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Template-Directed Synthesis of Metal-Organic Materials

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This tutorial review details the emergence of template-directed synthesis of metal-organic materials (MOMs) with emphasis upon reports of MOMs in which the template is retained, template@MOMs, and structurally characterized. Such MOMs enable analysis of the nature of the intermolecular interactions that occur between the template and the resulting host framework. The utilization of such understanding can enable template-directed synthesis to serve as a crystal engineering tool for the preparation of new MOMs, especially those that cannot be accessed without the use of a template. We anticipate that this review will guide future research by delineating several rules for identifying appropriate templates and molecular building blocks to afford MOMs with targeted structures and properties.

Key Learning Points

- Classification of the templates that have been thus far employed for the synthesis of MOMs according to chemical type
- Understanding of the importance of interactions between template and the resulting MOM framework
- That templates can afford new topologies that cannot be obtained directly
- Templates can be used to fine-tune pore size, pore volume, pore shape and interpenetration in MOMs
- The use of templates in MOM chemistry is likely to be as diverse and versatile as it is in zeolite chemistry

Introduction

Metal-organic materials (MOMs) represent an emerging class of materials comprised of molecular building blocks (MBBs), typically metal ions or metal clusters, that are linked by organic linker ligands.[1] MOMs exhibit great diversity of structure and composition and can range from discrete (e.g. nanoballs, metal-organic polyhedra, MOPs)[2] to polymeric 3-dimensional (3D) structures (e.g. porous coordination polymers, PCPs, porous coordination networks, PCNs, metal-organic frameworks, MOFs).[3] Early reports of coordination polymers can be traced back to the late 1950s and early 1960s.[4] However, it was their renaissance in the 1990s[5] that saw MOMs attract great attention thanks to their ability to exhibit permanent porosity, thereby enabling study of properties in the context of gas storage, gas separation, solid supports for sensors, catalysis, fluorescence, and magnetism.[1,6] Further, their amenability to crystal engineering[7] means that judicious selection of MBBs can facilitate exquisite control over structure with respect to topology and enable fine-tuning with respect to the size and chemistry of their pores.[8] In terms of crystal engineering, certain topologies are readily accessible using the "node and linker" approach first delineated by Robson.[5a] Topology plays an important role in the field of MOMs chemistry because it affords blueprints that enable the design of families of related compounds.[9] As delineated in reviews by Proserpio, O'Keeffe and Blatov, the program TOPOS has been developed to classify the structure of MOMs according to topological principles.[9] TOPOS and the RCSR searchable database provide 3-letter codes to classify topology.[9c,d,e] These codes are highlighted in bold in this tutorial review. Whereas it has become evident that there exists an effectively infinite number of possible topologies that can be generated by linking vertices and edges of MBBs, there are only a few network topologies that are accessible and robust enough to be easily fine-tuned and would thereby be regarded as "platforms". The synthesis of families of MOMs or MOM platforms is exemplified by several platforms that are accessible because of the ready availability of appropriate MBBs: **dia**, **pcu**, **nbo**, **acs**, **rht** and **tbo** nets. The 3-letter codes are not random. With the exception of **acs**, which is named in honor of the person who discovered the prototypal **acs** net,[9,10] the 3-letter codes are typically acronyms for existing parent structures (**dia**, **dia**mondoid; **pcu** **p**rimitive **cu**bic, **nbo**, **n**io**b**ium **o**xide; **tbo**, **t**wisted **bo**racite) or represent the nature of the MBBs (rht, **rh**ombicuboctahedra and **t**riangles). Such nets are robust from a design perspective because there are many appropriate MBBs that can serve as nodes, typically metal ions or metal clusters, but also polyfunctional organic ligands. Further, there are many bifunctional organic molecules or anions that can serve as linkers. The situation is exemplified by so-called "square paddlewheel" MBBs of formula $[M_2(COO)_4]$. A Cambridge Structural Database[11] (CSD version 5.35) survey of first row transition metals reveals that Cu(II) is by far the most commonly encountered metal in square paddlewheels (1217/1510 structures), presumably because of its inherent tendency to exhibit square pyramidal coordination geometry. Given the availability of di- and tri- carboxylate ligands, it is therefore unsurprising that $[Cu_2(COO)_4]$ square paddlewheel moieties are so well represented in MOM chemistry. Indeed, they form several prototypal MOM platforms as follows: with 3-connected nodes (1,3,5-benzenetricarboxylate, BTC) the prototypal **tbo** net HKUST-1 is afforded;[6g] with 2-connected linkers (1,4-

benzenedicarboxylate, 1,4-BDC) and axial pillars the DMOF class of **pcu** nets results;[10] with 1,4-BDC MOF-2 is generated;[12] with 1,3-BDC the prototypal nanoballs and MOPs[2] or isomeric 2-dimensional (2D) **sql** or **kag** nets result.[13] In this context, template-directed synthesis of MOMs remains relatively underexplored, especially when compared to other classes of porous material. This could be because, although MOMs have been studied for over 60 years, their porous nature was not systematically and widely explored until the early 1990's.[5] Indeed, permanent porosity was only first established in 1997 when Kitagawa investigated the gas adsorption behavior of $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4\}\cdot xH_2O$ compounds.[14] Shortly thereafter, extra-large surface area MOMs, exemplified by HKUST-1 and MOF-5,[5f] were reported. Nevertheless, as detailed herein, the study of templates is increasing as there are several motivations for studying template-directed synthesis of MOMs:

To access analogues of prototypal MOM platforms that cannot be prepared directly. Whereas Cu(II) cations readily and reliably form square paddlewheel clusters, other metals such as Co(II) and Mn(II) exhibit much lower propensity to generate $[M_2(COO)_4]$ paddlewheels, with only 31 and 13 structures, respectively, archived in the CSD. The tendency of Co^{2+} and Mn^{2+} to form different carboxylate clusters therefore mitigates, for example, against preparation of Co or Mn analogues of HKUST-1 directly by self-assembly of Co^{2+} or Mn^{2+} cations with BTC anions. Indeed, it was not until 2012 that the Co- and Mn-variants of HKUST-1 were successfully prepared by employing a template-directed synthesis strategy in our group.[15]

To create porous materials with new topologies. Another motivation for studying template-directed synthesis of MOMs is to generate porous materials with new topologies that cannot be prepared directly. Templation has long played a critical role in zeolite synthesis and has enabled their industrial-scale processing. Zeolites are amongst the longest known (over 150 years) classes of porous crystalline materials but they underwent a renaissance in the 1960s thanks to the use of templates such as quaternary ammonium cations during their synthesis.[16] Subsequently, ordered mesoporous silicates such as MCM-41, -48 and -50 were prepared by exploiting cationic surfactants as templates.[17] Template-directed synthesis quickly became a fixture in the study of other classes of porous materials including silicas, phosphates, organosilicas, carbons, polymers, metal oxides and zeolites.[18] Templation can likewise enable access to new classes of MOMs that cannot be prepared directly from the starting materials without the presence of the template (Table S1, see ESI).

Functional templates. A template may or may not be present within the pores or cages of a MOM framework after synthesis. If the template remains present after synthesis of the MOM, i.e. "template@MOMs", then there is an opportunity to study template-framework interactions such as hydrogen bonding, π···π interactions and electrostatic interactions. Further, if the template exhibits functionality such as catalytic activity, chirality or fluorescence then it can be transferred to the resulting template@MOM.

To exert fine control over structural features. Templates cover a wide variety of substances including organic molecules, inorganic compounds, dendrimers, ionic surfactants, block copolymers, ordered mesoporous silicas and carbons, colloids, colloidal crystals, anodic alumina, solvent, and lipid nanotubes.[18] Template-directed synthesis can enable adjustment of pore size, pore volume and pore shapes through careful selection of templates with different sizes and shapes.

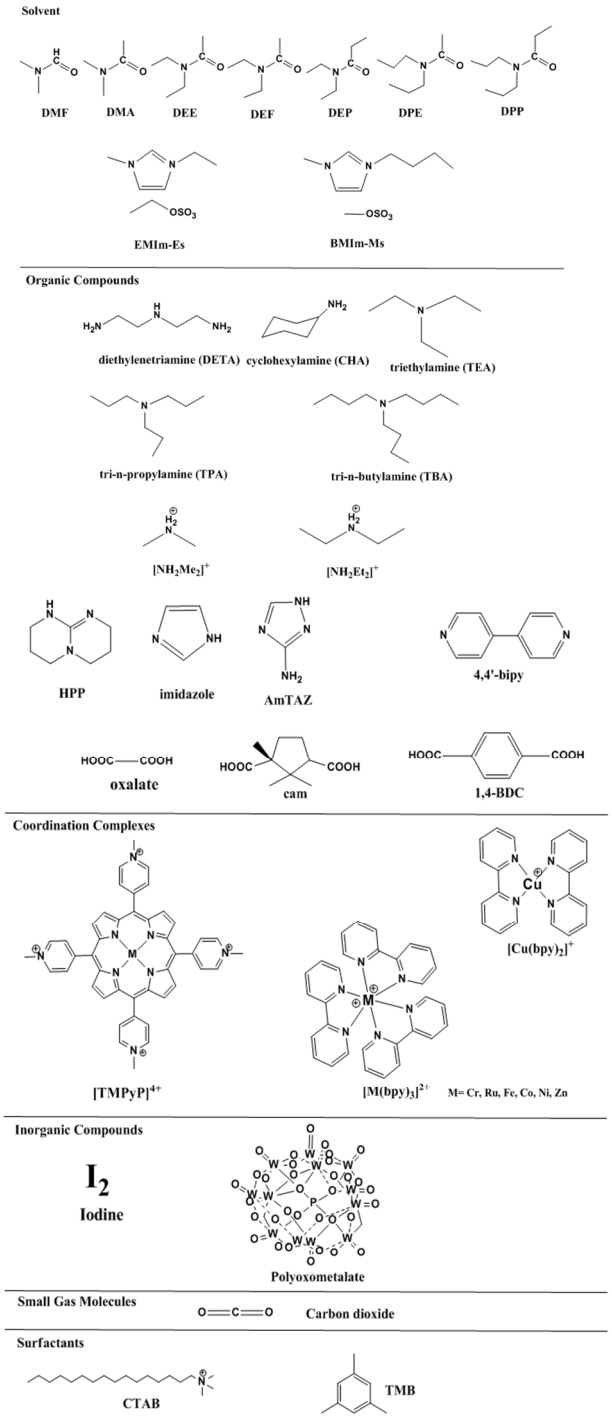

Fig. 1 Templates that have been used in synthesis of template-directed MOMs can be classified into six categories: (1) solvent; (2) organic compounds; (3) coordination complexes; (4) inorganic compounds; (5) small gas molecules; (6) surfactants.

Template-directed synthesis of MOMs

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Templates can afford control over the both the structure and functionality of a MOM and we could classify template@MOMs according to the end objective of the reaction. However, we classify template-directed syntheses of MOMs according to the nature of the template and, as detailed in Fig. 1, we identify six classifications of template: (1) solvent; (2) organic compounds; (3) coordination complexes; (4) inorganic compounds; (5) gas molecules; (6) surfactants. The organic linkers that have been most commonly used during template-directed synthesis of MOMs are illustrated in Fig. 2.

1. Solvent molecules serve as templates

Selection of solvent can play a crucial role with respect to MOM synthesis as most MOMs are prepared using solvothermal or layering methods that involve dissolution of starting materials. However, the template effect of solvent has not been broadly explored even though there are advantages associated with the use of solvent molecules as templates. For example, low-boiling-point solvents such as diethyl ether, dichloromethane and acetone can be removed from the MOM product through application of appropriate stress such as heat or vacuum. Indeed, this is perhaps the simplest method to activate MOMs for gas sorption studies since less volatile solvent can be exchanged for more volatile solvent in post-synthetic procedures. Solvent molecules can also be exploited to control the degree of interpenetration in MOMs.[19]

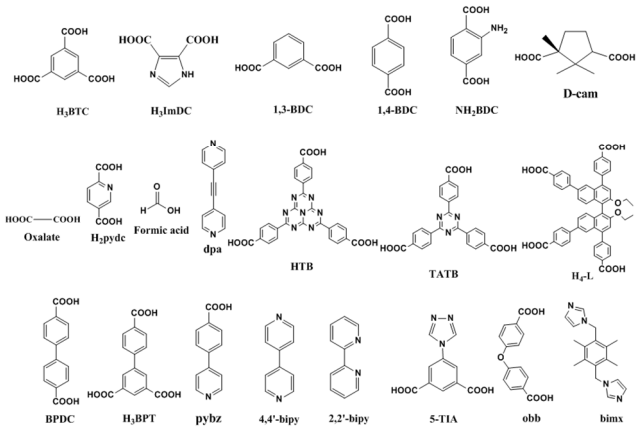

Fig. 2 Examples of linker ligands that have been used for the preparation of template-directed MOMs.

1.1 Organic solvents as templates

In 2005, we reported two zinc-based MOMs[20] formed by reaction of zinc nitrate, H_3BTC, and isoquinoline in MeOH. USF-3 formed in the presence of benzene whereas USF-4 resulted from the use of chlorobenzene. USF-3 and USF-4 are sustained by vertex linked triangular, square, and tetrahedral MBBs and represent early examples of ternary nets, i.e. nets formed from three types of node. These and the other MOMs presented herein are detailed in Table S1 (see ESI). Su's group further studied the template effect of solvent in the reaction of zinc nitrate and H_3BTC[21] and seven porous MOMs were synthesized solvothermally using DMF, DMA, DEE, DEF, DEP, DPE or DPP. Su *et al*. observed **srs**, **tfe** and **rtl** nets as well as nets with new topologies. This study revealed how solvent can profoundly influence structure and pore size, which ranged from 9 Å to 23 Å.

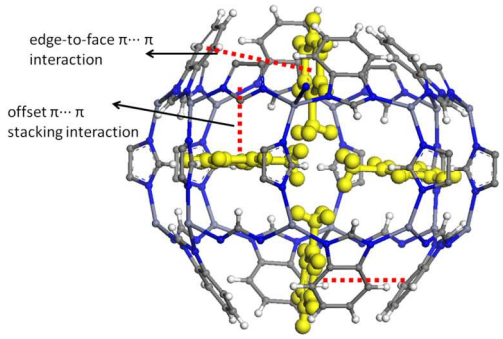

Fig. 3 The orientation of toluene molecules (yellow) in a ball/stick model of ZIF-11.

Wang and co-workers studied the template effect of toluene in the synthesis of ZIF-11 and ZIF-12, which exhibit zeolitic **rho** topology when prepared in alcohols.[22] The same reactions conducted without toluene afforded ZIF-7 and ZIF-9, which exhibit zeolitic **sod** topology. Structural studies conducted by Wang *et al*. revealed that toluene molecules remain in cavities and interact with imidazolate ligands in such a manner that π–π interactions force toluene molecules to adopt a specific orientation (Fig. 3).

1.2 Ionic liquids as templates

Ionic liquids are low melting salts that are finding applications as general purpose solvents and electrically conducting fluids. Ionic liquids have also been utilized as templates and/or solvent media to synthesize zeolites.[23] In 2004, Cooper and co-workers pioneered such use of ionic liquids and coined the term "ionothermal synthesis".[24] In 2008, Bu *et al*. reported the use of ionic liquids for the preparation of a series of 4-connected indium MOMs, ALF-1 to ALF-4 (Fig. 4), with **dia**, **cds** or **ths** topology.[25] The ability of ionic liquids to serve as solvent/template was demonstrated by ALF-1 and ALF-2, for which tetrapropylammonium cations served as structure-directing agents. In the case of ALF-3, which formed a **cds** net, both the cationic ($EMIm^+$) and anionic components (Es^-) of EMIm-Es (Fig. 1 and 4) were found to be located within cavities.

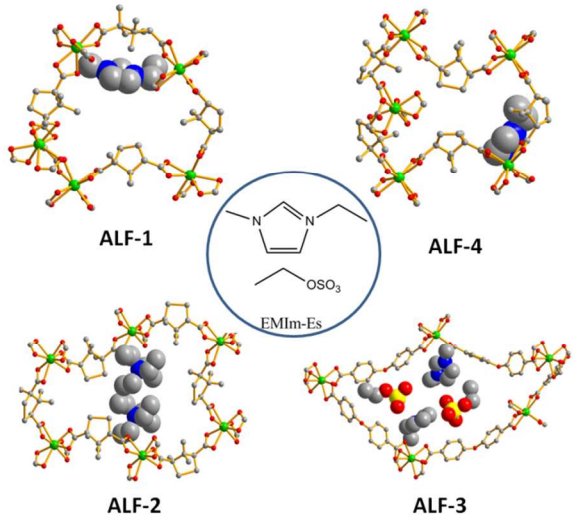

Fig. 4 Templates present in the structures of ALF-1, -2, -3 and -4.

1.3 Use of solvent to control interpenetration

Interpenetration is a well-studied phenomenon in MOMs and is particularly common in **dia**, **pcu** and **srs** nets.[1] Whereas interpenetration was once considered to be undesirable because it necessarily reduces surface area, recent studies have revealed that narrower pores in interpenetrated variants of nets can enhance binding energies for gases such as CO_2 and H_2.[26] There is now increased interest in understanding and controlling the levels of interpenetration that can occur in MOMs.

Our group recently reported a study that focused upon the non-interpenetrated and 2-fold interpenetrated variants of $[Cu(dpa)_2(SiF_6)]_n$, SIFSIX-2-Cu and SIFSIX-2-Cu-i, respectively (Fig. 5), which exhibit **pcu** topology.[26a] SIFSIX-2-Cu was synthesized by diffusing an ethanol solution of dpa into an ethylene glycol solution of $CuSiF_6$. SIFSIX-2-Cu-i was synthesized by diffusion of a methanol solution of $CuSiF_6$ into a DMSO solution of dpa. Although SIFSIX-2-Cu-i exhibits a much lower surface area, 735 $m^2 g^{-1}$, than SIFSIX-2-Cu, 3140 $m^2 g^{-1}$, and is twice as dense, SIFSIX-2-Cu-i was found to exhibit higher CO_2 uptake (both volumetric and gravimetric) and exceptional CO_2/CH_4 and CO_2/N_2 selectivity which exceeds that of other MOMs with coordinatively saturated metal centers. This performance can be attributed to the enhanced heat of adsorption (Q_{st}) of SIFSIX-2-Cu-i *vs.* SIFSIX-2-Cu, a feature that was ascribed to the better overlap of electrostatic potential fields in the relatively narrow pores in SIFSIX-2-Cu-i.

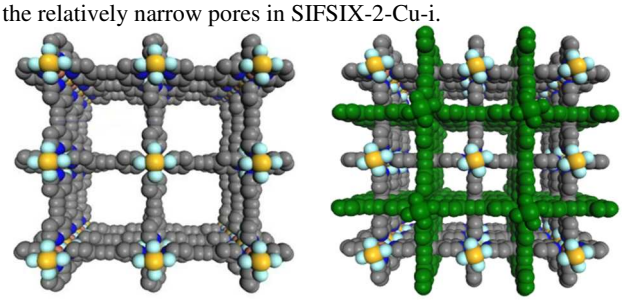

Fig. 5 The non-interpenetrated polymorph of SIFSIX-2-Cu (left) and its 2-fold interpenetrated variant, SIFSIX-2-Cu-i (right).

MOF-5 was first reported by Yaghi's group in 1999.[5f] MOF-5 is a prototypal **pcu** net comprised of 6-connected tetrahedral $[Zn_4O(COO)_6]$ MBBs that are linked at their edges by 1,4-BDC linkers. The non-interpenetrated variant of MOF-5 can be prepared by reaction of $Zn(NO_3)_2$ and 1,4-BDC in DEF whereas the 2-fold interpenetrated variant, MOF-5-i is formed in DMF (Fig. 6).[27] The larger size of DEF *vs.* DMF is presumably behind this solvent-directed template effect. The Langmuir surface area of MOF-5-i estimated from N_2 sorption isotherms is 1130 m^2/g, which is much lower than that of MOF-5 (4400 m^2/g). However, MOF-5-i was found to exhibit higher stability toward heat and moisture and significantly higher hydrogen uptake performance (23.3 *vs* 7.9 g/L), presumably due to the higher enthalpy of adsorption (7.6 *vs* 4.9 kJ/mol). Lin's group exploited a similar approach to control framework interpenetration in MOMs.[28] Reaction of $Cu(NO_3)_2$ and a racemic tetratopic carboxylate (L) in DMF/H_2O at 80°C afforded a 2-fold interpenetrated MOM, whereas the same reaction conducted in DEF/H_2O resulted in the non-interpenetrated variant.

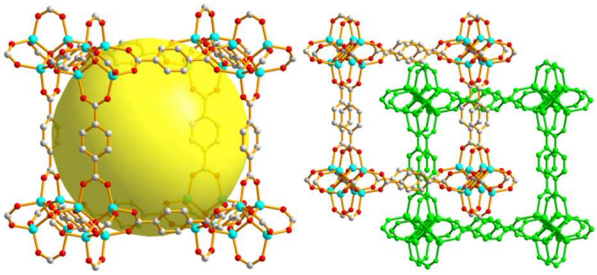

Fig. 6 The non-interpenetrated form of MOF-5 (left) and its 2-fold interpenetrated variant MOF-5-i (right).

2. Organic compounds as templates

2.1 Organic amines

Organic amines which are protonated *in situ* have been widely employed as templates in the synthesis of porous materials with anionic frameworks such as zeolites, aluminophosphates and anionic MOMs. Organic amines can play one or more of the following roles in the formation of MOMs: (i) deprotonation of O-donor ligands (e. g. carboxylic acids); (ii) templating the formation of specific MOM frameworks; (iii) following protonation, they can serve as counterions to balance the charge of anionic frameworks. Preformed ammonium cations can also serve as templates.

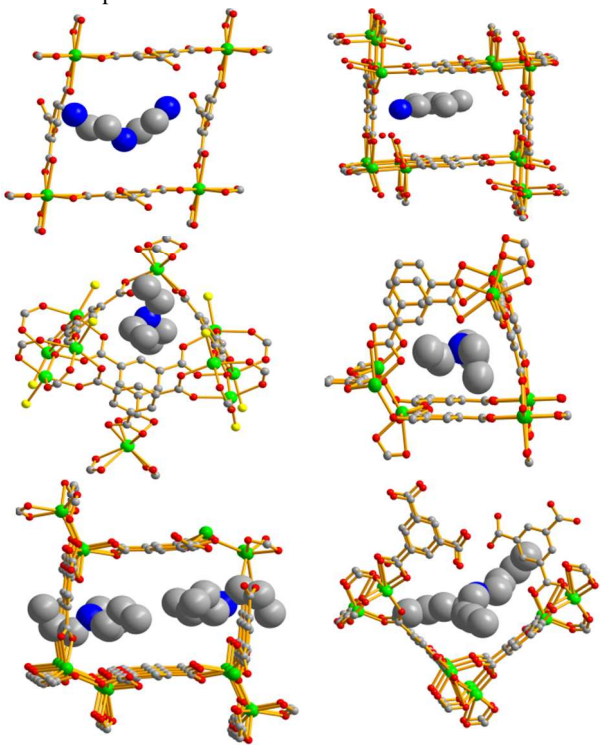

Fig. 7 Alkylammonium cations residing in the interlayer or channel spaces in a series of MOMs reported by Qiu and Zhu *et al.* (Color code: Cd, green; O, red; Cl, yellow; N, blue; C, gray).

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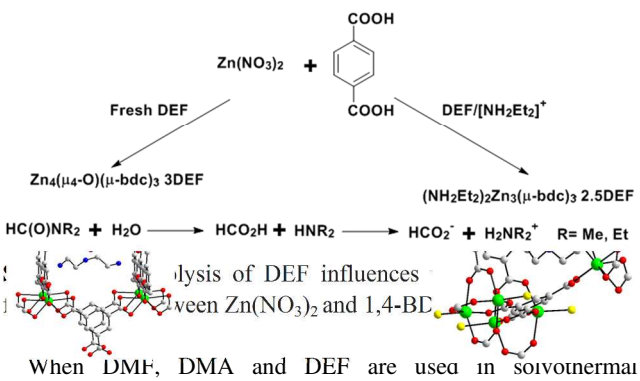
Qiu and Zhu *et al.* reported the synthesis and crystal structures of seven MOMs, JUC-49, -50, -51, -52, -53, -54 and -55, that resulted from the use of various alkylamines as templates (Fig. 7).[29] Specifically, diethylenetriamine, cyclohexylamine, triethylamine, tri-*n*propylamine, and tri-*n*-butylamine (Fig. 1) form alkylammonium cations which serve as structure-directing agents. JUC-49 and JUC-53 are 2D nets with **sql** and **fes** topology, respectively, in which the layers are cross-linked by hydrogen bonds between carboxylate oxygen atoms and NH groups of alkylammonium cations. JUC-50, JUC-52 and JUC-55 are 3D networks (see Table S1, ESI for network topology) in which alkylammonium cations are located in channels. The dimensions of the cations (HCHA: 5.4 Å, TEA: 4.9 Å and TBA: 9.7 Å) correspond to those of the channels (7.5 Å, 5.4 Å and 10.1 Å, respectively). Even though the size and shape of the organic amines vary, hydrogen bonding interactions play an important role in all of these structures. The hydrogen bonding interaction energies (E_{inter}) between the host frameworks and the organic templates was calculated to be -152.54, -20.27, -20.27, -12.17, -8.97, -11.13, and -19.97 kJ/mol per unit cell for JUC-49-55, respectively. In addition, post synthetic ion-exchange experiments revealed that the alkylammonium cations can be exchanged by inorganic cations such as K^+ with retention of framework integrity.



lysis of DEF influences
veen $Zn(NO_3)_2$ and 1,4-BD

When DMF, DMA and DEF are used in solvothermal reactions, alkyammonium cations can be formed by *in situ* solvent hydrolysis reactions. In 2005, Burrows *et al.* investigated the template effect of alkyammonium cations formed by hydrolysis of DEF.[30] Zinc nitrate and 1,4-BDC were heated in fresh DEF at 95 °C for 3 h, resulting in formation of crystals of compound 1. In contrast, when $Zn(NO_3)_2{\cdot}6H_2O$ and H_2bdc were heated under the same conditions but with DEF that had been in the laboratory for several weeks, small colorless crystals of compound 2 were isolated. The $[Et_2NH_2]^+$ cation in the product had been formed through hydrolysis of DEF (Scheme 1). In order to further investigate how $[Et_2NH_2]^+$ influences the formation of compound 2, zinc nitrate and 1,4-BDC were heated in fresh DEF to which $[NH_2Et_2]Cl$ had been added. This reaction resulted in compound 2, suggesting that $[Et_2NH_2]^+$ indeed templates the formation of compound 2. Simplification of the $[Zn_3(COOO)_6]$ building blocks in compound 2 to 8-connected nodes affords an 8-connected uninodal **bcg** network. Along the same lines, Su *et al.* reported two examples of MOMs synthesized from reaction of $Cd(NO_3)_2$ and Na_2BPDC/Na_2NH_2BDC in DMA/H_2O.[31] In order to investigate how $[Me_2NH_2]^+$ influences the reaction, $Cd(NO_3)_2$ and Na_2BPDC/Na_2NH_2BDC were heated in fresh DMA. It was observed that these two MOMs can only be obtained by addition of $[Me_2NH_2]Cl$ since introduction of NaCl, KCl or NH_4Cl did not afford the desired products. $[Me_2NH_2]^+$ cations therefore serve as templates for the formation of these materials.

2.2 N-Heterocyclic aromatic compounds

N-heterocyclic compounds such as pyridines and imidazoles can serve as templates and, when protonated to form cations, they balance the charge of anionic frameworks. They can also facilitate synthesis through deprotonation of carboxylic acids. Eddaoudi *et al.* reported the use of N-heterocyclic compounds as templates to prepare zeolite-like metal-organic frameworks (ZMOFs). HPP was used as a template during the reaction of $H_3ImDC$with $In(NO_3)_3$ to afford a *rho*-ZMOF with zeolitic **rho** topology (Fig. 8). By contrast, a *sod*-ZMOF with **sod** topology was formed in the presence of imidazole. It was found that the HPP cations are present in the product and that they can be exchanged by organic and inorganic cations such as Na^+.[32]

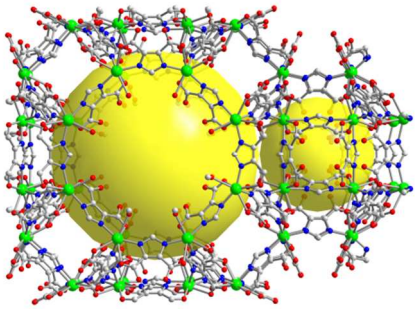


Fig. 8 Single-crystal structure of **rho**-ZMOF. Yellow spheres represent the largest sphere that would fit in the cavities without touching the van der Waals atoms of the framework.

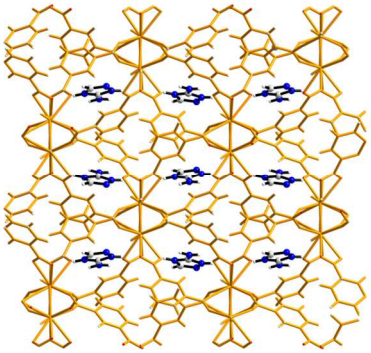


Fig. 9 The scu-3,6-Pnna topology of $[Ln(1,3\text{-}BDC)_2(H_2O)]_n$ can be regarded as a host–guest framework with $HAmTAZ^+$ cations lying in channels.

Yao and co-workers investigated the preparation of a series of isomorphous lanthanide MOMs employing $HAmTAZ^+$ cations as template.[33] The resulting anionic framework of formula $[Ln(1,3\text{-}BDC)_2(H_2O)]_n$ is based on rod-like $[Ln(COO)_4(H_2O)]_n$ MBBs and exhibits a rare (3,6)-connected scu-3,6-Pnna topology. Fig. 9 reveals that $HAmTAZ^+$ cations are located in 1D channels and are engaged in extensive and strong N-H···O and N···H-O hydrogen bonding that occurs between $HAmTAZ^+$ cations and carboxylate oxygen atoms or coordinated water molecules. The

structural information embedded in $HAmTAZ^+$ cations is therefore imparted to the host architecture.

In 2011, Banerjee *et al.* reported three Mn-based MOMs that were synthesized from 5-TIA and $Mn(NO_3)_2 \cdot xH_2O$ in DMF (Fig. 10).[34] Mn–5TIA-1 is a 3D nonporous net that was prepared without template. Mn–5TIA-2 and Mn–5TIA-3 exhibit cross-linked square grid nets and were prepared with pyrazine or 4,4′-bipy, respectively, as template. Mn–5TIA-2 and Mn–5TIA-2 exhibit 3,6-connected **apo** and **rtl** topologies, respectively, and possess pore apertures of ~2.56 Å and ~7.22 Å.

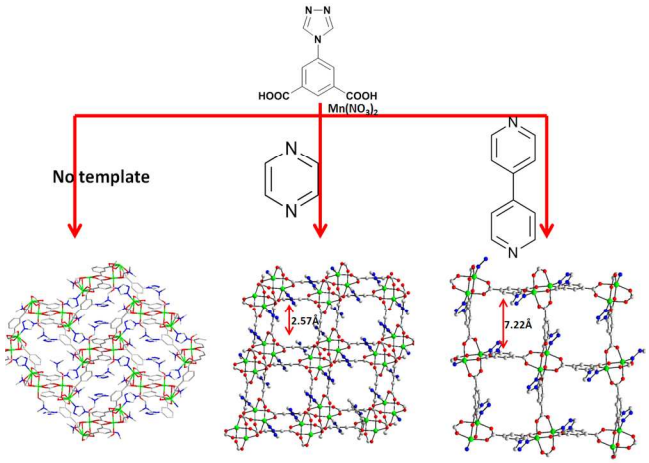


Fig. 10 Mn-MOMs can exhibit porosity that depends on the size of the template used during synthesis.

2.3 Other organic compounds

Organic compounds with carboxylate groups have been utilized to template the formation of cationic MOMs. In 2007, Bu *et al.* prepared a chiral Cu based MOM through the use of an enantiopure anionic template, d-(+)-camphoric acid.[35] Each Cu^+ ion is linked by four 4,4-bipy ligands to form a two-fold interpenetrated **dia** cationic network (Fig. 11). D-(+)-camphorate anions and 4,4-bipy ligands that lie within the cavities form hydrogen bonds with lattice water molecules. In addition, d-(+)-camphorate anions balance the charge of the cationic frameworks. Along the same lines, Wiebcke and co-workers reported a Zn MOM templated by 1,4-BDC.[36] This Zn MOM is a non-interpenetrated **pcu** network with 1D channels filled with 1,4-BDC molecules that interact with the host framework *via* hydrogen bonds between its carboxyl groups and the host framework (Fig. 12).

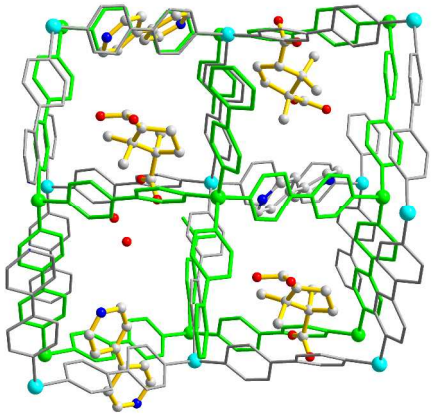


Fig. 11 d-Hcam and 4,4′-bipy lie in channels of a 2-fold **dia** network.

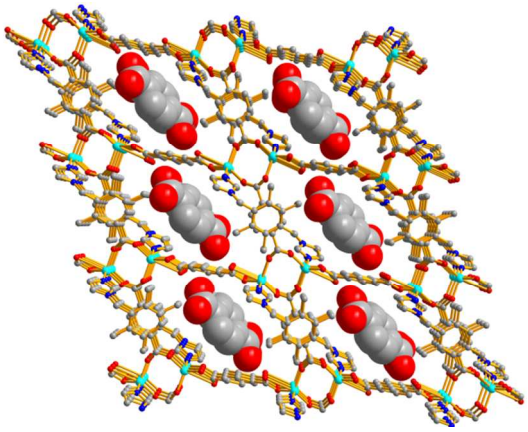


Fig. 12 1,4-BDC guest molecules in the **pcu** network of Zn MOM are presented in space-filling mode.

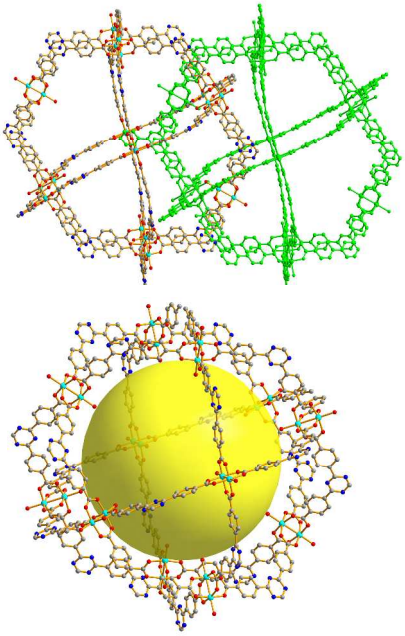


Fig. 13 The structures of PCN-6 (top) and PCN-6′ (bottom).

Ma and Zhou *et al.* reported the template effect of oxalate as a means to exert control over interpenetration in MOMs (Fig. 13).[26b] Reaction of TATB and $Cu(NO_3)_2 \cdot 2.5H_2O$ in DMA afforded a 2-fold interpenetrated MOM, PCN-6. PCN-6 is a 3,4-connected **tbo** net constructed from square paddlewheel MBBs linked by 3-connected TATB ligands. In contrast, a non-interpenetrated variant, PCN-6′, was synthesized by introducing oxalate anions during synthesis. Further studies on the synthetic conditions revealed that whether PCN-6 or PCN-6′ is afforded could not be controlled by varying temperature and solvent. The authors also studied another 3-connected ligand, HTB, which was reacted with $Cu(NO_3)_2 \cdot 2.5H_2O$ under conditions similar to those

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used to form PCN-6 and PCN-6′. PCN-6 was found to exhibit higher Langmuir surface area (3800 m^2/g vs. 2700 m^2/g) and volumetric hydrogen uptake (133% increase) than PCN-6′.

3. Coordination compounds as templates

3.1 Metalloporphyrins

MOMs that incorporate metalloporphyrins have attracted considerable attention in the past decade because they offer potential to serve as catalysts that combine the advantages of heterogeneous and homogenous catalysts in a single system. Two general approaches to incorporate metalloporphyrins into MOMs have been reported: porphMOMs, in which custom-designed porphyrins serve as organic linkers or nodes; porph@MOMs, in which porphyrins are encapsulated in the cages of MOMs. PorphMOMs are relatively well-studied[37] whereas porph@MOMs had until recently been limited to just three examples (porph@MOM-1 to -3), presumably because few existing MOMs contain cages with the requisite size, shape and geometry.[38] The syntheses of porph@MOM-1 to -3 were not achieved through templation because the porphyrin-free variants can be formed without porphyrins. In 2012, we reported a different approach to synthesize porph@MOMs, the use of TMPyP porphyrins as structure directing agents to template the formation of a series of hitherto unknown porph@MOMs, porph@MOM-4 to -11, in which metalloporphyrin moieties are trapped in a "ship-in-a-bottle" fashion.[15, 39] Fig. 14 details how transition metal cations react with BTC to form 2D layer structures in the absence of TMPyP. In contrast, octahemioctahedral cages are formed when TMPyP is present during the same reaction. These cages are well-suited to encapsulate tetrasubstituted porphyrins: their O_h symmetry matches the D_{4h} symmetry of TMPyP (as a subgroup); their cavity diameters of ~13 Å are a good fit for porphyrin rings, which exhibit diameters of ~10 Å; the four N-methyl-4-pyridyl arms of TMPyP can extend through four of the six square windows (~9 Å × 9 Å) of the cage. Porph@MOM-4 to -8 form **tbo** networks whereas porph@MOM-9 exhibits a new topology. Porph@MOM-4 is porous and can serve as a size-selective heterogeneous catalyst for oxidation of olefins.

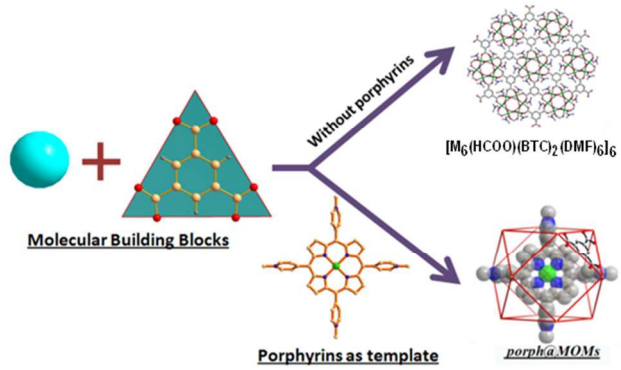

Fig. 14 The structure-directing effect of porphyrins enables the synthesis of porph@MOMs in which porphyrin moieties are encapsulated in a "ship-in-a-bottle" fashion.

TMPyP also templates the formation of porph@MOM-10 and porph@MOM-11, 3,6-connected **zzz** and **rtl** nets, respectively. The stoichiometry of the cationic porphyrin moieties is controlled by charge balance and they alternate in the square channels of these nets (Fig. 15).[39] Porph@MOM-10 is sustained by trimetallic $[Cd_3Cl_2(COO)_6]^{2-}$ MBBs whereas porph@MOM-11 is based upon dinuclear $[Cd_2(COOO)_6]^{2-}$ MBBs. The versatility of Cd with respect to its coordination to carboxylato ligands is a key factor in enabling templation. Permanent porosity and the presence of cadmium porpyrins make porph@MOM-10 and -11 amenable to post-synthetic modification (PSM). Porph@MOM-10 undergoes metal ion exchange to form variants that exhibit porosity and heterogeneous catalytic activity. Porph@MOM-11 undergoes PSM *via* cooperative addition of metal salts (e.g. NaCl and $BaCl_2$) to form porph@MOMs with enhanced CO_2 volumetric uptake and CO_2/CH_4 selectivity *vs.* porph@MOM-11.

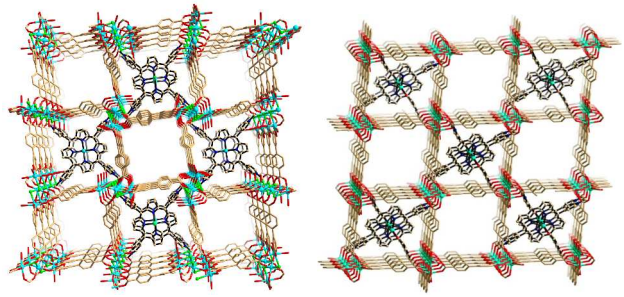

Fig. 15 The structures of porph@MOM-10 (left) and proph@MOM-11 (right).

3.2 $[M(2,2'\text{-bipy})_x]^{y+}$ cations

In 2004, Hong *et al.* reported a Gd-Cu heterobimetallic compound that was prepared by hydrothermal reaction of Gd_2O_3, $Cu(NO_3)_2{\cdot}3H_2O$, 1,3-BDC, and 2,2′-bipy at 170 °C.[40] Cu^{II} was reduced to Cu^{I} by 2,2′-bipy during synthesis and formed $[Cu(2,2'\text{-bipy})_2]^+$ cations which in turn template the formation of the resulting Gd-Cu 3D heterometallic framework. Fig. 16 reveals that two $[Cu(2,2'\text{-bipy})_2]^+$ cations lie in cages of the Gd-Cu framework and balance the charge of the anionic framework. $[Cu(2,2'\text{-bipy})_2]^+$ cations interact with the host framework *via* a series of weak interactions including π···π stacking between the pyridyl rings and the benzene rings of 1,3-BDC.

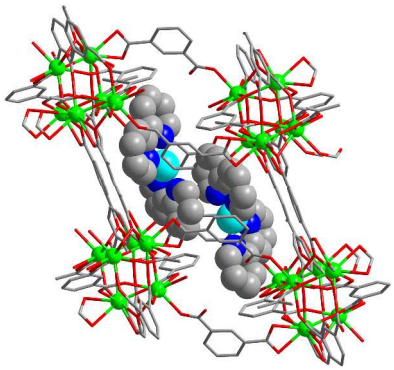

Fig. 16 The cage with two encapsulated $[Cu(2,2'\text{-bpy})_2]^+$ cations (space-filling) in a Gd-Cu framework.

The use of $[M^{II}(2,2'\text{-bipy})_3]^{2+}$ cations as templates in the synthesis of MOMs can be traced to at least 1993 when Decurtins and co-workers prepared a 3-connected **srs** net of formula

$[Fe_2(oxalate)_3]_n^{2n-}$ that wraps around $[Fe(2,2'\text{-bipy})_3]^{2+}$ cations (Fig. 17).[41] Interestingly, this MOM crystallizes in the chiral space group $P4_332$ as $[Fe(2,2'\text{-bipy})_3]^{2+}$ cations are chiral. Coronado *et al.* further studied $[M^{II}(2,2'\text{-bipy})_3]^{2+}$ templated nets when they reported a series of molecular magnets formulated as $\{[Z^{II}(2,2'\text{-bipy})_3]\cdot[ClO_4]\cdot[M^{II}Cr^{III}(ox)_3]\}_n$ (Z^{II} = Ru, Fe, Co, and Ni; M^{II} = Mn, Fe, Co, Ni, Cu, and Zn). These compounds exhibit chiral structures with M^{II} and Cr^{III} ions bridged by oxalate anions. They behave as soft ferromagnets with ordering temperatures up to 6.6 K in coercive fields up to 8 mT.

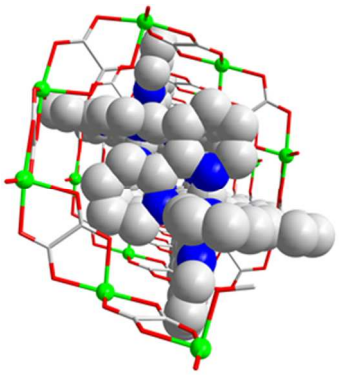

Fig. 17 $[Fe(2,2'\text{-bipy})_3]$ cations (space-filling) are encapsulated in a 3-connected **srs** net.

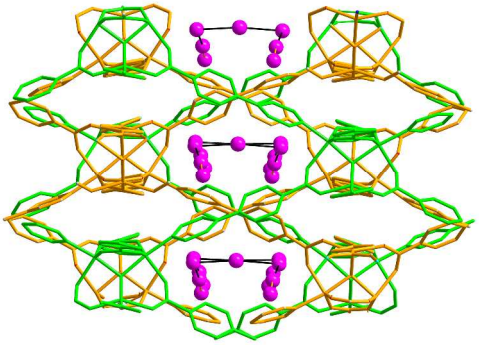

Fig. 18 Polyiodine anions (purple) lie in channels of $\{[Cu_6(pybz)_8(OH)_2]\}_n$.

4. Inorganic compounds as templates

4.1 Iodine

In recent years, there has been interest in incorporation of iodine into porous MOMs, most typically by post-synthetic diffusion. However, in 2012 Zeng's group reported a MOM in which iodine served as a template, thereby enabling the formation of an iodine encapsulating MOM, $\{[Cu_6(pybz)_8(OH)_2]\cdot I_5^-\cdot I_7^-\}_n$ (Fig. 18).[42] This MOM is interdigitated and exhibits 2-fold interpenetration based on a bipillared-bilayer framework. Polyiodide anions lie in channels and are tightly surrounded by the aromatic rings of the channel walls. Reaction without iodine afforded a previously known compound, $[Cu(pybz)_2]_n$, which has a dense and interlocking framework with two independent 3D networks based on single copper nodes. This MOM exhibits iodine release, partial iodine recovery, electrical conductivity and nonlinear optical activity modulated by crystalline transformation and decomposition of polyiodide ions. Su and co-workers recently employed a similar template-directed synthesis strategy to prepare a series of isomorphous 3d-4f heterometallic compounds via hydrothermal reaction of Ln_2O_3, $Cu(NO_3)_2\cdot 6H_2O$ and H_2pydc in the presence of iodine.[43] In the absence of iodine, blue crystals, a previously known compound, were obtained. Ma *et al.* reported another example of the use of iodine as a template to synthesize a MOM with a formula of $[In_2(pydc)_3(H_2O)]\cdot 0.5I_2\cdot 0.5H_2O$.[44]

4.2 Polyoxometalates

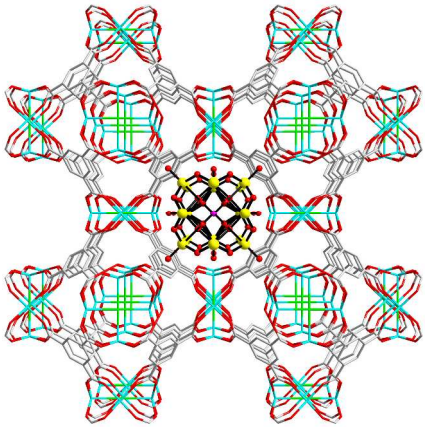

Fig. 19 NENU-11 exhibits eight sodalite-like cages that share square faces to form another cage that encapsulates Keggin polyanions. Hydrogen atoms and $(CH_3)_4N^+$ cations are omitted for clarity. Cu (cyan), O (red), C (gray), Cl (green), W (yellow).

Polyoxometalates (POMs) are a widely studied class of polyoxoanions of the early transition elements that are of particular interest for their ability to serve as catalysts. To address drawbacks associated with homogeneous catalysts such as short lifetime and non-recyclability, several groups have conducted studies aimed at the incorporation of POMs into MOMs. Template-directed synthesis of a "POM@MOM" was reported in 2012 by Su and Liu *et al.*, who prepared a porous MOM, NENU-11, utilising $[PW_{12}O_{40}]^{3-}$ as a template.[45] In the absence of POM only a small amount of HKUST-1 was isolated. NENU-11 consists of chloride-centered square-planar $[Cu_4Cl]^{7+}$ units linked by BTC ligands to afford a (3,8)-connected **the** net with sodalite-type cages (Fig. 19). NENU-11 has entatic metal centers (EMCs) and the multifunctional POM guests enable decontamination of nerve gas. Zhang's group reported an anionic MOM which exhibits the same framework as NENU-11.[46] $[(Me)_2NH_2]^+$ cations were generated by *in situ* solvent hydrolysis of DMA and they can be exchanged for other organic cations such as TMA, TEA and TPA, thereby tuning pore space for gas storage and separations applications.

5. Small gas molecules as templates

In 2007, Tian *et al.* used CO_2 to template the solvothermal synthesis of a series of metal(III) formate MOMs (M = Fe, Al, Ga and In) (Fig. 20).[47] These MOMs form 8-connected **reo** nets in which CO_2 molecules are encapsulated in *mmm* symmetry cages

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and hydrogen bond to formate CH groups (C-H···O = 2.665 Å). To validate the template effect of CO_2, the same reaction was conducted under Ar and was found to afford a previously known product with a formula of $\{[Al(OH)(HCOO)_2 \cdot H_2O]\}_n$. Removal of CO_2 resulted in decomposition of the framework.

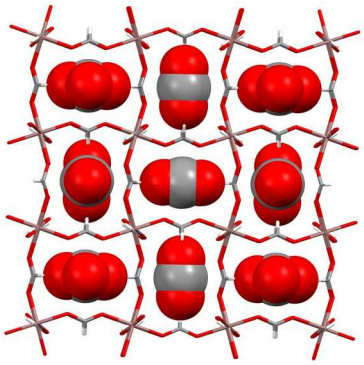
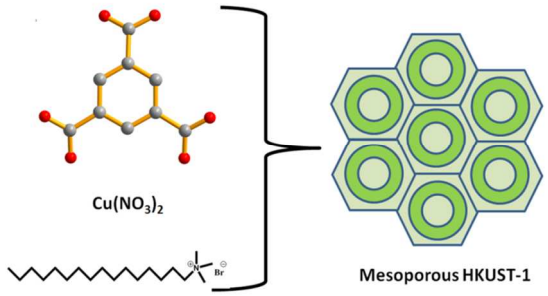


Fig. 20 8-connected **reo** nets with CO_2 molecules in 1D channels.

6. Surfactants as templates

Surfactant templates have been extensively used for preparation of mesoporous silicas and metal oxides to afford materials with high surface area and tunable pore size. However, surfactant templating remains underexplored in the synthesis of MOMs.[48] In 2008, Qiu *et al.* reported the use of CTAB to template a mesoporous variant of HKUST-1 (Scheme 2).[48a] The mesopore diameters in this variant of HKUST-1 can be up to ~5.6 nm. The use of 1,3,5-trimethylbenzene as a co-template extended the pore diameter of HKUST-1 to ~31 nm. In 2012, Zhou's group followed a similar approach to synthesize mesoporous HKUST-1 by using CTAB and citric acid as co-templates.[48b] Their study also revealed that if surfactant or citric acid are applied individually, mesoporous HKUST-1 is not obtained.



Scheme 2 Mesoporous HKUST-1 is self-assembled from copper ions and BTC in the presence of surfactant CTAB as template.

Conclusions

We have detailed herein that template-directed synthesis can be as effective for MOMs as it can be for traditional classes of porous materials. Further, new MOMs which cannot be directly prepared are now accessible. For example, HKUST-1 Co/Mn analogues with the prototypal **tbo** net can only be synthesized by using porphyrins as templates. Moreover, the **zzz** net (porph@MOM-10) cannot be prepared in the absence of templates. There are two important messages from the study of **zzz** nets. First, the use of metals that are promiscuous in terms of their coordination geometry, i.e. Cd^{2+} with carboxylate ligands, enables structural diversity at the level of the MBB which in turn facilitates templation of nets with novel topology. Second, the shape and size of the template profoundly impacts the self-assembly of MBBs as they form larger structures such as cages. Related to the latter, template-directed synthesis can rationally create micropores or mesopores in MOMs. In effect, templation offers a mechanism for fine-tuning of pore size, pore volume and pore shape through the systematic study of templates with different sizes and shapes. Solvent, organic complexes, coordination complexes, inorganic clusters, small gas molecules, and surfactants have all been successfully employed in this context. The templates detailed herein represent enormous diversity with respect to chemical type, size and shape. At one extreme, bulky templates (e.g. CTAB) enable formation of mesopores in MOMs, a difficult challenge for traditional synthetic approaches. At the other extreme, CO_2 can serve as a template and there is every reason to expect that other small gas molecules will also be able to serve as templates.

Future directions for template-directed synthesis of MOMs could involve their use to address industrial scale fabrication of MOMs by controlling the formation of specific MOMs and improving yield.[49] A second direction of practical utility would be to further explore the use of functional templates to transfer the functionality of the template into template@MOM products. A foreseeable extension of this strategy would be to encapsulate biomolecules, even proteins, to synthesize heterogeneous biocatalysts. A third application of template-directed synthesis would be in the area of drug loading and delivery in such a manner that drug molecules serve as templates to synthesize drug@MOMs. However, although there are already numerous examples of template-directed synthesis of MOMs, the mechanisms involved remain poorly understood. In this context, the work of Bajpe *et al.*[50] deserves to be highlighted since it has provided insight into the mechanism of templation. In particular, they discovered that strong electrostatic interactions between Cu^{2+} ions and Keggin templates afford the intermediates that enable the formation of a templated product. Further studies of this nature to address mechanistic issues are in order.

Abbreviations list

MOMs = metal-organic materials
MBBs = molecular building blocks
MOFs = metal-organic frameworks
PCNs = porous coordination networks
PCPs = porous coordination polymers
MOPs = metal-organic polyhedra
CSD = Cambridge Structural Database
BTC = 1,3,5-benzenetricarboxylate
3D = 3-dimensional
2D = 2-dimensional
1,4-BDC = 1,4-benzenedicarboxylate
1,3-BDC = 1,3-benzenedicarboxylate
@ = encapsulating
DMF = N,N′-dimethylformamide
DMA = N,N′-dimethylacetamide

DEE = N,N′-diethylformamide
DEE = N,N-Diethylacetamide
DEP = N,N-Diethylpropionamide
DPE= N,N-dipropylacetamide
DPP = N,N-Dipropylpropionamide
EMIm-Es = 1-Ethyl-3-methylimidazolium ethyl sulfate
dpa = 1,2-bis(4-pyridyl)acetylene
BPDC=4,4′-biphenyldicarboxylate
NH_2BDC=2-amino-1,4-benzenedicarboxylate
ZMOFs = zeolite-like metal-organic frameworks
HPP = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine
H_3ImDC = 4,5- imidazoledicarboxylic acid
AmTAZ = 3-amino-1,2,4-triazole
PSM = post-synthetic modification
bipy = bipyridine
5-TIA = 5-triazole isophthalic acid
bimx = 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene
TATB = 4,4′,4″-s-triazine-2,4,6-triyltribenzoate
HTB = s-heptazine tribenzoate
porph@MOMs = porphyrin encapsulating MOMs
TMPyP = meso-tetra(N-methyl-4-pyridyl) porphine tetratosylate
Pybz = 4-(4-pyridyl)benzoate
CTAB = cetyltrimethylammonium bromide
H_2pydc = pyridine-2,5-dicarboxylic acid

Notes and references

ESI: Table S1 The template@MOMs highlighted herein. Network topology was classified using TOPOS 4.0 software9f when not found in the RCSR database.

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Zhenjie Zhang was born in Hebei of China in 1984, and received his B.Sc and MS degrees from the Nankai University (advisor: Professor Peng Cheng). In the summer of 2010, Zhenjie joined Professor Michael J. Zaworotko's research group at University of South Florida as a Ph.D. graduate student. He currently conducts research in template-directed synthesis and post-synthetic modification of Porphyrin-Encapsulating Metal-Organic Materials (MOMs).

Dr. Mike Zaworotko currently serves as Bernal Chair of Crystal Engineering & Science Foundation of Ireland Research Professor at the University of Limerick, Ireland. He was born in Wales in 1956 and received his B.Sc. and Ph.D. degrees from Imperial College (1977) and the University of Alabama (1982), respectively. He served as a faculty member at Saint Mary's University, Nova Scotia, from 1985-1998 and at the University of South Florida, USA, from 1999-2013. Research activities have focused upon fundamental and applied aspects of crystal engineering since 1990. Currently, metal-organic materials, especially microporous and nanoporous sorbents, and multi-component pharmaceutical materials (MPMs) such as cocrystals, hydrates and ionic cocrystals are of particular interest. He currently serves as Associate Editor of the ACS published journal Crystal Growth & Design.

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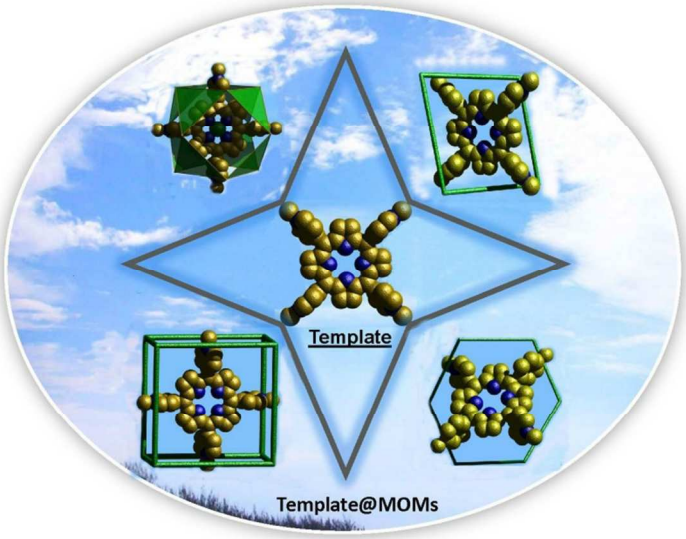
TOC



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