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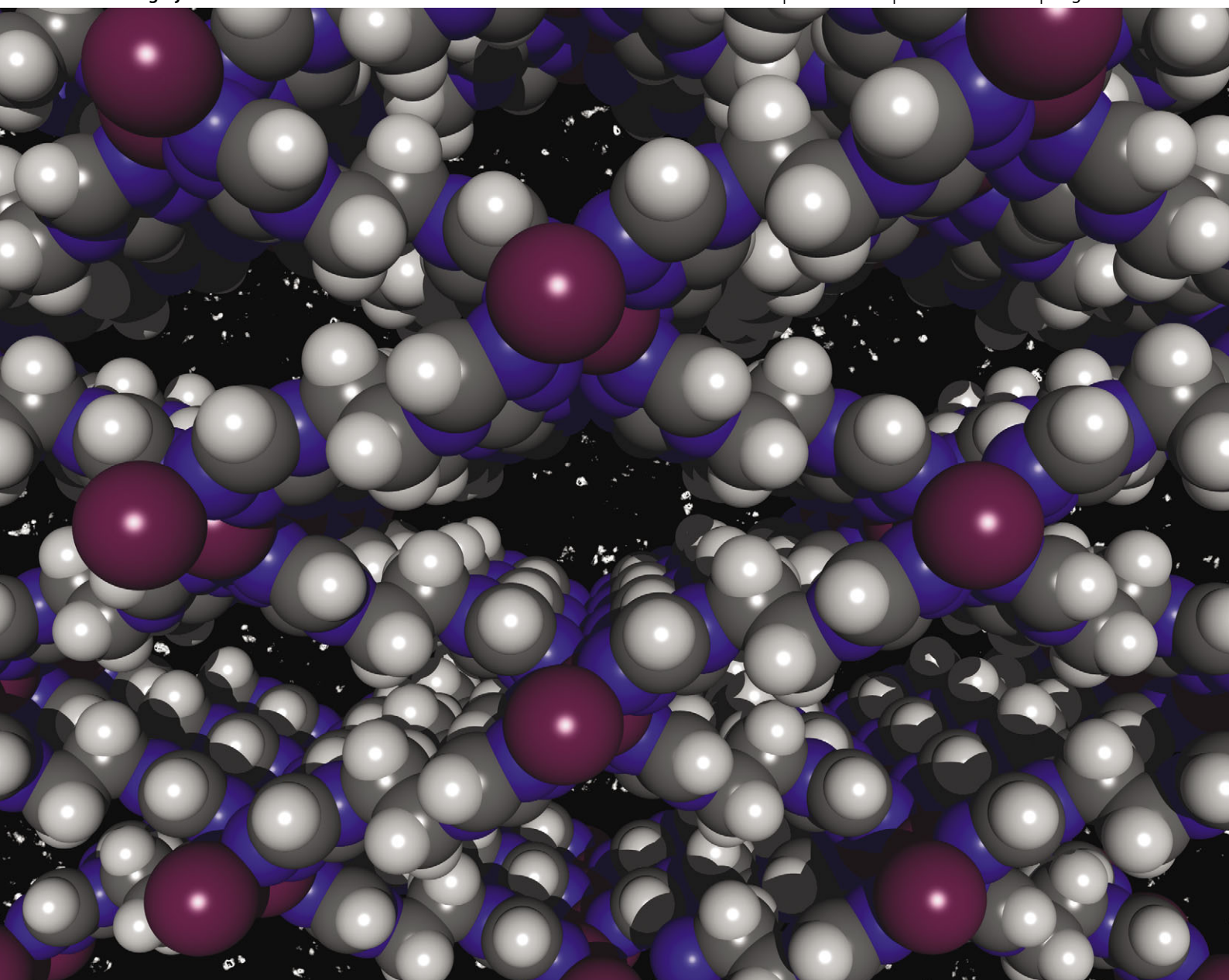

Themed issue: Coordination polymers: structure and function

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Christoph Janiak and Jana K. Vieth
MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs)

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MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs)†

Christoph Janiak* and Jana K. Vieth

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This review (over 380 references) summarizes metal–organic frameworks (MOFs), Materials Institute Lavoisier (MILs), iso-reticular metal–organic frameworks (IR-MOFs), porous coordination networks (PCNs), zeolitic metal–organic frameworks (ZMOFs) and porous coordination polymers (PCPs) with selected examples of their structures, concepts for linkers, syntheses, post-synthesis modifications, metal nanoparticle formations in MOFs, porosity and zeolitic behavior for applications in gas storage for hydrogen, carbon dioxide, methane and applications in conductivity, luminescence and catalysis.

Introduction

Infinitely extended metal–ligand networks with *metal nodes and bridging organic ligands* are called coordination polymers or metal–organic frameworks (MOFs).[1,2] MOFs have attracted tremendous attention over the past years.[3] This is due to the fact that they can be made porous, have large surface areas and tunable pore sizes and topologies, which leads to versatile architectures[4] and promising applications[1,5–8] such as ion exchange, adsorption—with a special emphasis on dihydrogen and other gas storage[1,9–21]—separation processes,[22] drug delivery,[23,24] for sensor technology,[25] heterogeneous catalysis,[1,26–45] hosts for metal colloids or nanoparticles,[46–48] hosts for (styrene, acetylene derivative and radical) polymerization reactions,[49,50] luminescence,[1,51–59] non-linear optics (NLO, frequency doubling),[1,60,61] magnetism,[1,54,55,62–64] and, recently, useful heat transformation including cooling applications through reversible water de- and adsorption.[65] Applications drive the interest in this class of compounds (Fig. 1).

Like zeolites and aluminophosphates, metal–organic frameworks are crystalline porous materials, but unlike zeolites they are not purely inorganic compounds and belong to organic–inorganic hybrid compounds. MOFs consist of metal atoms or metal clusters as nodes, which are linked through organic ligands (linkers). Because of their "infinite" connectivity from crystal edge to crystal edge MOFs belong to the group of coordination polymers (for a detailed definition of MOFs and suggestion of a classification see ref. 1 and 2).

Coordination polymers which date back to the 1960s were predecessors to MOFs[1] and since seminal papers primarily by Hoskins and Robson[66] but also others[67] in the early 1990s the interest in the MOF/PCP area has accelerated (Fig. 2) and it has become a fast-growing and very complex subject. The last decade has seen an almost exponential growth in publications on their structural topologies and potential applications.

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de
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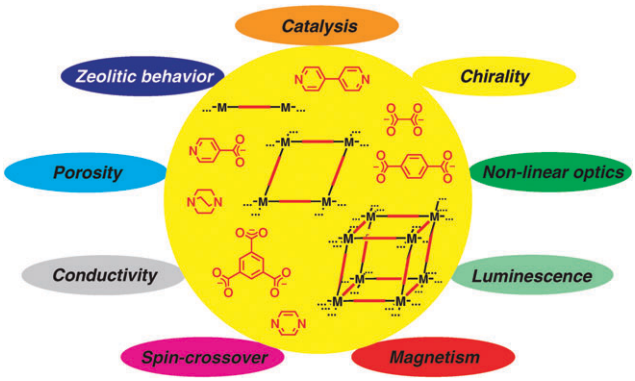


Fig. 1 Schematic presentation of application-oriented properties of MOFs (1D to 3D structures) with prototypical linkers in clockwise order: 4,4′-bipyridine, oxalate, benzene-1,4-dicarboxylate (terephthalate), pyrazine, benzene-1,3,5-tricarboxylate (trimesate), 1,4-diaza-bicyclo[2.2.2]octane, isonicotinoate.

The term metal–organic framework (MOF) was popularized by Yaghi *et al.* around 1995 in connection to three-dimensional (3D) porous coordination networks (PCNs).[68] Now MOFs are industrially prepared, for example, by BASF (marketed under the trademark BASOLITE™) and commercially available through Aldrich (Fig. 3).[69]

These metal–ligand network materials are synthesized from molecular building blocks (Scheme 1) in solution or hydro/solvothermal[71] procedures.

Anions are necessary for the charge balance to the metal cations, which typically function as nodes in the scaffolds. These anions can come from negatively charged bridging ligands such as carboxylates (Scheme 2).

Multi-carboxylate ligands with suitable spacers, especially benzene-multicarboxylato ligands, are frequent choices for metal–organic networks.[1,74] Benzene-1,4-dicarboxylate[75] (bdc^{2-}, terephthalate, Scheme 2), with a 180° angle between the two carboxylic groups, can form short bridges *via* one carboxylato end, thereby simultaneously linking up to four metal ions,[76–79] or it forms long bridges *via* the benzene ring, leading to a great variety of structures.[80,81] Also benzene-1,3-dicarboxylate (ip^{2-}, isophthalate),[82] in which the two

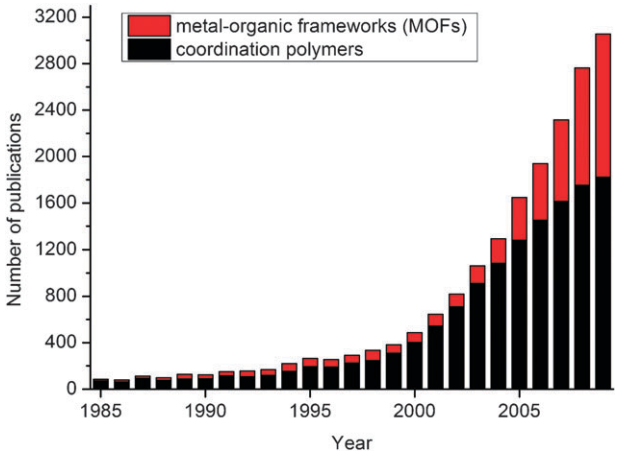


Fig. 2 Number of papers by year (since 1985) that use the concept (Scifinder) "metal organic framework", "MOF" or the term "coordination polymer". The numbers are based on a Scifinder search in April 2010 with one of the concepts "coordination polymer", "MOF" or "metal organic framework", but not containing (excluding) the concept "coordination polymerisation". The number of papers which contained both concepts "coordination polymer" and "MOF" or "metal organic framework" were limited, *e.g.*, 12 in 2003, 52 in 2005, 115 in 2007, 172 in 2008 and 180 in 2009.

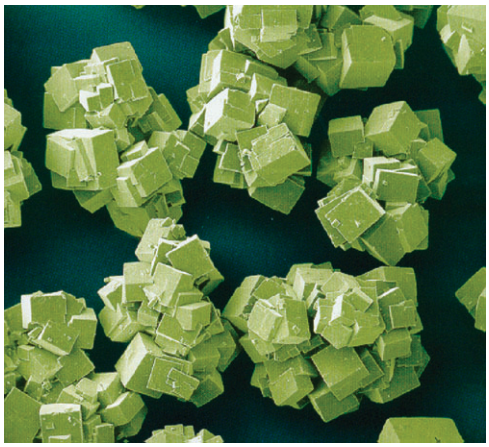
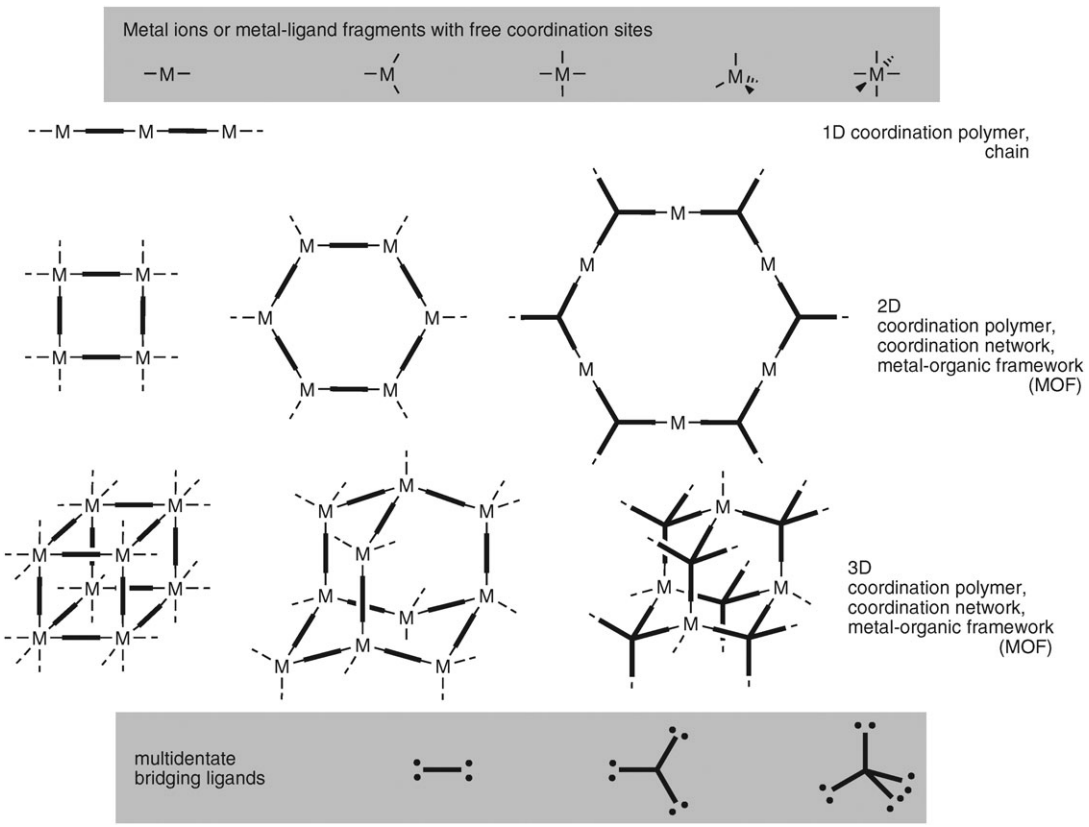
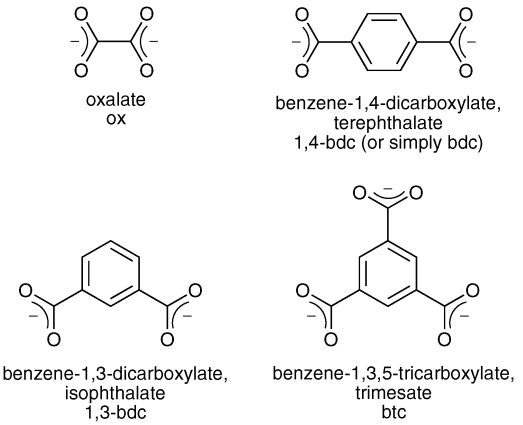


Fig. 3 Nanocubes of industrially prepared MOFs, also noted in connotation to nanomaterials and infinite coordination polymer particles (ICPs).[70]

carboxylate moieties are rigidly predisposed at 120° (Scheme 2), is a good oxygen donor for building metal–organic networks. Benzene-1,3,5-tricarboxylic acid ($btcH_3$, trimesic acid) is a rigid, planar molecule and has been extensively used in the form of its three benzene-1,3,5-tricarboxylate anions $btcH_n^{(3-n)-}$ (n = 0, 1, 2) as a bridging ligand in the synthesis of multidimensional MOFs. Recent examples (metals as cations and ligand bridging mode in parentheses) are for $btcH_2^-$ (Mn-μ_2),[83] for $btcH^{2-}$ (Mn-μ_2,[84] Mn-μ_3,[84,85] Co-μ_2,[86] Co-μ_3,[87,88] Ni-μ_3,[87] Cu-μ_2,[88] Zn-μ_2,[87–89] Zn-μ_3 and -μ_4,[88] and Cd-μ_3[90]) and for btc^{3-} (Fe-$\mu_{2,3}$,[91] Co-μ_2,[92] Co-μ_3,[93] Ni-μ_2,[54,94,95] Ni-μ_3,[95,96] Cu-$\mu_{2,3}$,[97] Cu-μ_3,[98] Zn-μ_3,[96,99] Ag-μ_3,[100] Ag-$\mu_{5,6}$,[101] In-μ_3,[102] and Y-μ_2[103]).



Scheme 1 Schematic presentation for the construction of typical coordination polymers/MOFs from molecular building blocks.

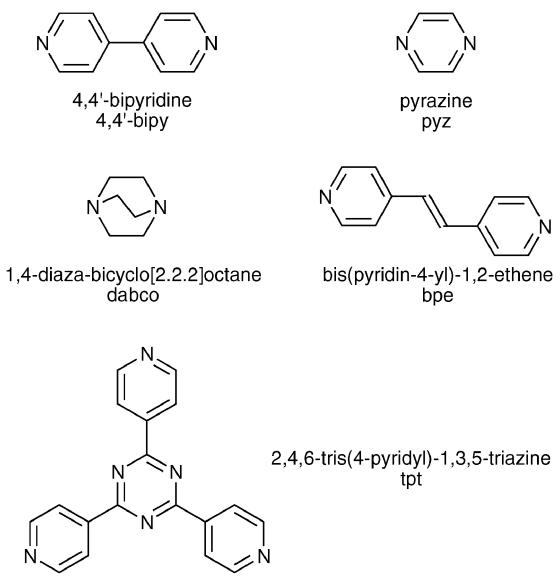


Scheme 2 Examples for prototypical anionic di- or tricarboxylate bridging ligands for MOFs.[72,73]

In the case of neutral bridging ligands (Scheme 3), charge balance is achieved by anions from the original metal salt, for example, Cl^-, NO_3^-, SO_4^{2-}, and BF_4^-.

The compound 4,4′-bipyridine (4,4′-bipy) is a prominent example for a prototypical bridging ligand and an attractive molecular building block for diverse architectures of metal–organic coordination networks[1,106–109] such as one-dimensional (1D) chains[110] or ladders,[111] two-dimensional (2D) grids[112–117] and three-dimensional frameworks.[118–120] 4,4′-Bipyridine functions not only as a linear spacer between metal connectors but can also act as a hydrogen-bond acceptor.[121] Several metal–organic coordination networks with two types of 4,4′-bipy bridging ligands—metal coordinating and hydrogen-bonding—have been reported.[106,122–141]

Rigid bridging linkers, as shown above, favor prominently among the linkers in the quest for thermally stable and robust porous frameworks that retain the MOF integrity in the absence of guest molecules (for a note on flexible linkers see section on 'Linker concepts').



Scheme 3 Examples for prototypical neutral nitrogen-heterocycle bridging ligands for MOFs.[73,104,105]

Prototypical MOFs

3D-$[Cu_3(btc)_2(H_2O)_3]$ (also called HKUST-1 or Cu-btc) is one of the first 3-dimensional porous coordination polymers that has been studied intensively. It contains $\{Cu_2\}$ units coordinated by four carboxylate groups in the well-known paddle-wheel structure of copper acetate (Fig. 4).[142,143] The 3D-coordination polymer $[Cu_3(btc)_2(H_2O)_3]$ crystallizes with the formation of a highly porous cubic structure with a complicated 3D network of channels. Along the *a*-axis there are large square channels of 9 × 9 Å (btc = benzene-1,3,5-tricarboxylate) (Fig. 4). Cu-btc is stable up to 240 °C. Both the water of crystallization and the aqua ligands coordinating the copper atoms can be removed thermally without loss of the structural integrity and exchanged by pyridine ligands.[142]

The paddle-wheel coordination in a MOF is also found for zinc with a 2D-structured extended framework of analogous alternating $\{Zn_2\}$- and organic terephthalate units (Fig. 5).[144]

Based on hydrothermally obtained tetranuclear and tetrahedral $\{Zn_4O\}$ building units a series of cubic *iso-reticular* MOF structures, IR-MOF-*n* (*n* = 1–16), with larger tunable pore sizes ranging from 3.8 to 29 Å, specific pore volumes up to 1 $cm^3\ g^{-1}$ and, thus, very high porosity were synthesized.[4] These materials were obtained using the geometric concept of *iso-reticular synthesis* with coordinated metal ions in the so-called secondary building unit (SBU) $\{Zn_4O\}$ and the organic carboxylate linkers shown in Scheme 4.[145–147] The structure of IR-MOF-1,[146] better known as MOF-5,[145] with the terephthalate linker (bdc) is probably one of the most widely recognized (Fig. 6). IR-MOF-16 has a record-high porosity of 91% of the unit-cell volume in the absence of guest molecules (Fig. 7).[146]

Porous metal carboxylates of the MIL-*n* type (for Materials Institute Lavoisier) associated with Férey *et al.* were derived using trivalent cations, such as vanadium(III), chromium(III) and iron(III), extended with the use of the p-elements such as aluminium(III), gallium(III) or indium(III). These open-framework MOFs resemble in part zeolite topologies, but differ in surface chemistry, density and pore sizes.[148–150] Important MIL-type structures like 3D-$[M(\mu_4\text{-bdc})(\mu\text{-OH})]$, MIL-53 (Fig. 8), consist of M = Al-, Cr- or Fe-terephthalate.[151–156] The framework of MIL-53 is highly flexible and it can assume different shapes depending on the strong host–guest interaction. Furthermore the formation of a porous Fe-MOF was an important step, because such Fe-MOFs are rare and Fe is a relevant element for prospective magnetic or catalytic properties.

The crystalline mesoporous material 3D-$[Cr_3(O)(bdc)_3(F)(H_2O)_2]\cdot\sim 25H_2O$, MIL-101, is a Cr-terephthalate with a hexagonal window of 16 Å opening and an inner free cage diameter of 34 Å. MIL-101 resembles an augmented MZN zeolite topology (Fig. 9).[157]

Linker concepts

Bridging benzene-di- or tri-carboxylate ligands as sole linkers are not prone to give interpenetrating networks. This general observation may be traced to the lower tendency of

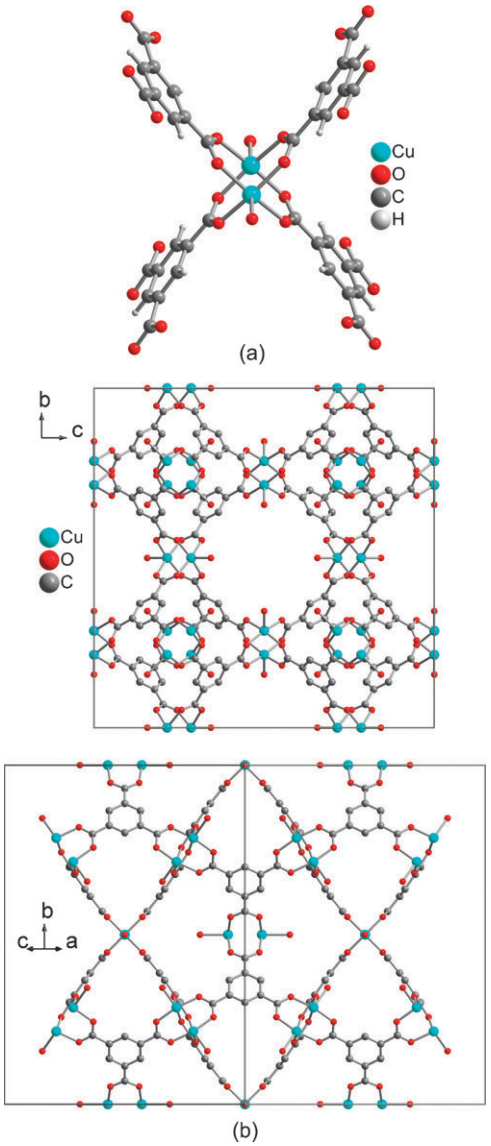


Fig. 4 (a) $\{Cu_2(btc)_4\}$ building unit and (b) two views of the packing diagram with the cubic unit cell of 3D-$[Cu_3(btc)_2(H_2O)_3]\cdot\sim 10H_2O$ (HKUST-1, a = 26.34 Å, CSD-Refcode FIQCEN)[142] to illustrate the zeolite analogy of this highly symmetric and porous framework. The disordered water molecules in the pores are not shown, nor are the H atoms on the aqua ligands and on carbon in the packing diagrams. The different objects in this figure are not drawn to scale.

benzene-polycarboxylates to enter into π-stacking interactions when compared with aromatic nitrogen heterocycle containing bridging ligands. In turn π-stacking is one of the primary weak intermolecular forces to control the intergrowth of interpenetrating networks (Fig. 10).[52,108,158] Hence, benzene-dicarboxylate (terephthalate) ligands with tetrahedral $\{Zn_4O\}$ or trigonal-prismatic $\{Cr_3(O)(F)(H_2O)_2\}$ clusters as secondary building units were successfully used for the constructions of *non*-interpenetrating—despite large pore sizes—cubic isoreticular MOFs (IRMOF-*n* with n = 1–16 of the MOF-5 structure type series) or MILs with large tunable pore sizes ranging from 3 to 19 Å.[145,157]

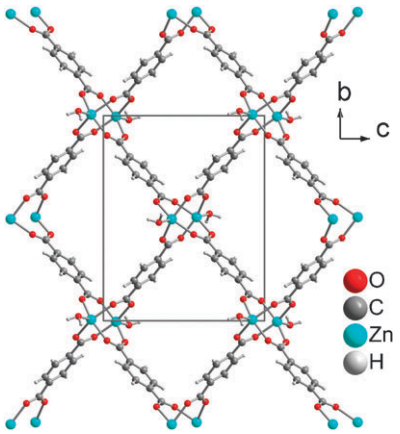
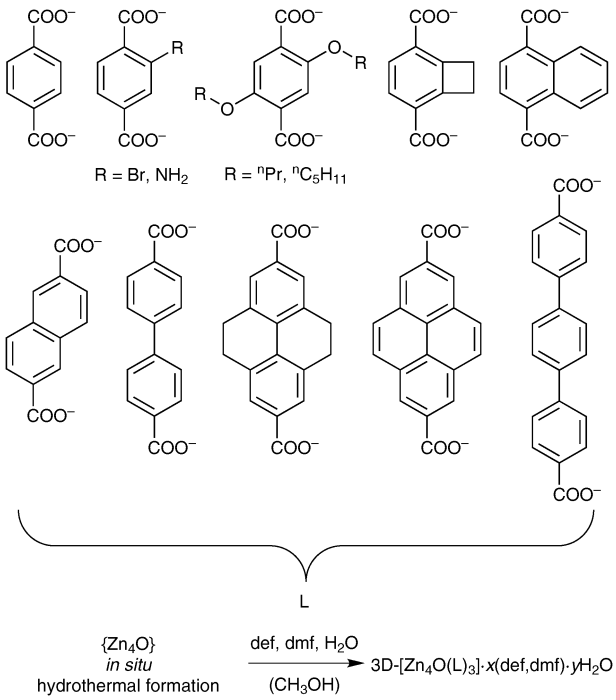


Fig. 5 Packing diagram for 2D-$[Zn_2(bdc)_2(H_2O)_2]$ (bdc = benzene-1,4-dicarboxylate, terephthalate, CSD-Refcode GECXUH).[144] Dimethylformamide guest molecules in the channels are omitted for clarity.



Scheme 4 Terephthalate-type linkers (L) for IR-MOF-*n* (n = 1–16), that is 3D-$[Zn_4O(L)_3]\cdot x$(def,dmf)$\cdot yH_2O$ (def = diethylformamide and dmf = dimethylformamide), spanning pore diameters from 3.8 to 28.8 Å and pore volumes from 56 to 91% of the unit cell volume in the solvent-guest free state (*cf.* Fig. 6 for IR-MOF-1, better known as MOF-5, and Fig. 7 for IR-MOF-15, -16).[145]

A MOF does not have to contain only one type of linker. Plenty of examples are known where two (or more) linkers build-up the framework structure.[53–55,65,159,160] Compound 3D-$[Ni_2(btc)_4(bipy)_6]$ is an example where benzene-1,3,5-tricarboxylate (btc) and 4,4′-bipyridine construct a MOF with 74% porous volume after solvent-guest removal (schematically shown in Fig. 11).[161]

The linkers do not have to be rigid but can also be flexible. At present, work on MOFs uses largely rigid spacer ligands,

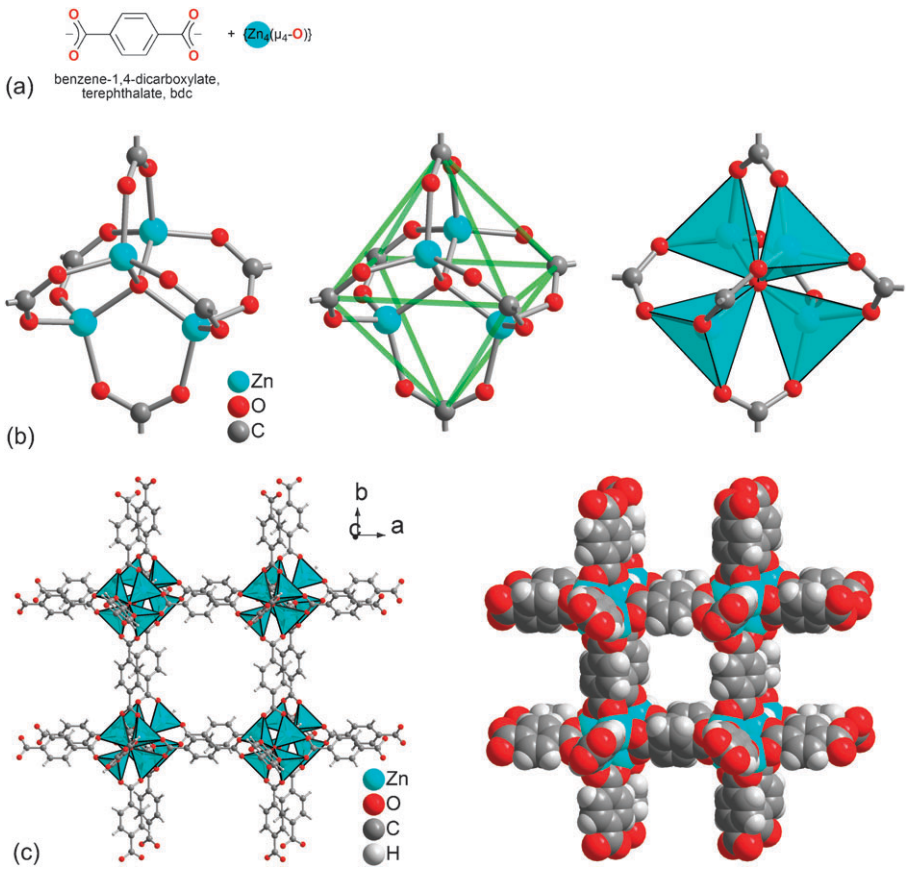


Fig. 6 (a) Building blocks for MOF-5 (IRMOF-1), 3D-[$Zn_4O(bdc)_3$], (b) ball-and-stick and polyhedral presentations of the tetrahedral {Zn_4O} secondary building unit with the carboxylate groups which span the edges of the {Zn_4O} tetrahedron in an octahedral fashion (green transparent lines) indicated and (c) the crystal structure packing diagram as ball-and-stick, with polyhedral {Zn_4O}, and as space-filling representation (CSD-Refcodes SAHYIK, SAHYOQ,[145] and EDUSIF[146] differing in the solvent-guest molecules, which are not shown). The objects in (b) *versus* (c) are not drawn to scale.

like benzene-di- or -tri-carboxylate. In the future we may see more flexible ligands, like the recent examples tci,[200] btre,[52–55,65] thioethers,[162] pypz[163] and others,[160,164] in the synthesis of new PCPs or MOFs (Schemes 5 and 6).

Flexible ligands still tend to give non-porous structures either through dense packing of a single network or through interpenetration[172,173] of two or more networks. An example of a potentially porous MOF from the flexible saccharato ligand is 3D-[Zn(μ_4-saccharate)] with alternating hydrophobic and hydrophilic channels (Fig. 12).[174]

The combination of a rigid and a flexible linker, namely benzene-1,3,5-tricarboxylate (btc) with bis(1,2,4-triazol-4-yl)-ethane (btre), also yields a dynamic porous,[19e] mixed-ligand MOF 3D-{[$Ni_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2]\cdot\sim 22H_2O$} (Fig. 13).[54,65]

Based on the prototypical negative carboxylate ligands (Scheme 2) or neutral pyridine linkers (Scheme 3) and cationic metal ions, most metal–ligand frameworks in MOFs are either neutral or cationic, respectively. Anionic frameworks which have the same charge as zeolites are, hence, called zeolite-*like* metal–organic frameworks (ZMOFs). Examples are *rho*-ZMOF and *sod*-ZMOF, which have been synthesized using protonated amines, cationic structural directing (templating) agents,[175] as in the preparation of zeolites (Fig. 14). ZMOFs combine zeolites and metal–organic frameworks as classes of porous functional materials. They show cation exchange properties, and the frameworks are expanded. These ZMOFs are expected to offer additional properties including tunability (pore size and organic functionality) and rational design of desirable properties.[176,177]

In *rho*-ZMOF the space occupied by guest molecules represents 56% of the cell volume (16 700 $Å^3$ per unit cell). The cage diameter is *ca.* 1.8 nm with a corresponding large aperture size. Cations can be fully exchanged by sodium ions. Moreover, cationic dyes (*e.g.* acridine) can be exchanged and are strongly bound by ionic interaction.[176]

New synthetic approaches

From solvent-free mechanochemical conditions in a ball mill over sonochemistry to resin-assisted preparations

Nowadays solvo- or hydrothermal synthesis[71] is one of the most popular methods to obtain coordination networks. Yet, MOFs can also be prepared using mechanochemistry, that is, grinding of two or more solids by using, for example, a mechanical ball mill (Fig. 15) and thereby avoid the use of solvents.[178,179]

An array-based approach of reacting 12 different metal salts and 5 bridging ligands in 60 potential reactions found

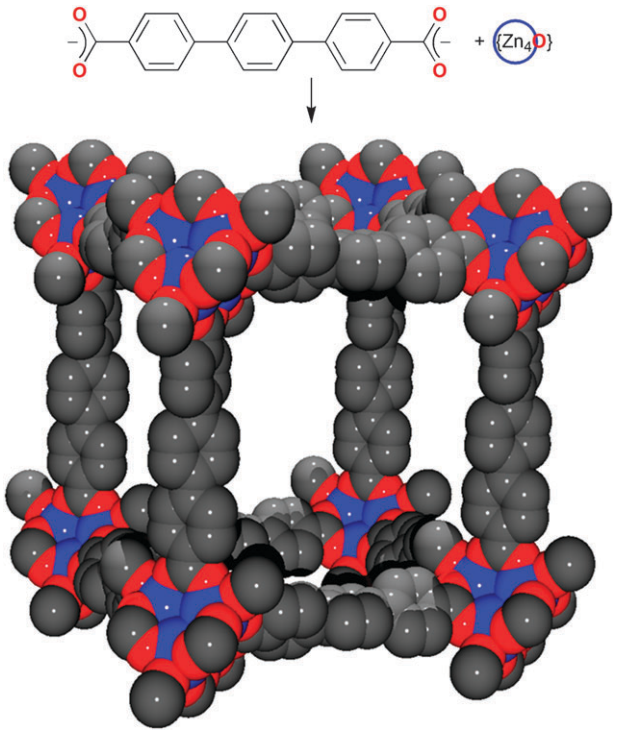


Fig. 7 Building blocks for IR-MOF-15, -16 and space-filling packing diagram of the resulting 3D-[$Zn_4O(L)_3$] (CSD-Refcode EDUVUU and EDUWAB[146] differing in the space group and solvent-guest molecules). IR-MOF-15, -16 has 91% pore volume in the absence of the solvent guest molecules (not shown). The distances between the centers of the {Zn_4O} nodes are 21.5 Å. Not shown are the H atoms and a crystallographically induced disorder where the linkers and the nodes are rotated by 90° along the linker axis. In the crystal structure of IRMOF-16 (EDUWAB) the Zn atoms are five-coordinated with methanol as a fifth ligand (as revealed from the deposited cif- or res-file).

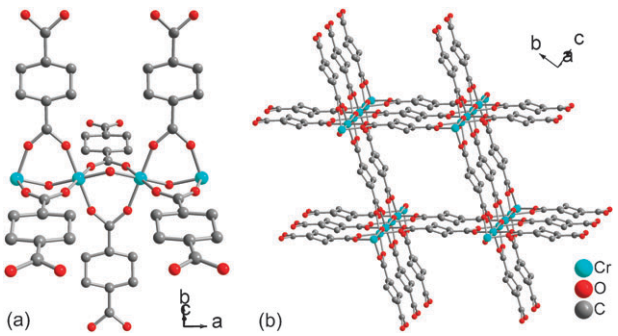


Fig. 8 (a) Terephthalato- and hydroxo-bridged metal strand as a subunit and (b) packing diagram of 3D-[M(μ_4-bdc)(μ-OH)] (M = Cr, Fe, and Al), MIL-53. The channels can contain guest molecules or be empty after a thermal guest removal (here M = Cr, CSD-Refcode MINVUA).[151,152]

solvent-free mechanochemical conditions (''ball-milling'') to be quite general for the synthesis of coordination polymers. Out of the 60 combinations, 38 gave microcrystalline products when characterized using X-ray powder diffractometry (XRPD). Six products could be identified by positively matching the measured XRPD pattern to a simulated one from single-crystal X-ray diffraction data in the Cambridge Structure Database, including the microporous MOFs $[Cu(ina)_2]_n$ and $[Cu_3(btc)_2]$ (HKUST-1, *cf.* Fig. 4) (ina = isonicotinate and btc = benzene-1,3,5-tricarboxylate) (Fig. 16).[181]

Scheme 7 summarizes the trends of reactivity under mechanochemical conditions which became apparent from the array-based study.

Another interesting alternative to conventional solution synthesis may be sonochemistry: high quality MOF-5 crystals of 5–25 μm in size were prepared using a sonochemical method in substantially reduced synthesis time (*ca.* 30 min) compared with conventional solvothermal synthesis (24 h).[182]

Transition metal-exchanged polymer resin beads have been used as a heterogeneous controlled-release source of metal cations in high yielding, phase pure solvothermal syntheses of novel transition metal–organic frameworks (Fig. 17).[183]

Combinatorial synthesis to new networks

A combinatorial approach with 2-amino-terephthalic acid ($bdcH_2$-NH_2) and $AlCl_3$ in methanol succeeded in leading to the new network 3D-$[Al_4(OH)_2(OCH_3)_4(bdc\text{-}NH_2)_3]\cdot xH_2O$ (named CAU-1, CAU = Christian-Albrechts-University) which is stable up to 580 K and built from $\{Al_8(OH)_4(OCH_3)_8\}^{12+}$ units. Each Al_8-SBU is surrounded and interconnected by 12 amino-terephthalate anions to enclose tetrahedrally- and octahedrally-shaped voids with inner diameters of 0.5 and 1.0 nm, respectively, and a Langmuir surface of 1700 $m^2\ g^{-1}$ (Fig. 18).[184]

Post-synthesis modifications

MOFs are usually prepared by combining metal ions (as salts) and the linkers in water or an organic solvent, perhaps with pH adjustment (to help deprotonation of an acid linker), and subjecting them to a solvothermal treatment. It would be ideal to have a building set of stable MOFs with different pore sizes, which could then be functionalized specifically to any need in a, so-called, post-synthesis treatment. This would allow systematic modification of the cavities and the design of a whole range of isostructural MOF networks with a range of chemical functionalities and therefore different chemical and physical properties. Programming the architectures in the cavity of the porous material could result in specifically designed and desired interactions of the given modified MOF with guest molecules.[185]

A successful chemical post-synthetic modification approach might have significant implications for MOF chemistry, with viable routes to the solid-state versions of diversity-oriented synthesis. The study and understanding of post-synthetic modifications might eventually lead to the development of combinatorial libraries of MOFs.

The first mentioned[185] post-synthetic modification was carried out on a Zn-MOF with the chiral ligand (derived from tartaric acid) (4*S*,5*S*)-5-(pyridin-4-ylcarbamoyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid (Fig. 19).[186] This ligand reacts with zinc ions to form a homochiral,[187] open 2D-network of formula $[2H_3O^+][\{Zn_3(\mu_3\text{-}O)(L)_6\}^{2-}]\ 12H_2O$. The trinuclear secondary building blocks $\{Zn_3(\mu_3\text{-}O)(L)_6\}^{2-}$ are connected

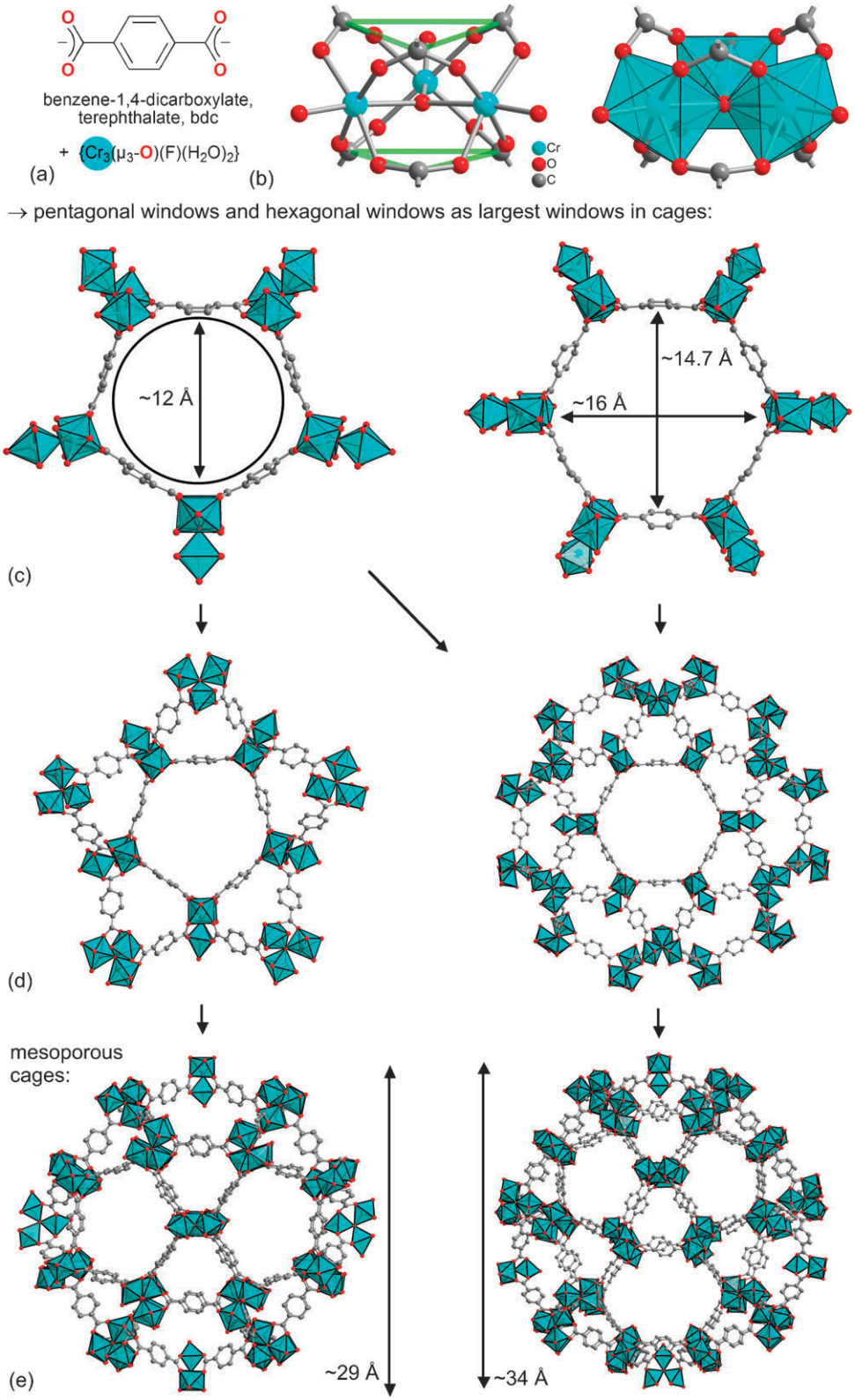


Fig. 9 (a) Building blocks for MIL-101, 3D-$[Cr_3(O)(bdc)_3(F)(H_2O)_2]\cdot\sim 25H_2O$, (b) ball-and-stick and polyhedral presentations of the trigonal-prismatic $\{Cr_3(O)(F)(H_2O)_2\}$ secondary building unit with the carboxylate groups that bridge between the Cr octahedra (green transparent lines) (Note: fluorine atoms could not be distinguished from aqua ligand), (c) the largest open windows around the mesoporous cages, (d) connectivity of pentagonal and trigonal or hexagonal, trigonal and pentagonal windows to construct the (e) mesoporous cages in the 3D framework (CSD-Refcode OCUNAK,[157] water-guest molecules are not shown.) The different objects in this figure are not drawn to scale.

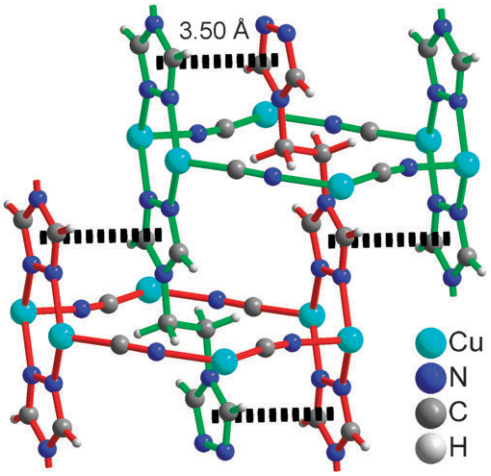


Fig. 10 Interpenetration of the two 3D frameworks (differentiated by the green and red bonds) in 3D-$[Cu_2(\mu\text{-}CN)_2(\mu_4\text{-btre})]$ (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane, *cf.* Scheme 5) with indication of the controlling π–π stacking interaction (dashed lines) of the parallel triazolyl rings (centroid–centroid distance 3.505(2) Å, interplanar separation 3.25 Å, CSD-Refcode FOQTIP).[52]

with each other *via* the pyridyl groups of the ligands to form the 2D-MOF. However, only three of the six pyridyl groups of the trinuclear unit are needed for the crosslinking (Fig. 19a). The remaining three pyridyl rings reach into the chiral 1D-channels. There, they can serve as anchor groups for substrate molecules. The pyridyl groups exposed in the channels provide the network with opportunities for chemical modification of the channel environment. The *N*-alkylation of all the pyridyl groups was carried out by adding an excess amount of iodomethane or iodohexane to a suspension of crystalline porous MOF material at room temperature and the framework charge changed from negative to positive. Furthermore, the presence of the pyridyl groups in the channels provides the MOF material with catalytic properties discussed in the referenced article.[186]

Several reports have been published concerning MOFs in which 2-aminoterephthalate (bdc-NH_2) was the linker and the amino group was modified post-synthetically with acetic acid anhydride (Scheme 8).[188–191]

Similarly, the pendant amino groups in isoreticular metal–organic framework-3 (IR-MOF-3) were subjected to post-synthetic modification with 10 linear alkyl anhydrides $O[CO(CH_2)_nCH_3]_2$ (where n = 1 to 18) to the corresponding amide frameworks[192] or with isocyanates to generate micro-porous urea-functionalized frameworks.[193]

Also, (Al)MIL-53-NH_2 with the 2-aminoterephthalate linker could be treated with formic acid after the synthesis to give the corresponding amide Al(OH)[bdc-NH-C(O)H] (denoted MIL-53-NHCHO).[194]

The flexibility of the metal–organic framework (the so-called "breathing")[195] can be triggered and controlled by modifying the amine groups on the linker. Post-synthetic modification of a mixed-ligand Zn-MOF from 1,4-diazabicyclo[2.2.2]-octane and 2-aminoterephthalate with alkyl anhydrides $O[CO(CH_2)_nCH_3]_2$ (where n = 1 to 5) forms amide groups that can control the pore opening and their breathing behavior to selectively absorb gases or other molecules (Scheme 9).[196]

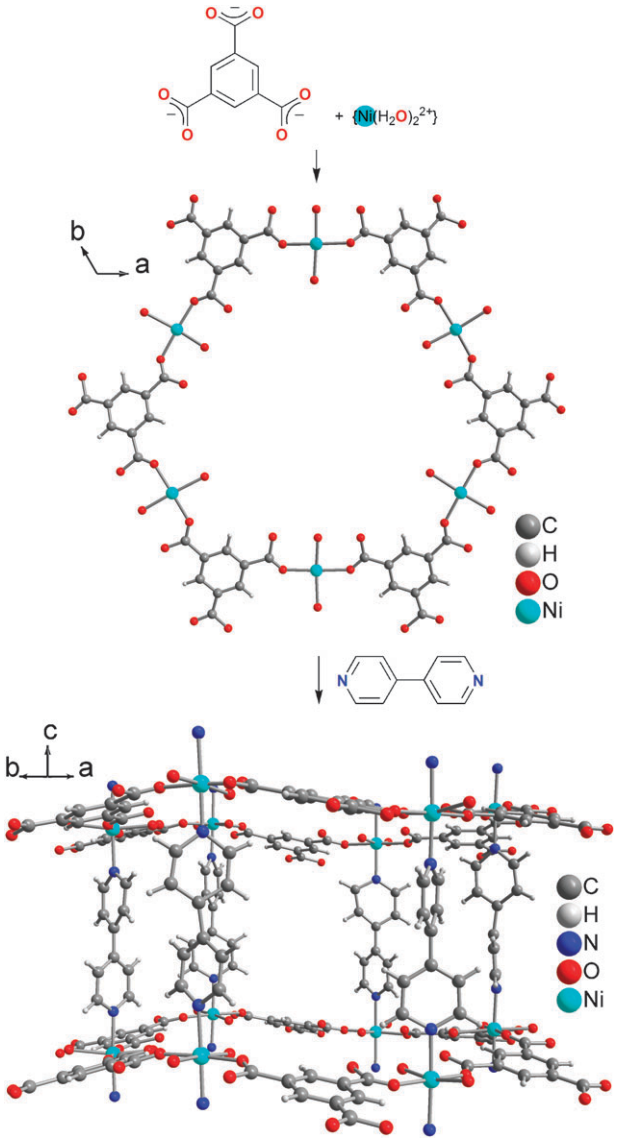
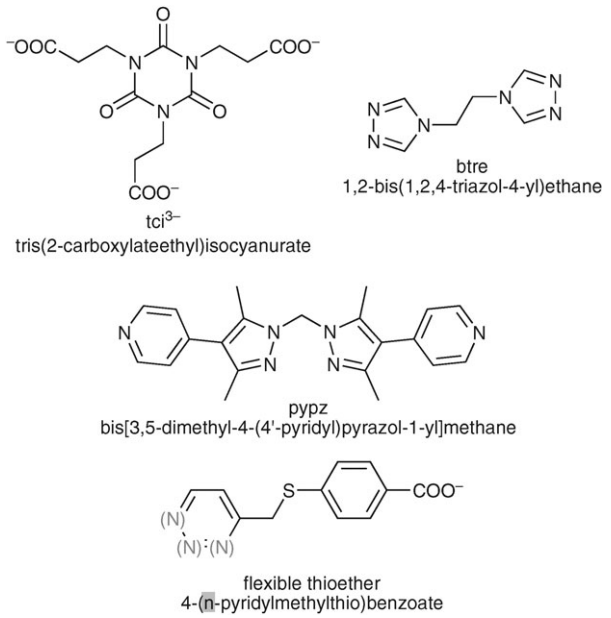


Fig. 11 Schematic presentation of the construction of 3D-$[Ni_2(btc)_4(bipy)_6]$ by two different bridging ligands. The (6,3)-nets from $\{Ni(H_2O)_2^{2+}\}$ and benzene-1,3,5-tricarboxylate (btc) lie in the *ab*-plane which are interconnected by 4,4′-bipyridine along the perpendicular *c*-axis. Guest molecules in the voids (74% of cell volume) are not shown (CSD-Refcode XUTQEI).[161]

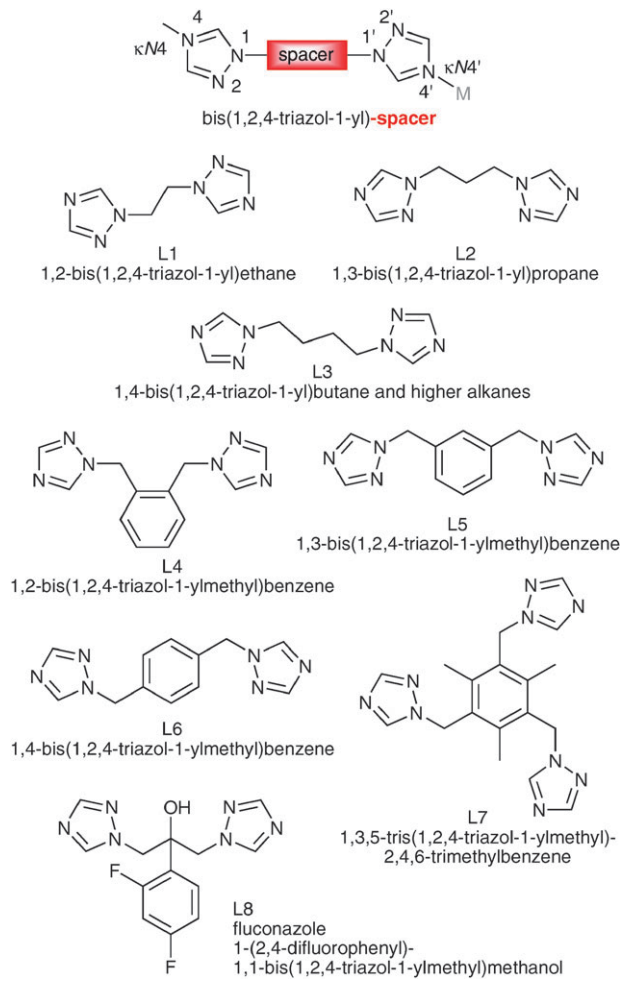
Nanoparticles inside MOFs

MOFs offer a means of combining caging effects of porous solid-state matrices with surfactant/particle interaction in a defined and molecularly controlled manner, going beyond the less-controlled embedding of guest molecules or nanoparticles into pure organic polymers.[46]

Some attention was focused on solvent-free loading *via* adsorption from the gas phase using volatile all-hydrocarbon organometallic compounds. These are known as precursors



Scheme 5 Examples of flexible bridging ligands, see also Scheme 6.



Scheme 6 Bis- and tris(1,2,4-triazol-1-yl) derived flexible bridging ligands with spacer modification between the typically κ*N*4:*N*4′ metal-coordinating triazole moieties. References: L1,[165] L2,[166] L3,[166,167] L4,[168] L5,[168,169] L6,[168,170] L7,[168] and L8.[171]

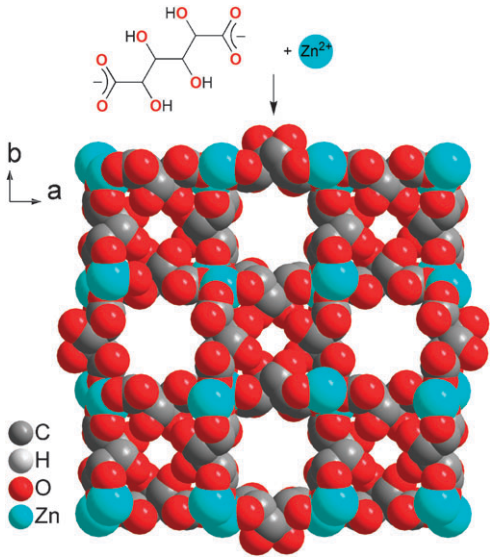


Fig. 12 Space-filling illustration of the checker game pattern of 3D-[Zn(μ4-saccharate)] with its large hydrophobic and small hydrophilic channels, when viewed along the tetragonal axis. The crystal water in the channels is not shown (CSD-Refcode TACPAP).[174]

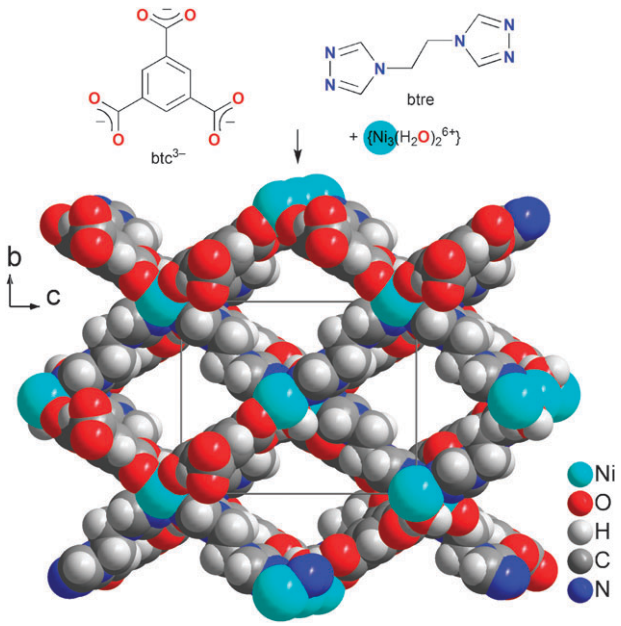


Fig. 13 Space-filling representation of dynamic porous 3D-{[Ni_3(μ3-btc)$_2$(μ4-btre)$_2$(μ-H_2O)$_2$]} with a total potential solvent volume of 1621 Å^3 or 52% per unit cell volume of 3116 Å^3; crystal water in the channels is not shown (CSD-Refcode LOBHAM).[54,65]

for metal–organic chemical vapour deposition (MOCVD) and allow a comparably high metal loading up to 30–40 wt% in a single loading step.[197] As MOFs can be chemically labile the loading procedure may affect or even destroy the MOF structure. The interaction of the nanoparticle itself with the host matrix may range from rather weak to quite strong, obviously depending on the chemistry of the particle/MOF interfaces. Much of the work in this area was done on MOF-5,

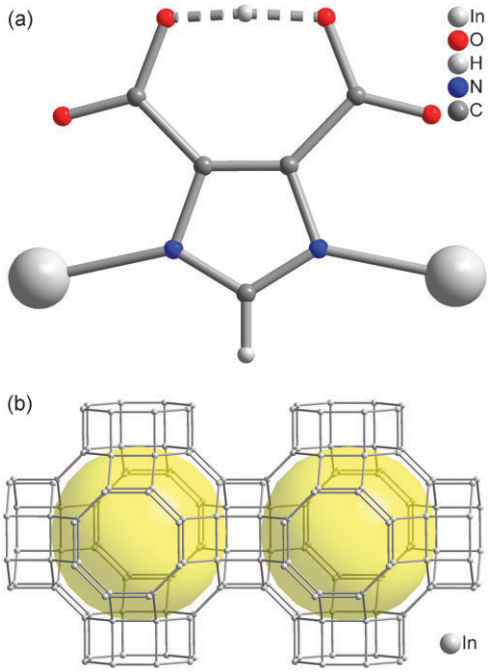


Fig. 14 (a) Metal–imidazole-4,5-dicarboxylato building unit and (b) structure of *rho*-ZMOF by depicting only the topological indium atom connectivity of the anionic framework 3D-$[In^{III}_2(\mu\text{-}C_5H_2N_2O_4^{2-})_4]^{2-}$. The guest molecules in the voids are not shown (CSD-Refcode TEFWIL).[176] The two objects in this figure are not drawn to scale.

Fig. 15 Ball mills which can generate microcrystalline products within minutes.[180]

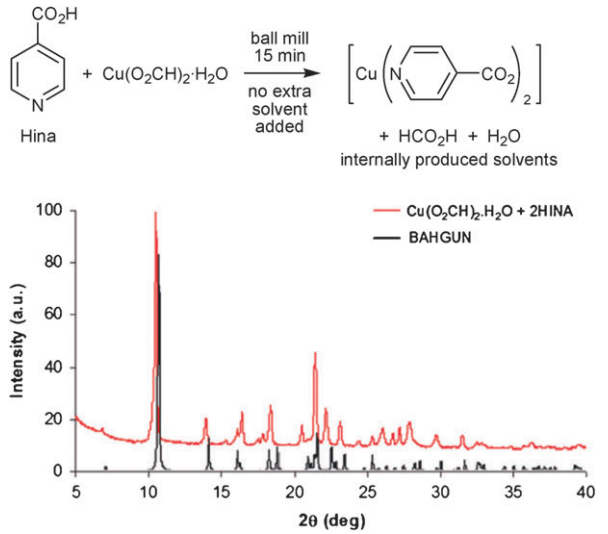
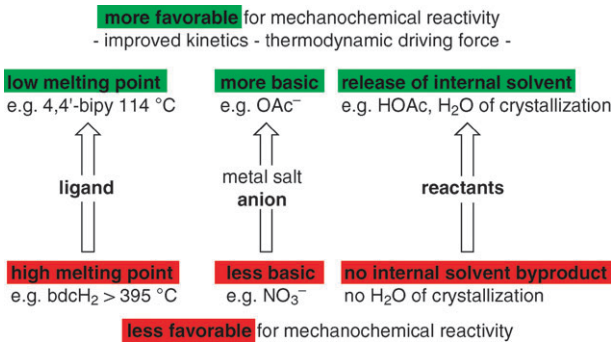


Fig. 16 Synthesis of $[Cu(ina)_2]$ (top) and comparison of the XRPD pattern of the product and the simulated pattern for $[Cu(ina)_2]\cdot 2H_2O$ (CSD-Refcode BAHGUN) based on single-crystal data (figure taken from ref. 181).



Scheme 7 Trends revealed by studying an array of 60 potential reactions between various ligands and metal salts in ref. 181. 4,4′-bipy = 4,4′-bipyridine, $bdcH_2$ = benzene-1,4-dicarboxylic acid, and OAc = CH_3COO.

3D-($[Zn_4O(bdc)_3]$) (Fig. 20, *cf.* Fig. 6).[46,48,197] It was expected to stabilize very small nanoparticles.

Several different metal–organic vapor deposition precursors, such as $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$, $[Cu(\eta^5\text{-}C_5H_5)(PMe_3)]$, $[Au(CH_3)(PMe_3)]$, $[Fe(CO)_5]$,[48] $[Zn(C_2H_5)_2]$[197] and [Ru(cod)(cot)],[46] were absorbed on the inner surface of MOF-5. The precursor $[Cu(OR)_2]$ (R = $CH(CH_3)CH_2NMe_2$) is not absorbed by MOF-5 but by IR-MOF-8 due to the pore opening diameter and the precursor size (8 Å and 9.5 Å). The Pd precursor is absorbed irreversibly while the others can be removed with a dynamic vacuum. The crystallinity of MOF-5 and the precursors remains unchanged. The treated MOFs react with H_2 or in a UV-photolysis to give nanoparticles of the respective metal (see Table 1). For example, for [Ru(cod)(cot)] (cod = 1,5-cyclooctadiene and cot = 1,3,5-cyclooctatriene) hydrogenolysis at 3 bar and 150 °C yields 1.5–1.7 nm Ru-nanoparticles embedded in the intact MOF-5 matrix (Fig. 20). Milder conditions lead to the formation of a ruthenium(cod)(arene) complex with the arene moiety of the bdc linkers.[46]

The Au particles are probably more mobile due to weaker interaction of Au with the MOF. Therefore, the particles can diffuse through the pores to the surface of the MOF where they can aggregate to form larger particles. For Au-NPs this aggregation is driven by the known strong aurophilic Au–Au interaction (Au cohesive energy 3.8 eV, ~88 kcal mol^{-1}).[198] All MOFs with the enclosed nanoparticles were tested for catalytic activity.[46–48]

Porosity and zeolitic behavior

Interesting properties of MOFs are—at present—mainly porosity and zeolite-type behavior for the reversible exchange of guest molecules (Scheme 10).[1,9,10,12–20] Porosity is the basis for what could be termed zeolitic behavior, for *e.g.*, ab/desorption of gases (gas storage), ion exchange, enantiomer

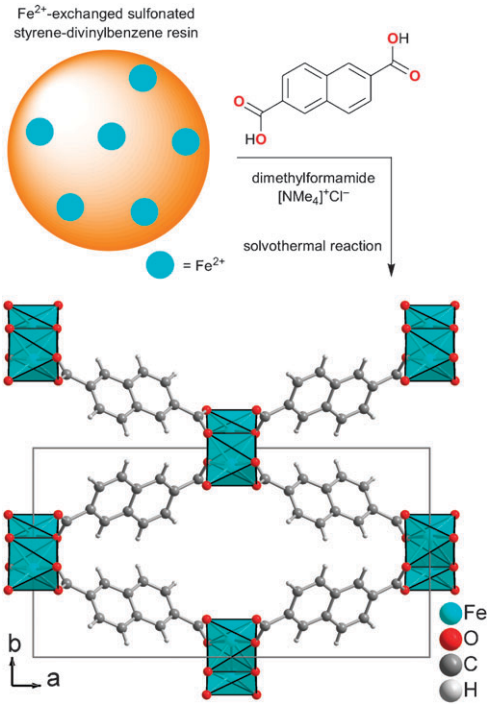


Fig. 17 Slow release of Fe^{2+} ions from a polymer resin to yield the MOF 3D-[Fe^{II}(μ_6-naphthalene-2,6-dicarboxylato)] in solvothermal reaction; guest molecules are not shown (CSD-Refcode TONBII).[183]

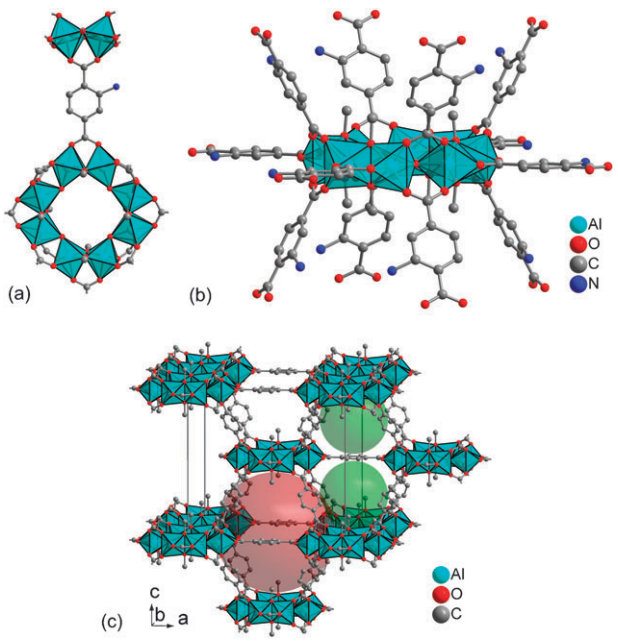


Fig. 18 $\{Al_8(OH)_4(OCH_3)_8\}^{12+}$ building unit in polyhedral presentation in (a) top view showing only one of the 12 bdc-NH_2 connections and (b) side view with all 12 connecting bdc-NH_2 linkers to adjacent units and (c) packing diagram of 3D-[$Al_4(OH)_2(OCH_3)_4$(bdc-NH_2)$_3$]·$x$$H_2O$ (CAU-1) with the two main types of octahedral (red) and tetrahedral (green) voids. Crystal water molecules in the voids are not shown. The NH_2-groups on the aromatic terephthalate ring are disordered.[184] The three objects in this figure are not drawn to scale.

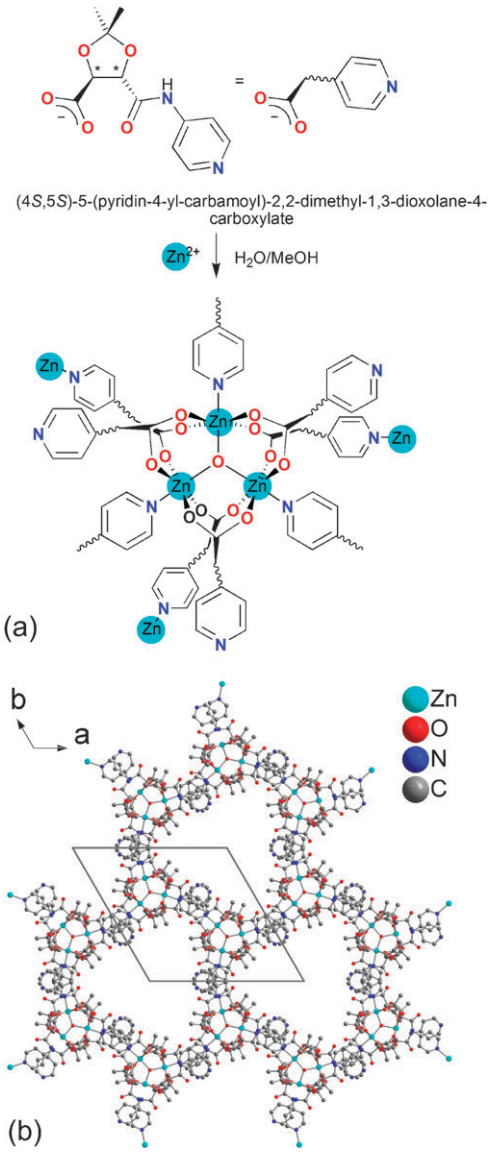
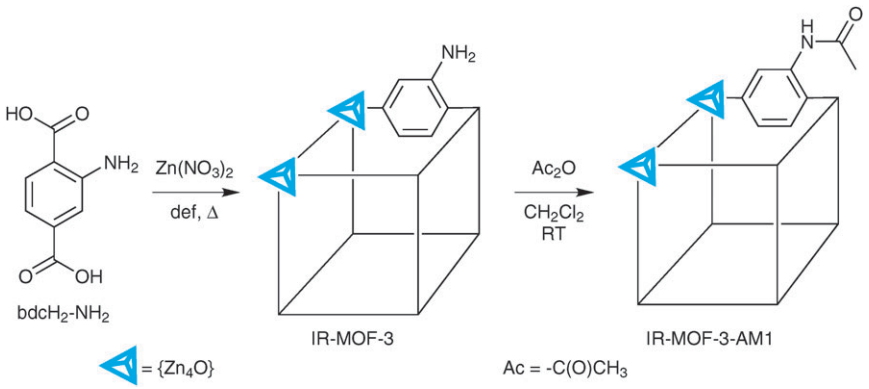


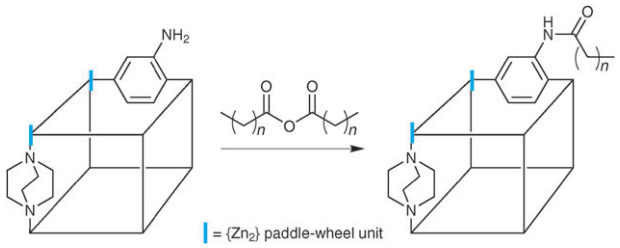
Fig. 19 (a) Schematic presentation of the oxo-bridged trinuclear $\{Zn_3(\mu_3\text{-}O)(L)_6\}^{2-}$ secondary building unit and (b) packing diagram of 2D-[$2H_3O^+$][$\{Zn_3(\mu_3\text{-}O)(L)_6\}^{2-}$] $12H_2O$; guest molecules in the 1D channels are not shown. The channels have the form of equilateral triangles with edge lengths of about 13 Å. The channel volume is approximately 47% of the total volume. The porous structure is stable in the presence of solvents. The H_3O^+-cations and water molecules of crystallization can be exchanged against other guest molecules (CSD-Refcode UHOPUC[186]).

separation or selective catalysis. Advantages of MOFs over classical zeolites are the manifold design aspects through the organic linkers and metal nodes.[4,147,199] General problems of porosity in MOFs deal with the host/framework stability in the absence of guests. It still remains a synthetic challenge to "design" metal–organic networks with porosity and zeolite-type behaviour in porous coordination polymers (PCPs) or MOFs for the reversible exchange of guest molecules in molecular sieves, gas storage and catalysis.[200]

The benzene-1,3,5-diphenylphosphane (bdp) ligand yields the MOF 2D-[Ag_4(bdp)$_3$](CF_3SO_3)$_4$·$x$$MeNO_2$·$y$EtOH with



Scheme 8 Formation of an isoreticular MOF with 2-aminoterephthalic acid and its post-synthesis modification with acetic acid anhydride to the corresponding amide framework. IR-MOF-3 is a Zn-MOF with $\{Zn_4O\}$ units as nodes (see above Fig. 6 and 7).[188]



Scheme 9 Conversion of the amine groups in a mixed-ligand MOF can activate the breathing of the pores: for $n = 0$ the pores are narrowed and for $n = 3$–5 the pores are held open but for $n = 1$ or 2 a bistable framework is formed that leads to controlled breathing.[196]

adjacent layers directly on top of each other, so as to give a channel structure (Fig. 21). The counter anions, the nitromethane and ethanol solvent molecules reside in the channels. The latter can be exchanged against diethyl ether or water molecules with retention of the framework channel structure.[201]

Gas storage

Gas storage based on the porosity and zeolitic behavior of MOFs is currently one of the most highlighted and most visible application-oriented works in the field of MOFs. A note of caution may be in place for the long-term perspective: at present, the gas storage results are based on small scale lab experiments with pure gases or selected gas mixtures. It will still be a challenge to bring such systems onto a larger scale with the heat (absorption energy) dissipation upon gas absorption, the fast kinetics, and the important property of stability especially to water vapor and reactive gas impurities—all necessary for real-life technical applications.[6,24] A better understanding of mechanism and thermodynamics of adsorption and better knowledge of adsorption sites is necessary for a purposeful improvement of the adsorption performance.[24] The well-known $\{Zn_4O\}$-terephthalate-based MOFs, such as prototypical MOF-5, are not stable towards water vapor. At the same time technical H_2 will always contain some ppm water from its steam reforming or water electrolytic synthesis.

It has been shown[13] that the claimed gas-storage performance of a MOF strongly depends on the method of synthesis, the scale of production and efficiency of activation (guest removal) (for a comparison of different H_2 storage abilities of MOF-5 see ref. 14, 18, and 202). Thus, there is a need for normalization with a complete data set as different groups may measure different materials, even if

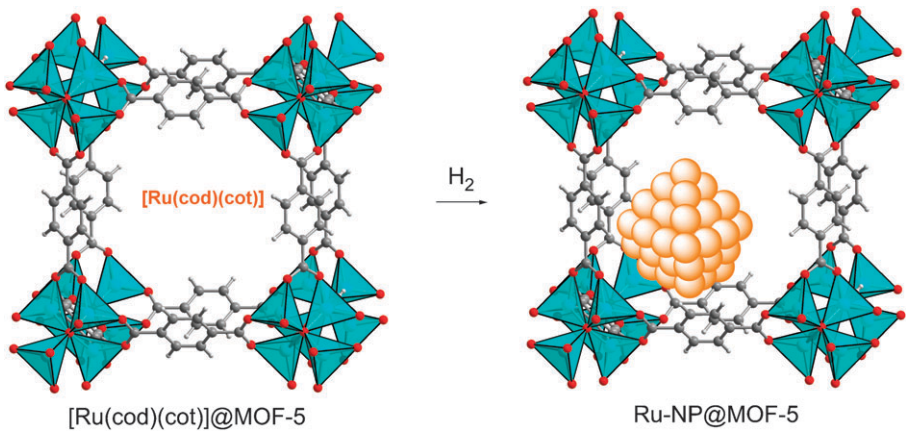
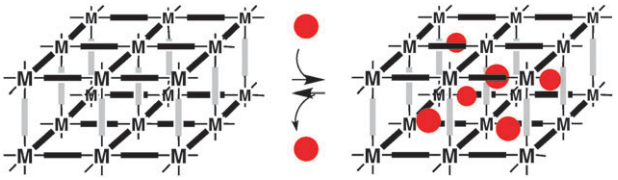


Fig. 20 Schematic presentation of the formation of Ru-nanoparticles (Ru-NP) from [Ru(cod)(cot)] by dihydrogen reduction inside MOF-5 (*cf.* Fig. 6).[46]

Table 1 Nanoparticle formation from organometallic precursors in MOF-5

Precursor	[Pd(η^5-C_5H_5)-(η^3-C_3H_5)][48]	[Cu(η^5-C_5H_5)-(PMe_3)][48]	[Au(CH_3)-(PMe_3)][48]	[Ru(cod)(cot)][46]	[Zn(C_2H_5)$_2$][197]
Nanoparticle inducing agent: H_2	1.4 nm (±0.1) (MOF very reactive)	3–4 nm	5–20 nm (polydisperse)	1.5–1.7 nm (can be oxidized to RuO nanoparticles)	ZnO nanoparticles, no data about size
Host crystallinity	Changed	Intact	Intact	Intact	No information
UV	1–2 nm (clusters)				



Scheme 10 Schematic representation of the zeolitic behavior of MOFs with the reversible guest exchange through the porous framework. The possibility of having two (or more) different linkers in mixed-ligand MOFs (*cf.* Fig. 11, 13 and Scheme 9) is indicated by gray and black bars.

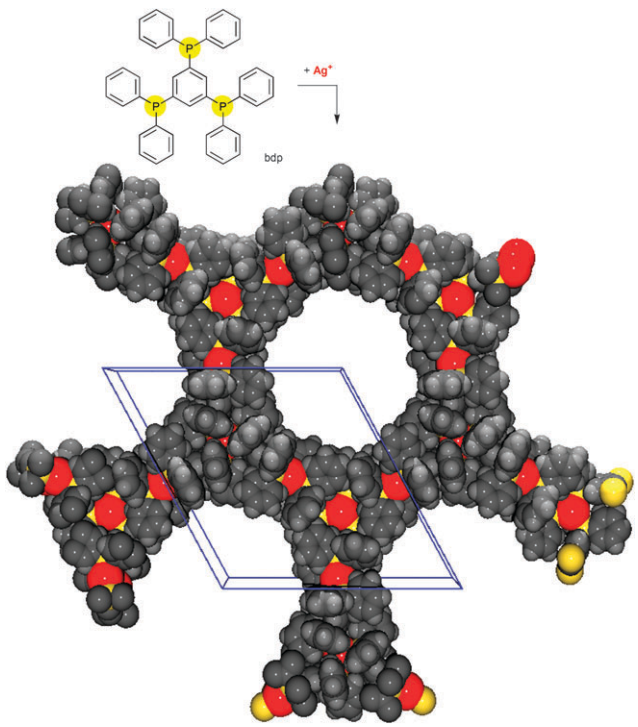


Fig. 21 Building blocks and space-filling representation (viewed along *c*) of the crystal structure of the 2D-[Ag_4(bdp)$_3$](CF_3SO_3)$_4$·*x*$MeNO_2$·*y*EtOH framework with anions and solvent molecules omitted to show the channel structure (bdp = benzene-1,3,5-diphenylphosphane). The channel diameter is 16 Å and the solvent-accessible unit cell volume 36% (*a* = *b*-axis = 29.95 Å) (CSD-Refcode ODIPAS).[201]

superficially termed the same MOF.[24] Validation of published values by other groups are necessary before values become credible as was, for example, done with MOF-5 (*cf.* Fig. 6), MIL-53 (*cf.* Fig. 8) and HKUST-1 (*cf.* Fig. 4).[24]

Hydrogen storage

A crucial aspect for H_2/O_2 fuel cells in mobile applications is the dihydrogen storage. The storage of gaseous hydrogen at high pressure (up to 700 bar) or of liquid hydrogen at very low temperatures (−250 °C) in mass-scale, for example in automotive applications, raises issues of safety, handling, insulation, leakage, volumetric and gravimetric storage density. Metal–organic frameworks (MOFs) and also covalent organic frameworks (COFs)[203] have raised some hopes as potential hydrogen storage media because of their high porosity and large specific surface area (Fig. 22).[204]

MOFs store hydrogen mainly by physisorption. The binding energy of H_2 in MOFs is about 4–8 kJ mol^{-1}. This requires cooling to 77 K for an efficient storage of dihydrogen. Many MOFs are investigated for hydrogen storage. However, the H_2 storage capacity only yields record numbers when measured at 77 K. On the other hand, MOFs require little thermal energy for the H_2 release, compared to transition metal hydrides with their much higher release temperatures. Theoretical estimates suggest an optimal binding energy of about 15 kJ mol^{-1} to store H_2 at room temperature and pressures between 1.5–20 bar.[205]

Two strategies can be envisioned to reach this stronger physisorption energy: (a) smaller pore sizes, so that the H_2 molecule interacts with more pore walls simultaneously; (b) incorporation of coordinatively unsaturated metal atoms which bind H_2. The most prominent example for unsaturated metal sites is probably the Cu_2 paddle-wheel unit, which can be found, for example in the MOF 3D-[Cu_3(btc)$_2$] (HKUST-1, *cf.* Fig. 4 with the aqua ligands on Cu removed). Neutron-scattering experiments have verified that H_2 binds at these sites first, most likely, as a side-on dihydrogen complex.[206] In the MOF 3D-[Cu_6(μ_8-5,5′-methylenedi(isophthalato)(H_2O)$_6$], termed PCN-12 (PCN = porous coordination network, Fig. 23), the number of nearest neighboring "open metal sites" of each H_2-hosting void was increased by aligning these sites in a way that they can interact directly with the guests (H_2 molecules) inside the void. Subsequently, PCN-12 exhibits the highest hydrogen storage capacity at 77 K and 1 bar (3.05 wt%) reported to date.[207] The system PCN-12-Si has the methylene bridged between the isophthalate groups exchanged by dimethylsilicanediyl ($Me_2Si<$) and thereby enables a higher polarizability compared to PCN-12 which leads to stronger H_2 binding. The structure of PCN-12-Si is isoreticular to PCN-12 and stable up to 210 °C. At 77 K 2.6 mass% H_2 can be stored at 1 bar which is among the five highest present values. Simulations indicate that the H_2 is not only deposited at the metal sites but also in small pores of the host structure.[208]

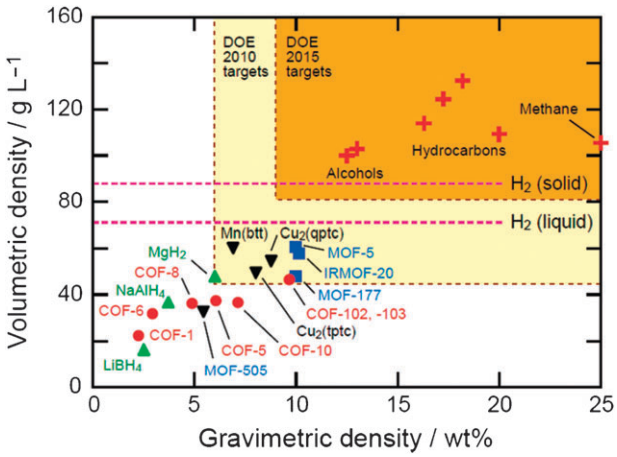


Fig. 22 Storage density of dihydrogen, H_2 per mass and per volume. Figure taken from ref. 204 (reprinted with permission from the American Chemical Society).

CO_2 storage

The MOF of composition 3D-[$Mg_2(\mu_8$-dot$)(H_2O)_2$] (dot = 2,5-dioxidoterephthalate) (also called CPO-27-Mg or Mg-MOF-74) (Fig. 24) was able to filter and retain only the CO_2 out of a mixture of 20% CO_2 and 80% CH_4 under pressure. The CO_2 sorption capacity of Mg-MOF-74 was 89 g kg^{-1}. The material released 90% of the trapped CO_2 at room temperature under ambient conditions. Upon heating to 80 °C the CO_2 was fully desorbed. It is suggested that the magnesium ions interact weakly but selectively with the CO_2.[209]

Gas-pressurized MOFs still contain unfilled open volume. When MOF-5 filled with CO_2 at 400 psi pressure was probed with positrons (e^+) 20–30% of the open volume was still present. Probing the porosity with positrons also revealed that the crystals contain 6 nm long defects and that heat treatments degrade the crystal structure and form pores of a broad range of sizes.[211]

CH_4 storage[10]

Square channels of 8 × 8 Å as part of a 3D channel network are found in the neutral framework of 3D-[$Cu(\mu$-$SiF_6)(4,4'$-bipy$)_2]\cdot 8H_2O$ (4,4′-bipy = 4,4′-bipyridine). The three-dimensionality is achieved by bridging of the 2D-{$Cu(4,4'$-bipy$)_2$} nets through the SiF_6 dianions (Fig. 25). The porous MOF is stable in the absence of the initially-incorporated water molecules of crystallization. Adsorption experiments with methane indicated that above a pressure of 5 bar the framework 3D-[$Cu(\mu$-$SiF_6)(4,4'$-bipy$)_2$] can take up significantly more methane than zeolite 5A, which has the highest methane adsorption capacity of all zeolites.[212]

Light-weight metals as nodes in networks

So far, transition metals of the 3d (Ti–Zn) and in part the 4d series (Ag and Cd) featured prominently as nodes in MOFs or MILs. Recently, coordination networks with the light-metals aluminium and magnesium have been highlighted for their porosity, such as 3D-[$Al_4(OH)_2(OCH_3)_4(H_2N$-bdc$)_3]\cdot x H_2O$

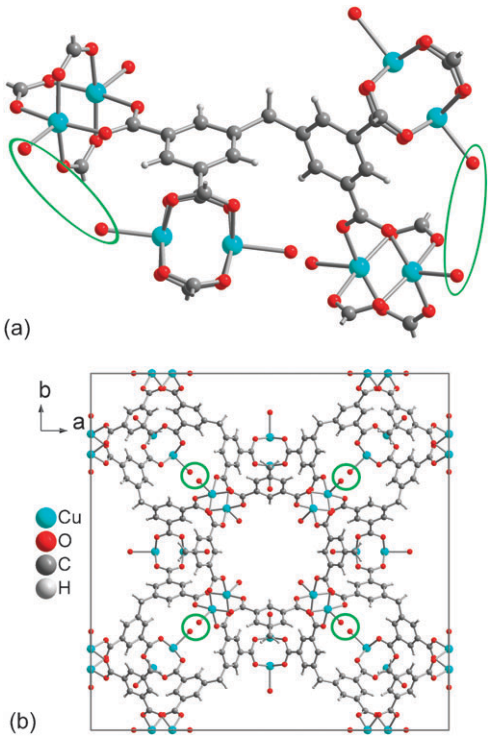


Fig. 23 (a) {Cu_2} paddle-wheel SBUs with one μ_8-bridging 5,5′-methylenedi(isophthalato) ligand and also indicating the alignment of the aqua-ligands (green ellipsoids) and, thus, nearest neighboring "open metal sites" into the voids to enhance the H_2 binding and storage capacity and (b) packing diagram with the tetragonal unit cell of 3D-[$Cu_6(\mu_8$-5,5′-methylenedi(isophthalato$)(H_2O)_6$] (PCN-12, $a = b$ = 32.87 Å, c = 22.63 Å, CSD-Refcode HOGLEV).[207] The dimethylsulfoxide (DMSO) guest molecules are not shown.

(see above),[184] or for their CO_2 filter and storage capacity such as 3D-[$Mg_2(\mu_8$-dot$)(H_2O)_2$] (dot = 2,5-dioxidoterephthalate) (CPO-27-Mg or Mg-MOF-74) (see above, Fig. 24).[209] Lithium-doping of a hydroxy-modified MIL-53(Al) with the 2-hydroxyterephthalate linker (bdc-OH) and formulated as 3D-[Al(OH)(bdc-OH)] resulted in a further increase of the H_2-adsorption capacity.[213]

Porous frameworks for drug ab/desorption in medicine

MILs can function as containers for drug delivery. Frameworks of the MIL series could absorb anti-tumor and anti-AIDS active agents (busulfan, azidothymidine triphosphate, doxorubicin and cidofovir) and release them again in human organs like the liver. The release of the drug from the MIL container was detectable after 30 min of an *in vivo* intravenous administration in rats and could last for 14 days. The storage capacity depended on the pore size, pore functionalization and the MIL-particle size. For example, 40 mass% of doxorubin could be stored in (aminoterephthalato)iron(III) (MIL-101-NH_2).[214]

A MOF from terbium ion nodes and *cis*,*cis*,*trans*-(diammine-dichloro-disuccinato)platinum(IV) bridging metallo-ligands was precipitated from an aqueous solution as nanoparticles through the addition of methanol. To avoid

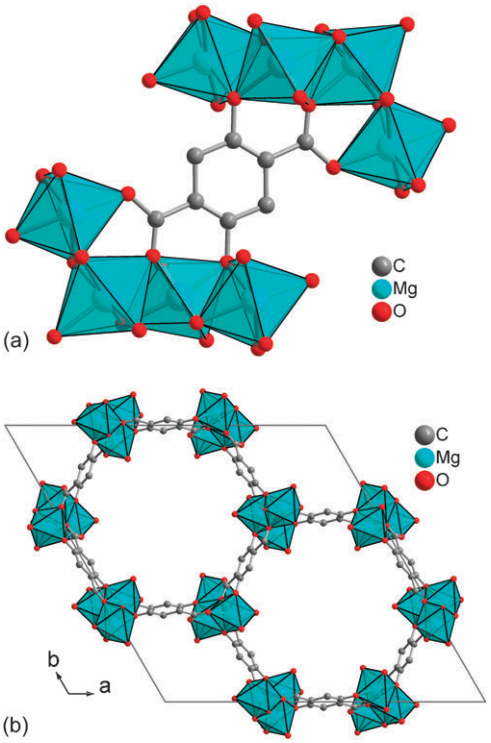


Fig. 24 (a) 2,5-Dicarboxylatobenzene-1,4-diolato($^{4-}$) (dot = 2,5-dioxidoterephthalate) ligand μ_8-bridging between octahedrally coordinated Mg atoms (polyhedral presentation) and (b) packing diagram of the rhombohedral unit cell of 3D-[$Mg_2(\mu_8\text{-dot})(H_2O)_2$] (CPO-27-Mg, Mg-MOF-74, $a = b = 26.03$ Å), which was shown to filter CO_2 out of a CO_2/CH_4 gas mixture.[209] Water of crystallization in the channels ($8H_2O$ per formula unit) is not shown (CSD-Refcode VOGTIV).[210]

hydrolysis of the nano-MOF before reaching the cellular destination, the MOF was encapsulated in amorphous silica. The thickness of the silica shell allowed to control the release of the Pt(IV) ligands which then convert into antitumor active Pt(II) species inside the cells. For cancer cell selectivity the silica was coated on the outside with a cyclic pentapeptide known to coax cancer cells to take the peptide *via* endocytosis.[215]

Sensing through guest molecules

Guest molecules can influence the spin crossover behavior of the framework 2D-[$Fe(NCS)_2$(4,4′-azopyridine)$_2$]·$\frac{1}{2}$EtOH formed by the *trans*-4,4′-azopyridine ligand with $Fe(NCS)_2$ units. In the empty MOF no spin transition of the Fe(II) atoms is observed. When guest molecules like ethanol are absorbed by the host lattice (Fig. 26), a temperature-dependent spin equilibrium between Fe(II) low- and high-spin occurs. This behavior finds its origin in a lattice expansion through the guest molecules which in addition fine-tune the electronic situation of the iron atoms through H-bonds to the S-atoms of the isothiocyanate ligands.[216]

For the sensing properties of MOFs a direct contact with an electrically conducting material would be desirable. One possibility is to grow oriented MOFs on a two-dimensional

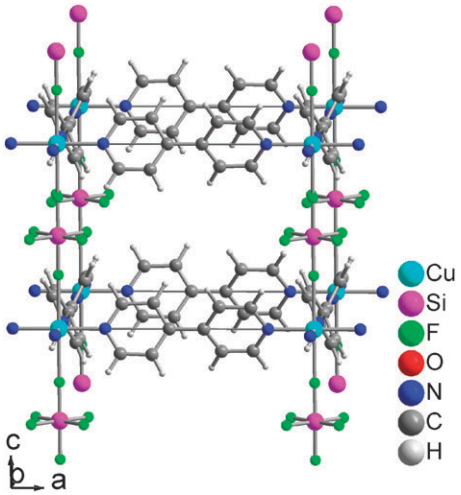


Fig. 25 Packing diagram of 3D-[Cu(μ-SiF_6)(μ-4,4′-bipy)$_2$] with a high CH_4 storage capacity (tetragonal, $a = b = 11.11$ Å, $c = 8.11$ Å, CSD-Refcode GORWUF).[212] Neither the crystallographically-induced mirror disorder of the pyridyl rings nor the water guest molecules are shown.

pre-structured surface substrate like a self-assembled monolayer (SAM).[217,218] The SAM with a –COOH-terminated surface is first constructed through the adsorption of an appropriate phenyl- or alkyl-thiol onto a gold surface. Then the MOF can be deposited upon cooling from the hot mother liquor which contains pre-nucleated MOF particles.[219] An alternative is the layer-by-layer deposition of the MOF: the –COOH-terminated surface is, for example, dipped alternately into a solution of copper diacetate, $Cu(OOCCH_3)_2$ and into a solution of benzene-1,3,5-tricarboxylic acid, $btcH_3$ to prepare the surface-MOF HKUST-1 (*cf.* Fig. 6). X-Ray diffraction and surface plasmon resonance (SPR) experiments show the formation of well-ordered MOF layers.[220]

Luminescence

Luminescent stable metal–organic coordination polymers or now MOFs have been an active research area for decades because of their potential applications in materials science.[1,51,52,56–59,221] Mixed-ligand coordination polymers[53–55,65,159,160] based on a luminescent and a non-luminescent ligand should allow for a dilution of the luminescent centers to avoid concentration quenching effects. Luminescence favors prominently in coordination polymers with d^{10}-elements and nitrogen or oxygen-containing bridging ligands. Benzenedi- or -tricarboxylates can exhibit luminescence in coordination polymers with metal nodes such as zinc or cadmium.[51,222]

Metal–bis(1,2,4-triazol-4-yl)ethane (btre) frameworks exhibit broad band luminescence under UV excitation (Fig. 27).[52] The free flexible ligand btre (*cf.* Scheme 5) did not show fluorescence probably due to a photoinduced electron transfer because of its flexibility.[223] Incorporation of the ligand into a metal–ligand coordination network freezes internal ligand rotation and, thus, turns on luminescence properties. The isomorphous zinc and cadmium MOFs

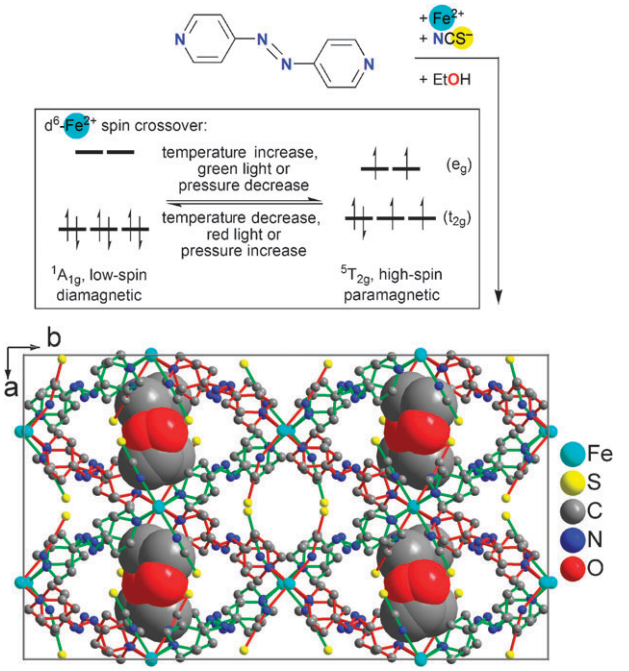


Fig. 26 Building blocks, principle of Fe^{2+} spin crossover and packing diagram of the 2D-[$Fe(NCS)_2$(4,4′-azopyridine)$_2$]·½EtOH framework with guest-dependent spin-crossover of the Fe(II) atoms. An interpenetration of the 2D nets (running along the viewing direction and differentiated by red and green bonds) creates the 3D MOF-structure. The EtOH guest molecules (in space-filling mode) are disordered. H-atoms are not shown (CSD-Refcode GUTDOO).[216]

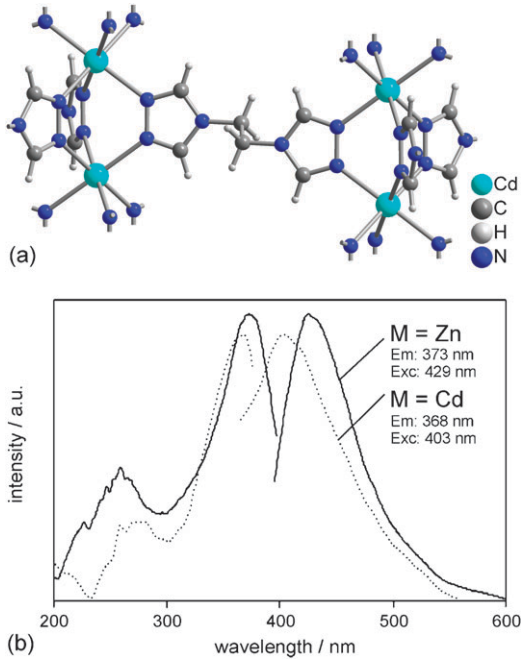


Fig. 27 (a) Building unit and (b) fluorescence excitation and emission spectra of 3D-[M(μ_4-btre)(μ_2-btre)](ClO_4)$_2$ (M = Zn; M = Cd). The respective excitation (emission spectra) and monitored wavelengths (excitation spectra) are indicated (CSD-Refcodes FOQTAH for Zn, FOQTEL for Cd).[52]

3D-[M(μ_4-btre)(μ_2-btre)](ClO_4)$_2$ show an emission peaking at 429 nm (M = Zn) and 403 nm (M = Cd) when excited around 370 nm. Additionally, the zinc derivative shows a more intense fluorescence than the cadmium derivative.[52] One often observes a significant decrease of fluorescence intensity caused by the coordination of ligands to heavier atoms like cadmium(II) due to the heavy-atom effect. With increasing atom number these ions promote intersystem crossings leading to quenching of fluorescence and in some cases increasing phosphorescence.[224]

MOFs have been built with varying amounts of luminescent lanthanoids into the framework. Such a single MOF-compound of composition Er_xYb_{1-x}-PVDC-1 (Fig. 28) emits a unique light spectrum that reads like a colored barcode. The MOFs have been prepared with two or three different lanthanoids which emit in the near-infrared. Variation of the amount of lanthanoid starting salts in the synthesis tailors the emission spectrum of the framework.[225]

Catalysis

Catalysis is of continuous importance. Advantages of MOFs as catalyst are seen in the easy separation of a heterogeneous catalyst, the tailoring of the pore size to yield selectivity, regioselectivity and/or shape and size selectivity by creating an appropriate environment around the catalytic center in the restricted space available. Incorporating, locking and shielding the active sites into a protective solid framework (akin to an enzyme) might prevent chemical and practical problems that are associated with catalyst degradation and product/catalyst separation known from homogeneous systems.[26,226]

It is important when the catalytic properties of MOFs are investigated to prove that they are indeed heterogeneous catalysts. It must be insured that there is no leaching of molecular species into the substrate solution. Despite the large number and variety of MOF-structures little is known, so far, about their properties as solid-state catalysts.[6,19f,227] Infrared microspectroscopy has been applied to monitor catalytic reactions as they occur within the pores of zeolite crystals.[228] The technique offers a new procedure for probing the detailed relationship between a catalyst's structure and its function. The method offers a means for elucidating reaction pathways mediated by industrially relevant catalysts such as zeolites. The new IR method, used either by itself or in conjunction with fluorescence and UV-Vis techniques, may provide resolution of the time and spatial mapping of reactant, intermediate, and product molecules in catalytically active microporous systems under actual catalytic working conditions.[228]

MOFs can work as catalysts through (i) coordinatively unsaturated nodes (metal centers), (ii) ligands functionalized with organic groups (*e.g.* as Brönsted acids akin to organocatalysis), (iii) metal-complexes (as in homogeneous catalysis) which are incorporated into the linking ligand (*e.g.* as metalloligands) or the pores. Examples are:

– cyanosilylation [Ar–C(O)R + Me_3SiCN → Ar–C($OSiM_3$)-(CN)R] with MIL-101 (*cf.* Fig. 9);[28]

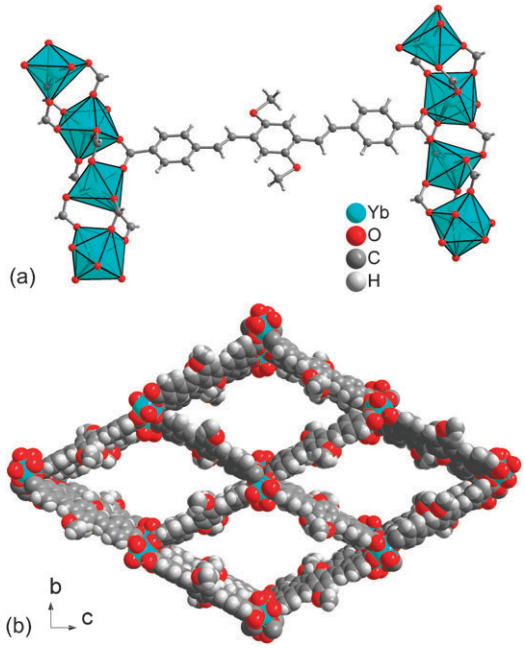


Fig. 28 (a) Building unit of 3D-$[Yb_2(pvdc)_3(H_2O)_2]\cdot(dmf)_6(H_2O)_{8.5}$ (named Yb-PVDC-1, $pvdc^{2-}$ = 4,4′-[(2,5-dimethoxy-1,4-phenylene)-di-2,1-ethenediyl]bis-benzoate, dmf = dimethylformamide) showing the ligand bridging action between chains of hexa- and octa-coordinated Yb^{3+}; (b) packing diagram in space-filling representation of the luminescent framework (solvent guest molecules in the channels omitted). Yb atoms can non-stoichiometrically be replaced by Er atoms to tune the emission spectrum in Er_xYb_{1-x}-PVDC-1.[225]

– cyanosilylation of carbonyl substrates with the MOF acting as Lewis acid catalyst and Mukaiyama aldol reaction [Ar–CHO + $R_2C{=}C(OSiMe_3)R'$ → $Ar–C(OSiMe_3)–CR_2–C(O)R'$]; it was proven that activation takes place in the pores and not on outer surface;[229]

– aromatic *para*-alkylation with IRMOF-1 and -8 (*cf.* Scheme 4, Fig. 6);[29]

– acetalization of benzaldehyde with trimethyl orthoformate using different In(III)-MOFs;[30]

– condensation of benzaldehyde with malonitrile [Knoevenagel-reaction, here Ph–CHO + $H_2C(CN)_2$ → $Ph–C(H){=}C(CN)_2$] with a Cd-MOF as base; it was shown that the MOF and not the solution is active; the MOF shows very good recyclability;[31]

– enantioselective addition of diethylzinc to 1-naphthaldehyde and other aromatic aldehydes as a heterogeneous asymmetric catalysis with homochiral metal organic frameworks; network-structure dependent catalytic activity;[32]

– oxidative coupling of propylthiol, PrSH, with O_2, air or *tert*-butyl hydroperoxide to the disulfide PrSSPr; this may have an environmental application to destroy residues or toxins;[33]

– oxidation of sulfides;[34]

– oxidative coupling of 2,6-dimethylphenol to poly-(1,4-phenylene ether) (PPE) and diphenoquinone (DPQ) with H_2O_2 as oxidant and NaOMe as co-catalyst at room temperature;[35]

– oxidation of benzylalcohol to benzaldehyde with 100% selectivity and up to 87% yield,[230]

– cyclohexane oxidation;[36]

– peroxidative oxidation of alkanes;[37]

– tetralin oxidation with bleading effects from the Cu- and Co-MOF tested and ruled out;[38]

– enantioselective olefin epoxidation;[39]

– transesterification of a range of esters with MeOH under mild conditions at room temperature;[231]

– CO to CO_2 oxidation;[40]

– olive oil degradation of mill waste water with $[Cu_3(btc)_2]$ (*cf.* Fig. 4);[41]

– photocatalytic degradation of organic dyes;[42]

– (i) rearrangement of α-pinene oxide to campholenic aldehyde, (ii) cyclization of citronellal to isopulegol (with relatively good selectivity for some diastereoisomers) and (iii) rearrangement of ethylene acetal of 2-bromo-propiophenone (which is a very good reaction to examine the character of active sites) all with $[Cu_3(btc)_2]$ (*cf.* Fig. 4); tests for heterogeneous reactions were carried out, no leaching occurred but the catalyst crystals suffered from fragmentation during reaction; the catalyst activity decreases slowly due to deposits in the pores;[43]

– ring-opening polymerization of cyclic esters;[44]

– styrene, acetylene derivative and other radical polymerization reactions;[49,50]

– NO decomposition to N_2 and O_2 and reduction of NO with *n*-hexane in the presence of O_2.[232]

For (iii) a metalloporphyrin complex immobilized inside a ZMOF was shown to perform better than the same molecule used in solution or attached to other types of solid support. The anionic indium–imidazoledicarboxylate ZMOF grows around the cationic protonated porphyrin template and thereby anchors and isolates the porphyrin inside the cages. In a post-synthesis step the porphyrin rings were then metallated.[233] Catalysis experiments show that the Mn–porphyrin@ZMOF oxidizes cyclohexane to a mixture of cyclohexanone and cyclohexanol in greater than 90% yield. There was no activity for leaching and other control reactions. The catalyst could be recycled and reused a dozen times without loss of activity.[233]

The MOF 3D-$[Zn_2(bdc)(L\text{-lac})dmf]\cdot dmf$ (L-lac = L-lactate, dmf = dimethylformamide) catalyzed heterogeneously the oxidation of aromatic sulfides (Ar–S–R′) to chiral sulfoxides ($Ar–S^*(=O)R'$) chemoselectively over sulfones($Ar–S(=O)_2R'$). Despite the enantiopure chirality of 3D-$[Zn_2(bdc)(L\text{-lac})dmf]\cdot dmf$ no asymmetric induction in the catalytic sulfoxidation was observed but there was an enantiomeric excess (ee) for the adsorption of the obtained sulfoxides. Subsequently, a one-pot process in which 3D-$[Zn_2(bdc)(L\text{-lac})dmf]\cdot dmf$ acts as both the heterogeneous catalyst and a chiral stationary phase in a column chromatography separation was feasible. Thereby, the racemic sulfoxide $Ph–S^*(=O)Me$ was obtained in enantiomerically and chemically pure form (Fig. 29).[234]

Perspectives

Metal–organic frameworks, be they named MOFs, MILs, PCN, PCPs or simply coordination polymers, have developed into a mature discipline. By publication statistics there is still

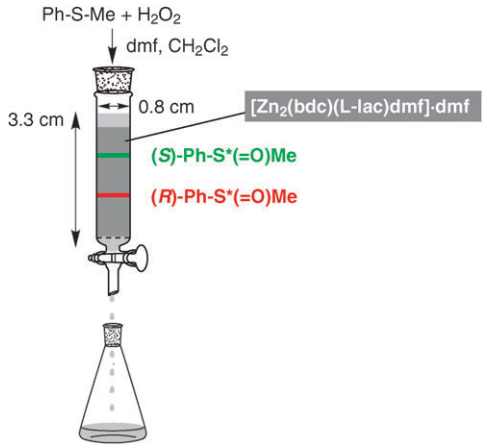


Fig. 29 Schematic procedure of the catalytic sulfide oxidation and concomitant chromatographic enantiomeric separation of the chiral sulfoxide product by 3D-[Zn_2(bdc)(L-lac)dmf]·dmf acting both as a catalyst and a chiral stationary phase (L-lac = L-lactate, bdc = benzene-1,4-dicarboxylate (terephthalate), dmf = dimethylformamide).[234]

no end to the boom. Eventually, however, it has to come down to real application emerging from this class of compounds. Many applications are envisioned as outlined above and in numerous other reviews, but so far, to the best of our knowledge, none has materialized.[6] We are neither aware of a MOF built into a technical device nor used as an industrial catalyst. It is hard to be a prophet where the breakthrough in a technological application will occur. Clearly, the high porosity and inner surface area render a zeolite-type application for reversible gas storage, separation or heterogeneous catalysis most likely. It is here where most people focus their research activities. The future will tell but as scientists we should not exclude any venues and be open for surprises. It does not need only to be hydrogen storage where MOF applications have to lie. Many other gases are industrially important[6,10,15,16] and even the reversible uptake of simply water in a MOF holds potential.[65,235]

Acknowledgements

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