn-ε-Keggin ions, and three novel electroactive POM-based MOF compounds based on monomeric, dimeric or chain-like Zn-ε-Keggin units for hydrogen evolution reaction were generated under hydrothermal conditions (Fig. 1).[54] Given the recognized advantages of graphene and the well-known strong chemisorption between POMs and carbon materials, Rodriguez-Albelo et al. prepared POM@graphene hybrids (POM@G) via a reduction process of graphite oxide (GO) in which Zn-ε-Keggin-based MOFs were worked as reducing agents.[55] The POM@G hybrids with the high quality of the graphene constituent, enhanced electrochemical properties, large surface area and remarkable stability under various conditions, offer great promise for producing a new class of nanomaterials for a wide range of applications in the photo/electro catalytic and electroanalytical domains.

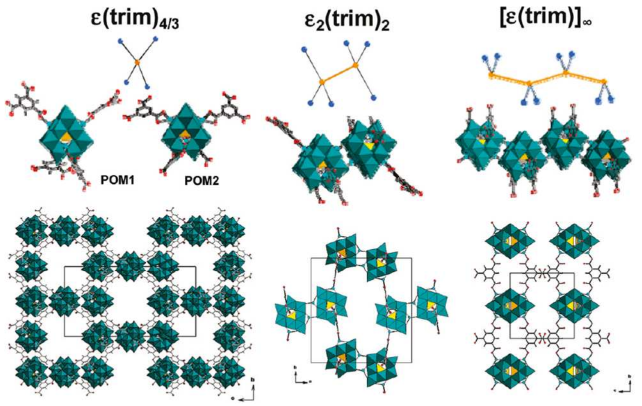


Fig. 1 POM building blocks of $\varepsilon(trim)_{4/3}$, $\varepsilon_2(trim)_2$ and $[\varepsilon(trim)]_\infty$, a view of their unit cell, and their schematic representation; black lines indicate connections between POMs and trim linkers, while orange lines symbolize condensation reactions between POMs. Adapted with permission from ref. 54. Copyright 2011 American Chemical Society.

In 2007, Yang and co-workers extended the preparation of transition-metal-substituted polyoxotungsates (POTs) from a conventional aqueous solution method to hydrothermal technique. A series of novel Ni_6-substituted POTs, $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6L_3(B\text{-}\alpha\text{-}XW_9O_{34})]$ ($\{\mathbf{Ni_6XW_9}(H_2O)_6\}$, where $\mathbf{Ni_6} = [Ni_6(\mu_3\text{-}OH)_3L_n]^{9+}$, $\mathbf{XW_9} = \{B\text{-}\alpha\text{-}[XW_9O_{34}]\}$ and B indicates the type of isomer of $\alpha\text{-}XW_9O_{34}$, X = Si or P, L = en or enMe; en = ethylenediamine, enMe = 1,2-diaminopropane), were isolated by studying the new reaction systems containing vacant POM precursors, metal ions, and organic amines under hydrothermal conditions.[56] The Ni_6-substituted POTs are composed of rich terminal water ligands with different orientations, which offers the possibility for making new derivatives by replacing the water ligands with other inorganic or organic groups. They introduced various rigid carboxylate ligands into the well-defined hydrothermal systems for *in situ* generation of Ni_6-substituted POTs and successfully isolated three POM-based MOF compounds (Fig. 2).[57] As a continuation of their work, tris(hydroxymethyl)aminomethane (noted as Tris) was successfully grafted onto the surface of a Ni_6-substituted POTs formed *in situ* to further generate a 3-connected building block. The cooperative assembly of Tris functionalized 3-connected building blocks and 1,3,5-H_3btc result in a cubic POM-organic molecular cage with high thermal and hydrothermal stability.[58] The key points of the synthetic procedures have been well established, which indicates that this strategy offers an effective and feasible way for designing and making new POM-based MOF materials.[59]

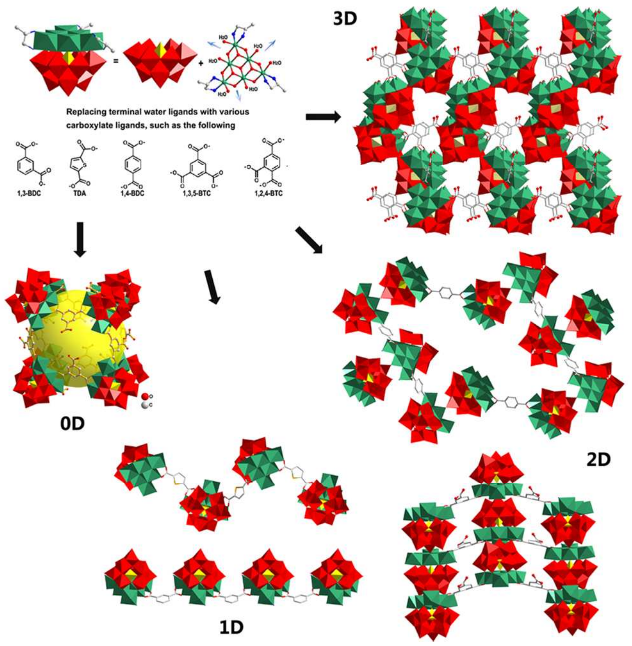


Fig. 2 Designed syntheses of TMSP-based cluster organic frameworks. WO_6: red, NiO_4N_2 or NiO_6: green, PO_4: yellow. Adapted with permission from refs. 57 and 58. Copyright 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2010 American Chemical Society.

As is known, eight isomeric forms of octamolybdates have been documented, that is, the *α*-, *β*-, *γ*-, *δ*-, *ε*-, *ζ*-, *η*- and *θ*-isomers, sorted by different numbers of $[MoO_4]$, $[MoO_5]$ and $[MoO_6]$ clusters. These isomers are easily transformed into each other under mild environmental changes and can be conveniently obtained under hydrothermal conditions with controlled pH values. It is worth mentioning that γ-Mo_8 anion, which has six $[MoO_6]$ and two $[MoO_5]$ units, possesses the unique merits to construct organically functionalized 3D POM-based frameworks containing Mo–N bonds.[60-62]

Conventionally, POMs are comprised of early-transition metal with d^0 or d^1 electronic configurations. The metal oxide clusters entirely consisted of late transition metal ions with d^{10} electronic configuration are rarely available owing to the instability of extremely high negative charge. Compared with conventional POM clusters, d^{10} metal-oxygen clusters may have some special properties resulting from the inherent characteristics of late transition metals. In this sense, how to lower the overall negative charge to obtain d^{10} metal-oxygen clusters is a significant and challenging task in synthetic chemistry and material science. Lan and Su et al. employed a semirigid ligand containing eight carboxyl groups, 5,5'-(2,2-bis((3,5-dicarboxyphenoxy)methyl) propane-1,3-diyl)bis(oxy)diisophthalic acid (**L^1**), to study the system of crystalline catalysts containing d^{10} metal-oxygen clusters. Fortunately, an unprecedented 3D heteropolyoxozincate organic compound with (3,4,24)-connected **ddy** topology, $[Zn_{16}(HPO_3)_4]L^1_3$ (**IFMC-200**), has been isolated, which contains the first example of 24-connected node constructed from a single d^{10} metal cluster (Fig. 3).[63] The new strategy with "carboxyl group-stabilized polyoxozincate cluster" mode helps to lower the overall negative charge, and successfully proved that it is an efficient method to isolate a late transition metal-oxygen cluster. **IFMC-200** exhibits superior thermal stability, good water-stability, tolerance to acid and base, and Lewis acidity, which enables its catalytic activity in the esterification reaction of free fatty acids with different alcohols. Surprisingly, **IFMC-200** exhibits abnormal catalytic result that is favour for the conversion of long-chain fatty acids under the same conditions compared as the previous reports.

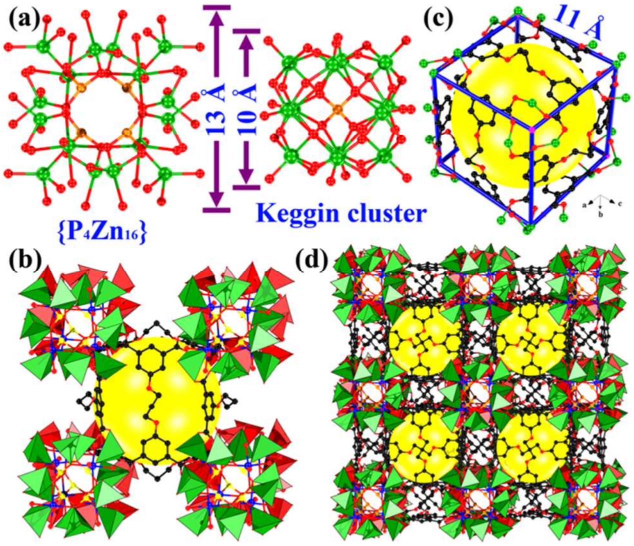


Fig. 3 (a) The structures of $\{P_4Zn_{16}\}$ (left) and Keggin-type cluster (right); (b) and (c) the cage structure in **IFMC-200**; and (d) the 3D framework of **IFMC-200**.

In most of the above cases, POM clusters were involved in M-□-Keggin or $\{Ni_6XW_9(H_2O)_6\}$ (M = Zn or La; X = P or Si), while organic ligand were limited to N-containing or carboxylic-containing rigid organic species. In this type of POM-based MOF materials, well-defined POM units directly connect with organic ligands. POM unit without modification is difficult to directly connect with organic species to form multidimensional structures. As a result of POM units and deprotonated organic ligands always exist in anionic forms; it is difficult to form neutral compounds from these two anionic moieties. In this regard, it is necessary to modify POM anions with d/f-bolck metal cations for the first step. The grafting makes it easier to obtain such POM-based MOF single-crystal materials, modified POM units directly connecting with organic ligands. It is suggested that lowering the negative charge of POM moieties through TM-decorated/substituted POM clusters is an efficient and promising method to obtain POM-based MOF compounds. However, this kind of POM-based MOF materials is not a diverse family and rarely reported. The reason for this perhaps associated with that either carboxylic-containing or N-containing ligands are liable to be protonated in acidic media and difficult to connect with anionic POM units. From the experimental point of view, the modification of POM anions by metal cations always generated in situ through hydrothermal technique. If the organic ligand can also be generated in situ, it can coordinate to the modified POM units immediately, in order to avoid being protonated. Therefore, it is a promising method to generate ligand in situ in further research. In addition, the modification of POM units is limited to saturated or vacant Keggin units. Maybe the POM units will expand to more species in the future. More importantly, as for M-□-Keggin system, the electrochemical behaviours were investigated, while for $\{Ni_6XW_9(H_2O)_6\}$ system, the magnetic properties were surveyed in details. New properties of as-synthesized materials, such as catalysis, will be explored, which is to ensure the vitality of such materials.

3.1.2 POM anions resided within cages of MOFs as templates

New porous materials with regular, bulky, accessible cages and channels, for instance, zeolites and zeolite-like compounds, have aroused increasing interest owing to their potential applications in gas storage, heterogeneous catalysis, chemical separations, and proton conductivity.[64-68] The use of templates such as organic amine cations is a current important synthetic strategy in this area. In addition, large inorganic anions can also be employed as templates to construct novel porous frameworks.[69] In this aspect, POM anions are one of the suitable inorganic templates due to their versatile structural topologies and abundant chemical combinations that endow them with controllable shape, size and high negative charges (Table 2).[70-72] For instance, Zubieta prepared a $\{Mo_6O_{19}\}$-templated 3D $[\{Fe(tpypor)\}_3Fe]_n^{4n+}$ framework (tpypor = tetrapyridylporphyrin),[70] and Keller employed $PW_{12}O_{40}^{3-}$ as a non-coordinating anionic template to construct a 3D Cu^{I}-4,4'-bipy (4,4'-bipy = 4,4'-bipyridine) MOF.[71] In 2009, the structures of POM containing coordination polymers in which the combination of POMs and metal-organic polymers is through host-guest supramolecular interactions, such as weak coordination interactions, electrostatic interaction, and hydrogen bonding, were well-summarized by Lu and co-workers.[73] In this section, we mainly focused on the 3D MOFs with POM anions as templates.

Naruke and co-workers prepared three nanoporous crystalline compounds that consists of $[Cu_3(1,3,5\text{-btc})_2(H_2O)_3]_n$ framework (also known as **HKUST-1**) accommodating α-Keggin anions as evidenced by IR, and ^{29}Si and ^{31}P MAS NMR spectra.[74] Similar system was thoroughly characterized by Hundal's group.[75] In 2009, Liu and Su et al. obtained a series of crystalline compounds from a simple one-step hydrothermal reaction, in which the catalytically active Keggin anions were alternately arrayed as noncoordinating guests in the cuboctahedral cages of **HKUST-1** host matrix, named as **NENU-n** series (Fig. 4).[76] In **NENU-n**, the main properties of the framework were preserved, and high POM loadings (35–45 wt%) were observed, which exceeded that of loadings in traditional supports. Moreover, agglomeration is avoided owing to the confinement within MOF cavities. The acid catalytic performance of **NENU-3** was assessed through the hydrolysis of esters in excess water, which showed high catalytic activity and can be used repeatedly without activity loss.

Furthermore, **NENU-29** and **-30** were prepared by immersing the crystals of as-synthesized **NENU-3** and **-4** in saturated solutions of $LiNO_3$ for a week, respectively.[77] In these two compounds, the POM anions and Li^+ ions act as guests within the **HKUST-1** hosts. H_2 adsorption studies demonstrated that the guests play a key role in increasing the H_2 adsorption capacity of the frameworks. Later, **NENU-28** were synthesized with an analogy method and used as adsorbent towards volatile organic compounds.[78]

Table 2 Summary of POM-templated MOF compounds

No.	Compounds	Space group	Topology[a]	POM units	Organic linkers	Dimensionality	Ref.
1	$[\{Fe(tpypor)\}_3Fe(Mo_6O_{19})_2]\cdot xH_2O$	*Pn*-3	pcu	$\{Mo_6O_{19}\}$	tpypor	3D	70
2	$[Cu_3(4,4'\text{-bipy})_5(MeCN)_2]PW_{12}O_{40}\cdot 2C_6H_5CN$	*C*2/*c*	(3,3,4)-connected	$\{PW_{12}O_{40}\}$	4,4'-bipy	3D	71
3	$[Cu_3(1,3,5\text{-btc})_2(H_2O)_3]_2Na_3PW_{12}O_{40}\cdot nH_2O$	*Fm*-3*m*	tbo	$\{PW_{12}O_{40}\}$	1,3,5-H_3btc	3D	75
4	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6$ $[H_2SiW_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-1**)	*Fm*-3*m*	tbo	$\{SiW_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
5	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6$ $[H_2GeW_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-2**)	*Fm*-3*m*	tbo	$\{GeW_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
6	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6$ $[HPW_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-3**)	*Fm*-3*m*	tbo	$\{PW_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
7	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6$ $[H_2SiMo_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-4**)	*Fm*-3*m*	tbo	$\{SiMo_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
8	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6[HPMo_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-5**)	*Fm*-3*m*	tbo	$\{PMo_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
9	$[Cu_2(1,3,5\text{-btc})_{4/3}(H_2O)_2]_6$ $[HAsMo_{12}O_{40}]\cdot(TMA)_2\cdot xH_2O$ (**NENU-6**)	*Fm*-3*m*	tbo	$\{AsMo_{12}O_{40}\}$	1,3,5-H_3btc	3D	76
10	$Li_2[Cu_{12}(1,3,5\text{-btc})_8\cdot 12H_2O][HPW_{12}O_{40}]\cdot 27H_2O$ (**NENU-29**)	*Fm*-3*m*	tbo	$\{PW_{12}O_{40}\}$	1,3,5-H_3btc	3D	77
11	$Li_2[Cu_{12}(1,3,5\text{-btc})_8\cdot 12H_2O][H_2SiMo_{12}O_{40}]\cdot 25H_2O$ (**NENU-30**)	*Fm*-3*m*	tbo	$\{SiMo_{12}O_{40}\}$	1,3,5-H_3btc	3D	77
12	$K_2[Cu_{12}(1,3,5\text{-btc})_8H_2O_n][HPW_{12}O_{40}]$ (**NENU-28**)	*Fm*-3*m*	tbo	$\{PW_{12}O_{40}\}$	1,3,5-H_3btc	3D	78
13	$H_3[(Cu_4Cl)_3(1,3,5\text{-btc})_8]_2[PW_{12}O_{40}]\cdot(TMA)_6\cdot 3H_2O$ (**NENU-11**)	*Fm*-3*m*	sod	$\{PW_{12}O_{40}\}$	1,3,5-H_3btc	3D	79
14	$H_4[(Cu_4Cl)_3(1,3,5\text{-btc})_8]_2[SiW_{12}O_{40}]\cdot(TMA)_6\cdot 3H_2O$ (**NENU-15**)	*Fm*-3*m*	tbo	$\{SiW_{12}O_{40}\}$	1,3,5-H_3btc	3D	80
15	$[Cu_3(1,3,5\text{-btc})_2]_4[(TMA)_4CuPW_{11}O_{39}H]$	*Fm*-3*m*	tbo	$\{CuPW_{11}O_{39}\}$	1,3,5-H_3btc	3D	81
16	$[Co_4(dpdo)_{12}][H(H_2O)_{27}(CH_3CN)_{12}][PW_{12}O_{40}]_3$	*Im*-3	pcu	$\{PW_{12}O_{40}\}$	dpdo[b]	3D	82
17	$\{[Ni(dpdo)_3]_4(PW_{12}O_{40})_3[H(H_2O)_{27}(CH_3CN)_{12}]\}_n$	*Im*-3	pcu	$\{PW_{12}O_{40}\}$	dpdo	3D	83
18	$[Cu_2(H_2O)_2(bpp)_2Cl][PM_{12}O_{40}]\cdot\sim 20H_2O$ (M = W or Mo)	*P*4$_2$/*n*	bcu	$\{PM_{12}O_{40}\}$	bpp	3D	85
19	$[Cu_4(bmtp)_4][SiW_{12}O_{40}]$	*P*2$_1$/*c*	pcu	$\{SiW_{12}O_{40}\}$	bmtp[c]	3D	86
20	$[Cu(3,4\text{-bpo})_2(H_2O)(SiW_{12}O_{40})]\cdot(3,4\text{-}H_2bpo)\cdot 7H_2O$	*Pna*2$_1$	sql	$\{SiW_{12}O_{40}\}$	3,4-bpo[d]	2D	87
21	$\{[Ln(H_2O)_4(pydc)]_4\}[XMo_{12}O_{40}]\cdot 2H_2O$ (Ln = La, Ce and Nd; X = Si or Ge)	*C*2/*c*	gis	$\{XMo_{12}O_{40}\}$	H_2pydc	3D	88
22	$[Ln(H_2O)_4(pydc)]_4[SiW_{12}O_{40}]\cdot 2H_2O$ (Ln = La, Ce and Nd)	*I*4$_1$/*a*	gis	$\{SiW_{12}O_{40}\}$	H_2pydc	3D	89
23	$Ln_4(pydc)_4[SiW_{12}O_{40}]\cdot 19H_2O$ (Ln = Eu, Gd, Tb and Dy)	*C*2/*c*	gis	$\{SiW_{12}O_{40}\}$	H_2pydc	3D	90
24	$[Ln(pydc)(H_2O)_n]_4[SiW_{12}O_{40}]\cdot 4H_2O$ (Ln = Tm, Y, Pr, La, Sm and Eu)	*I*4$_1$/*a*	gis	$\{SiW_{12}O_{40}\}$	H_2pydc	3D	91
25	$Cu_3(bimb)_5(bim)_2(PMo_{12}O_{40})_2$	*P*2$_1$/*n*	dmp	$\{PMo_{12}O_{40}\}$	bimb[e] and bim[f]	3D	92
26	$\{[Ag_2(trz)_2][Ag_{24}(trz)_{18}]\}[PW_{12}O_{40}]_2$	*Pn*-3*m*	pcu	$\{PW_{12}O_{40}\}$	Htrz	3D	93
27	$\{[Cd\text{-}(DMF)_2Mn^{III}(DMF)_2tpypor]$ $(PW_{12}O_{40})\}\cdot 2DMF\cdot 5H_2O$	*C*2/*c*	sql	$\{PW_{12}O_{40}\}$	tpypor	2D	94
28	$[M_2(4,4'\text{-bipy})_3(H_2O)_2(ox)][P_2W_{18}O_{62}]\cdot 2(4,4'\text{-}H_2bipy)\cdot 3H_2O$ (M = Co and Ni)	*P*2$_1$/*m*	pcu	$\{P_2W_{18}O_{62}\}$	4,4'-bipy	3D	95

[a] the topology of MOF structures; [b] dpdo = 4,4'-bipyridine-N,N'-dioxide; [c] bmtp = 1,5-bis(1-methyl-5-mercapto-1,2,3,4-tetrazole)pentane; [d] 3,4-bpo = 2-(3-pyridyl)-5-(4-pyridyl)-1,3,4-oxadiazole; [e] bimb = 1,4-bis(1-imidazolyl)benzene; [f] bim = 1-(4-bromophenyl)-1*H*-imidazole.

As a continuation of the above works, Liu and Su et al. hydrothermally isolated a sodalite-type porous POM-based framework, **NENU-11**, with Keggin ions as templates in 2011 (Fig. 5).[79] **NENU-11** displayed its potential application in the removal of nerve gas with encapsulated $\{PW_{12}O_{40}\}$ as catalytically active center. **NENU-11** shows a rapid adsorption of dimethyl methylphosphonate (DMMP), reaching 1.92 mmol g^{-1} within 100 minutes (15.5 DMMP molecules per formula unit), which is much higher than previous data reported for other MOFs with higher surface areas. The conversion of DMMP to methyl alcohol was 34% at room temperature, which increased gradually with temperature, reaching the optimum with 93% at 50 °C. Later, they employed **NENU-15** to assess its synergistic effect between host frameworks and guest POMs in NO removal.[80] **NENU-15** not only displayed good adsorption behavior for NO, but also exhibited superior activity in NO decomposition.

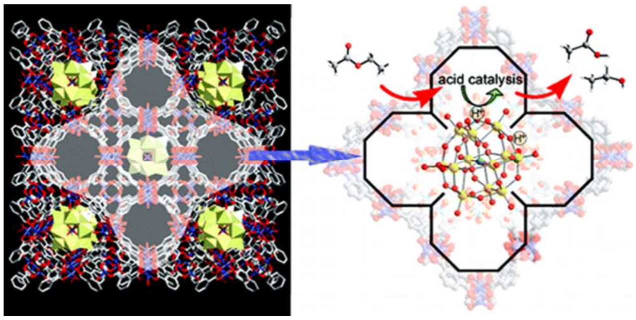


Fig. 4 View of a (001) sheet with two kinds of pores in **NENU-n**, and **NENU-3** was used as catalyst in the hydrolysis of esters. Reprinted with permission from ref. 76. Copyright 2009 American Chemical Society.

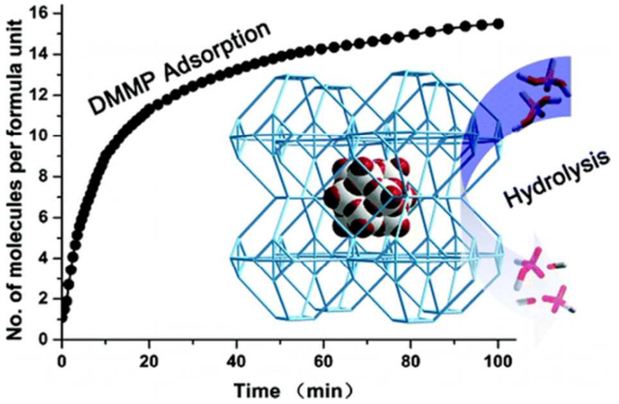


Fig. 5 Variation of DMMP uptake over time for **NENU-11** at 298 K and 1 bar under flowing He. Reprinted with permission from ref. 79. Copyright 2011 American Chemical Society.

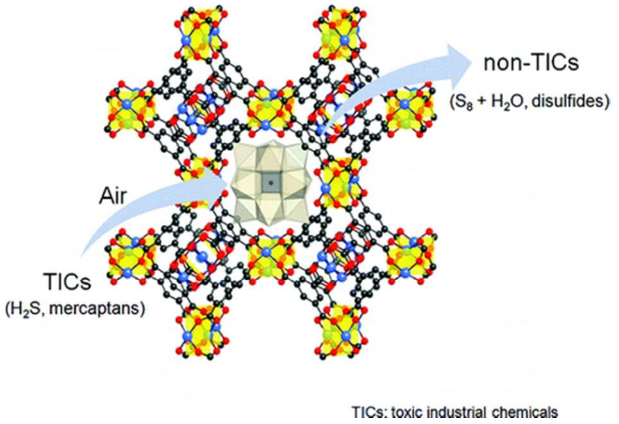


Fig. 6 The oxidation of H_2S to S_8 catalyzed by $[Cu_3(C_9H_3O_6)_2]_4[\{(CH_3)_4N\}_4CuPW_{11}O_{39}H]$. Reprinted with permission from ref. 81. Copyright 2011 American Chemical Society.

In 2011, Hill et al. employed $[CuPW_{11}O_{39}]^{5-}$ to fit the pores of **HKUST-1**, resulting in a new crystalline catalyst, $[Cu_3(C_9H_3O_6)_2]_4[\{(CH_3)_4N\}_4CuPW_{11}O_{39}H]$ (Fig. 6), which efficiently catalyzes the detoxification of various sulfur compounds including H_2S to S_8 using only ambient air.[81] The results suggested that it is a readily reisolated and reused heterogeneous catalyst that requires only the ambient environment for some oxidation processes, indicating its potential value as a versatile and robust catalytic decontaminant.

Besides this kind of POM-templated Cu-trimesic acid materials, there are many other MOF networks containing POM anions as templates. They will be described as follows.

In 2006, Duan and co-workers reported a family of 3D non-interwoven POM-based MOF compounds with cubic cavities occupied by the Keggin anions $[PW_{12}O_{40}]^{3-}$ and water clusters $[H(H_2O)_{27}]^+$ (Fig. 7).[82] The results of both the X-ray diffraction study and the calculation suggest that the excess proton is positioned in the centre of the protonated water cluster, which encouraged them to extensively study this system.[83,84] They employed the as-synthesized compounds as heterogeneous acid catalysts for the hydrolysis of phosphodiester bond cleavage for the first time.[84]

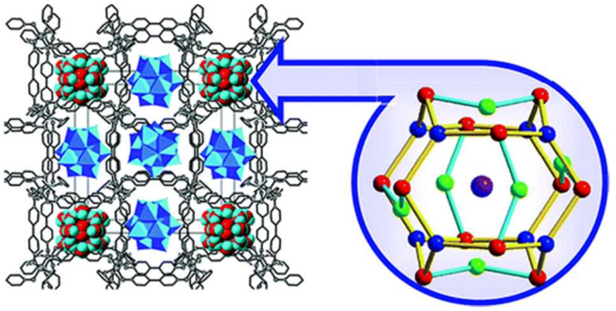


Fig. 7 The 3D non-interwoven POM-based MOF compounds with cubic cavities occupied by the Keggin anions $[PW_{12}O_{40}]^{3-}$ and water clusters $[H(H_2O)_{27}]^+$. Reprinted with permission from ref. 82. Copyright 2006 American Chemical Society.

In 2008, Wang et al. reported two Keggin-templated porous frameworks, which constructed by 3D eight-connected coordination polymer hosts $[Cu_2(H_2O)_2(bpp)_2Cl]_n^{3n+}$ and ball-shaped Keggin-type guests $[PM_{12}O_{40}]^{3-}$ as templates (bpp = 1,3-bis(4-pyridyl)propane).[85] The photoluminescent properties at ambient temperature and the electrochemical behaviors were investigated, which displays good electrocatalytic activity toward the reduction of nitrite. Furthermore, a series of Keggin-templated porous frameworks based on flexible or rigid N-containing ligands have been prepared by the same group.[86,87] In recent years, Hu et al. synthesized a family of 3D 4-connected cationic framework $\{[Ln(H_2O)_4(pydc)]_4\}^{4+}$ (Ln = La, Ce and Nd, H_2pydc = pyridine-2,6-dicarboxylic acid) with gismondine topology, in which ball-shaped Keggin $[XM_{12}O_{40}]^{4-}$ (X = Si and Ge, M = Mo and W) were acted as templates.[88,89] Soon after, Niu et al. and Huang et al. studied the Ln-pydc/Keggin system and isolated a series of 3D MOFs that contain $[SiW_{12}O_{40}]^{4-}$ anions as templates.[90,91] Although the nonlinear channels of 3D host frameworks are filled with Keggin ions, some of these compounds exhibit ethanol-sorption properties. A peanut-like POM-based MOF compound with (4,5)-connected topology was successfully constructed by Su and co-workers, in which Keggin anions embed in the voids of peanut-like shell to act as cores.[92]

Lu and co-workers carried out a study on Ag^+/Htrz/Keggin system (Htrz = 1*H*-1,2,4-triazole)[93] and reported a 3D polycatenated framework with Keggin ions encapsulated in the adamantine-like nanocages formed by triazole ligands,

$[Ag_2(trz)_2][Ag_{24}(trz)_{18}][PW_{12}O_{40}]_2$ (Fig. 8). The Keggin ions work as templates to directly form a 3D polycatenated framework, while a 2D $[Ag(trz)]_\infty$ network would be obtained by the self-assembly of Ag^+ cations and triazole in the absence of Keggin ions. This result indicates that understanding the encapsulation mechanism will ultimately enable the rational design of new generations of POM-based MOF structures.

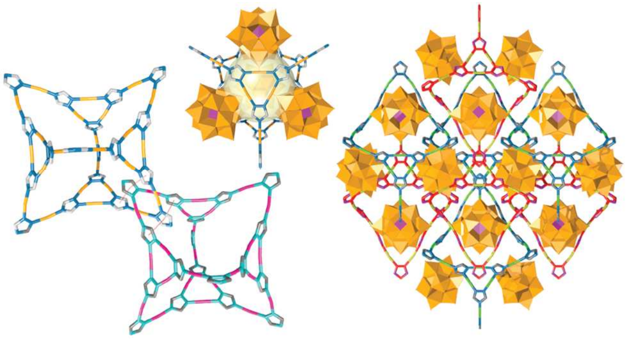


Fig. 8 The 3D structure of $[Ag_2(trz)_2][Ag_{24}(trz)_{18}][PW_{12}O_{40}]_2$. Adapted with permission from ref. 93. Copyright 2010 Nature Publishing Group.

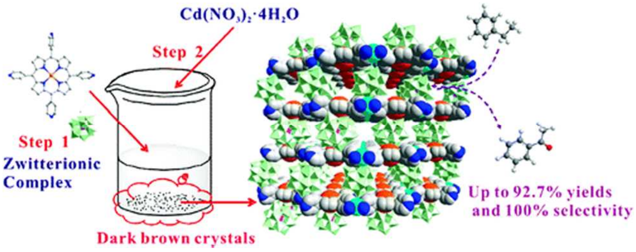


Fig. 9 A Keggin-templated Mn^{III}-metalloporphyrin-based hybrid layered framework as a highly effective heterogeneous catalyst. Reprinted with permission from ref. 94. Copyright 2012 American Chemical Society.

Recently, Wu et al. developed a two-step synthesis strategy for the effective preparation of a novel layered POM-Mn^{III}-metalloporphyrin-based hybrid framework (Fig. 9)[94] The hybrid solid demonstrates remarkable capability for scavenging of dyes and for heterogeneous selective oxidation of alkylbenzenes with excellent product yields and 100% selectivity. This work provides a new pathway for the future synthesis of POM-porphyrin hybrid materials with merged functionality for potential applications.

Moreover, three Wells-Dawson-templated MOFs were reported by Liu et al. and the electrochemistry experiments indicate they have good electrocatalytic activities toward the reduction of nitrite ions.[95,96]

In summary, this kind of POM-based MOF materials was always isolated by hydrothermal method. In the previous reports, most of transition metal ions in use are Cu^{2+} ions, while there are also several examples involved in lanthanide ions. As for POM-templated MOF materials, templates are mainly Keggin anions, while Dawson and homopolyoxometalate ions have occasionally been employed. A major reason for this result can be ascribed to the requirement of size matching between POM units and MOF networks. Hence, it is an important challenge to design and prepare new MOFs composed of metal ions (or metal clusters) and organic ligands, in which the sizes of MOF cavities and POM blocks are well-matched. POM-templated MOF materials combine well-defined crystalline structures, high surface areas, regular and tunable cavities, and high catalytic active site density. Therefore, their catalytic performances have caught the attention of researchers worldwide in recent years. We believe that further research in the preparation of POM-templated MOF materials and their application in catalysis will be a highlight in MOFs science and will be strengthened in the future. Moreover, their application in other fields will be worthy to be explored.

Table 3 Summary of 3D porous POM-pillared MOF compounds

No.	Compounds	Space group	Topology	POM units	Organic linkers	Ref.
1	$KH_2[(D\text{-}/L\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}]·5H_2O$	$P4_32_12$/ $P4_12_12$	(3,3,4,4)-connected	$\{BW_{12}O_{40}\}$	D-/L-proline	13
2	$(TBA)_2[Cu^{II}(bbtz)_2(\beta\text{-}Mo_8O_{26})]$	$P2_1/c$	pcu	$\{\beta\text{-}Mo_8O_{26}\}$	bbtz	30
3	$(TBA)_2[Cu^{II}(bbtz)_2(\alpha\text{-}Mo_8O_{26})]$	$C2/c$	sxd	$\{\alpha\text{-}Mo_8O_{26}\}$	bbtz	30
4	$(TBA)_2[Cu^{II}(bbtz)_2(\alpha\text{-}Mo_8O_{26})]$	$P2_1/c$	pcu	$\{\alpha\text{-}Mo_8O_{26}\}$	bbtz	30
5	$[Cu^ICu^{II}(Cu^{II}fcz)_2(H_2O)_5(PMo^{VI}{}_{10}Mo^V{}_2O_{40})]·6H_2O$	$P2_1/n$	(3,4,5,6)-connected	$\{PMo^{VI}{}_{10}Mo^V{}_2O_{40}\}$	Hfcz	100
6	$[Cu^I{}_2(Cu^{II}fcz)_2(H_2O)_2(PMo^{VI}{}_8V^V{}_3V^{IV}{}_3O_{42})]·6H_2O$	$C2/c$	(3,4,6)-connected	$\{PMo^{VI}{}_8V^V{}_3V^{IV}{}_3O_{42}\}$	Hfcz	100

3.1.3 Porous inorganic-organic materials with POMs anions as pillars

Another remarkable approach for construction of multifunctional POM-based materials is the use of the coordination ability of polyanions to combine with different transition metal-organic fragments (Table 3). As a result, many POM-based inorganic-organic hybrid materials have been reported recently besides the above-mentioned two kinds. And this kind of POM-based inorganic-organic materials has been well-reviewed by Dolbecq et al. in 2010.[11] In most cases, this kind of POM-based materials consisting of organic ligands, transition metal (or lanthanide) ions, and POM units was isolated by hydrothermal method. Only a few examples were prepared by conventional aqueous or ionothermal approach. In addition, this kind of POM-based materials exhibit diverse properties ranging from optical, electronic to magnetic fields. However, it is difficult to obtain POM-based inorganic-organic frameworks with open networks due to the limitations of the choice of organic ligands, the characteristics of POM anions and synthesis methods. Although a lot of researchers adopt the concept of POM-based MOF in the literatures, only three POM-based CP compounds with 3D open networks were introduced as examples in this part. In these cases, POM units play the role of pillars in the formation of POM-based MOF single-crystal materials.

We try to analyse and explain the reasons why these POM-based hybrid compounds do not form porous networks. Firstly, the preparation strategy: most of such materials were synthesized at higher temperature by employing water as solvent (usually above 140 °C). It is contrary to the classical preparation conditions of MOFs. MOFs were commonly synthesized in organic solvents at lower temperature, in which organic solvents play the role of templates, favouring in the formation of porous frameworks. In addition, solvothermal reactions at lower temperature can effectively avoid the formation of interpenetrating and generate porous architecture. Certainly, this is also related to the nature of POM anions, which like to crystallize in water phase. It is not easy to synthesize POM-based hybrid materials in organic solvents. It is perhaps a difficult and challenge topic to synthesize porous POM-based MOF compounds in an organic or mixed solvent medium in the future. Secondly, the choice of organic ligands: in the reported POM-based hybrid compounds, most of the organic ligands used were flexible or semirigid ligands (for instance, imidazole, pyridine and their derivatives). The employment of flexible or semirigid ligands tends to form interpenetrating structure rather than porous structure at higher temperature. Finally, the channels always occupied by water molecules in the few resulting porous materials. Moreover, the water molecules resided in the channels is difficult to remove owing to the stronger hydrogen bonding between water molecules and frameworks. Thus, the as-synthesized POM-based materials are difficult to have high specific surface areas. So far, only a few specific surface areas of such materials were successfully measured. That is to say, it is difficult to obtain a real porous POM-based MOF materials. Herein, we chose the following examples as the representatives of porous inorganic-organic materials with POM anions as pillars to introduce from such materials according to the synthesis methods.

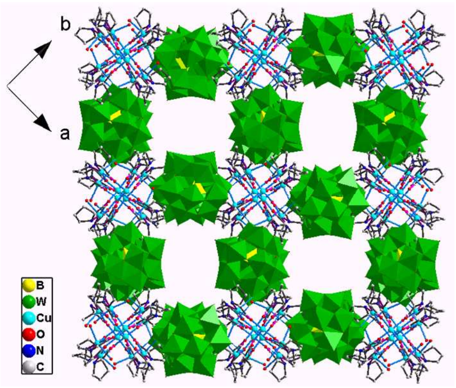


Fig. 10 The 3D structure of $KH_2[(D\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}]\cdot 5H_2O$. Reprinted with permission from ref. 13. Copyright 2006 John Wiley and Sons.

In 2006, Wang and Su et al. prepared two chiral POM-based architectures, $KH_2[(D\text{-}/L\text{-}C_5H_8NO_2)_4(H_2O)Cu_3][BW_{12}O_{40}]\cdot 5H_2O$ by conventional aqueous solution method (Fig. 10).[13] In these two compounds, the copper(II) centres are connected together by proline ligands to yield a 1D coordination polymer chain, which are further covalently bonded to terminal oxo groups of the Keggin clusters to form a unique 3D open framework. The ICD in the POM clusters can be clearly seen in the CD spectrum owing to the chirality transfer from chiral proline ligands to POM clusters through the copper bridges leading to a lowering of the symmetry. The CD spectra were virtually unchanged with time, indicating that both enantiopure compounds are enantiomerically stable in aqueous solution. Subsequently, this work was highlighted in *Nature Materials*.

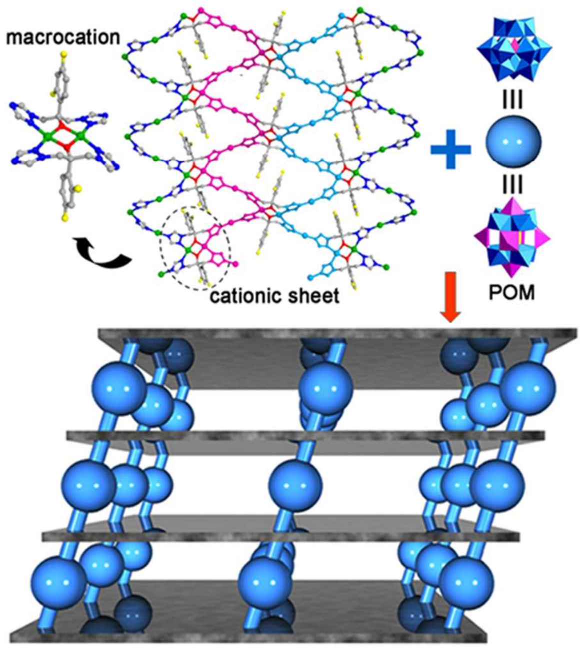


Fig. 11 Ball-and-stick representations of macrocation $(Cufcz)_2^{2+}$, the cationic sheet consisting of $(Cufcz)_2^{2+}$ and Cu cations, two kinds of POM units, and schematic view of the two POM-pillared open MOFs.

In 2007, Lan and Su et al. carried out an extensive survey on the system of metal-fluconazole (Hfcz) and POMs.[97-99] They hydrothermally synthesized two POM-pillared 3D open MOFs based on deliberately designed metal-fcz macrocations and Keggin ions (Fig. 11),[100] enlightened by the work of Mizuno's group on the construction of zeolite-type ionic crystals.[101,102] The $(Cufcz)_2^{2+}$ macrocations linked copper cations to generate a 2D wavelike cationic sheet, and then the POM anions served as pillars to bridge the cationic sheets to form POM-pillared 3D frameworks. Additionally, the electrochemical behaviours were investigated. Furthermore, they isolated two $\{\beta\text{-}Mo_8O_{26}\}$-pillared 3D frameworks, when the transformation of Cu^{II} ions into Cu^{I} ones in different degrees were studied through step by step increasing of the amount of organic amine.[103,104]

With 1-ethyl-3-methylimidazolium bromide as solvent, a family of 3D porous $\{Mo_8O_{26}\}$-based structures were ionothermally obtained by Wang and Su et al. in 2012 (Fig. 12).[30] The structural integrity remains unchanged until 300 °C; most importantly, the bulky organic cations within their nanosized channels can be replaced by transition-metal ions through a cation-exchange process, and subsequent gas adsorption measurements confirm their permanent porosity.

In summary, the preparation of this kind of POM-based materials is involved in several methods, conventional aqueous method, hydrothermal and ionothermal techniques. Additionally, there are many reports on POM-pillared inorganic-organic hybrid coordination polymers; however, most of them did not possess porous frameworks. The reason for this result perhaps associates with the fact that most of organic ligands were linear linkers in the previous works, which favors to form interpenetration rather than structures with pores. Furthermore, it is more difficult to obtain a porous POM-pillared inorganic-organic material, compared with the isolation of POM-templated MOF materials. There will be more crystalline materials with strange topology and structure to emerge through adjusting POM units, organic ligands and metal ions. However, the relationship between the structure and property of these materials is an important issue for researchers in the future.

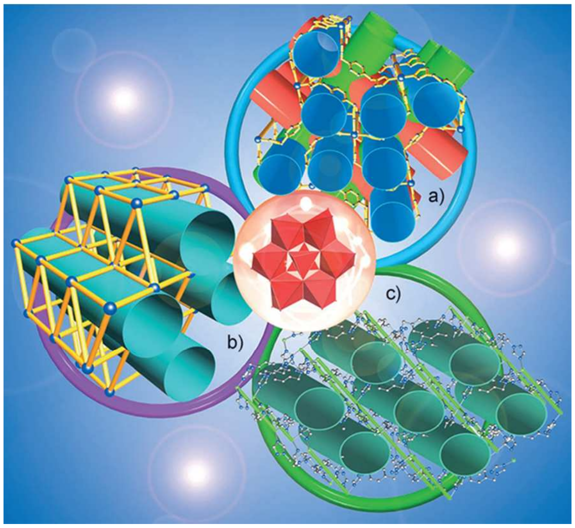


Fig. 12 The three $\{Mo_8O_{26}\}$-based porous MOF materials prepared by ionothermal method. Reprinted with permission from ref. 30. Copyright 2012 John Wiley and Sons.

3.1.4 Nanoscale POM-based MOF crystalline materials

The reported synthetic methods for POM-based MOF materials typically result in large crystal sizes (in millimetre), which are expected to be less suitable for catalytic application due to potential mass transport limitation, especially in catalytic processes in the liquid phase. In this context, some researchers focus their study on selecting the optimum particle size of POM-based MOF nanomaterials for different catalytic reactions.

Through the control of hydrothermal synthesis and some simple treatments, **NENU-1** samples with average particle diameters of 23, 105 and 450 μm, respectively, were prepared by Liu and co-workers.[105] The catalytic activity was fully assessed in the dehydration of methanol to dimethyl ether. The effect of particle size on the catalytic activity of **NENU-1** was studied, in order to select the particle size appropriate for avoiding the diffusion limitation in heterogeneous gas-phase catalysis. It exhibited higher catalytic activity than the copper-based MOF, *γ*-alumina, and *γ*-alumina-supported 12-tungstosilicic acid catalysts. Furthermore, nanoscale **NENU-1** was also preliminarily assessed in the formation of ethyl acetate from acetic acid and ethylene. It also exhibited a high activity which was comparable with that of silica-supported 12-tungstosilicic acid catalyst.

Martens and co-workers reported the convenient synthesis of similar POM/**HKUST-1** composites at room temperature.[106,107] And the acid catalytic activity of the as-synthesized nanomaterials was assessed by the esterification reaction of acetic acid and 1-propanol in the absence of solvent. Moreover, template effects during POM encapsulation in MOF were first studied by Bajpe, who described the instantaneous and stoichiometric formation of a **HKUST-1** with intact Keggin-type $H_3PW_{12}O_{40}$ molecules trapped in the pores.[108] The stability of as-synthesized nanomaterials was thoroughly studied by Breynaert.[109] Direct evidence of strong electrostatic interaction between Cu^{2+} ions and POM anions was observed from a significant shift in ^{31}P NMR. The self-assembly of the POM/**HKUST-1** composite was studied by means of ex situ NMR, SAXS, DLS, NIR, XANES and EPR.[110]

So far, the work on nano-functionalized POM-based MOF materials was rarely reported. The research in this area is still in its infancy. It is a difficult issue to prepare nanocrystals with the same structure of a known POM-based MOF compound. Correspondingly, the research on nanotechnology of MOF materials provides us with much experience. Perhaps it is a promising method to learn from nano-scientists to synthesize more nanosized POM-based MOF materials. It will be research topic to design and prepare more excellent POM-based MOF nanomaterials with proper particle size and shape which can be employed in a series of catalysis reactions. Continued engagement in the synthesis of POM-based MOF nanomaterials for catalysis and other applications will be encouraged in future work.

3.1.5 The gas adsorption study of POM-based MOF crystalline materials

POM-based MOF crystalline materials possess the features of both POMs and MOFs. In this context, the gas adsorption study and determination of Brunauer-Emmett-Teller (BET) surface areas is inevitable to be performed. However, there is scare work to be reported on the BET data of POM-based MOF materials until now (Table 4). Perhaps some researchers did not try to carry out the adsorption measurements of their new materials. It needs further treatment to obtain a larger specific surface area due to the characteristics of such materials.

Table 4 Summary of BET surface areas in the reported literatures.

No.	Compounds	BET / $m^2 \cdot g^{-1}$ [a]	Ref.
1	$(TBA)_2[Cu^{II}(bbtz)_2(\alpha\text{-}Mo_8O_{26})]$	772	30
2	$[Cu_3(1,3,5\text{-btc})_2(H_2O)_3]_2Na_3PW_{12}O_{40}\cdot nH_2O$	519	75
3	**NENU-3**	460[b]	76
4	**NENU-29**	466	77
5	**NENU-30**	487	77
6	**NENU-28**	470	78
7	**NENU-11**	572	79
8	**NENU-15**	547	80
9	$[Cu_3(1,3,5\text{-btc})_2]_4[(TMA)_4CuPW_{11}O_{39}H]$	462	81

[a] The BET surface areas obtained from the N_2 isotherms at 77 K; [b] Langmuir surface area.

Generally speaking, there are three species occupied in the porosities of the porous POM-based materials: POM anions, water molecules or organic cations (such as TMA^+ or TBA^+). In order to successfully assess the adsorption data, the channels must be vacated. According to different species occupied within the porosities, it can be divided into the following situations: (i) POM anions: POM anions cannot be removed for the reason that it will not be POM-based materials after POM units were removed. (ii) water molecules: the as-synthesized sample was heated overnight under vacuum at high temperature to remove guest water molecules from the framework. For example, Liu and Su et al. successfully removed the water molecules resided in the framework of **NENU-3** under vacuum at 200 °C, and successfully measured its BET surface area.[76] (iii) organic cations: it can be clearly seen that bulky cations (such as TMA^+ or TBA^+) always serve as countercations resided in the channels or cavities when POM-based MOF compounds with POM anions as templates were isolated. Some researchers performed the cationic exchange experiments of bulky organic cations with suitable small metal ions. The integrity of POM-based porous MOF materials is retained, as confirmed by the subsequent N_2 adsorption experiments. The most successful example is that Wang and co-workers utilized d-block transition-metal Co^{2+} cations to exchange with bulky TBA^+ cations when considering its size and stability. After the immersion of the crystals in acetone containing Co^{2+} ions for 16 h and then heating at 150 °C for 8 h in a vacuum, they obtained an activated material with BET surface area of 772 $m^2\ g^{-1}$.[30] Subsequently, it exhibits high CO_2 uptake capacity at saturation of 165 $cm^3 \cdot g^{-1}$ (7.4 $mmol \cdot g^{-1}$, 231.6 $L \cdot L^{-1}$) at 195 K and 87.7 $cm^3 \cdot g^{-1}$ (3.9 $mmol \cdot g^{-1}$, 122.5 $L \cdot L^{-1}$) at 273 K, which is comparable to the highest value of classical zeolite-like MOFs. In addition, Liu and co-workers employed alkali metal ion Li^+ to exchange with TMA^+ cations, leading to an increase in the H_2 adsorption capacity.[77] Of course, there will be other types and methods; further research is currently underway.

It is well-known that the catalysis reaction depends on the concentration of substrates around the catalytic sites. A suitable porosity of POM-based MOF materials perhaps favors to the contact between the reaction substrate and the catalytically active sites, improving the catalytic activity of POM-based MOF materials. Therefore, we anticipate that these three examples may provide a platform for gas adsorption, and that further more POM-based MOF materials with porosities that will exhibit better catalytic activity can be prepared.

Table 5 Summary of the encapsulation of POMs into the cages of MOF materials and catalytic study

No.	MOFs	BET[a]	POM units	BET[b]	Synthetic Methods[c]	Catalytic study	Ref.
1	**MIL-101(Cr)**	5900[d]	$\{PW_{11}O_{39}\}$	3750[d]	**Method C**	—[e]	32
2	**MIL-101(Cr)**	2200[f]	$\{PW_{11}TiO_{39}\}$	1930[f]	**Method C**[g]	alkenes oxidation with O_2 or H_2O_2	33
3	**MIL-101(Cr)**	2200[f]	$\{PW_{11}CoO_{39}\}$	2050[f]	**Method C**[g]	alkenes oxidation with O_2 or H_2O_2	33
4	**MIL-101(Cr)**	2200[f]	$\{PW_4O_{24}\}$	1800[f]	**Method C**	alkenes oxidation with H_2O_2	115
5	**MIL-101(Cr)**	2200[f]	$\{PW_{12}O_{40}\}$	1700[f]	**Method C**	alkenes oxidation with H_2O_2	115
6	**MIL-101(Cr)**	2800	$\{PW_{12}O_{40}\}$	2340[h]	**Methods A** and **C**	Knoevenagel condensation; esterification of acetic acid and n-butanol and dehydration of methanol	118
7	**MIL-101(Cr)**	4004[i]/3460[j]	$\{PW_{12}O_{40}\}$	1020	**Methods A** and **C**	Baeyer condensations and epoxidation reactions	119
8	**MIL-101(Cr)**	—[e]	$\{PW_{11}O_{39}\}$	—[e]	**Method C**	—[e]	120
9	**MIL-101(Cr)**	—[e]	$\{SiW_{11}O_{39}\}$	—[e]	**Method C**	—[e]	120
10	**NH_2-MIL-101(Al)**	—[e]	$\{PW_{12}O_{40}\}$	—[e]	**Method A**	—[e]	121
11	**NH_2-MIL-101(Al)**	—[e]	$\{PW_{12}O_{40}\}$	1260	**Method A**[k]	oxidation of CO and hydrogenation of toluene	36
12	**MIL-101(Cr)**	2772	$\{PW_{12}O_{40}\}$	2508[l]	**Method A**	dehydration of carbohydrates to HMF	122
13	**MIL-100(Cr)**	1295	$\{PW_{12}O_{40}\}$	1080[m]	**Method C**[n]	—[e]	35
14	**MIL-100(Fe)**	2800[d]	$\{PMo_{12}O_{40}\}$	1000[d]	**Methods A, B,** and **C**	—[e]	124

[a] the BET surface areas of MOFs ($m^2 \cdot g^{-1}$); [b] the BET surface areas of POM@MOFs ($m^2 \cdot g^{-1}$); [c] **Method A**: synthesis of MOF in the presence of POM; **Method B**: synthesis of POM inside the cages of formed MOF, and **Method C**: impregnation of MOF with an aqueous solution of POM; [d] Langmuir surface area; [e] No relevant study; [f] Specific surface area; [g] **Method C** with CH_3CN as solvent; [h] 10 wt% encapsulated; [i] **MIL-101** synthesized in water at pH 2.6 under microwave condition; [j] **MIL-101** synthesized in water at pH 2.6 under autoclave condition; [k] **Method A** under microwave condition; [l] 11.9 wt% encapsulated; [m] 16.6 wt% encapsulated; [n] **Method C** under both hydrothermal and microwave conditions for pure aqueous or organic phase and biphasic mixtures systems.

3.2 POM-loaded MOF materials and their applications

POMs have received increasing attention owing to their numerous applications in acid and oxidation catalysis. POMs with strong Brønsted acidity and multi-step reversible redox transformations under rather mild conditions show promise as solid-acid catalysts and electron transfer catalysts for many organic transformations and industrial applications. It should be noted that their acid-base and redox properties can be tuned over a wide range by varying the chemical composition. Meanwhile, POMs have a good thermal stability in the solid state, better than other strong solid acids like ion exchange resins. However, their applications are limited by their relatively small surface areas (< 10 $m^2 \cdot g^{-1}$), low stability under catalytic conditions and high solubility in aqueous solution. One way to overcome these drawbacks is to encapsulate POMs within porous solid matrixes, such as various acidic or neutral porous supports, silica, activated carbon, ion-exchange resin, and mesoporous molecular sieves included.[111-113] However, several drawbacks are associated with these materials, including low POM loading, POM leaching, the conglomeration of POM particles, active sites that are nonuniform, and the deactivation of acid sites by water. The immobilization of POMs in a suitable solid matrix, which can overcome these drawbacks, is an important step toward the challenging goal of catalysis.

The possibilities to tailor the pore size over a wide range and to allow further functionalities in the framework render MOFs particularly interesting for catalytic applications. Moreover, this fact makes "POM-loaded MOF materials" systems especially interesting for heterogeneous catalysis, which has been widely studied (Table 5).[114]

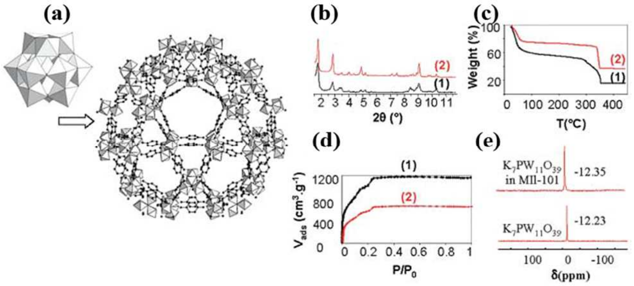


Fig. 13 (a) Schematic view of the insertion of Keggin anions within the largest pore of **MIL-101**, (b) XRD of **MIL-101** (1) and **MIL-101**(Keggin) (2), (c) TGA of **MIL-101** (1) and **MIL-101**(Keggin) (2), (d) Nitrogen sorption-desorption isotherms at 78 K of **MIL-101** (1) and **MIL-101**(Keggin) (2), (e) ^{31}P solid-state NMR spectra of the Keggin salt and **MIL-101**(Keggin). Reprinted with permission from ref. 32. Copyright 2005 American Association for the Advancement of Science.

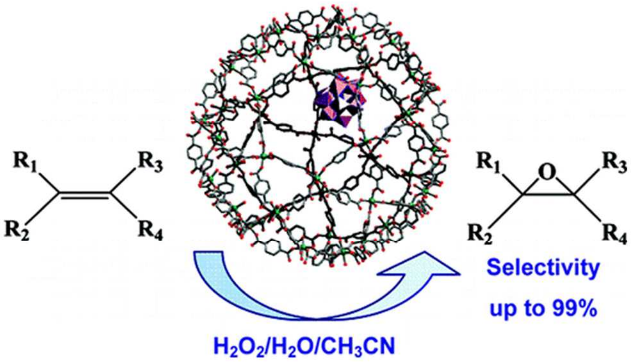


Fig. 14 The alkene epoxidation reaction over $\{PW_4O_{24}\}$/**MIL-101(Cr)** and $\{PW_{12}O_{40}\}$/**MIL-101(Cr)**. Reprinted with permission from ref. 115. Copyright 2010 American Chemical Society.

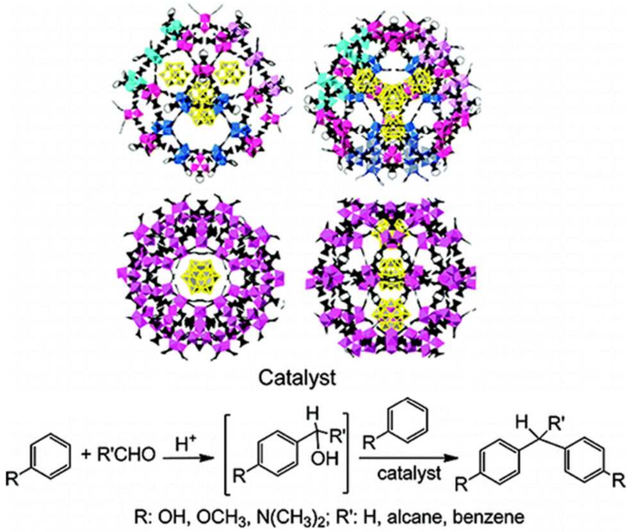


Fig. 15 The encapsulation of phosphotungstic acid into the cages of **MIL-101(Cr)** and Baeyer condensations catalytic study. Adapted with permission from ref. 119. Copyright 2012 American Chemical Society.

POM-loaded MOF material was firstly reported by Férey and co-workers. **MIL-101** with a formula of $Cr_3F(H_2O)_2O(1,4\text{-}bdc)_3{\cdot}nH_2O$, has a chromium carboxylate cubic structure and is an ideal carrier due to its very large pore size, large surface area and good stability.[32] Férey et al. successfully incorporated the lacunary heteropolytungstate $K_7PW_{11}O_{39}$ within the cages of **MIL-101** for the first time (Fig. 13). Later, titanium/cobalt-mono-substituted Keggin, $[PW_4O_{24}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ anions were electrostatically bound to **MIL-101**(Cr) and used as heterogeneous catalysts for oxidation reactions (Fig. 14).[33,115] The related work were fully reviewed by Kholdeeva and co-workers.[116,117] A similar method was followed by Gascon et al., the introduction of phosphotungstic acid to the synthesis mixture of **MIL-101**(Cr) yields the direct encapsulation of POMs inside **MIL-101**(Cr).[118] Furthermore, by simply impregnating the as-prepared **MIL-101**(Cr) or by adding phosphotungstic acid to the aqueous **MIL-101**(Cr) followed by heating by either a conventional oven or microwave, Hatton's group obtained POM/**MIL101**(Cr) composites. Furthermore, POM/**MIL101**(Cr) composites were used as catalysts for Baeyer condensations and epoxidation reactions, exhibiting high turnover numbers (Fig. 15).[119] Recently, the electrochemical investigation of encapsulation of monovacant Keggin-type POMs in **MIL-101**(Cr) were also reported.[120]

By using SAXS/WAXS, Gascon et al. *in situ* prepared phosphotungstic acid/NH$_2$–**MIL-101(Al)** composites.[121] The relative intensity of the Bragg peaks changes dramatically in the case of the POM templated synthesis, which was attributed to the successful encapsulation of Keggin units in both middle and large cavities, pointing to a very efficient encapsulation. Furthermore, the highly dispersed phosphotungstic acid in NH$_2$-**MIL-101(Al)** served as anchoring sites for the Pt precursor species, was synthesized and tested as catalyst in the oxidation of CO, the preferential oxidation of CO in the presence of H$_2$, and the hydrogenation of toluene.[36]

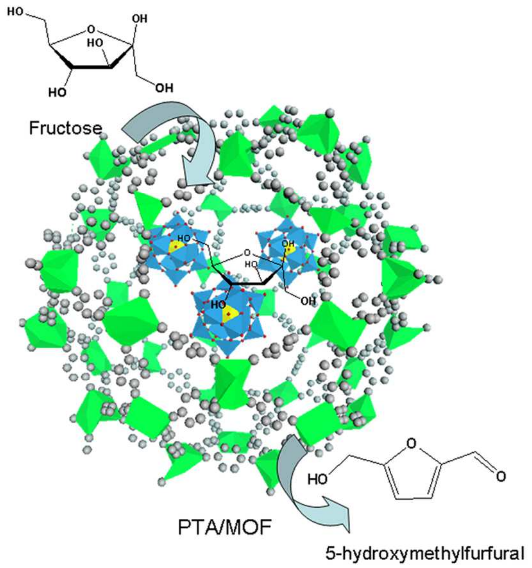


Fig. 16 $H_3PW_{12}O_{40}$/**MIL-101** catalysed dehydration of carbohydrates to 5-hydroxymethylfurfural in ionic liquids. Reprinted with permission from ref. 122. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5-Hydroxymethylfurfural (HMF) has been considered as a renewable chemical platform for the production of liquid fuels and fine chemicals. Li and Hensen et al. performed a study on the encapsulation of $H_3PW_{12}O_{40}$ into **MIL-101** to evaluate it as a solid acid catalyst for the selective dehydration of carbohydrates to HMF in ionic liquids.[122] The result indicates that $H_3PW_{12}O_{40}$/**MIL-101** is effective for HMF production from fructose in DMSO (Fig. 16). The catalytic activities depended on the $H_3PW_{12}O_{40}$ loadings, and the catalyst can be recycled under the same reaction conditions. This is the first application of a MOF material in carbohydrate dehydration.

Another interesting MOF with such exceptional properties is **MIL-100(Cr)** with a formula of $Cr_3F(H_2O)_3O(1,3,5\text{-btc})_2{\cdot}nH_2O$. **MIL-100(Cr)**, a crystalline MOF material with a hierarchical pore system (micro: ~5–9 Å; mesoporous: ~25–30 Å) and a very high surface area (3100 m^2g^{-1}), was also reported by Férey.[123] Successful encapsulation of POMs within **MIL-100(Fe)** sample has been achieved through several methods: (i) synthesis of **MIL-100(Fe)** in the presence of heteropolyacid, (ii) synthesis of heteropolyanion inside the cages of formed **MIL-100(Fe)**, and (iii) impregnation of **MIL-100(Fe)** with an aqueous solution of heteropolyanion.[124] Furthermore, the stabilities towards leaching of the different solid samples were evaluated, suggesting that they are stable in aqueous solution with no POM leaching even after more than 2 months. Juan-Alcañiz and co-workers performed a study on the one-pot encapsulation of phosphotungstic acid in **MIL-100(Cr)** under conventional and microwave heating conditions for three different solvent systems.[35] This interaction decreases the Lewis acidity associated with the MOF framework and only slightly increases the Brønsted acidity.

In addition, porous solids with organized multiple porosity are of scientific and technological importance for broadening the application range from traditional areas of catalysis and adsorption/separation to drug release and biomedical imaging. However, preparation of crystalline porous materials offering a network with uniform micro- and mesopores remains a major scientific challenge. Kirschhock et al. demonstrated a strategy based on variation of synthesis parameters, and a new material coined **COK-15** (COK = Centrum voor Oppervlaktechemie en Katalyse) was synthesized via a dual-templating approach.[125] **COK-15** has substantially wide permanent mesopores demonstrating excellent catalytic activity and selectivity in methanolysis of styrene oxide under mild reaction conditions.

Recently, POM-loaded MOF materials have been attracted increasing attention owing to their potential applications in diverse organic reactions. However, only **MIL-100** and **MIL-101** were successfully selected as carriers due to the strict requirements of stabilities in the presence of POM anions and the pore sizes of MOF networks matched with POM anions (1~2 nm). So far, it is a great challenge to prepare stable MOF materials with suitable pore sizes to employ as carriers and much space in choosing MOF carries need to be explored. We also anticipate that more MOFs will provide as carriers and more POMs with different functions for broad potential in preparation of POM-loaded MOF materials, and that more POM-loaded MOF materials perhaps not only be employed as heterogeneous catalysts in various organic reactions but also be used in other fields, such as proton conductivity and capacitor, will be investigated in the future.

4. Outlook and conclusions

In this review, the classification, synthesis strategies and relevant applications of porous POM-based MOF materials are presented. The study of porous POM-based MOF materials is very topical in synthetic chemistry and material science. POM-based MOF single-crystal materials and POM-loaded MOF materials provide illustrations of this trend. Beside its academic interest, this research is motivated by diverse applications related to this gigantism, especially their use in catalysis domain. As for POM-based MOF materials, POM-templated and -loaded MOF materials are better able to simultaneously reflect the common characteristics of POMs and MOFs compared with other two types, modified POM units directly connecting with organic ligands and porous inorganic-organic materials with POMs anions as pillars. In this context, it is a better choice to prepare POM-templated and -loaded MOF materials for the isolation of porous POM-based MOF materials.

However, the investigation on POM-based MOF materials is still in its infancy. Firstly, controllable synthesis is a relatively difficult issue in the design and preparation of POM-based MOF materials owing to the exact information of the formation process being unclear and usually assigned to self-assembly. Secondly, the choice of POMs, metal ions and ligands is seldom. For example, as for modified POMs directly connecting with organic ligands, the POM unit is limited to Zn/La-ε-Keggin and {$\mathbf{Ni_6XW_9}$} (X = P or Si); as for the preparation of POM-loaded MOF materials, only the encapsulation of POMs into the cages of **MIL-100**, **MIL-101** and **HKUST-1** has successful examples. So far, it is a challenge to prepare POM-based MOF materials with diverse structures and multifunctionalities. Thirdly, the study of the unique properties that corresponds to POM-based MOF materials is extremely rare. The study of application is focused on catalysis, less involved in other aspects. Thus, there is a clear need to develop approaches to bridge the gap between POMs and MOFs so that the mechanism of their self-assembly and relevant applications can be explored in a more systematic way. Finally, the preparation of POM-based MOF materials with desirable properties has also not been achieved yet. In consequence, there is still a strong need to develop new types of materials in the ever growing domain of POM-based MOF materials.

Until now, the most likely potential application of POM-based MOF materials perhaps is catalysis for the following advantages: (i) POM-based MOF materials usually have high thermal stability, and can be easily recycled for several times as heterogeneous catalyst; (ii) crystalline POM-based MOF materials with exact chemical composition and structure is beneficial to the study of catalytic mechanism; (iii) as for POM-loaded MOF materials, MOF moiety with a high specific surface area serves as a carrier not only increasing the dispersion of POMs, but perhaps facilitating the effective contact between POM and substrates; and (iv) the organic fragments of POM-based MOF catalysts can be easily tailored by organic synthesis in order to meet the requirements of catalysis reactions, such as the hydrophilic and lipophilic property of catalysts, which better improved the catalytic performance of such materials. Moreover, the size of catalysts is one of important factors to influence the catalytic activity, thus the investigation on POM-based MOF nanomaterials will be a focus in the future. Except for the application in the catalysis area, the magnetic properties and electrocatalytic behaviours of porous POM-based MOF materials perhaps would be extensively explored in the future, as well as their proton conductivity and capacitive performance.

Anyway, POM-based MOF materials integrate water-soluble

POM units and insoluble crystalline MOF materials, offering the possibility to make POMs become "material", which expands the scope of applications of POMs. Moreover, the introduction of POM ions possessed different functions to MOF system, adding a new active point for MOF materials, will become a new focus in POM and MOF sciences in the future.

We sincerely hope that this article will represent a snapshot of recent progress in POM-based MOF materials, serving as a reference to those who wish to learn more about this area and also help new researchers become inspired, interested, and involved in the subject.

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1 Y. Kikukawa, S. Yamaguchi, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi and N. Mizuno, *J. Am. Chem. Soc.*, 2008, **130**, 5472–5478.

2 D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1736–1758.

3 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34–48.

4 C. L. Hill, *Chem. Rev.*, 1998, **98**, 1–2.

5 L. Cronin and A. Müller, *Chem. Soc. Rev.*, 2012, **41**, 7333–7334.

6 J.-P. Zhang, X.-C. Huang and X.-M. Chen, *Chem. Soc. Rev.*, 2009, **38**, 2385–2396.

7 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, doi:10.1126/science.1230444.

8 M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343–1370.

9 A. Müller and C. Serain, *Acc. Chem. Res.*, 2000, **33**, 2–10.

10 H. N. Miras, E. F. Wilson and L. Cronin, *Chem. Commun.*, 2009, 1297–1311.

11 A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009–6048.

12 D.-Y. Du, L.-K. Yan, Z.-M. Su, S.-L. Li, Y.-Q. Lan and E.-B. Wang, *Coord. Chem. Rev.*, 2013, **257**, 702–717.

13 H.-Y. An, E.-B. Wang, D.-R. Xiao, Y.-G. Li, Z.-M. Su and L. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 904–908.

14 H. An, E. Wang, Y. Li, Z. Zhang and L. Xu, *Inorg. Chem. Commun.*, 2007, **10**, 299–302.

15 R. Cao, S. Liu, Y. Liu, Q. Tang, L. Wang, L. Xie and Z. Su, *J. Solid State Chem.*, 2009, **182**, 49–54.

16 C.-H. Zhang, C.-J. Zhang, Y.-G. Chen and S.-X. Liu, *Inorg. Chem. Commun.*, 2011, **14**, 1465–1468.

17 J.-X. Meng, Y. Lu, Y.-G. Li, H. Fu and E.-B. Wang, *Cryst. Growth Des.*, 2009, **9**, 4116–4126.

18 H. Pang, C. Zhang, J. Peng, Y. Wang, J. Sha, A. Tian, P. Zhang, Y. Chen, M. Zhu and Z. Su, *Eur. J. Inorg. Chem.*, 2009, 5175–5180.

19 X. Wang, J. Peng, K. Alimaje and Z.-Y. Shi, *CrystEngComm*, 2012, **14**, 8509–8514.

20 D.-Y. Du, J.-S. Qin, T.-T. Wang, S.-L. Li, Z.-M. Su, K.-Z. Shao, Y.-Q. Lan, X.-L. Wang and E.-B. Wang, *Chem. Sci.*, 2012, **3**, 705–710.

21 D. Du, J. Qin, C. Wang, X. Liu, S. Li, Z. Su, X. Wang, Y. Lan and E. Wang, *J. Mater. Chem.*, 2012, **22**, 21040–21044.

22 H.-Y. Liu, H. Wu, J. Yang, Y.-Y. Liu, J.-F. Ma and H.-Y. Bai, *Cryst. Growth Des.*, 2011, **11**, 1786–1797.

23 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012–1016.

24 F. H. Aidoudi, D. W. Aldous, R. J. Goff, A. M. Z. Slawin, J. P. Attfield, R. E. Morris and P. Lightfoot, *Nature Chem.*, 2011, **3**, 801–806.

25 N. Zou, W. Chen, Y. Li, W. Liu and E. Wang, *Inorg. Chem. Commun.*, 2008, **11**, 1367–1370.

26 S. Lin, W. Liu, Y. Li, Q. Wu, E. Wang and Z. Zhang, *Dalton Trans.*, 2010, **39**, 1740–1744.

27 A. S. Pakhomova and S. V. Krivovichev, *Inorg. Chem. Commun.*, 2010, **13**, 1463–1465.

28 H. Fu, Y. Li, Y. Lu, W. Chen, Q. Wu, J. Meng, X. Wang, Z. Zhang and E. Wang, *Cryst. Growth Des.*, 2011, **11**, 458–465.

29 H. Fu, Y. Lu, Z. Wang, C. Liang, Z. Zhang and E. Wang, *Dalton Trans.*, 2012, **41**, 4084–4090.

30 H. Fu, C. Qin, Y. Lu, Z.-M. Zhang, Y.-G. Li, Z.-M. Su, W.-L. Li and E.-B. Wang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7985–7989.

31 E. Ahmed and M. Ruck, *Angew. Chem., Int. Ed.*, 2012, **51**, 308–309.

32 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.

33 N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315–323.

34 S. Kayaert, S. Bajpe, K. Masschaele, E. Breynaert, C. E. A. Kirschhock and J. A. Martens, *Thin Solid Films*, 2011, **519**, 5437–5440.

35 J. Juan-Alcañiz, M. G. Goesten, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *New J. Chem.*, 2012, **36**, 977–987.

36 E. V. Ramos-Fernandez, C. Pieters, B. van der Linden, J. Juan-Alcañiz, P. Serra-Crespo, M. W. G. M. Verhoeven, H. Niemantsverdriet, J. Gascon and F. Kapteijn, *J. Catal.*, 2012, **289**, 42–52.

37 A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, 1837–1852.

38 A. Dobecq, E. dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009–6048.

39 G. Sazani and M. T. Pope, *Dalton Trans.*, 2004, 1989–1994.

40 S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacôte, S. Thorimbert and M. Malacria, *J. Am. Chem. Soc.*, 2005, **127**, 6788–6794.

41 Y. F. Song, D. L. Long and L. Cronin, *Angew. Chem., Int. Ed.*, 2007, **46**, 3900–3904.

42 M. H. Rosnes, C. Musumeci, C. P. Pradeep, J. S. Mathieson, D. L. Long, Y. F. Song, B. Pignataro, R. Cogdell and L. Cronin, *J. Am. Chem. Soc.*, 2010, **132**, 15490–15492.

43 C. P. Pradeep, D. L. Long, G. N. Newton, Y. F. Song and L. Cronin, *Angew. Chem., Int. Ed.*, 2008, **47**, 4388–4391.

44 L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng and D. R. Powell, *Angew. Chem., Int. Ed.*, 2002, **41**, 4129–4132.

45 Z. Peng, *Angew. Chem., Int. Ed.*, 2004, **43**, 930–935.

46 J. Zhang, J. Hao, Y. Wei, F. Xiao, P. Yin and L. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 14–15.

47 P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2002, **41**, 2398−2401.

48 A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot and F. Sécheresse, *Chem. Eur. J.*, 2003, **9**, 2914−2920.

49 A. Dolbecq, C. Mellot-Draznieks, P. Mialane, J. Marrot, G. Férey, and F. Sécheresse, *Eur. J. Inorg. Chem.*, 2005, 3009–3018.

50 C. Lei, J.-G. Mao, Y.-Q. Sun and J.-L. Song, *Inorg. Chem.*, 2004, **43**, 1964–1968.

51 W. Wang, L. Xu, G. Gao, L. Liu and X. Liu, *CrystEngComm*, 2009, **11**, 2488–2493.

52 L. M. Rodriguez-Albelo, A. R. Ruiz-Salvador, A. Sampieri, D. W. Lewis, A. Gómez, B. Nohra, P. Mialane, J. Marrot, F. Sécheresse, C. Mellot-Draznieks, R. N. Biboum, B. Keita, L. Nadjo and A. Dolbecq, *J. Am. Chem. Soc.*, 2009, **131**, 16078–16087.

53 L. M. Rodriguez-Albelo, A. R. Ruiz-Salvador, D. W. Lewis, A. Gómez, P. Mialane, J. Marrot, A. Dolbecq, A. Sampieri and C. Mellot-Draznieks, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8632–8639.

54 B. Nohra, H. E. Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo and A. Dolbecq, *J. Am. Chem. Soc.*, 2011, **133**, 13363–13374.

55 L. M. Rodriguez-Albelo, G. Rousseau, P. Mialane, J. Marrot, C. Mellot-Draznieks, A. R. Ruiz-Salvador, S. Li, R. Liu, G. Zhang, B. Keita and A. Dolbecq, *Dalton Trans.*, 2012, **41**, 9989–9999.

56 S. T. Zheng, D. Q. Yuan, H. P. Jia, J. Zhang and G. Y. Yang, *Chem. Commun.*, 2007, 1858–1860.

57 S.-T. Zheng, J. Zhang and G.-Y. Yang, *Angew. Chem., Int. Ed.*, 2008, **47**, 3909–3913.

58 S.-T. Zheng, J. Zhang, X.-X. Li, W.-H. Fang and G.-Y. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 15102–15103.

59 S.-T. Zheng and G.-Y. Yang, *Chem. Soc. Rev.*, 2012, **41**, 7623–7646.

60 X. Wang, J. Li, A. Tian, G. Liu, Q. Gao, H. Lin and D. Zhao, *CrystEngComm*, 2011, **13**, 2194–2196.

61 A. Tian, X. Liu, J. Ying, D. Zhu, X. Wang and J. Peng, *CrystEngComm*, 2011, **13**, 6680–6687.

62 H.-Y. Zang, Y.-Q. Lan, S.-L. Li, G.-S. Yang, K.-Z. Shao, X.-L. Wang, L.-K. Yan and Z.-M. Su, *Dalton Trans.*, 2011, **40**, 3176–3182.

63 D. Du, J. Qin, Z. Sun, L. Yan, M. O'Keeffe, Z. Su, S. Li, X. Wang, X. Wang and Y. Lan, *Sci. Rep.*, 2013, **3**, 2616, doi: 10.1038/srep02616.

64 J. Qin, D. Du, W. Li, J. Zhang, S. Li, Z. Su, X. Wang, Q. Xu, K. Shao and Y. Lan, *Chem. Sci.*, 2012, **3**, 2114–2118.

65 A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2009, **131**, 4204–4205.

66 H.-L. Jiang, Y. Tatsu, Z.-H. Lu and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5586–5587.

67 M. Yoon, K. Suh, S. Natarajan and K. Kim, *Angew. Chem., Int. Ed.*, 2013, **52**, 2688–2700.

68 S.-L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656–1683.

69 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638–2684.

70 D. Hagrman, P. J. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 3165–3168.

71 C. Inman, J. M. Knaust and S. W. Keller, *Chem. Commun.*, 2002, 156–157.

72 Y.-G. Li, L.-M. Dai, Y.-H. Wang, X.-L. Wang, E.-B. Wang, Z.-M. Su and L. Xu, *Chem. Commun.*, 2007, 2593–2595.

73 R. Yu, X.-F. Kuang, X.-Y. Wu, C.-Z. Lu and J. P. Donahue, *Coord. Chem. Rev.*, 2009, **253**, 2872–2890.

74 L. Yang, H. Naruke and T. Yamase, *Inorg. Chem. Commun.*, 2003, **6**, 1020–1024.

75 G. Hundal, Y. K. Hwang and J.-S. Chang, *Polyhedron*, 2009, **28**, 2450–2458.

76 C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren and Z.-M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883–1888.

77 F. Ma, S. Liu, D. Liang, G. Ren, C. Zhang, F. Wei and Z. Su, *Eur. J. Inorg. Chem.*, 2010, 3756–3761.

78 F.-J. Ma, S.-X. Liu, D.-D. Liang, G.-J. Ren, F. Wei, Y.-G. Chen and Z.-M. Su, *J. Solid State Chem.*, 2011, **184**, 3034–3039.

79 F.-J. Ma, S.-X. Liu, C.-Y. Sun, D.-D. Liang, G.-J. Ren, F. Wei, Y.-G. Chen and Z.-M. Su, *J. Am. Chem. Soc.*, 2011, **133**, 4178–4181.

80 F.-J. Ma, S.-X. Liu, G.-J. Ren, D.-D. Liang and S. Sha, *Inorg. Chem. Commun.*, 2012, **22**, 174–177.

81 J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839–16846.

82 M. Wei, C. He, W. Hua, C. Duan, S. Li and Q. Meng, *J. Am. Chem. Soc.*, 2006, **128**, 13318−13319.

83 M. Wei, C. He, Q. Sun, Q. Meng and C. Duan, *Inorg. Chem.*, 2007, **46**, 5957-5966.

84 Q. Han, L. Zhang, C. He, J. Niu and C. Duan, *Inorg. Chem.*, 2012, **51**, 5118−5127.

85 X. Wang, Y. Bi, B. Chen, H. Lin and G. Liu, *Inorg. Chem.*, 2008, **47**, 2442–2448.

86 X. Wang, H. Hu, A. Tian, H. Lin and J. Li, *Inorg. Chem.*, 2010, **49**, 10299–10306.

87 X. Wang, H. Hu, B. Chen, H. Lin, A. Tian and J. Li, *Solid State Sci.*, 2011, **13**, 344–349.

88 C.-H. Li, K.-L. Huang, Y.-N. Chi, X. Liu, Z.-G. Han, L. Shen and C.-W. Hu, *Inorg. Chem.*, 2009, **48**, 2010–2017.

89 Y. Gao, Y. Xu, Z. Han, C. Li, F. Cui, Y. Chi and C. Hu, *J. Solid State Chem.*, 2010, **183**, 1000–1006.

90 X. Liu, Y. Jia, Y. Zhang and R. Huang, *Eur. J. Inorg. Chem.*, 2010, 4027–4033.

91 S. Li, D. Zhang, Y. Guo, P. Ma, J. Zhao, J. Wang and J. Niu, *Eur. J. Inorg. Chem.*, 2011, 5397–5404.

92 H. Zang, K. Tan, Y. Lan, G. Yang, K. Shao and Z. Su, *Inorg. Chem. Commun.*, 2010, **13**, 1473–1475.

93 X. Kuang, X. Wu, R. Yu, J. P. Donahue, J. Huang and C. Lu, *Nature Chem.*, 2010, **2**, 461–465.

94 C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C.-D. Wu, *J. Am. Chem.Soc.*, 2012, **134**, 87−90.

95 X. Zhao, D. Liang, S. Liu, C. Sun, R. Cao, C. Gao, Y. Ren and Z. Su, *Inorg. Chem.*, 2008, **47**, 7133–7138.

96 Y. Yang, S. Liu, C. Li, S. Li, G. Ren, F. Wei and Q. Tang, *Inorg. Chem. Commun.*, 2012, **17**, 54–57.

97 S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, X.-H. Wang and Z.-M. Su, *Inorg. Chem.*, 2007, **46**, 8283–8290.

98 Y.-Q. Lan, S.-L. Li, K.-Z. Shao, X.-L. Wang and Z.-M. Su, *Dalton Trans.*, 2008, 3824–3835.

99 S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, J. Liu, Y.-M. Fu and Z.-M. Su, *Dalton Trans.*, 2008, 2015–2025.

100 Y.-Q. Lan, S.-L. Li, K.-Z. Shao, X.-L. Wang, X.-R. Hao and Z.-M. Su, *Dalton Trans.*, 2009, 940–947.

101 S. Uchida, M. Hashimoto and N. Mizuno, *Angew. Chem., Int. Ed.*, 2002, **41**, 2814–2817.

102 C. Jiang, A. Lesbani, R. Kawamoto, S. Uchida and N. Mizuno, *J. Am. Chem. Soc.*, 2006, **128**, 14240–14241.

103 Y.-Q. Lan, S.-L. Li, X.-L. Wang, K.-Z. Shao, Z.-M. Su and E.-B. Wang, *Inorg. Chem.*, 2008, **47**, 529–534.

104 Y.-Q. Lan, S.-L. Li, X.-L. Wang, K.-Z. Shao, D.-Y. Du, H.-Y. Zang and Z.-M. Su, *Inorg. Chem.*, 2008, **47**, 8179–8187.

105 D.-D. Liang, S.-X. Liu, F.-J. Ma, F. Wei and Y.-G. Chen, *Adv. Synth. Catal.*, 2011, **353**, 733–742.

106 L. H. Wee, S. R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C. E. A. Kirschhock and J. A. Martens, *Chem. Commun.*, 2010, **46**, 8186–8188.

107 L. H. Wee, N. Janssens, S. R. Bajpe, C. E. A. Kirschhock and J. A. Martens, *Catal. Today*, 2011, **171**, 275–280.

108 S. R. Bajpe, C. E. A. Kirschhock, A. Aerts, E. Breynaert, G. Absillis, T. N. Parac-Vogt, L. Giebeler and J. A. Martens, *Chem. Eur. J.*, 2010, **16**, 3926–3932.

109 D. Mustafa, E. Breynaert, S. R. Bajpe, J. A. Martens and C. E. A. Kirschhock, *Chem. Commun.*, 2011, **47**, 8037–8039.

110 S. R. Bajpe, E. Breynaert, D. Mustafa, M. Jobbágy, A. Maes, J. A. Martens and C. E. A. Kirschhock, *J. Mater. Chem.*, 2011, **21**, 9768–9771.

111 W. Qi, Y. Wang, W. Li and L. Wu, *Chem. Eur. J.*, 2010, **16**, 1068–1078.

112 S. Rana, S. Mallick, L. Mohapatra, G. B. B. Varadwaj and K. M. Parida, *Catal. Today*, 2012, **198**, 52–58.

113 N. Kawasaki, H. Wang, R. Nakanishi, S. Hamanaka, R. Kitaura, H. Shinohara, T. Yokoyama, H. Yoshikawa and K. Awaga, *Angew. Chem., Int. Ed.*, 2011, **50**, 3471–3474.

114J. Juan-Alcaňiz, J. Gascon and F. Kapteijn, *J. Mater. Chem.*, 2012, **22**, 10102–10118.

115 N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin and O. A. Kholdeeva, *Inorg. Chem.*, 2010, **49**, 2920–2930.

116 O. A. Kholdeeva, N. V. Maksimchuk and G. M. Maksimov, *Catal. Today*, 2010, **157**, 107–113.

117 N. V. Maksimchuk, O. A. Kholdeeva, K. A. Kovalenko and V. P. Fedin, *Isr. J. Chem.*, 2011, **51**, 281–289.

118 J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon and F. Kapteijn, *J. Catal.*, 2010, **269**, 229–241.

119 L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mater.*, 2012, **24**, 1664−1675.

120 P. M. P. de Sousa, R. Grazin, A. D. S. Barbosa, B. de Castro, J. J. G. Moura, L. Cunha-Silva and S. S. Balula, *Electrochim. Acta*, 2013, **87**, 853–859.

121 J. Juan-Alcaňiz, M. Goesten, A. Martinez-Joaristi, E. Stavitski, A. V. Petukhov, J. Gascon and F. Kapteijn, *Chem. Commun.*, 2011, **47**, 8578–8580.

122 Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2011, **4**, 59–64.

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

124 R. Canioni, C. Roch-Marchal, F. Sécheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Férey, J. Grenèche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner and G. V. Tendeloo, *J. Mater. Chem.*, 2011, **21**, 1226–1233.

125 L. H. Wee, C. Wiktor, S. Turner, W. Vanderlinden, N. Janssens, S. R. Bajpe, K. Houthoofd, G. V. Tendeloo, S. D. Feyter, C. E. A. Kirschhock and J. A. Martens, *J. Am. Chem. Soc.*, 2012, **134**, 10911−10919.

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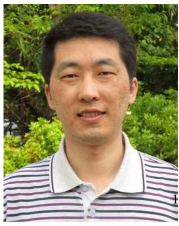

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