Available online at www.sciencedirect.com
ScienceDirect
Focus Article, *Mendeleev Commun.*, 2017, **27**, 321–331

Mendeleev Communications

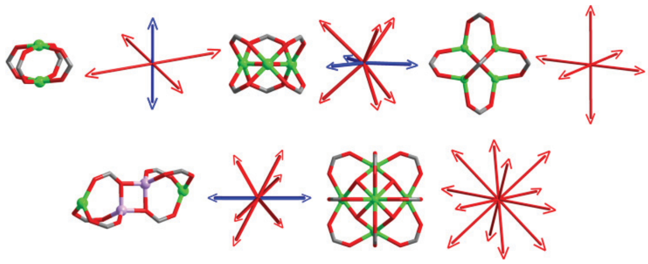
Pre-synthesized secondary building units in the rational synthesis of porous coordination polymers

Danil N. Dybtsev,[a,b] Aleksandr A. Sapianik[a] and Vladimir P. Fedin*[a,b]

[a] *A.V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: cluster@niic.nsc.ru*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*

DOI: 10.1016/j.mencom.2017.07.001

The tailored synthesis of periodic coordination structures is fundamentally important for the design of porous compounds with desired functionalities. The building block approach allows a rational and modular design of metal-organic frameworks to be accomplished from the scratch. This concept takes the advantage of the structural robustness and fixed geometry of ligands in the pre-synthesized complexes. Moreover, such a synthetic protocol can lead to otherwise unaccessible coordination structures. This review outlines the examples of the successful creation of metal-organic frameworks from discrete polynuclear complexes. We hope this work will inspire researchers in their everlasting quest for the targeted design of the materials with desired functionalities.



Introduction

Porous coordination polymers or metal-organic frameworks (MOFs) emerged about two decades ago, and they have quickly become an extensively developed area of modern chemistry and materials science. These crystalline solids are typically constructed from metal ions or clusters as inorganic units connected through structurally rigid organic ligands into coordination networks. The numbers of MOF structures and their functional properties are almost infinite. The most important applications of MOFs arise from their record-high porosity and great structural tunability. A lot of resourceful review articles on gas storage,[1–5] selective separation of gases[6] and other molecules,[7–9] drug delivery,[10] ion transport,[11–13] catalysis,[14,15] luminescence,[16,17] sensing,[18,19] optic properties,[20] magnetic properties,[21,22] electric properties,[23–25] electrochemical applications,[26] using MOF compounds have been publishing for the last decade. As in any other material type, the crystal structure greatly affects the functionality of MOF compounds. This makes the targeted synthesis of porous coordination frameworks fundamentally important in the design of materials with desired properties. The building block concept, which was introduced and developed by G. Ferey,[27] M. Schröder,[28] O. Yaghi and M. O'Keeffe,[29] allows one to achieve the simplification and topological visualization of complex coordination structures. More importantly, the building block approach makes it possible to rationalize the modular design of a particular MOF from scratch.

The inorganic building blocks are usually composed of several metal nuclei linked by multidentate oxo/hydroxo/halido anions or donor groups of organic ligands.[30–32] The overwhelming majority of such polynuclear metal units are self-assembled from the mononuclear cations and salts during the crystallization of a MOF under optimized reaction conditions. However, in many

Danil N. Dybtsev received his PhD degree in 2002 under the supervision of Professor V. P. Fedin and Dr. Sci. degree in 2014. He got an extensive post-doctoral experience in the research groups of Professor K. Kim (POSTECH, Korea) and Professor G. Férey (Versailles University, France). After several years of visiting professorship in Pohang University of Science and Technology, he joined A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences (SB RAS), where he is a deputy director for science. His research interests include coordination chemistry, metal-organic frameworks and porous materials.

Aleksandr A. Sapianik, graduate student at A. V. Nikolaev Institute of Inorganic Chemistry, SB RAS. His research interests include metal-organic frameworks based on preorganized polynuclear complexes.

Professor **Vladimir P. Fedin** received his PhD degree from M. V. Lomonosov Moscow State University (Professor A. N. Nesmeyanov). He performed his postdoctoral work with Professor A. Muller (AvH Fellowship), Professor A. G. Sykes (RCS Rapitza Fellowship) and Professor T. Saito (JSPS Fellowship). He is director of A. V. Nikolaev Institute of Inorganic Chemistry, SB RAS, and head of the Chair of Inorganic Chemistry at Novosibirsk State University. His research interests focus on inorganic, coordination, cluster and supramolecular chemistry.

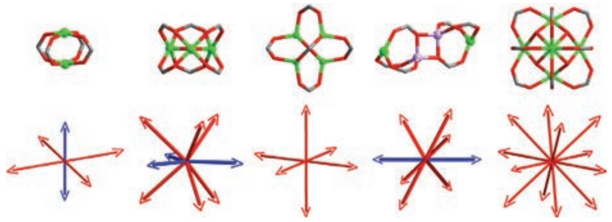


Figure 1 MOF building blocks (from left to right, $\{M_2(CO_2)_4\}$, $\{M_3O(CO_2)_6\}$, $\{Zn_4O(CO_2)_6\}$, $\{Li_2M_2(CO_2)_6\}$ and $\{Zr_6O_8(CO_2)_{12}\}$) and possible directions of structure extension: red, carboxylate linkers; blue, electron donating linkers.

cases, these units occur as discrete polynuclear complexes soluble in common solvents, and they are stable enough to sustain (partial) ligand substitution during the crystal growth of MOFs. Therefore, the synthesis of a particular MOF could be rationalized by choosing a pre-synthesized soluble complex with the fixed structure of metal nuclei and local geometry of the inner sphere ligands as a starting compound. Though such a two-step synthetic route could be time consuming, it is more rational and more predictable, as compared with a simple one-pot reaction, which relies completely on a self-assembly. In some cases, MOF products can be obtained only from the pre-synthesized metal complexes as starting materials. In addition, the use of the polynuclear complexes is especially rewarding in the preparation of MOFs based on heterometallic polynuclear units since complex multicomponent reaction mixtures rarely yield the desired phase-pure crystalline product with a regular chemical composition.

Since the discovery of first highly porous copper(II) trimesate (HKUST-1) and zinc(II) oxoterephthalate (MOF-5) in 1999,[33,34] metal-carboxylate frameworks absolutely dominate among MOF compounds.[35,36] Carboxylate anion ($RCOO^-$) possesses two donor oxygen atoms with two lone electron pairs; therefore, up to four metal cations could be coordinated to one carboxylate. As a result, metal-carboxylate frameworks are often based on polynuclear carboxylate complexes as inorganic building blocks. In many cases, those complexes are well-known in classical coordination chemistry of monocarboxylate ligands (acetate, pivalate, benzoate, *etc*.). Despite the fact that many convenient polynuclear metal complexes are well-known and readily available, the step-by-step syntheses of coordination frameworks from the pre-assembled units are rarely used, which is disappointing. This review summarizes the examples of the successful design of MOFs from discrete complexes, and it could be an inspiration for those who attempt to obtain particular coordination structures with desired functionality. The review is composed of two sections: (i) homo- and heterometallic polynuclear metal complexes as nodes for MOF synthesis (Figure 1) and (ii) metal clusters as building units for MOF synthesis. Each section is further ranked by an increasing nuclearity of metal complexes/clusters.

M_2 building blocks

Binuclear metal carboxylates $[M_2(RCOO)_4(L)_2]$ are the simplest polynuclear metal units featured in MOF structures as building blocks. Many acetates with the above formula ($M = Cr^{2+}$, Cu^{2+}, Mo^{2+}, Ru^{2+}, Rh^{2+}, *etc.*) are known in classical coordination chemistry as so-called paddle-wheel complexes. Moreover, for certain complexes, *e.g.* $[Cu_2(OAc)_4(H_2O)_2]$, the formation of such binuclear carboxylate structures is almost inevitable. As a result, many examples of the targeted design of MOF structures based on the paddle-wheel complexes have been reported. The geometry of $[M_2(RCOO)_4(L)_2]$ molecular complexes represents an octahedron with four carboxylate ligands directed around a square and two axillary ligands (L) perpendicular to the plane of the square. The four carboxylate bridges are connected to two metal centers by *syn-syn* mode, while the apical L molecules are typically N- or O-donor monodentate ligands. As a result, the paddle-wheel complexes $[M_2(RCOO)_4(L)_2]$ could be extended onto regular periodic networks in different ways: (i) connection through axillary positions; (ii) connection through dicarboxylate ligands and (iii) substitution of both carboxylates and L ligands.[37] The first way seems simpler since it does not affect the metal carboxylate core, while the substitution of carboxylate ligands should involve apparently less stable intermediates with a distorted coordination environment. In 1974, Soos *et al*. obtained the crystal structure of a 1D polymer, where the binuclear copper(II) acetate units $[Cu_2(OAc)_4]$ were linked by ditopic pyrazine (pz, see Figure 2) ligands.[38] Similar results were reported later.[39–42] More complicated topologies prepared by connecting the paddle-wheel units through polytopic organic ligands are discussed below.

In 2000, Robson *et al*.[43] synthesized a layered coordination framework with a honeycomb structure by the reaction of $[Cu_2(OAc)_4]$ solution in methanol with 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) solution in benzyl alcohol. MacGillivray *et al*.[44] employed *rctt*-tetrakis(4-pyridyl)cyclobutane (4,4′-tpcb) as an axial linker for $[Cu_2(OAc)_4]$, resulting in a 2D coordination polymer $[Cu_2(OAc)_4(4,4'\text{-tpcb})_{1/2}]$ with an open structure of isolated 1D channels formed by the stacking of layers one above another. In 2006, Ohmura *et al*.[45] synthesized a 2D MOF based on pyridylporphyrin (H_2tpyp) and copper(II) acetate dinuclear complexes. Similarly, the structure of $[Cu_2(AcO)_4\{Cu(tpyt)\}_{1/2}]$ is made of intersecting layered motives. The permanent porosity of $[Cu_2(AcO)_4\{Cu(tpyt)\}_{1/2}]$ was further confirmed by gas adsorption isotherm measurements, featuring a reversible type I isotherm characteristic of the microporous materials.

The first periodic coordination network based on a pentagon tiling was obtained by the group of Zaworotko[46] using the slow diffusion of a methanol solution of urotropin (hexamethylenetetramine) into a solution of $[Cu_2(EtCOO)_4(MeOH)_2]$. The dinuclear copper carboxylate spacers link the three- and four-connected ur moieties into a (5,4/3)-net, as illustrated in Figure 3. The two crucial design elements that direct the formation of a particular coordination topology in such systems were emphasized: the carboxylate anion in the pre-built dinuclear units $[Cu_2(RCOO)_4]$ and the ratio between these $\{Cu_2\}$ complexes and ur. For example, the 1D zigzag structure[47] is observed when ur coordinates to two $[Cu_2(RCOO)_4]$ linkers (R = Me or Bu^t), and a diamondoid structure[48] results from the coordination of four binuclear $\{Cu_2\}$ units to ur.

In 2010, Dunbar *et al*.[49,50] synthesized a series of ruthenium(II) and rhodium(III) based two-dimensional fishnet-type networks containing the paddle-wheel complexes linked by 7,7,8,8-tetracyanoquinodimethane (TCNQ) ligands. The resulting materials exhibited interesting magnetic and conducting properties.

The dinuclear metal paddle-wheel complexes $[M_2(RCOO)_4(L)_2]$ could also be connected into extended coordination structures through polycarboxylate linkers. The research group of Mori succeeded in obtaining a wide range of 2D and 3D coordination polymers from pre-synthesized copper(II) carboxylate complexes. For example, the layered copper(II) terephthalate $[Cu_2(bdc)_2]$ (bdc^{2-} = terephthalate) with a square-grid topology was synthesized by adding a methanol solution of copper(II) formate to a methanol solution of terephthalic (H_2bdc) and formic acids to result in blue plate-like crystals.[51] Later, the family of these layered coordination structures was expanded by the use of other dicarboxylate linkers (fumaric acid and *trans*-1,4-cyclohexanedicarboxylic acid) under the same reaction conditions. All of the three compounds can be activated by heating *in vacuo*. In turn, the activated compounds are capable of adsorbing gases, and this fact supports their permanent porosity. In particular, methane uptakes of 71, 82 and 60 $cm^3\ g^{-1}$ were achieved at 3.5 MPa by the samples of terephthalate-, fumarate- and *trans*-

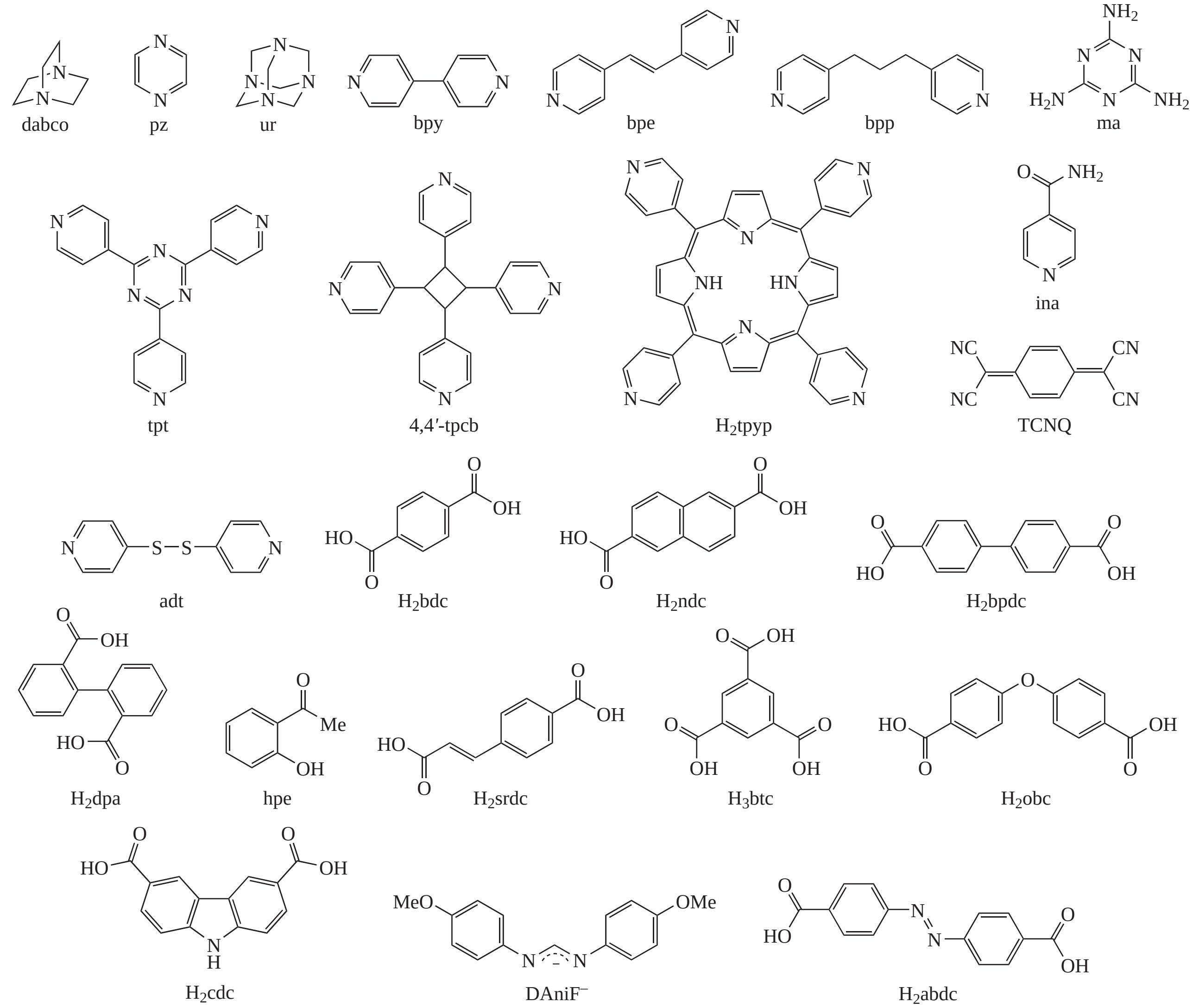


Figure 2 Organic reagents structures and their abbreviations used in the text.

1,4-cyclohexanedicarboxylate-based MOFs, respectively. These values are similar to those for zeolite 5A.[52] The addition of dabco as a second linker to the reaction mixture of $[Cu_2(RCOO)_4]$ (R = H or Me) and rigid stryrenedicarboxylic acid (H_2sdc) or biphenyldicarboxylic acid (H_2bpdc) results in the formation of 3D structures where the octahedral units $[Cu_2(RCOO)_4]$ are connected through the corresponding dicarboxylate and dabco pillars in all six directions, making the highly porous scaffold-like MOFs. The adsorption isotherm measurements confirmed the stability and excellent gas uptake properties of such materials as the BET surface areas of 3129 and 3265 $m^2 g^{-1}$ were reported for $[Cu_2(sdc)_2(dabco)]$ and $[Cu_2(bpdc)_2(dabco)]$, respectively, and these values are much higher than those for any porous zeolite.[53]

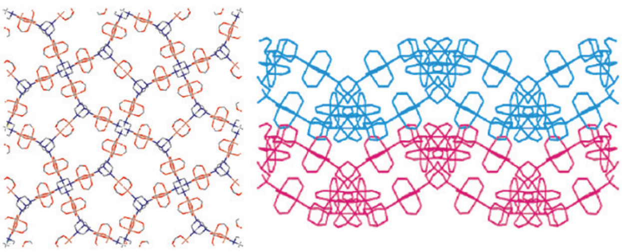


Figure 3 (*a*) Overhead and (*b*) perspective views of the (5,4/3)-network (H atoms omitted for clarity) in the crystal structure of $[ur]_3[Cu_2(\mu\text{-}O_2CEt)_4]_5$. Reproduced with permission from ref. 46. © 2001 American Chemical Society.

Being structurally similar to a carboxylate anion, the *N*,*N*′-di-(*p*-anisyl)formamidinate anion ($DAniF^–$) also stabilizes the formation of binuclear transition metal complexes. The complexes $[M_2(DAniF)_2L_4]$ and $[M_2(DAniF)_3L_2]$ (M = Mo, Rh, *etc.*; L = = MeCN) are of particular interest since the presence of poorly coordinated acetonitrile ligands allows the targeted design of extended coordination structures to be accomplished from these complexes. In the simplest example, two anionic $[Mo_2(DAniF)_3(CH_2CN)_2]^{4-}$ units could be connected to a dimer through the replacement of the CH_2CN ligands by a dicarboxylate (fumarate, malonate, succinate, *trans*-1,4-cyclohexanedicarboxylate, *etc.*). More complex molecular units, such as loops, triangles, squares or even molecular polyhedra, could be assembled from the $[M_2(DAniF)_2L_4]$ complexes and the dicarboxylate linkers under certain reaction conditions. Furthermore, the molecular loops or squares were extended into 1D tubular structures by employing additional N-donor ditopic ligands, such as *trans*-1,2-bis(4-pyridyl)-ethylene or 1,4-dicyanobenzene. More than 40 coordination compounds were obtained in the rational step-by-step manner, as outlined by Cotton *et al.*[39] They proposed abundant opportunities for the further development of such complex structures and the exploration of their functional properties in molecular separation, redox activity and host–guest chemistry.

The discovery of porous copper(II) trimesate $[Cu_2(btc)_{2/3}]$ (also known as HKUST-1) boosted the research area of the porous MOFs tremendously.[33] Although the original synthesis was carried out using a simple copper(II) nitrate salt and trimesic acid (H_3btc), the employment of pre-assembled dinuclear carboxylate complexes made it possible to introduce new interesting aspects to the rational preparation of the HKUST-1. In particular, Pichon and James[54] employed solvent-free mechanochemical synthetic conditions to obtain coordination frameworks, including HKUST-1, using the paddle-wheel acetate, formate and trifluoroacetate $[Cu_2(RCOO)_4]$ complexes. Remarkably, HKUST-1 was prepared in a quantitative yield within minutes, which emphasizes the structure-directing role of the pre-assembled dinuclear copper(II) carboxylate units. The reaction between copper(II) acetate and H_3btc in a mixed solution of DMF/EtOH/H_2O under ultrasonic treatment at ambient temperature for short reaction times (5–60 min) yielded nanosized $[Cu_2(btc)_{2/3}]$ crystals with no significant loss in physicochemical properties, such as specific surface area, pore volume and gas storage capacity, compared with HKUST-1 microcrystals obtained by a conventional solvothermal method.[55] A number of mixed-valence Ru analogues of the HKUST-1 $[Ru_2(btc)_{2/3}X]$ (anion X = Cl, Cl/OH, F/OH, OH) were synthesized from dinuclear Ru(II,III) acetate or pivalate precursors and H_3btc. It was demonstrated that the bulkier *tert*-butyl group in the ruthenium pivalate results in a striking improvement of the crystallinity of the final MOFs, compared with the ruthenium acetate precursor. The counter ion X also affects the number of coordinatively unsaturated metal sites in the activated framework $[Ru_2(btc)_{2/3}]$, which is crucial for the catalytic, adsorption and other important functional properties of porous materials.[56]

A very interesting example of the step-by-step design of the 3D architecture was reported by the group of Zhou.[57] The reaction between copper(II) nitrate and carbazole-3,6-dicarboxylic acid (H_2cdc) leads to the large hollow metal-organic octahedron $[Cu_2(cdc)_2L_2]$ (L = solvent), where $[Cu_2(COO)_4]$ paddle-wheel units reside at the vertexes and the carbazoledicarboxylate moieties link these $\{Cu_2\}$ units to form the edges of the octahedron (Figure 4). These large metal-organic octahedrons are soluble in organic media with the retention of their structure. More importantly, such pre-assembled octahedral blocks could be connected through linear bpy linkers, which coordinate to the apical positions of the $\{Cu_2\}$ carboxylate units on the outer surface of the polyhedron. The resulting 3D metal-organic network was dimensionally reduced back to a molecular octahedron and further deconstructed to form a 1D chain, representing the first example of the reversible assembly of a MOF from a presynthesized molecular polyhedral block.

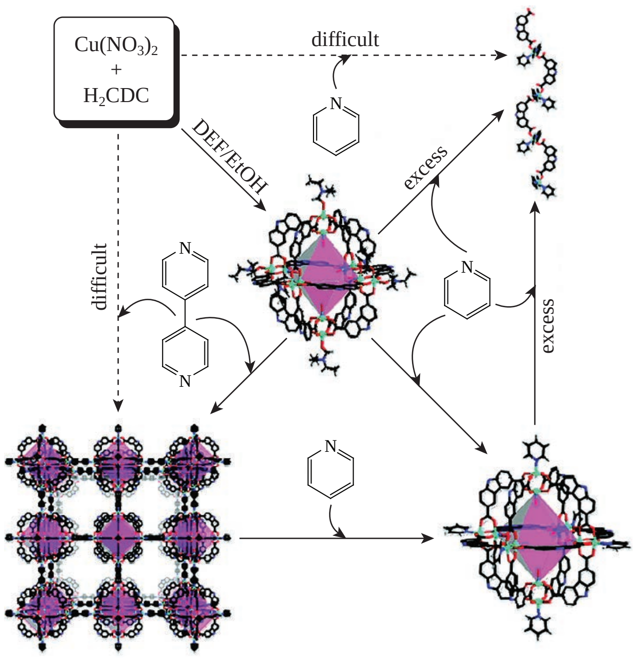
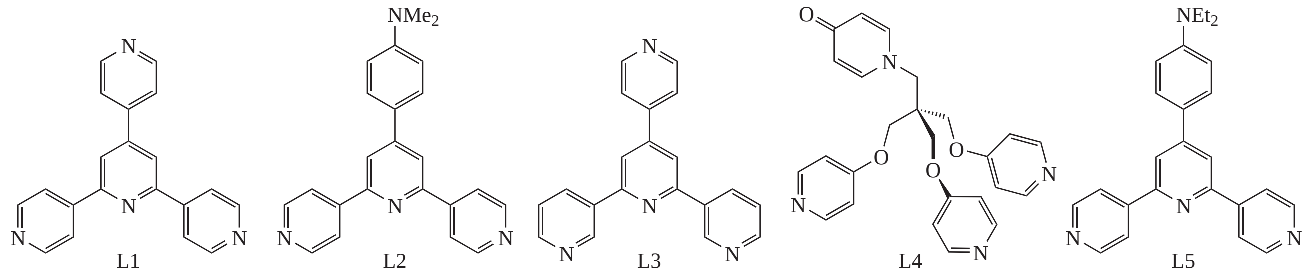


Figure 4 Reaction scheme and drawings of crystal structures of coordination assemblies. Most of the H atoms have been omitted for clarity. Color scheme: Cu, aqua; O, red; N, blue; C, black. Reproduced with permission from ref. 57. © 2009 American Chemical Society.

M_3 triangle building block

Trinuclear basic carboxylate units $[M_3O(RCOO)_6L_3]$ are a common type of the complexes of transition metals in the oxidation states +2 and +3, (sometimes, +4). Basic metal acetates are typically crystallized from the aqueous solutions of acetic acid and the corresponding metal salts. Three metal cations form a triangle with a bridging μ_3-O oxo anion. Six bridging carboxylate ligands connect each pair of metal cations above and below the M_3 plane, forming an incomplete octahedral environment of oxygen atoms around each metal cation. The sixth coordination position in this octahedron is occupied by a solvent molecule, such as H_2O, or additional axillary monodentate ligand (*e.g.*, pyridine). Moreover, the trinuclear metal oxocarboxylate core is a platform for numerous heterometallic complexes $[M'M_2O(RCOO)_6L_3]$, typically, with 3*d* metals. Such complexes are very convenient starting materials for the rational design of heterometallic coordination frameworks. The trinuclear complexes $[M_3O(RCOO)_6L_3]$ could be extended through either axillary ligands, carboxylate ligands or both. In the first case, the complex serves as a triangular node. In the second case, it is a six-connected node with trigonal prismatic geometry. Both cases were extensively explored in the design of the metal-organic coordination structures. As a result, significant progress has been achieved in the investigation of the mechanism of the directed assembly of the trinuclear building blocks $[M_3O(RCOO)_6L_3]$ into extended frameworks.

The research group of I. L. Eremenko developed the use of polydentate N-containing bridging linkers to connect heterometallic pivalate complexes $[M'M_2O(piv)_6(Hpiv)_3]$ (piv = Bu^tCOO^-) into an array of extended structures. Two isostructural coordination polymers $[Fe_2MO(piv)_6(bpy)_{3/2}]$ (M = Ni^{2+} or Co^{2+}) were prepared by linking the corresponding trinuclear heterometallic pivalates with linear bpy linkers. The triangular direction of the bpy linkers of the trinuclear pivalate building units $[M'M_2O(piv)_6(bpy)_3]$ gives rise to the layered honeycomb structure of the coordination polymers. The crystal structure of both compounds comprised three such interpenetrated honeycomb layers with zigzag channels in the interstitial space. Microporous nature of both compounds was confirmed by the measurements of N_2 and H_2 adsorption isotherms (S_{BET} = 520 m^2 g^{-1} for M = Ni, S_{BET} = 273 m^2 g^{-1} for M = Co). The structures of the trinuclear heterometallic pivalate complexes are successfully retained in the coordination polymers and so are magnetic properties as the magnetic behavior of $[Fe_2MO(piv)_6(bpy)_{3/2}]$ was found to be governed by exchange interactions in trinuclear blocks.[58] Moreover, the crystal structures of the porous coordination polymers $[Fe_2MO(piv)_6(bpy)_{3/2}]$ were found flexible in terms of changes in distances between the independent layers, which led to a variation in the pore volume. Such changes are completely reversible and induced by solvent exchange. A strong difference between the sorption of alkanes and alcohols was found: while alkane (*n*-hexane and *n*-octane) sorption isotherms were typical of microporous sorbents, the adsorption of alcohols (methanol and ethanol) was probably associated with structural rearrangements, which continuously occurred with increasing the sorbate pressure. This distinction and the higher sorption capacity for ethanol, as compared with that for methanol, is consistent with the hydrophobic nature of the channels (due to the presence of multiple *tert*-butyl groups in their structure).[59]



Linking the trinuclear complexes through organic pseudo-D_{3h} symmetric ligands led to the formation of 2D coordination polymer $[Fe_2NiO(piv)_6(L1)]$ (L is a bridging ligand). The crystal structure of this compound was stable to desolvation, and the desolvated structure was capable of adsorbing significant quantities of N_2 and H_2. The dimensionality of the product was reduced by removing a donor group from the ligand. This change transformed the ligand into a C2v symmetric bridge and caused a structural change from an infinite 2D polymer to a discrete 24-nuclear molecule $[\{Fe_2NiO(piv)_6\}_8\{L_2\}_{12}]$, which possessed a nanocube structure. Therefore, the desolvation of this compound led to the collapse of the crystal structure, and the compound was characterized by much lower sorption capacity compared to 2-D coordination polymer. The magnetic properties of the compounds were governed by those of the trinuclear $\{Fe_2NiO(piv)_6\}$ unit.[60] Further investigation in linking the same trigonal complex $[Fe_2NiO(piv)_6(Hpiv)_3]$ (piv^- = pivalate) by a bigger series of polypyridine ligands resulted in obtaining novel layered $[Fe_2NiO(piv)_6(tpt)]$, $[Fe_2NiO(piv)_6(L3)]$, $[Fe_2NiO(piv)_6(L4)]$ and chain-like $[\{Fe_2NiO(piv)_6\}_4(L5)_6]$ coordination polymers (Figure 5). It was shown that the polypyridine spacer played a key structure-driven role in the dimensionality and topology of the

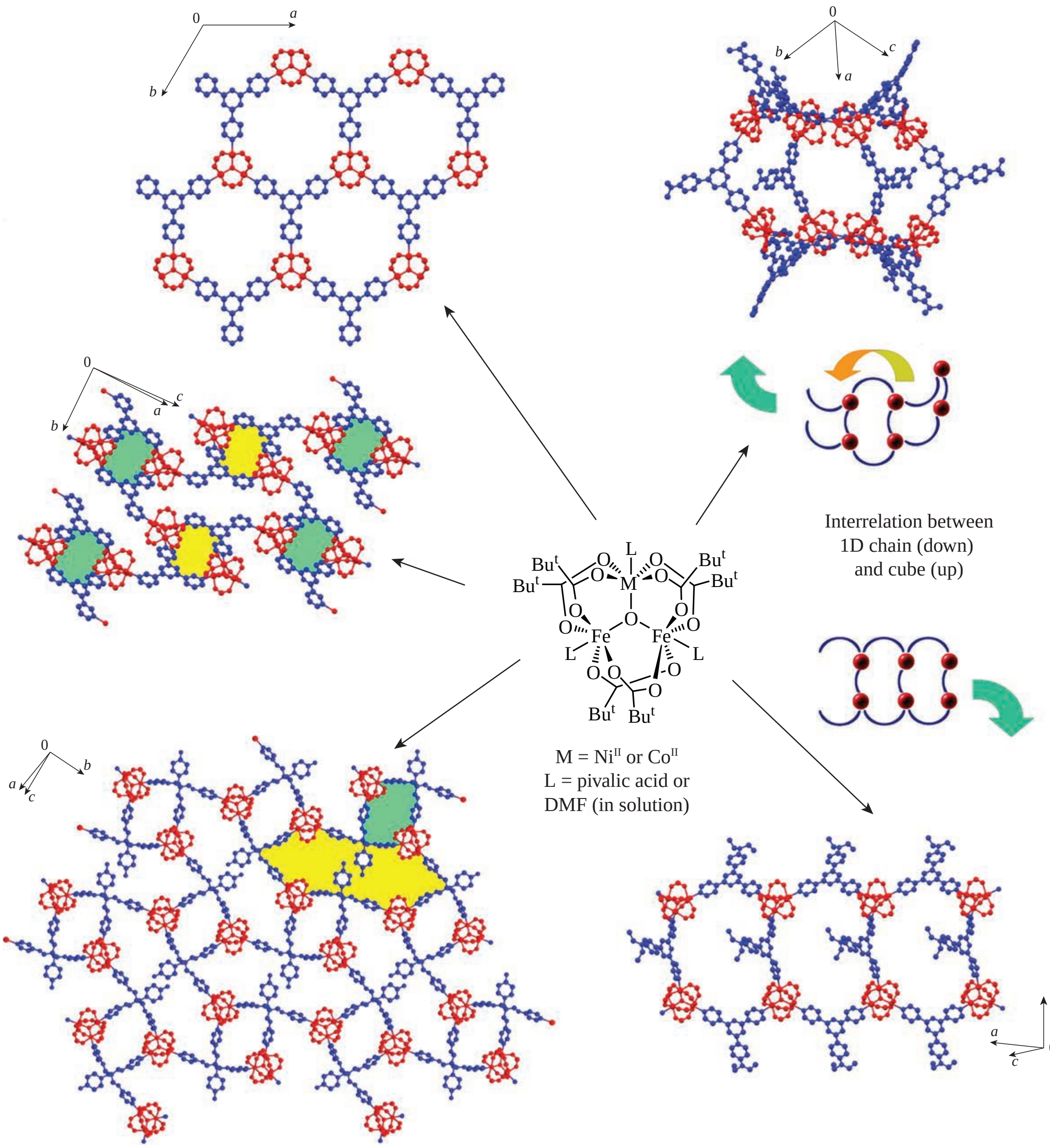


Figure 5 Coordination polymers based on the $\{Fe_2MO(RCOO)_6\}$ fragment. All H atoms, Bu^t groups, and noncoordinated molecules (if any) are omitted for clarity. Reproduced with permission from ref. 61. © 2015 American Chemical Society.

resulting coordination network. Compounds $[Fe_2NiO(piv)_6(L2)]$ and $[Fe_2NiO(piv)_6(L3)]$ possess porous structures, as confirmed by the sorption of N_2 and H_2 at 78 K. Additionally, porous coordination polymer $[Fe_2NiO(piv)_6(L2)]$ was used as a heterogeneous catalyst for the condensation of salicylaldehyde or 9-anthracenecarbaldehyde with malononitrile. The best activity was observed in the case of a salicylaldehyde substrate, resulting in up to 88% conversion into 2-imino-2*H*-chromene-3-carbonitrile.[61]

Linking the trinuclear pivalate $[Fe_2CoO(piv)_6]$ fragment by the redox-active bridge $[Ni(L6)_2]$ (L6H is Schiff base from the hydrazide of 4-pyridinecarboxylic acid and 2-pyridinecarbaldehyde) afforded new porous coordination polymer $[\{Fe_2CoO(piv)_6\}\{Ni(L6)_2\}_{3/2}]$. The crystal lattice of this compound is built of stacked 2D layers where each $[Ni(L6)_2]$ unit binds two $[Fe_2CoO(piv)_6]$ ones. The magnetic properties of the coordination polymer mainly depend on the magnetism of trinuclear pivalate and the $[Ni(L6)_2]$ bridge as the interactions between these components are minor. Redox activity studies of the coordination polymer showed potentials similar to that of the $[Ni(L6)_2]$ complex in solution, providing that the electronic influence of $\{Fe_2Co\}$ units on $[Ni(L6)_2]$ is not significant, which is consistent with magnetochemical data. The catalytic activity of $[\{Fe_2CoO(piv)_6\}\{Ni(L6)_2\}_{3/2}]$ in $CHCl_3$ dehalogenation was demonstrated.[62]

Significant progress in exploring the secondary building unit (SBU) approach was achieved by the research group of Ferrey.[63] A series of the coordination polymers were prepared from the trimeric acetate complexes $[M_3O(OAc)_6L_3]$ (M = Fe, Cr, V, Ru, Mn, and Co) in the presence of dicarboxylic acids at elevated temperatures, which promoted direct exchange between the acetate and dicarboxylate moieties while the trimeric units remained intact throughout the MOF formation.

The two new isostructural 3D coordination polymers $[Fe_3O(MeOH)_3(succ)_3]$ and $[Fe_3O(MeOH)_3(adip)_3]$ were prepared from trinuclear iron(III) acetates and succinic $[HOOC(CH_2)_2COOH]$ or adipic $[HOOC(CH_2)_4COOH]$ acid, respectively (Figure 6).[63] In these crystal structures, the trinuclear $\{Fe_3\}$ prismatic units are connected by dicarboxylate linkers into hexagonal topology. Similar frameworks were obtained using longer terephthalate (bdc^{2-}), 2,6-naphthalenedicarboxylate (ndc^{2-}) and 4,4′-biphenyldicarboxylate ($bpdc^{2-}$) linkers. The experiments showed that these solids exhibit remarkable structural dynamics (breathing) upon gas sorption and a gate-opening phenomenon featured by a huge hysteresis between the adsorption and desorption plots. Such a behavior could enlarge the field of applications for such materials.[64] Further investigations of trimeric iron oxocarboxylate with the involvement of EXAFS data measured from amorphous intermediates and crystallization solutions provided the first evidence that the trinuclear building units remain intact during the crystallization of MOFs.[65] Particularly, the crystallization of $[Fe_3O(adip)_3]$ occurs *via* the initial formation of an amorphous phase, which then dissolves before being consumed completely

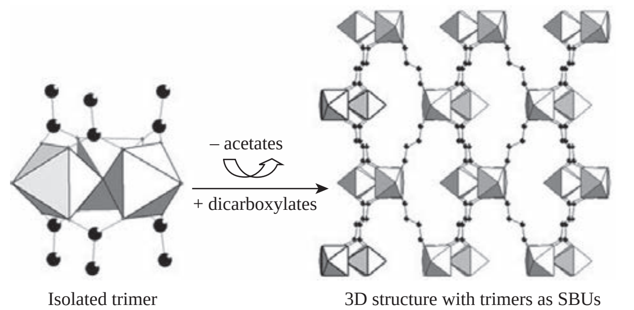


Figure 6 Schematic representation of the synthetic route involving trimeric SBUs with MIL-88 given as an example. Reproduced with permission from ref 63. © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

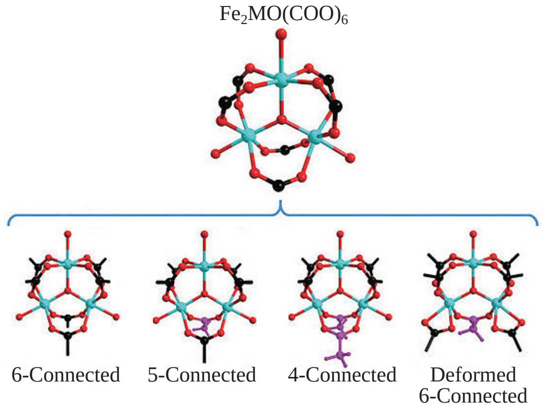


Figure 7 Four connecting modes of the $[Fe_2M(\mu_3\text{-}O)]$ cluster. Carboxylates on ligands and terminal acetates are represented in black and purple, respectively. Reproduced with permission from ref. 68. © 2014 Macmillan Publishers Ltd.: Nature.

to yield solely the final crystalline product. This process is analogous to that revealed for the hydrothermal crystallization of classical aluminosilicate zeolites, where an amorphous intermediate phase is commonly found prior to the formation of the zeolite.[66] Recently, the oxo-centered trimeric mixed metal acetates $[Fe_2M(\mu_3\text{-}O)(AcO)_6]$ (M = Ni, Co, and Mg) were used as building blocks for the environmentally friendly and scalable preparation of mixed-metal MOFs. The trinuclear complexes were linked by azobenzenetetracarboxylate linkers ($abdc^{2-}$) to result in a series of isostructural porous networks ($S_{BET} > 1300\ m^2\ g^{-1}$) with practically interesting aspects, such as the hydrothermal stability and accessibility of active metal sites, as confirmed by spectroscopic techniques and adsorption studies.[67]

Feng *et al*. used $[Fe_2M(\mu_3\text{-}O)(OAc)_6]$ (M = Fe, Cr, Al, Sc, V, and In) complexes as the sources of 4,5,6-connected nods (Figure 7) for coordination polymer synthesis by the acetate anion replacement with polycarboxylate linkers and their combinations. Through this versatile synthetic route, they obtained the single crystals of 34 iron-containing MOFs. Even though the ligands vary in symmetry, functionality, connectivity and size, the structure of the $\{Fe_2M\}$ building block is maintained in these frameworks. The synthetic strategy included a dimensional augmentation from zero-dimensional trinuclear nodes $\{Fe_2M\}$ to three-dimensional nets. Partial substitution for the ligands in the $[Fe_2M(\mu_3\text{-}O)(OAc)_6]$ clusters proceeds when complete substitution becomes incompatible with some of the ligands because of symmetry requirements or steric hindrance. Although all of the above Fe-MOFs are synthesized under similar conditions, the varying amount of acetic acid as a modulator agent was added in each case to avoid the precipitation of amorphous products. An excess of acetic acid slows down the ligand substitution reaction, which, in turn, slows the rate of the MOF crystal growth and improves the crystallinity of the product. However, when the concentration of acetic acid is too high, reaction solutions remain clear with no solid products even after a long period, which suggests a favorable thermodynamic equilibrium for the molecular species over the insoluble coordination polymers. It was found that, for ligands with similar size and connectivity, MOFs containing the trinuclear $\{Fe_2M\}$ units with lower connectivity always need a lower concentration of acetic acid as the modulator reagent. Meanwhile, for $\{Fe_2M\}$ units with the same connectivity, ligands with higher connecting numbers always require more acetic acid.[68]

M_3 linear 'pin-wheel' unit

Another type of trinuclear metal(II) carboxylate complexes represents a rod-like unit with a six-coordinated metal cation at the center and four- or five-coordinated metal cations at the ends

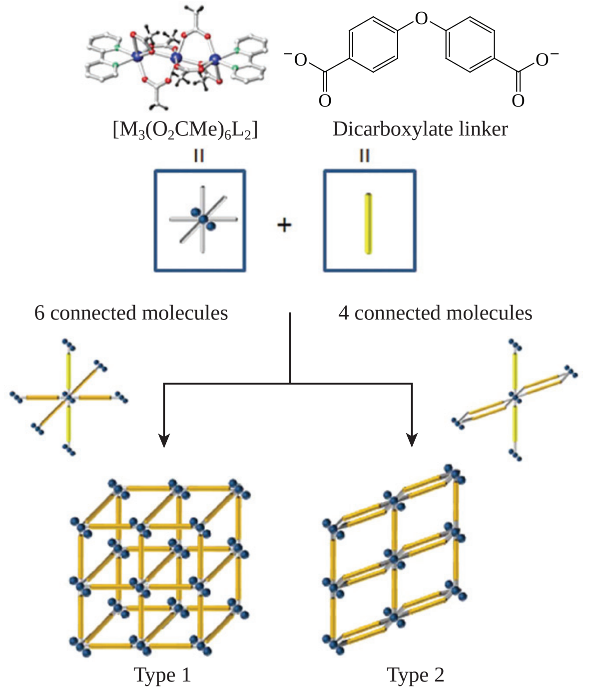


Figure 8 Synthesis of an extended trinuclear MOF starting from a dicarboxylate linker and a linear trinuclear complex. Yellow sticks and blue ball clusters represent obc ligands and linear trinuclear complexes, respectively. Reproduced with permission from ref. 69. © 2012 The Royal Society of Chemistry.

of the rod. Three carboxylate groups bridge central metal atom with either one of two terminal cations forming the overall six-connected pin-wheel geometry of the carboxylate groups. The coordination number of the terminal cations could be four or five, depending on the metal cation radius and the denticity of the terminal ligand. Even though such trinuclear fragments are quite common in MOF structures, the molecular complexes are less abundant than the above triangular ones. There is one published example of the rational framework engineering from the pin-wheel $[M_3(AcO)_6(2,2'\text{-bpy})_2]$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}; 2,2′-bpy = 2,2′-bipyridyl) complexes reported by Kim and Jung.[69] They prepared trinuclear complexes as starting materials for the synthesis of MOFs, which preserved the local structures of pristine trinuclear units. Linear trinuclear molecules were used as SBUs due to their potential catalytic and magnetic properties. 4,4-Oxybis(benzoic acid) (H_2obc) was used as a networking linker to provide rigid benzyl groups (Figure 8). Rotating its central, articulate oxygen at suitable lengths is expected to interconnect the trinuclear units by ligand exchange. The six acetate groups were replaced by three dicarboxylate ligands to produce $M^{II}_3(obc)_3(L)_2$. All of the five compounds contained the parent linear SBU and had a 3D porous structure (type 1) or a 2D open channel structure (type 2), as shown in Figure 8. The 3D structure created 1D channel along the *a* axis.[69]

M_4 building block

Tetrahedron. The tetranuclear zinc(II) basic acetate $[Zn_4O(AcO)_6]$ is one of the common types of carboxylate complexes also known for beryllium(II) and cobalt(II). The central μ_4-O^{2-} oxo anion connects together four metal cations in a tetrahedron fashion. In turn, each pair of the cations is connected by carboxylate anions in a *syn-syn* mode to form the tetrahedron edges. The perfect octahedral geometry of carboxylate ligands in the tetrahedral basic carboxylate complexes $[M_4O(RCOO)_6]$ implies the possibility of the extension of such blocks *via* linear dicarboxylate ligands into highly porous frameworks with scaffold-like primitive cubic topology (Figure 9). Such an idea was proposed by Yaghi and O'Keeffe,[34] although the originally reported synthesis of the famous IRMOF family of porous frameworks utilized simple zinc(II) salts.

Hausdorf *et al*. were the first to implement the step-by-step synthesis of both classical zinc carboxylate frameworks (IRMOF series) and the cobalt and beryllium homologues of the most prominent MOF-5 compound. The acetates $[Zn_4O(OAc)_6]$ and $[Be_4O(OAc)_6]$ and the dimeric pivalate $[Co_4O(Bu^tCOO)_6]$ were used as precursors in coordination polymer synthesis. The use of

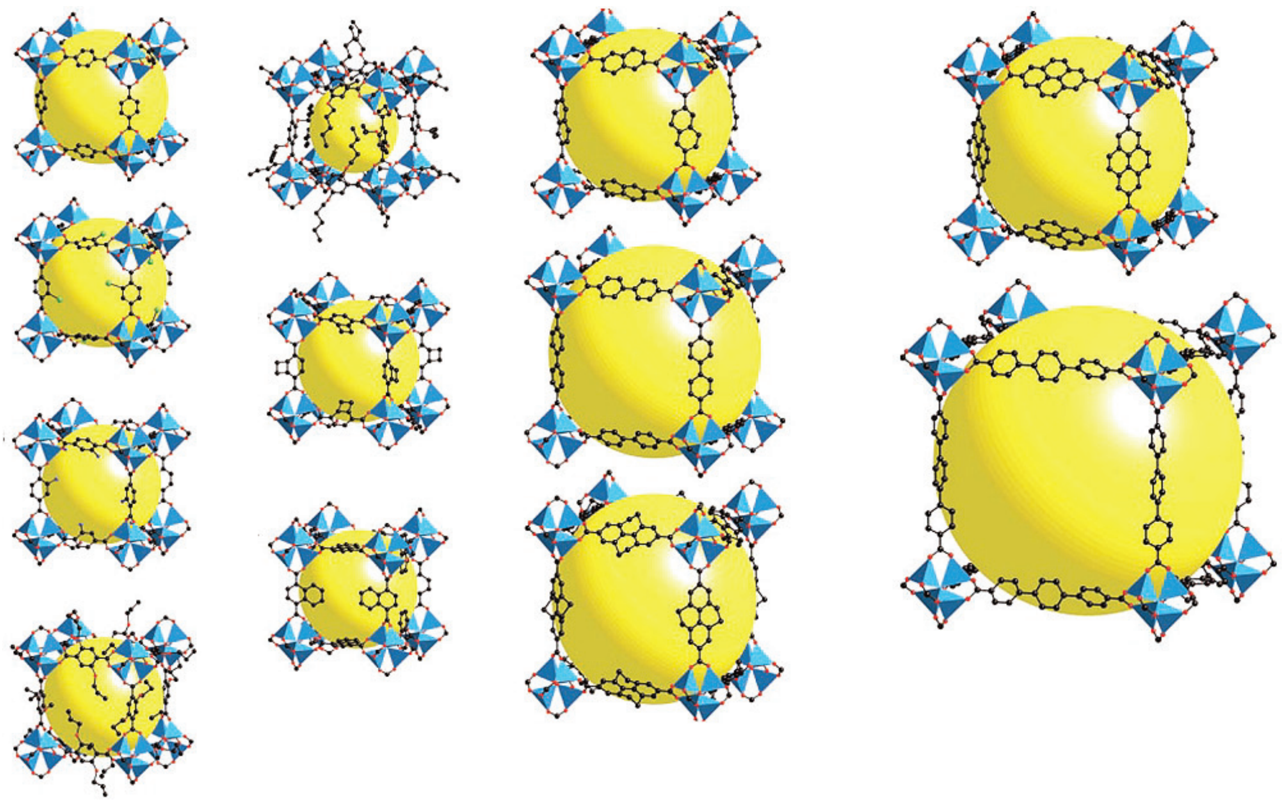


Figure 9 IRMOF series with different carboxylate linkers.

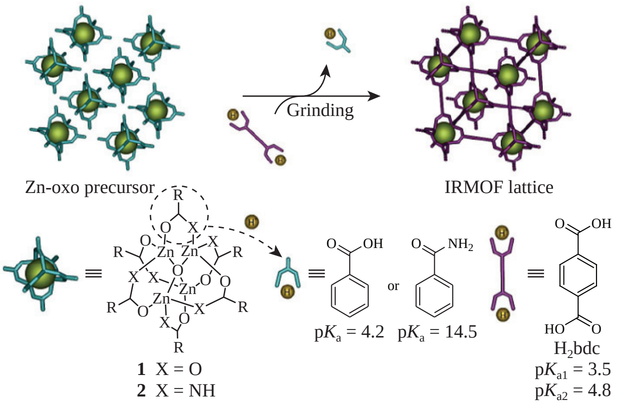


Figure 10 Schematic diagram of a mechanochemical strategy for the synthesis of MOF-5. Reproduced with permission from ref. 74. © 2015 The Royal Society of Chemistry.

cobalt centers adds new features to the existing IRMOF structures, such as magnetic properties.[70]

The nanoparticles of MOF-5 were prepared in a dilute suspension by mixing two solutions of $[Zn_4O(PhCOO)_6]$ and H_2bdc.[71] Scattering analysis revealed a significant impact of the molar ratio between two components in the reaction mixture as particle formation induced by the heating of a solution of $Zn(NO_3)_2$ and terephthalic acid led to an entirely different particle formation pattern.[72] Interestingly, the addition of a modulator after the initiation of nucleation and growth by a combination of two constituents results in an accelerated focusing of the width of the particle size distribution. This effect is achieved by forming a shell of monodentate modulator molecules, which covalently bind to the particle surfaces.[73] The result thus suggests the use of *in situ* formed surface-decorated MOF nanoparticles as carriers for functional additives and for the fabrication of MOF-based bioconjugates.

Recently, a mechanochemical strategy for the solvent-free preparation of MOFs based on oxo-centered tetranuclear complexes was demonstrated.[74] An important role of the interplay between the acidity strength of a carboxylate (pK_a = 4.2) or amidate (pK_a = 14.5) group in the tetranuclear Zn^{II} precursors, on the one hand, and the acidity of the carboxylate group of terephthalate anions in the product, on the other hand, was elucidated for the successful preparation of MOF-5, revealing a pre-assembled oxo-zinc amidate cluster as the most efficient precursor (Figure 10). However, Cubillas *et al*. showed no evidence for replacement of a benzoate group from the intact $[Zn_4O(PhCOO)_6]$ complex by a surface-attached terephthalate unit *via* nucleophilic substitution. This indicates that the precursor molecules undergo dissociation before incorporation into the MOF-5 framework. The $[Zn_4O(PhCOO)_6]$-containing growth solutions were found to influence the relative growth rates along different crystallographic directions and to lead to a faster nucleation rate under certain conditions, as compared to growth solutions containing simpler zinc salts. This suggests a degree of remnant association of the zinc species derived from the $[Zn_4O(PhCOO)_6]$ cluster during crystal growth under these conditions.[75]

Heterometallic Li_2M_2 building unit

The first example of the heterometallic tetranuclear complex $[Li_2Co_2(piv)_6(NEt_3)_2]$ containing lithium and *d*-element cations was prepared by the group of Eremenko.[76] Now, such complexes are known for many metals (M = Cu^{2+}, Zn^{2+}, Ni^{2+}, *etc.*). In the crystal structure of $[Li_2M_2(RCOO)_6L_2]$, each Li^+ cation adopts a tetrahedron environment, while each heavier metal could have a coordination number of 4 or 5, depending on the metal and axillary ligands L. Six carboxylate ligands are connected to one *d*-metal (*syn* mode) and one Li^+ cation (*syn* mode). Two of six carboxylate ligands feature an additional coordination to the second Li^+ cation by *anti* mode, forming a $\{Li_2O_2\}$ rhombus. The metal carboxylate core is centrosymmetrical; therefore, the tetranuclear complex $[Li_2M_2(RCOO)_6]$ could also be viewed as a dimer of two asymmetrical bimetallic carboxylate units $[LiM(RCOO)_3]$. The overall geometry of the organic ligands in the heterometallic $[Li_2M_2(RCOO)_6L_2]$ complexes resembles one in the above trinuclear pin-wheel complexes $[M_3(RCOO)_6L_2]$. Indeed, the two topological Li^+ cations serve as the octahedron node of a carboxylate environment. The robust geometry of organic ligands, versatile tunability of the chemical composition and well-developed coordination chemistry of such tetranuclear molecular complexes make them attractive building blocks for the rational design of the heterometallic MOF structures.[77]

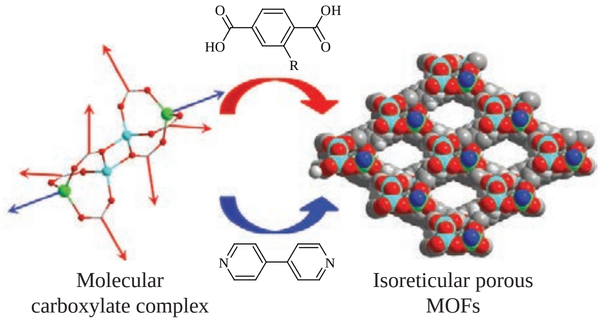


Figure 11 General scheme of obtaining new MOFs based on 8-connected secondary building unit from heterometallic pivalate complex.

Recently, the complex $[Li_2Zn_2(piv)_6(py)_2]$ was used as a starting material for the synthesis of isostructural coordination polymers by linking tetranuclear units through the derivatives of terephthalate anions R-bdc (R = H, Br, NO_2, NH_2) and bpy (Figure 11). Note that the pre-synthesized tetranuclear complex is a necessary reaction component as the use of a mixture of Li^I and Zn^{II} salts instead of $[Li_2Zn_2(piv)_6(py)_2]$ only results in either an amorphous precipitate or the crystallization of other products. The single crystal X-ray analysis of obtained samples confirmed the successful step-by-step strategy as all products are based on the same eight-connected tetranuclear heterometallic $[Li_2Zn_2(COO)_6L_2]$ node. Each tetranuclear complex is connected to eight others by six terephthalate and two bpy linear linkers forming an open 3D metal-organic framework with complicated self-penetrated topology. Most interestingly, porous channels could be identified within these structures, determining the luminescent and sorption properties of compounds. The permanent porosity of the activated frameworks was confirmed by the measurements of gas adsorption isotherms (N_2, CO_2, and CH_4). The substituents (R) in the terephthalate moieties R-bdc decorate the inner surface and control the aperture of channels, the volume of micropores, and the overall surface area thus affecting both the gas uptakes and adsorption selectivity. The photoluminescent properties of the prototypic porous framework $[Li_2Zn_2(bdc)_3(bpy)]$ and the corresponding host–guest compounds with various aromatic molecules (benzene, toluene, anisole and nitrobenzene) were systematically investigated.[78]

M_6 building block

Lillerud *et al*. reported the synthesis of isoreticular porous MOFs based on the hexanuclear Zr^{IV} oxohydroxocarboxylate core $[Zr_6O_4(OH)_4(RCOO)_{12}]$ from the molecular salt $ZrCl_4$.[79] Due to an exceptional chemical and thermal stability and versatile chemical tunability, this series of frameworks, particularly, the simplest derivative based on terephthalic acid $[Zr_6O_4(OH)_4(bdc)_6]$ also known as UiO-66, quickly become the most extensively

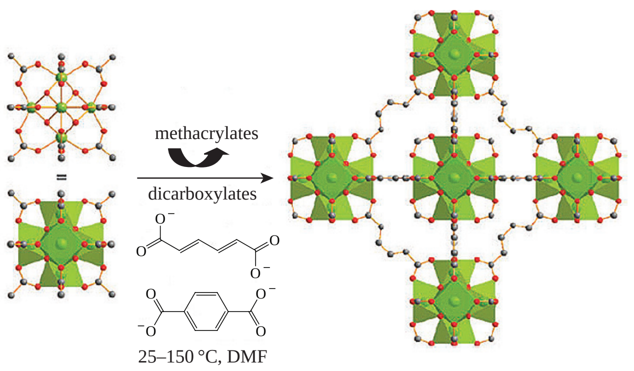


Figure 12 Schematic diagram of the synthesis of porous zirconium dicarboxylate (right) starting from Zr_6 methacrylate oxoclusters (left). Metal polyhedral, carbon atoms and oxygen atoms are shown in yellow, grey and red, respectively. Reproduced with permission from ref. 80. © 2010 The Royal Society of Chemistry.

studied model MOFs. Later, Guillerm *et al*. reported the rational synthesis of such compounds by the exchange of the monocarboxylate ligand of the hexanuclear zirconium methacrylate (met^-) $[Zr_6O_4(OH)_4(met)_{12}]$ with dicarboxylic terephthalic or *trans*,*trans*-muconic acid leading to the above UiO-66 or related isoreticular UiO-type framework, respectively (Figure 12). Interestingly, no crystalline product can be obtained starting from $ZrCl_4$ as a molecular precursor regardless of the synthesis temperature (25–200 °C) or time (1 h–4 days). On the contrary, the use of a hexanuclear Zr^{IV} oxo complex easily leads to the formation of a white crystalline phase in a broad range of the metal/ligand stoichiometries, concentrations, temperatures and reaction times.[80]

Surprisingly, the gram amounts of microporous MOFs were obtainable by the directed assembly of an organic linker with the readily accessible carboxylate-capped zirconium cluster $[Zr_6O_4(OH)_4]^{12+}$ simply by exposing a physical mixture of reactants to milling liquid vapor.[81] It offers a smooth route to highly porous catalytically active UiO-type frameworks under conditions resembling mild processes of small molecule self-assembly, contrasting conventional approaches that require highly corrosive reagents (HCl, $ZrCl_4$, $ZrOCl_2$) under solvothermal conditions. These results demonstrate the potential of the rational step-by-step approach as a large-scale preparation method for the UiO-type MOFs.

The synthesis of the 1D coordination polymer $[Mn_6O_2(piv)_{10}(bpy)(Hpiv)_2]$ from the corresponding hexanuclear complex $[Mn_6O_2(piv)_{10}(Hpiv)_2]$ was reported recently.[82] The Mn ions include two groups comprising the inner core of two Mn^{III} ions and outer four Mn^{II} ions to give a mixed valence six nuclear core. All Mn ions are surrounded by μ_2- and μ_3-pivalate groups to form the $Mn_6O_2(Bu^tCO_2)_{10}$ cluster. Four vacant sites on the outer Mn^{II} ions are distinguishably occupied by two ligands in a *cis* arrangement: the first type of Mn^{II} cations are capped by monodentate pivalic acids, and the second type of Mn^{II} cations are occupied by a bridging bpy molecule to form a 1D zigzag chain.

Ovcharenko *et al*.[83] found that the reaction of similar $[Mn_6O_2(piv)_{10}(thf)_4]$ complex with 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl (NIT-Me) produced different heterospin compounds depending on solvent used in the synthesis. Among them are two coordination polymers with chain $[Mn_6O_2(piv)_{10}(thf)_2(NIT\text{-}Me)Mn_6O_2(piv)_{10}(thf)(CH_2Cl_2)(NIT\text{-}Me)]$ and diamond-like framework $[Mn_6O_2(piv)_{10}(NIT\text{-}Me)_2]$ structures depending on the degree of coordinated solvent molecules substitution (Figure 13).

Three new 2D coordination polymers were constructed from $[Mn_6O_2(RCOO)_{10}]$ (R = Pr^i and Bu^t) clusters and bridging ligands different in flexibility and length. Two compounds are built by interlinking hexanuclear $\{Mn_6\}$ pivalate cluster complex with rigid isonicotinamide (ina) or semirigid aldrithiol (adt) linkers to yield $[Mn_6O_2(piv)_{10}(ina)_2]$ or $[Mn_6O_2(piv)_{10}(adt)_2]$, respectively, with a 2D (4,4) square-grid topology network. In another example, $[Mn_6O_2(Pr^iCOO)_{10}(adt)_2]$, the hexanuclear $\{Mn_6\}$ isobutyrate clusters are linked by aldrithiol (adt) into an unprecedented bilayer motif containing cluster-based T-shaped secondary building blocks.[84]

Noncabroxylate complexes as building units

The so-called Kuratowski-type pentanuclear 1,2,3-triazolate coordination complexes $[M_5(tz)_6L_4]^{n+/-}$ are known since 1978,[85] and they received their name after the work of Volkmer.[86] Four metal cations form a regular tetrahedron with the fifth one placed in the center of the tetrahedron. Six triazolate anions occupy the tetrahedron edges, simultaneously coordinating to two cationic vertexes and one cation in the center. Such complexes are most abundant for Cu^{II}, Zn^{II} and, to a lesser extent, Cd^{II}, Ni^{II}, and Co^{II}. The auxiliary anionic ligands (L) are directed outward the center of the tetranuclear complex forming regular tetrahedron geometry. These anionic ligands are apparent candidates to extend these Kuratowski complexes into coordination frameworks. Wang *et al.* demonstrated that the nitrate anions in $[Zn_5(btz)_6(NO_3)_4]$ (btz is

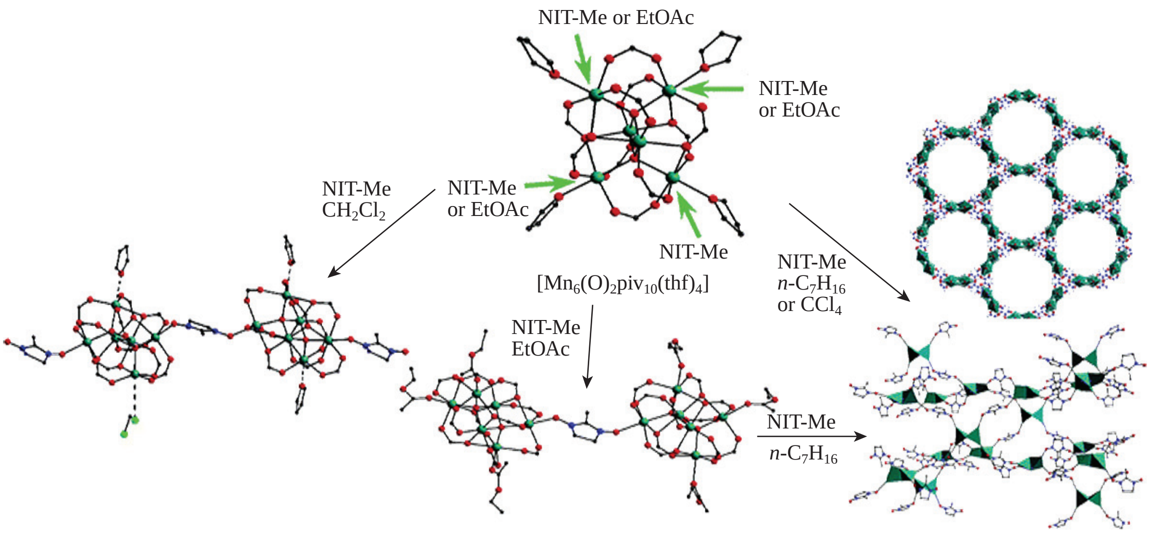


Figure 13 Formation of 3D diamond-like framework (right), chain structure (left) and dumbbell-like molecules (middle) (Me and Bu^t groups of ligands are omitted for clarity). Reproduced with permission from ref. 83. © 2004 American Chemical Society.

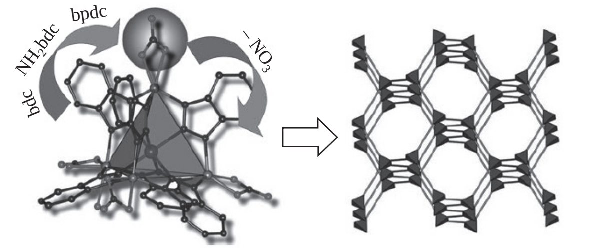


Figure 14 Replacement of nitrate groups by linear organic linkers to form extended dia nets. Reproduced with permission from ref. 87. © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

benzotriazolate) could be replaced by linear dicarboxylate ligands, such as terephthalate (bdc^{2-}), aminoterephthalate (NH_2-bdc^{2-}) or 4,4′-biphenyldicarboxylate ($bpdc^{2-}$), forming four-connected diamondoid networks with different degrees of interpenetration (Figure 14).[87] The terephthalate-based compounds $[Zn_5(btz)_6(bdc)_2]$ and $[Zn_5(btz)_6(NH_2\text{-}bdc)_2]$ are isostructural, forming four-fold interpenetrated networks. The free solvent accessible volume in $[Zn_5(btz)_6(bdc)_2]$ reaches 46%, and its microporous nature was confirmed by the gas adsorption measurements (V_{pore} = 0.41 ml g^{-1}; S_{BET} = 850 m^2 g^{-1}). The longer $bpdc^{2-}$ linker in $[Zn_5(btz)_6(bpdc)_2]$ provides as much as six-fold interpenetration with a solvent accessible volume of 45%. Interestingly, the arrangements of independent diamondoid nets in the crystal structures of $[Zn_5(btz)_6(bdc)_2]$ and $[Zn_5(btz)_6(bpdc)_2]$ are different, demonstrating the potential of the step-by-step synthetic approach to maintain the structure of the building unit and the general topology of a metal-organic network while controlling the degree of the interpenetration and the relative arrangement of the independent nets.

The tridecanuclear mixed-valence $Mn^{II/III}$ complex $[(Mn_{13}\text{-}(\mu_4\text{-}O)_6(\mu\text{-}OH)_2(\mu\text{-}MeO)_4(MeOH)_2(Bu^tPO_3)_{10}(4\text{-picoline})_4]$ was prepared by a reaction of $MnCl_2$ and $KMnO_4$ in the presence of *tert*-butyl phosphonic acid ($Bu^tPO_3H_2$) and 4-picoline in methanol.[88] Thirteen Mn cations are connected by bridging oxo, hydroxo, methanolate and phosphinate anions. The outer periphery of the polynuclear unit is additionally decorated by monodentate picoline and methanol ligands. The authors proposed and successfully demonstrated that outer ligands in the $\{Mn_{13}\}$ complexes could be replaced by bridging 4,4′-trimethylenedipyridine ligands (bpp) to produce a chain-like 1D coordination polymer containing large voids and channels. The X-ray diffraction and ESI-MS analyses confirmed that the composition and geometrical parameters of $\{Mn_{13}\}$ units in the coordination polymer are identical to those in the molecular complex thus proving the concept of the step-by-step rational design. Furthermore, a post-synthetic treatment of the coordination polymer by a TCNQ solution leads to the coordination of $TCNQ^{\bullet-}$ radical anions to the reduced $\{Mn^{III}_{13}\}$ units, which remain structurally intact during the treatment. The final product was characterized by magnetic measurements to confirm a ferrimagnetic arrangement of the $\{Mn^{III}_{13}\}$ spin carriers with S = 2 and TCNQ radical anion species (S = 1/2).

The tetranuclear copper(II) oxochlorido complexes $[Cu_4OCl_6L_4]$ (L is a monodentate ligand or solvent) are known for the last decades. The complex has a tetrahedron structure with four Cu^{II} cations at the corners and six μ_2-Cl^- bridging anions at the tetrahedron edges, centered by μ_4-O^{2-} anion. The solvent molecules are attached to Cu cations, suggesting the four-connected tetrahedral geometry of coordination bonds for this tetranuclear building unit. A coordination polymer based on such units was prepared by a solvothermal reaction of $[Cu_4OCl_6(MeOH)_4]$ with dabco in methanol.[89] Structural analysis revealed a doubly interpenetrated four-connected open framework with zeolite-like topology. Relatively large hexagonal channels of 11.4 Å, filled with solvated molecules, run along the *c* crystallographic direction. Thermal analysis, mass spectrometry and X-ray diffraction study showed that the compound is stable up to 170 °C.

Prospects

The structure of a material directly affects its properties. The tailored synthesis of periodic coordination frameworks is fundamentally important for the design of porous compounds with desired functionalities. The building block concept demonstrated here allows one to accomplish a rational and modular design of metal-organic frameworks from the scratch when pre-synthesized polynuclear complexes with the robust structure and geometry of ligands are utilized as starting compounds. Moreover, this step-by-step synthesis can lead to otherwise unobtainable metal-organic coordination structures. Many convenient polynuclear metal complexes are known and readily available as precursors for the step-by-step syntheses of coordination frameworks. Nevertheless, a serendipitous self-assembly from the mononuclear species is so far dominating among the synthetic methods for new porous coordination frameworks. This review not only summarizes the examples of the successful design of metal-organic frameworks from the discrete complexes but also serves as an inspiration for the researchers engaged in the development of particular materials with desired functionality.

Dedicated to Professor Dr. D. Fenske on the occasion of his 75^{th} birthday.

This work was supported by the Russian Foundation for Basic Research (grant no. 17-53-16015).

References

1 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
2 Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868.
3 J. Sculley, D. Yuan and H.-C. Zhou, *Energy Environ. Sci*., 2011, **4**, 2721.
4 M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782.
5 Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657.
6 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869.
7 B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev*., 2014, **43**, 5766.
8 Y. Liu, W. Xuan and Y. Cui, *Adv. Mater.*, 2010, **22**, 4112.
9 M. P. Yutkin, D. N. Dybtsev and V. P. Fedin, *Russ. Chem. Rev.*, 2011, **80**, 1009 (*Usp. Khim.*, 2011, **80**, 1061).
10 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.
11 S. Horike, D. Umeyama and S. Kitagawa, *Acc. Chem. Res.*, 2013, **46**, 2376.
12 P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913.
13 T. Yamada, K. Otsubo, R. Makiura and H. Kitagawa, *Chem. Soc. Rev.*, 2013, **42**, 6655.
14 J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011.
15 M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196.
16 Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev*., 2012, **112**, 1126.
17 J. Heine and K. Müller-Buschbaum, *Chem. Soc. Rev.*, 2013, **42**, 9232.
18 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815.
19 K. Müller-Buschbaum, F. Beuerle and C. Feldmann, *Microporous Mesoporous Mater*., 2015, **216**, 171.
20 C. Wang, T. Zhang and W. Lin, *Chem. Rev.*, 2012, **112**, 1084.
21 M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.
22 N. Roques, V. Mugnaini and J. Veciana, *Top. Curr. Chem.*, 2010, **293**, 207.
23 W. Zhang and R.-G. Xiong, *Chem. Rev.*, 2012, **112**, 1163.
24 L. Sun, M. G. Campbell and M. Dincă, *Angew. Chem. Int. Ed.*, 2016, **55**, 3566.
25 G. Givaja, P. Amo-Ochoa, C. J. Gómez-García and F. Zamora, *Chem. Soc. Rev.*, 2012, **41**, 115.
26 A. Morozan and F. Jaouen, *Energy Environ. Sci.*, 2012, **5**, 9269.
27 G. Férey, *J. Solid State Chem.*, 2000, **152**, 37.

28 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.
29 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
30 W.-X. Zhang, P.-Q. Liao, R.-B. Lin, Y.-S. Wei, M.-H. Zeng and X.-M. Chen, *Coord. Chem. Rev.*, 2015, **293**–**294**, 263.
31 D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257.
32 J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400.
33 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
34 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
35 C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem. Int. Ed*., 2004, **43**, 1466.
36 D. N. Dybtsev, D. G. Samsonenko and V. P. Fedin, *Russ. J. Coord. Chem.*, 2016, **42**, 557 (*Koord. Khim.*, 2016, **42**, 515).
37 W. Mori and S. Takamizawa, *J. Solid State Chem.*, 2000, **152**, 120.
38 J. S. Valentine, A. J. Silverstein and Z. G. Soos, *J. Am. Chem. Soc.*, 1974, **96**, 97.
39 F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759.
40 L. K. Knight, V. N. Vukotic, E. Viljoen, C. B. Caputo and S. J. Loeb, *Chem. Commun.*, 2009, **37**, 5585.
41 W. J. Belcher, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun*., 2002, 1602.
42 X.-J. Luan, X.-H. Cai, Y.-Y. Wang, D.-S. Li, C.-J. Wang, P. Liu, H.-M. Hu, Q.-Z. Shi and S.-M. Peng, *Chem. Eur. J.*, 2006, **12**, 6281.
43 S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 2000, 1095.
44 G. S. Papaefstathiou and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2002, **41**, 2070.
45 T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito and K. Tatsumi, *Inorg. Chem.*, 2006, **45**, 7988.
46 B. Moulton, J. Lu and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2001, **123**, 9224.
47 J. Pickardt, *Acta Crystallogr.*, 1981, **B37**, 1753.
48 H. Ackermann, F. Weller, R. Stief and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1496.
49 H. Miyasaka, N. Motokawa, S. Matsunga, M. Yamashita, K. Sugimoto, T. Mori, N. Toyota and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 1532.
50 H. Miyasaka, C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2000, **39**, 3831.
51 W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa and M. Kishita, *Chem. Lett.*, 1997, **26**, 1219.
52 K. Seki, S. Takamizawa and W. Mori, *Chem. Lett.*, 2001, **30**, 122.
53 K. Seki and W. Mori, *J. Phys. Chem. B*, 2002, **106**, 1380.
54 A. Pichon and S. L. James, *CrystEngComm*, 2008, **10**, 1839.
55 Z.-Q. Li, L.-G. Qiu, T. Xu, Y. Wu, W. Wang, Z.-Y. Wu and X. Jiang, *Mater. Lett*., 2009, **63**, 78.
56 W. Zhang, O. Kozachuk, R. Medishetty, A. Schneemann, R. Wagner, K. Khaletskaya, K. Epp and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2015, 3913.
57 J.-R. Li, D. J. Timmons and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368.
58 R. A. Polunin, S. V. Kolotilov, M. A. Kiskin, O. Cador, E. A. Mikhalyova, A. S. Lytvynenko, S. Golhen, L. Ouahab, V. I. Ovcharenko, I. L. Eremenko, V. M. Novotortsev and V. V. Pavlishchuk, *Eur. J. Inorg. Chem.*, 2010, 5055.
59 R. A. Polunin, S. V. Kolotilov, M. A. Kiskin, O. Cador, S. Golhen, O. V. Shvets, L. Ouahab, Z. V. Dobrokhotova, V. I. Ovcharenko, I. L. Eremenko, V. M. Novotortsev and V. V. Pavlishchuk, *Eur. J. Inorg. Chem*., 2011, 4985.
60 V. N. Dorofeeva, S. V. Kolotilov, M. A. Kiskin, R. A. Polunin, Z. V. Dobrokhotova, O. Cador, S. Golhen, L. Ouahab, I. L. Eremenko and V. M. Novotortsev, *Chem. Eur. J.*, 2012, **18**, 5006.
61 S. A. Sotnik, R. A. Polunin, M. A. Kiskin, A. M. Kirillov, V. N. Dorofeeva, K. S. Gavrilenko, I. L. Eremenko, V. M. Novotortsev and S. V. Kolotilov, *Inorg. Chem.*, 2015, **54**, 5169.
62 A. S. Lytvynenko, S. V. Kolotilov, M. A. Kiskin, O. Cador, S. Golhen, G. G. Aleksandrov, A. M. Mishura, V. E. Titov, L. Ouahab, I. L. Eremenko and V. M. Novotortsev, *Inorg. Chem.*, 2014, **53**, 4970.
63 C. Serre, F. Millange, S. Surblé and G. Férey, *Angew. Chem. Int. Ed.*, 2004, **43**, 6285.
64 S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange and G. Férey, *Chem. Commun.*, 2006, 284.
65 S. Surblé, F. Millange, C. Serre, G. Férey and R. I. Walton, *Chem. Commun*., 2006, 1518.
66 C. S. Cundy and P. A. Cox, *Microporous Mesoporous Mater*., 2005, **82**, 1.
67 S. Wongsakulphasatch, F. Nouar, J. Rodriguez, L. Scott, C. Le Guillouzer, T. Devic, P. Horcajada, J.-M. Grenèche, P. L. Llewellyn, A. Vimont, G. Clet, M. Daturi and C. Serre, *Chem. Commun.*, 2015, **51**, 10194.
68 D. Feng, K. Wang, Z. Wei, Y.-P. Chen, C. M. Simon, R. K. Arvapally, R. L. Martin, M. Bosch, T.-F. Liu, S. Fordham, D. Yuan, M. A. Omary, M. Haranczyk, B. Smit and H.-C. Zhou, *Nature Commun*., 2014, **5**, 5723.
69 Y.-J. Kim and D.-Y. Jung, *CrystEngComm*, 2012, **14**, 4567.
70 S. Hausdorf, F. Baitalow, T. Böhle, D. Rafaja and F. O. R. L. Mertens, *J. Am. Chem. Soc*., 2010, **132**, 10978.
71 R. Nayuk, D. Zacher, R. Schweins, C. Wiktor, R. A. Fischer, G. van Tendeloo and K. Huber, *J. Phys. Chem. C*, 2012, **116**, 6127.
72 S. Hermes, T. Witte, T. Hikov, D. Zacher, S. Bahnmüller, G. Langstein, K. Huber and R. A. Fischer, *J. Am. Chem. Soc.*, 2007, **129**, 5324.
73 D. Zacher, R. Nayuk, R. Schweins, R. A. Fischer and K. Huber, *Cryst. Growth Des*., 2014, **14**, 4859.
74 D. Prochowicz, K. Sokołowski, I. Justyniak, A. Kornowicz, D. Fairen-Jimenez, T. Friščić and J. Lewiński, *Chem. Commun.*, 2015, **51**, 4032.
75 P. Cubillas, K. Etherington, M. W. Anderson and M. P. Attfield, *CrystEngComm*, 2014, **16**, 9834.
76 Zn. V. Dobrohotova, A. A. Sidorov, M. A. Kiskin, G. G. Aleksandrov, K. S. Gavrichev, A. V. Tyurin, A. L. Emelina, M. A. Bykov, A. S. Bogomyakov, I. P. Malkerova, A. S. Alihanian, V. M. Novotortsev and I. L. Eremenko, *J. Solid State Chem.*, 2010, **183**, 2475.
77 A. A. Sapianik, I. A. Lutsenko, M. A. Kiskin, A. A. Sidorov, I. L. Eremenko, D. G. Samsonenko, D. N. Dybtsev and V. P. Fedin, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 2601 (*Izv. Akad. Nauk, Ser. Khim*., 2016, 2601).
78 A. A. Sapianik, E. N. Zorina-Tikhonova, M. A. Kiskin, D. G. Samsonenko, K. A. Kovalenko, A. A. Sidorov, I. L. Eremenko, D. N. Dybtsev, A. J. Blake, S. P. Argent, M. Schröder and V. P. Fedin, *Inorg. Chem.*, 2017, **56**, 1599.
79 J. Hafizovic Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc*., 2008, **130**, 13850.
80 V. Guillerm, S. Gross, C. Serre, T. Devic, M. Bauer and G. Férey, *Chem. Commun*., 2010, **46**, 767.
81 K. Užarević, T. C. Wang, S.-Y. Moon, A. M. Fidelli, J. T. Hupp, O. K. Farha and T. Friščić, *Chem. Commun.*, 2016, **52**, 2133.
82 K. Nakata, H. Miyasaka, K. Sugimoto, T. Ishii, K. Sugiura and M. Yamashita, *Chem. Lett.*, 2002, **31**, 658.
83 V. Ovcharenko, E. Fursova, G. Romanenko and V. Ikorskii, *Inorg. Chem*., 2004, **43**, 3332.
84 I. L. Malaestean, A. Ellern, J. van Leusen, V. C. Kravtsov, P. Kögerler and S. G. Baca, *CrystEngComm*, 2014, **16**, 6523.
85 J. H. Marshall, *Inorg. Chem.*, 1978, **17**, 3711.
86 S. Biswas, M. Tonigold and D. Volkmer, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2532.
87 X.-L. Wang, C. Qin, S.-X. Wu, K.-Z. Shao, Y.-Q. Lan, S. Wang, D.-X. Zhu, Z.-M. Su and E.-B. Wang, *Angew. Chem. Int. Ed.*, 2009, **48**, 5291.
88 L. Zhang, R. Clérac, C. I. Onet, M. Venkatesan, P. Heijboer and W. Schmitt, *Chem. Eur. J.*, 2012, **18**, 13984.
89 Y.-Y. Liu, M. Grzywa, M. Weil and D. Volkmer, *J. Solid State Chem.*, 2010, **183**, 208.

Received: 24th April 2017; Com. 17/5233