High Valence 3p and transition metals based MOFs

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High Valence 3p and transition metals based MOFs

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This article focuses on high valence 3p and transition metal based Metal Organic Frameworks. In the first part we will discuss the complex solution chemistry of these metals which makes this sub-class of MOFs more of a challenge than the traditional low valence MOFs will first be discussed. This is followed by a short review of the different classes of solids based on phosphonates, carboxylates and other linkers. Finally, we report some of the most relevant/important properties of these solids such as their chemical or thermal stability as well as their catalytic, redox- and photo-activities.

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Introduction

Metal-organic frameworks (MOFs) or Porous Coordination Polymers are one of the most recent and rapidly growing classes of crystalline porous solids.[1-5] This is due to their huge compositional and structural diversity allowing for numerous potential applications such as gas storage, separation of fluids, catalysis, sensors, inclusion, biomedicine etc... Amongst the thousands of MOFs structures reported so far, the majority are built up from divalent cations (Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}…) and are typically based on carboxylates, phosphonates or N donating linkers, or a combination of them. This leads to MOFs with a wide range of structure types and pore sizes, from the micro to the meso domain and with or without functional groups on the organic spacer. MOFs built up from higher valence cations (+III, +IV…) are not very (far less) common,[6-16] except maybe for Ln^{3+} cations and more recently uranyl moieties.[17] Such a discrepancy arises mainly from the differences in terms of chemical reactivity compared to lower valence metals, for example their higher charge density often results in less control (makes it harder to control) over the crystallization process and/or to the formation of metal hydroxide or oxides. This makes the discovery of new topologies based on these cations and (the formation) obtaining single crystals suitable for fast structure determination more difficult. Although still scarce, there are (however) several reasons which justify the continuous effort for developing new porous high valence MOFs. One of the most significant problems is the low chemical stability of this class of materials.[18, 19] The often poor water stability of most limits their use in real applications, while recent studies have shown that for a given linker, increasing the charge of the metal usually leads to an enhancement of the hydrothermal stability of the MOF.[18] Other important perspectives concern/include the possibility of enlarging the range of MOF chemistries to develop new architectures of interest associated with specific properties arising from the intrinsic properties of these highly charged cations (redox or photo-activity, catalysis…).

This article aims first at compiling the studies related to the use of these less familiar cations, focusing on 3p (Al^{3+}, Ga^{3+}, In^{3+}) or transition metal cations (Fe^{3+}, Cr^{3+}, Sc^{3+}, Zr^{4+}, Ti^{4+},...) excluding therefore lanthanides, actinides and POM-MOFs (POM : PolyOxoMetallates).[20, 21] Particular attention will be devoted to analysing: i) the different parameters that affect the chemical reactivity of high valence cations (+III, +IV…), ii) the structural features of the resulting MOFs and iii) (discussing) the consequences in terms of stability and properties.

The Solution Chemistry

MOFs are built up from the ionocovalent association of a cation and a negatively charged linker bearing a complexing function (carboxylate, phosphonate, azolate…). Prior to any reaction with an organic linker, the physicochemical properties of the cation such ascharge, size, electronegativity… have to be considered in order to gain some understanding of the differences in terms of chemical reactivity of the various cations.

It appears that the charge density, which results from a combination of ionic radius and charge, has a strong impact on the nature of the condensation processes in aqueous solution (Figure 1). For divalent cations, water only induces the formation of hydroxide or oxide groups (at room temperature) under basic conditions while/whereas tri or tetravalent cations typically form hydroxide or oxides over a much larger pH range.

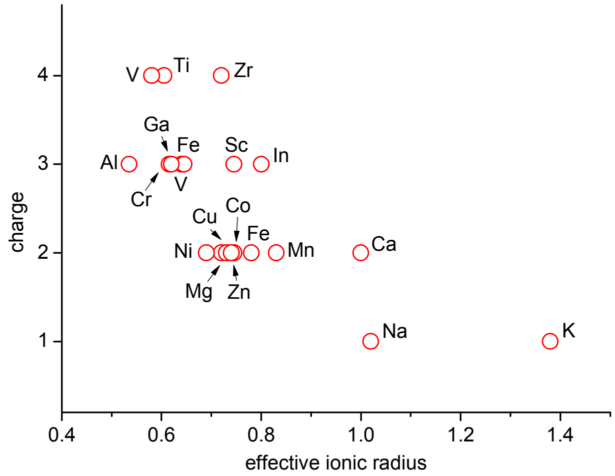

Figure 1 Ionic radius and charge of selected 6-fold coordinated cations (for Mn and Fe, the high spin state is considered).[22]

Indeed, the charge (density) of the cation drastically impacts on the phase diagram of the species in aqueous solution. A typical set of cations traditionally bearing a +2, +3 or +4 oxidation state over most of the pH domain in water, is shown on Figure 2 through the Pourbaix diagrams of Zn, Fe and Ti in water.[23, 24] It appears that the higher the charge the larger the range of pH where oxide or hydroxides dominate, even under quite acidic conditions (see Fe and Ti in Figure 2). Therefore, for higher valence cations the domain of pH where molecular species are available in solution considerably shrinks.

For titanium, TiO_2 dominates in water over the entire pH range and the existence of titanium complexes, such as Ti^{4+} oxoclusters, only occurs under highly acidic conditions (pH<0), while/whereas zinc hydroxides only appear when turning to basic conditions. The situation for iron is in between that of titanium and zinc: soluble iron(III) species are present under acidic conditions but hydroxides appear at higher pH than for the Ti system. Note that at lower potential, iron(II) is present which leads to an increased domain of solubility which then extends up to the basic pH.

The charge is not the only parameter; the ionic radius also plays an important role as shown below for the tetravalent cations (Ti, Zr, Hf): for a given charge, the smaller the cation the more acidic and the less soluble in water (Figure 3). The consequences in terms of metal to ligand complexation are obvious.

While at room temperature, divalent cation species are readily soluble under basic conditions, the increase in cationic charge necessitates either dissolving metal oxides or hydroxides or shifting the reaction pH towards acidic or very acidic conditions.

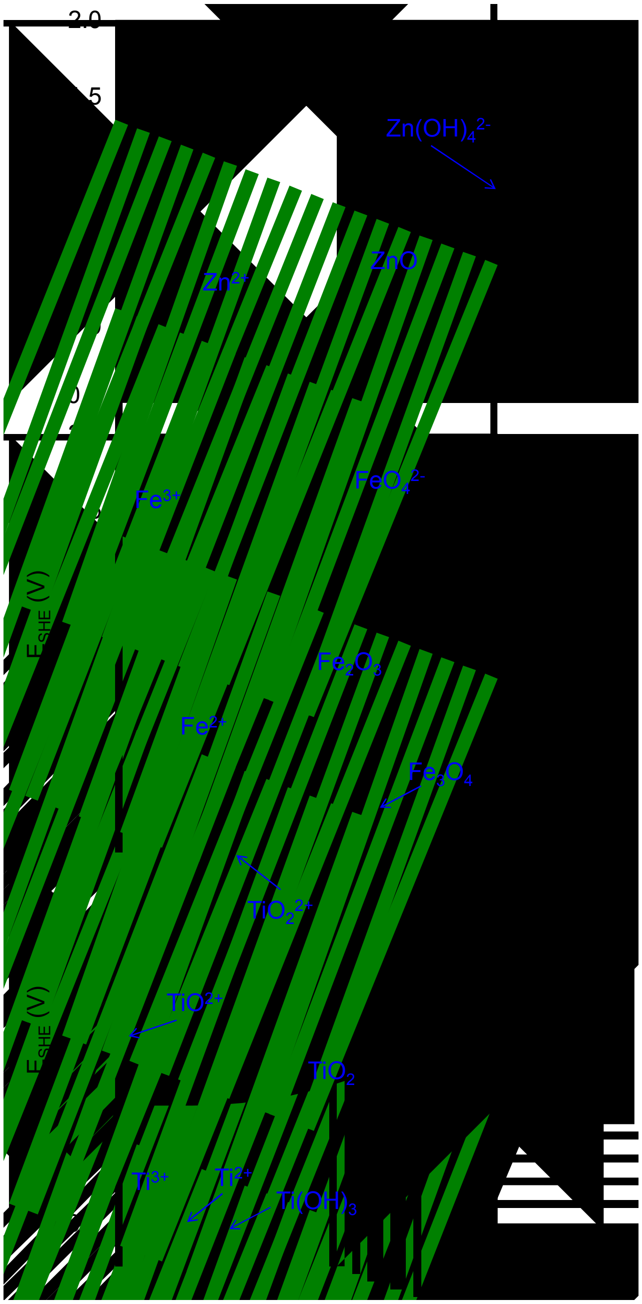

Figure 2 Pourbaix diagrams of zinc (top), iron (center) and titanium (bottom) calculated for $[M^{n+}] = 10^{-3}$ mol. L^{-1} at 25°C using the Hydra and Medusa softwares.[24] Green dashed lines: O_2/H_2O and H_2O/H_2 redox couples.

In other words, the chemistry of MOFs formed with higher valence cations involves a (much) stronger competition between the inorganic polymerisation and the formation of metal-ligand complexes. Of course, these Pourbaix phase diagrams are provided only in water at room temperature for a given concentration and counter-anion and one expects that using other polar solvents at different temperatures in the presence of linkers will certainly strongly impact the phase diagrams. However, it is likely that this global trend will remain unaffected, particularly since polar solvents and/or metal precursors contain a significant amount of water that can favour inorganic condensation during the synthesis process.

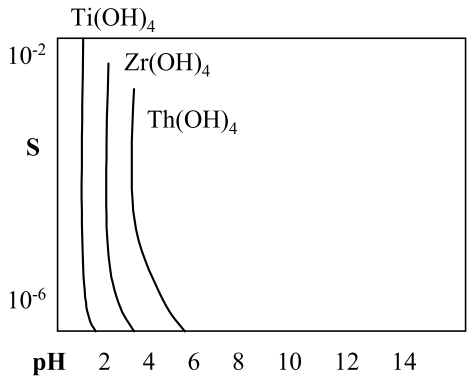

Figure 3 Effect of the size of the cation (water, RT) on the solubility of the hydroxyl, according to Charlot et al. [25]

As a consequence, most synthesis reactions using tri or tetravalent cations are performed under slightly acidic conditions and sometimes require higher temperatures or the use of additives such as HF[9, 16, 26, 27], HCl[28] or monocarboxylic acids[29]. This is in order either to dissolve or avoid the formation of metal hydroxides or oxides or to maintain a sufficient concentration of metal complexes necessary for the formation of hybrid framework in solution.. In the last/latter case, the competition between the coordination of the mono- and poly-carboxylate species to the cation also slows down the nucleation and leads to larger crystallites.[29]

Finally, even for a given oxidation state, the reactivity is dependent on the nature of the cation. As an example, Fe(III) is far more reactive than Cr^{3+} due to the intrinsic slower ligand-metal exchange constant of Cr^{3+}.[30] As a consequence, although most Fe^{3+} based MOFs can be prepared from Fe^{3+} salts under mild conditions (typically T < 150°C), Cr^{3+} materials require higher temperatures, usually above 180°C.[9, 16, 26] This discrepancy needs to be taken into account when bimetallic M^{3+} solids are prepared.[31]

The Solids

Phosphonates

This topic was recently reviewed by Clearfield and collaborators.[32] The first systematic assays of synthesis of high valence tri- or tetra-valent based MOFs were performed using poly-phosphonates as linkers. Alberti et al. were the first to explore systematically, under mild hydrothermal conditions, the formation of derivatives of the well known layered metal phosphates α or γ- ZrP, by replacing the phosphate groups with alkyl or aromatic monophosphonate groups.[33] Following this work, Clearfield et al. further used diphosphonates in order to connect these metal phosphonate layers and form (allowing the formation of) pillared three-dimensional structures.[34] Since these pioneering results, several other groups succeeded in producing arrays of layered or open framework metal(III, IV or V) phosphonates, based on various cations such as vanadium(III, IV or V),[35-37] aluminum,[38] gallium,[39] iron(III),[39, 40] lanthanides,[41] titanium(IV),[42-44] tin(IV),[45, 46] molybdenum[47] or cerium(IV).[48]

Altough the intensive synthetic effort to develop porous phosphonates, a permanent porosity was rarely achieved. A concept was thus proposed by Clearfield et al, in order to enhance/improve the porous character of metal phosphonates, which involves carefully controlling the substitution rate of diphosphonates by monophosphonates. Open framework metal diphosphonates were obtained,[13] however the resulting porous character was established in a disordered non periodic manner. This approach was later extended to other metal(III) phosphonates materials.[49] A similar approach was developed in parallel that consisted of mixing diphosphonates and phosphites, in a 1:3 ratio, in another attempt to build up open framework architectures.[50, 51]

Although a relatively large number of three dimensional metal(III, IV or V) phosphonates structures have been reported to date,[52] "real/true" porous phosphonates based solids that exhibit an organised permanent porosity are still very scarce: as mentioned above, one can cite the Zr mono- / di-phosphonates of formula $Zr(O_3P\text{-}R\text{-}PO_3)_x(O_3P\text{-}R')_{2-2x}$ (R, R': organic spacers)[13] and the Zr phosphites/3,3′,5,5′-tetramethylbiphenyl)diphosphonate[50] of formula $Zr(HPO_3)_{1.33}(O_3P\text{-}R\text{-}PO_3)_{0.33}$, R = 3,3',5,5'-tetramethylbiphenyl which both exhibit a 1D small pore system leading to a low porosity (S_{BET} ~ 375 $m^2\ g^{-1}$). In parallel, significant results were obtained through the synthesis of a porous Al methyl phosphonate MOF denoted AlMePo-β of formula $Al_3(CH_2PO_3)_2.nH_2O$ (Figure 4);[53] here, the porosity (S_{BET} ~ 300 $m^2\ g^{-1}$) is not achieved through the presence of alternatingmono- (or phosphites) and di-phosphonates within a pillared structure but through the direct formation of an open framework Al phosphonate MOF. More recently, porous piperazine metal (III or IV) diphosphonates denoted MIL-91[14] or $MX[OHO_2P(CH_2)\text{-}L\text{-}(CH_2)PO_2OH].nH_2O$ ($M=Al^{3+}$ or Ti^{4+}, X=OH or O; L: piperazine) were reported bearing a 2D small pore system (ϕ ~ 4Å; S_{BET} ~ 300 $m^2\ g^{-1}$) built up from corner sharing chains of octahedra linked by diphosphonate groups (Figure 5). It should be noted that, over the past two decades, (several?) series of porous metal phosphonates (M = Al, Ti, Zr, Sn…) obtained under solvothermal conditions and lacking from long range order were also reported, mostly by Clearfield et al.[32, 54, 55] The authors proposed that local defects of the (in the) linkers are at the origin of the porosity of these solids.

Despite these interesting results, pore size and surface areas are still a long way from (far smaller) those of the recent series of large pore metal(II) diphosphonates STA-12, which exceed 1000 $m^2\ g^{-1}$ in agreement with their larger pore size (~ 10Å),[56] or its very recent larger isoreticular form STA-16.[57]

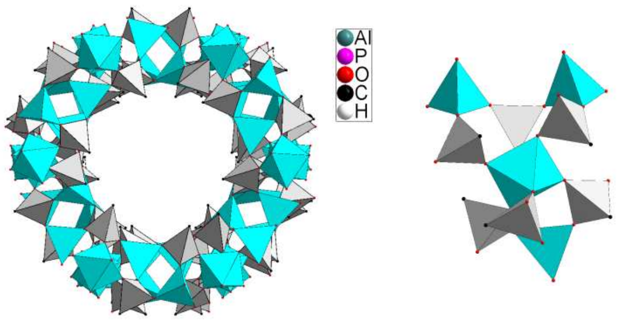

Figure 4 Crystal structure of the porous Al phosphonate AlMePo-β (left) and its constitutive structure building unit (right). [53]

Another approach to broaden the structural diversity of metal phosphonates consists in using auxiliary complexing or functional groups, such as amine, carboxylate or iminoacetate groups, that either increase the number of connectivies and/or increase the solubility of the linker to boost the cristallisation process [58].

In conclusion, metal phosphonates are not the most common MOFs whatever the oxidation state of the metal. Our opinion is that two concomitant factors are in play: commercially available linkers are very scarce and the need to connect the three oxygen atoms of the phosphonates (versus two oxygen atoms for carboxylates) decreases the geometrical degree of freedom for building open architectures, if one accepts/ takes into account the use of auxiliary groups. This is nicely illustrated through the case of the titanium diphosphonates MIL-25 and MIL-91(Ti): whilst in MIL-25 solids or $Ti(O_3P\text{-}(CH_2)n\text{-}PO_3)$ (n=2, 3),[59] all three oxygen atoms from the phosphonates are connected to Ti atoms resulting in a pillared non porous structure, in MIL-91(Ti) only two of the three oxygen atoms from the phosphonate groups connect Ti cations (Figure 5) leading to the formation of a microporous material.

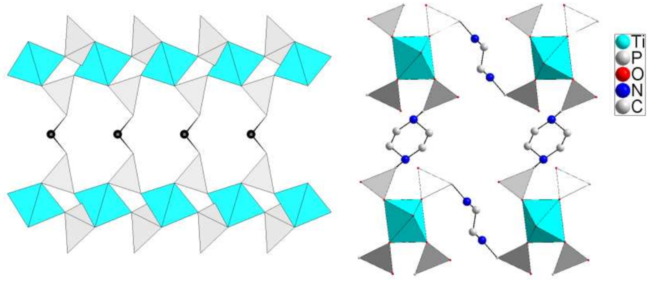

Figure 5 Comparison of the crystal structures of the Ti diphosphonates MIL-25 (left) and MIL-91 (right).

In terms of chemical reactivity, although phosphonates offer three oxygen atoms and two pKa (rather than the two oxygen atoms and one pKa for carboxylates) which might at first suggest greater possibilities for forming new architectures, on the whole there is less structural diversity for metal phosphonates compared with the huge variety of metal carboxylates (or azolates). Typically, the SBU varies with the metal (III to V): from simple polyhedra isolated by phosphonate groups, to clusters (dimers, trimers…) and chains or layers of metal polyhedra bearing connectivities depending on the nature of the metal.[60]

In terms of synthesis conditions, it is worthy of note that most synthesis of metal(III or IV) phosphonates are performed in water because of the high polarity of the phosphonates despite some recent attempts using non aqueous solvents, and they often require high temperatures (150-220°C). HF is also often used as a mineralisation agent to increase the solubility of the metal(III or IV) complexes and/or to slowdown the cristallisation process due to the very fast metal(III or IV) reactivity towards phosphonates.[61]

Carboxylates

As with the M^{2+} cations, the most prominent M^{3+} and M^{4+} porous coordination polymers belong to this family.

When coupled with poly-carboxylate ligands, M^{3+} cations lead to /form two main Secondary Building Units (SBUs): a chain built up from μ_2-hydroxo corner sharing octahedra formulated $[M(OH)(CO_2)_2]_n$ and a μ_3-oxo centered trimer of MO_6 octahedra formulated $M_3O(CO_2)_6X(S)_n$ (X = anion, S = solvent) with n = 2 if X is bound to M and 3 otherwise (Figure 6). Both SBUs are robust and have been reported with most of the M^{3+} cations (Al, Sc, V, Cr, Fe, Ga, In) in a low dimensional form (1-D compounds and molecular clusters for the trimer and the chain respectively). They can be formed under various synthetic conditions: at room temperature or under solvothermal conditions; in polar solvents, particularly water, DMF and alcohols. It should be noted that, in general, most of the chemically robust motifs found in MOFs were already known to coordination chemists as molecular species, often both in solution and in the solid state.[62, 63] Most M^{3+} cations can also give rise to specific iSBU, which will be discussed later in this section.

When coupled with linear dicarboxylate ligands (such as terephthalate or BDC), the above mentioned chain SBU gave rise typically to two microporous solids, namely the MIL-53 (M = Al,[64] Cr,[16] Fe,[65, 66] Ga,[67-69] In,[70] Sc,[71] V[6, 72]) and its polymorph MIL-68.

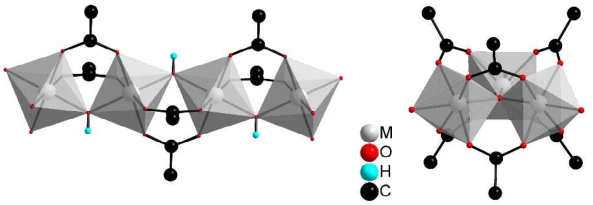

Figure 6 Prototypical SBUs found in the M^{3+}/carboxylate system. Left: $[M(OH)(CO_2)_2]_n$ chain; right: $M_3O(CO_2)_6X(S)_n$ trimer.

Both solids are formulated M(OH)(BDC) and are built up from corner-sharing chains of $MO_4(OH)_2$ octahedra connected through the ligand to define 1-D pores, which are either diamond-shaped in the case of MIL-53 or triangular and hexagonal shaped in the case of MIL-68 (Figure 7). Whereas the first solid exhibits a flexible framework (see below), the second one is rigid and possesses an experimental BET surface area ranging from 800 to 1700 m^2 g^{-1}. Both polymorphs can be obtained with one single (using the same)cation (Al, Fe,[73] Ga,[74] V,[75] In[74]) although the key feature driving to the formation of one solid *preferentially over* the other is not obvious. MIL-53 is generally more easily obtained than MIL-68, *i.e.* it can be prepared under a broader range of reaction conditions: depending on the cation, either water and/or an organic solvent such as DMF can be used. The inorganic precursor can be either a salt or the reduced metal (Fe^0). Moreover, their properties can be easily modified through the functionalization of the terephthalate linker with polar/apolar or acidic/basic groups,[76-81] whereas only an amino functionalized MIL-68 has been reported up to now.[82] Analogues of MIL-53 based on either longer aromatic (naphthalendicarboxylate, biphenyldicarboxylate)[83-85] or alkylated (cyclohexanedicarboxylate)[86] ligands were also produced, while the shorter fumarate analogue A520 is the first MOF ever prepared at/on the industrial scale by BASF.[87] Regarding the MIL-68 solids, DMF seems to favour their formation, possibly through a templating effect which stabilises the triangle-shaped 1-D pore specific to this structure.[73, 74] Alternatively, the combination of similar chain-like motifs with bent dicarboxylate ligands gives rise to new topologies, such as the benzophenone derivative CAU-8[88] or isophthalates CAU-10.[89]

Thus far, no solid based on tricarboxylate linkers and pure chains has been reported. The only structurally related solid is the MIL-96(Al,[90] Cr[91] or Ga[92]) series formulated $M_{12}O(OH)_{18}(H_2O)_3(M_2(OH)_4)(BTC)_6 6\bullet(H_2O)_n$. This solid is built up from theafore-mentioned trimers together with corrugated chains of corner-sharing MO_6 octahedra leading to micropores (diameter ~ 9 Å) connected through very small windows (3-4 Å).

Regarding the trimeric SBU, it acts as a trigonal prismatic node, which leads to various topologies depending on the symmetry of the ligand. For the linear dicarboxylate ligand (terephthalate and analogues), two polymorphs based on trimers formulated $M_3O(L)_3X(H_2O)_2\bullet(solvent)_x$, namely the MIL-88 (or MOF-235) and MIL-101 solids, can be obtained. Both have been reported mainly for M = Cr, Fe, but can be found with other cations (such as Sc[93-95]). The MIL-88 structure (or *acs* topology[96, 97]) consists of triangle-based hybrid bipyramids, with each corner being occupied by a trimer, and the linker lying at the edges along the axis of the bipyramid only (Figure 7).

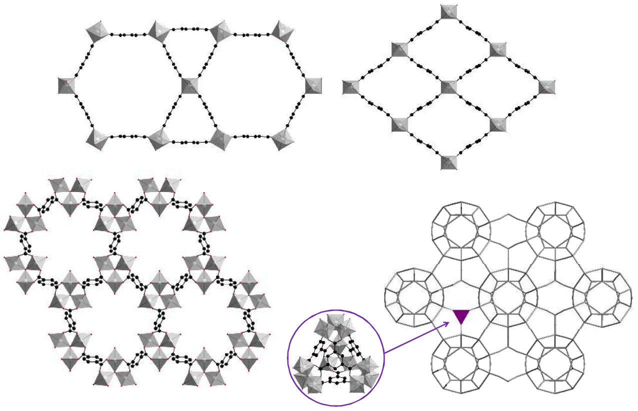

Figure 7 Most common structure types found in the M^{3+}/di- and tri-carboxylate systems. Top left: MIL-53, top right: MIL-68; bottom left: MIL-88; bottom right: MIL-100. Metal polyhedra, and carbon atoms are in grey and black, respectively.

The connection of these bipyramids ensure the formation of two types of micropores, one along the axis of the bipyramid and one perpendicular.[98] This topology is compatible with a very high degree of structural flexibility, up to 230 % in cell volume.[99] As a consequence, the MIL-88 and its analogues (with functionalized[100] or elongated linkers[15]) present a pronounced flexible behaviour (see below). Most of these appear to be non-porous towards adsorption of nitrogen at 77 K but easily adsorbs various guests, this adsorption being associated with a pore re-opening that becomes easier when bulky functional group or non aromatic spacers are used.[100, 101] The same SBU and BDC linker can give also rise to the MIL-101 topology. This structure is based on hybrid super-tetrahedra built up from trimers (at the corners) and linkers (on the edges) giving rise to a zeolitic MTN-type structure exhibiting two types of spherical mesopores (Φ~29 and 34 Å) connected through microporous windows (Φ~ 12 and 16 Å) (Figure 7). Initially reported with Cr,[9] the V,[102] Fe,[103] Al,[104] and Sc[95] analogues have also been recently described, together with larger analogues based on 2,6-nathphalendicarboxylate and Cr[105] and 4,4'-biphenyldicarboxylate and Fe.[106] The reactivity of some specific ligand/cation pairs (pairings) was studied in order to shed some light on the parameters driving the formation of one polymorph *preferentially over* the other (MIL-101 / MIL-88), and one SBU *vs.* the other (trimer *vs.* chain).[104, 107, 108] In particular, the reactivity of the BDC-NH_2 and Fe was investigated systematically using high-throughput techniques.[107] In the case of MIL-101 and MIL-88 (or MOF-235), it was highlighted that the key parameter is the concentration of the reactants: the most porous solid (MIL-101) is preferentially formed at lower concentration,[104, 107] whilst the MIL-88 is obtained at higher concentration. Regarding the SBU, it was broadly found that trimers are favoured with shorter reaction times,[108] at lower temperature and in basic medium, whereas the chain-based solids (MIL-53) are favoured in acidic medium and/or at higher temperature. A recent EDXRPD study involving the solvothermal (DMF/water) Al / BDC-NH_2 system and the MIL-53, MOF-235 and MIL-101 MOFs, has shown that upon addition of water to the reaction media, the trimer based MOFs MOF-235 and MIL-101 convert into the more thermodynamically stable MIL-53 phase.[104]

Although these parameters need to be re-investigated when a new ligand is considered, these findings might drastically speed-up/accelerate the studies of new M^{3+} / dicarboxylate systems.

In the case of the trimesate ligand (BTC), the MIL-100 structure type can be obtained. This solid, formulated $M_3O(BTC)_2X(H_2O)_2$•(solvent)$_x$, was initially reported with Cr,[26] and then the series was extended to Al,[109] Fe,[110] V,[111] Sc[95] and Mn.[112] Its structure consists of hybrid super-tetrahedra built up from trimers (at each corner) and linkers (along on the faces) assembling in the same way as in MIL-101 to define two types of spherical mesopores (Φ~24 and 29 Å) connected through microporous windows (Φ~ 5.5 and 8.6 Å) (Figure 7). (Thanks to)Because of its high BET surface area (>2000 $m^2 g^{-1}$) and pore volume (> 1cm^3 g^{-1}), rather easy preparation and high chemical stability (at least for M = Cr, Fe, see below), this family now appears as one of the archetypical mesoporous MOFs. Using a longer sulfurated linker and Fe, Zhou et al. recently reported a pseudo-polymorph of MIL-100, based this time on hybrid super-octahedra,[113] while Schröder et al., using Sc and the BTB linker obtained a hexagonal porous compound.[94] Using the same extended tritopic linker, we also recently isolated the larger analogue of MIL-100(Fe).[106] Another recent approach to generate (for generating) new solids is the mixed linker strategy, which consists in/involves the combination of ligands of different symmetry. Using a mixture of linear dicarboxylates and a tritopic linker (BTB), resulted in a series of new microporous or mesoporous iron(III) carboxylate MOFs of the MIL-142 or MIL-143 structure type.[114]

When tetracarboxylate linkers are used, the number of microporous solids (decreases) becomes scarcer. Denser solids based on the 1,2,4,5-benzenetetracarboxylate (or BTeC) and the chain have been obtained leading to rather low surface areas, including a series of aluminium BTeC MOFs (see below).[115-117] Only larger linkers, such as porphyrin derivatives lead to significantly porous solids.[118] One can also cite the very small pore MIL-102 solid based on Cr trimer and 1,4,5,8-benzentetracarboxylate[119] as well as the microporous *soc*-MOF (or MIL-127) (free diameter of ca 7 Å) based on azobenzenetetracarboxylate and In[11] or Fe that bear a more significant surface area above 1200 $m^2 g^{-1}$.[120]

Finally, the molecular trimeric Cr units built up from pyridine carboxylate were also recently used to prepare heterometallic Cr/Ag framework in a two-step fashion.[121]

One of the main interests of MOFs based on the trimeric SBU comes from the possibility of generating coordinatively unsaturated sites (CUS). In most cases, 2/3 of the metallic cations possess a labile solvent molecule in a terminal position, which can be eliminated upon heating to generate a free Lewis and/or redox metal site. This will be developed in detail in the 'properties' section.

In addition to these common SBUs, few cations lead to specific SBUs (and then MOFs), either because of serendipity (the experimental conditions leading to this phase with other cations have not been yet determined) or because of the intrinsic characteristic of the cation, such as its large radius / low charge density (Sc, In) or specific solution chemistry (Al).

In the case of scandium, a few porous solids based either on isolated ScO_6 octahedra (in $Sc_2(BDC)_3$[122, 123]) or on dimers of octahedra formulated $Sc_2(\mu_2\text{-}OH)(CO_2)_5$ [124] have been reported. For indium, the combination and deformation of the afore mentioned SBU lead to a series of porous materials.[125] For this cation, the large ionic radius (see Figure 1) also favours a coordination number higher than six. In this context, Eddaoudi et al. developed a series of zeolitic MOFs (ZMOFs) built up from mixed nitrogenated/oxygenated linkers such as imidazolatedicarboxylate and isolated 8-fold coordinated In^{3+} ions,[12, 126] while Allendorf et al. reported a porous solid based on the tritopic BTB linker and similar isolated eight-fold connected In^{3+} ions.[127]

In the case of iron, by benefiting from the partial degradation of the trimeric iron(III) acetate in the presence of terephtalic acid under solvothermal conditions, one could (it was possible to) obtain the microporous MIL-85 solid, built up from one-dimensional helical inorganic chains (Serer et al. Chem Mater 2004). Later, isolated Fe^{3+} octahedra were also observed in the porphyrintetracarboxylate based solid MIL-141, whose structure is built up from three interpenetrated nets presenting the PtS topology.[128] With the extented tritopic linker BTB, a microporous solid formulated $Fe_4(\mu_3\text{-}O)_2(BTB)_{8/3}(DMF)_2(H_2O)_2$•(solvent)$_x$ and based on eight-connected tetrameric units of FeO_6 octahedra has been reported (Figure 8).[129] The structure was described as a partially augmented *the* net.

With vanadium(III), a solid (MIL-71) formulated $V^{3+}_2(OH)_2F_2(BDC)\bullet H_2O$ was reported, which can further be oxidised into its vanadium(IV) analogue with a $V^{4+}_2O_2F_2(BDC)$ formula.[130] The interest of this compound lies in its unusual 2-D SBU, rather than its porosity (it only presents ultra-micropores), This SBU can be described as the condensation of the chain of MIL-53, or better still as a layered perovskite sheet, *i.e.* built up from corner sharing VO_4F_2 octahedra. This unusual structure, together with the redox chemistry of vanadium results, in a distinctive magnetic behavior.

Finally, the richness of the chemistry of Al in solution gives rise to numerous specific(notable) porous solids, of which a few typical examples are described below. Firstly, the aluminium trimesate MIL-110(Al), built up this time from octanuclear cluster of AlO_6 octahedra and formulated $Al_8(OH)_{15}(H_2O)_3(BTC)_3\bullet(solvent)_x$ was evidenced (Figure 8).[131] Regarding the three microporous Al trimesates currently reported (MIL-96, MIL-100 and MIL-110), the key synthetic parameters favouring one solid *over* the other appear to be the pH and the reaction time.[132]

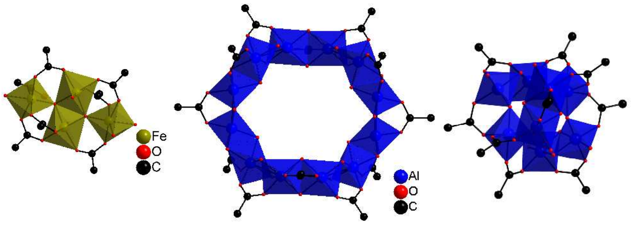

Figure 8 Some specific molecular SBUs found in M^{3+}/carboxylate systems. Left: $Fe_4(\mu_3\text{-}O)_2(CO_2)_8$; middle: $Al_{12}(OCH_3)_{24}(CO_2)_2$; right: $Al_8(OH)_{15}(H_2O)_3(CO_2)_9$.

In the BTeC / Al system, among the various solids identified, a microporous solid formulated $Al_4(\mu_2\text{-}OH)_8(BTec)$ (MIL-120) was isolated.[133] This compound is built up of chains of edge-sharing octahedra, rather than the corner-sharing octahedra encountered/found in the MIL-53 and MIL-68 series. as well as this unusual 1-D SBU, a few molecular SBU were also obtained. As an example, the CAU-3 series, formulated $Al_2(OCH_3)_4L$[134] (L = BDC, NDC, BDC-NH$_2$) is built up from 12-member rings of edge-sharing octahedra (Figure 8), connected through 12 linkers to define a *fcu* topology. [134] The same *fcu* topology can be found in CAU-1, which is formulated $Al_8(OH)_4(OCH_3)_8(BDC\text{-}NH_2)_6]\bullet(solvent)_x$ and built up from 8-member rings of corner- and edge- sharing AlO_6 octahedra (Figure 9).[135] In both cases, the use of methanol as reaction medium seems to play a major role in the formation of the solids, as exemplified by the presence of methanolate bridges in the SBU. As a matter of fact, the octameric ring found is CAU-1 is similar to few molecular complexes of Cr, Fe and V (see [136] and references therein), and (a slightly modified version)can be found in a slightly modified form in the Ti(IV) terephthalate MIL-125 (see below).[8]

In the case of tetravalent cations (Ti^{4+}, Zr^{4+}, Hf^{4+}), all known porous solids were published only very recently: the first porous carboxylates based on Zr and Ti were published in 2008[7] and 2009,[8] respectively. In the case of Ti, the very limited number of porous compounds (a single porous 3-D structure type known, see below) certainly does not result from a lack of interest in this particular cation (incorporating the photophysical properties of Ti^{4+} into a porous MOF certainly crossed the mind of many chemists...), but rather from its challenging solution chemistry (see the 'chemistry in solution' section).

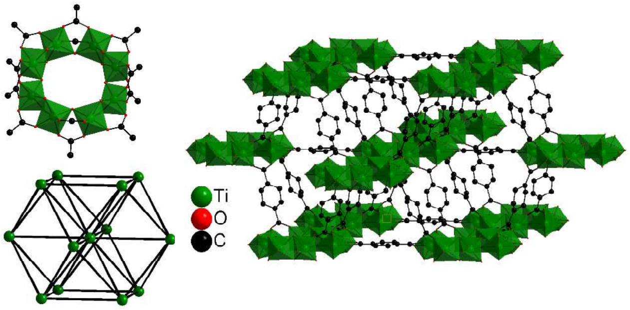

Figure 9 Structure of MIL-125 (or CAU-1). Top left: $Ti_8O_8(OH)_4(CO_2)_{12}$ unit; right: crystal structure; bottom left: *fcu* topology.

Indeed, previous attempts to grow crystallized polycarboxylate Ti MOFs led to amorphous solids.[137] (At present) Up to 2014, the only crystallized solid is the Ti terephthalate MIL-125 formulated $Ti_8O_8(OH)_4(BDC)_6\bullet(solvent)_x$.[8] The structure is similar to that of CAU-1 described above, but here half of the μ_2-OH and μ_2-OCH$_3$ are replaced by μ_2-O bridges in order to maintain the charge balance (Figure 9). The amino-functionalized version was also reported.[138, 139] With regards to its synthesis;the high reactivity of titanium in the presence of water leads to the (very) rapid formation of TiO_2 which makes the use of hydrothermal conditions very difficult, and thus organic solvents such as DMF and MeOH are required.

Zr based MOFs have recently been reviewed by Cohen et al.[10, 140] Most of them are built up from the robust $Zr_6O_n(OH)_m$ unit (Figure 10), whose chemistry in solution was already established by Schubert et al.[141] While most Zr-based MOFs incorporating this SBU are prepared in DMF starting from a dicarboxylic acid and zirconium chloride, the robustness of the Zr_6 units, which can form under a broad range of experimental conditions, allows the use of alternative organic solvents such as N,N'-diethylformamide (DEF), N,N'-diamethylacetamide (DMA)[142] or even water[143] in the case of polar, soluble ligands. Up to the beginning of 2012, all the reported solids were Zr^{4+} dicarboxylate isotructural with the pristine UiO-66 solid.[7] This Zr^{4+} terephthalate, formulated $Zr_6O_4(OH)_4(BDC)_6\bullet(solvent)_x$, is built up from $Zr_6(OH)_4(O_4(CO_2)_{12}$ clusters (Figure 10, left) connected through twelve terephthalate linkers to define a *fcu* topology (see Figure 9). Two types of micropores, tetrahedral and octahedral, are thus generated, leading to a surface area close to 1200 m^2 g^{-1}. Over/In the last few years, this compound has dethroned MOF-5 and HKUST-1 as benchmark MOF material. Its success relies on its high stability (see below), easy synthesis and functionalization. Indeed, numerous analogues (sometimes interpenetrated) based on elongated[144] or functionalized (even highly sophisticated[145, 146]) linkers have been published.

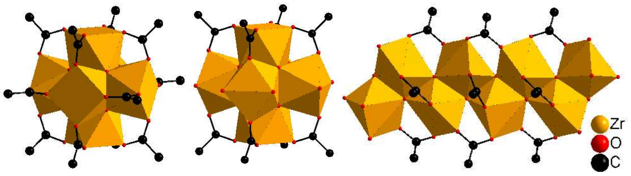

Figure 10 Zr-based SBUs Left: $Zr_6O_4(OH)_4(CO_2)_{12}$ unit; middle: $Zr_6O_8(CO_2)_8S_8$ (S = solvent) unit; right: $[ZrO(CO_2)_2]_n$ chain.

Behrens et al. established the role of monocarboxylic acid as a growth inhibitor to tailor and often drastically increase the crystallite size of UiO-66 type solids.[29, 147] This strategy was generalized to other Zr_6-based solids to grow either single crystals suitable for laboratory diffractometers or prepare nanoparticles.[148, 149] The addition of inorganic acids, such as HCl,[150] or even water, was also shown to dramatically influence both the kinetics of crystallization and the final size of the crystallites.[151] Moreover, the robustness of the SBU allowed for the preparation of MOFs from pre-built Zr_6 units by/through ligand exchange, either in solution through the use of soluble molecular clusters,[152] or in the solid state.[153] Finally, it should be noted that the Zr_6 unit can be reversibly dehydrated (transformation from $Zr_6(OH)_4O_4(CO_2)_{12}$ to $Zr_6O_6(CO_2)_{12}$), this phenomenon is associated with a change in the coordination number of the Zr ions (from 8 to 7).[28, 154]

More recently, two highly porous solids based on extended tetracarboxylate linkers and the afore mentioned SBU $Zr_6(OH)_4O_4(CO_2)_{12}$ were reported.[155] Interestingly/Importantly, a third phase, based this time the carboxylate-deficient form of the Zr_6 cluster $Zr_6O_8(CO_2)_8$ was also isolated (Figure 10). This later cluster, already seen in molecular complexes, exhibits an 8-fold cubic connectivity, leading to a completely different topology. Following (on from) this work, a few structures based on similar 8-fold connected Zr_6 units and tetracarboxylates (square planar[149] or tetrahedral[156]) or dicarboxylates[148] were then reported. While the charge distribution on the Zr_6 unit is not always fully deciphered (both μ_3-O and μ_3-OH groups are present along withterminal ligands (replacing the carboxylate group) which can be either anionic of neutral), the stability of such solids upon guest departure (especially bound solvent molecules) is often limited. Nevertheless, post-synthetic treatment with HCl solution seems to enhance such stability, this effect is probably associated with terminal ligand exchange and acid-base reactions.[149]

More recently, other solids based on low symmetry deficient Zr_6 units, either 10-fold[157] or even 6-fold[158, 159] connected, were found. To summarise, while the Zr_6 unit appears rather robust, its versatile connection number (from 6 to 12), combined with the use of di- to tetra-carboxylate ligands, recently lead to a drastic increase of the number of porous Zr MOFs, presenting novel topologies and in many cases high porosity (surface area often above 1500 $m^2\ g^{-1}$).

In these studies, analogues based on Hf rather than Zr were also isolated, once again all built up from Hf_6 units.[148, 158, 160]

Finally, we recently reported a new series of Zr^{4+} dicarboxylates formulated ZrO(L) (L = BDC, NDC, DPDC,...) and labelled MIL-140. Their structure is not built up from molecular inorganic SBU, but from polymeric double chains of edge sharing ZrO_7 polyhedra (Figure 10), connected through the ligands to define triangle-shaped 1-D pores. Whereas the smallest member of the series (L = BDC) exhibits a rather low surface area (400 $m^2\ g^{-1}$), the longest ones present a significant porosity together with a marked hydrophobic character as well as an improved mechanical and chemical stability compared to their Zr_6 clusters polymorphs (see below).[161] The MIL-140 family was also extended to functionalized ligands terephthalate.[162]

Although the carboxylate-based solids define the largest family of high valence porous MOFs, it is clear that new members will appear in the near future. For example, many carboxylate clusters of high nuclearity, which are known molecular species, have not been yet incorporated within polymeric networks.[136] This will of course lead to new topologies. Finally, for some specific cations, such as Al^{3+}, the richness of their chemistry in water can also be found in other solvents, such as alcohol, as exemplified/shown/demonstrated/highlighted by the work of Stock et al. who recently reported the solvothermal preparation of new solids based on unusual SBUs.[134, 135] Such a strategy will also obviously lead to new materials.

Other ligands

Basic azolate ligands, such as tetrazolate and pyrazolate derivatives, were recently found to significantly enhance the chemical stability (especially towards water) of M^{2+} based MOFs.[163] This phenomenon was rationalized by comparing/through the comparison of the pKa of the complexing groups: the higher the basicity, the stronger the cation-ligand bonds and hence the higher chemical stability.[164] Nevertheless, highly charged cations (M^{3+}, M^{4+}) usually hold a strong oxophilic character, which renders the isolation of derived azolate based MOFs challenging. Indeed, up to now only one single example of a benzenedipyrazolate (BDP) Fe^{3+} MOF was reported by Long et al.[165] This solid, formulated $Fe_2(BDP)_3$, is built up from chains of isolated FeN_6 octahedra connected through the ligands to define triangular channels (Figure 11). This MOF was prepared in anhydrous DMF, probably to avoid the competition with oxygenated ligands such as water.

Mixed phenolate-carboxylate ligands have lead to interesting materials with M^{2+} cations, the most prominent example being the M_2(DOBDC) or CPO-27 series (DOBDC = dioxyterephthalate).[166] In the same vein, Zhang et al. very recently reported a solid formulated $Ti_2(HDOBDC)_2(H_2DOBDC)$ (labelled NTU-9) built up from this ligand and Ti^{4+}, whose structure is made of isolated TiO_6 octahedra connected through the ligands to define honeycomb-like 2-D sheets (Figure 11).[167] This solid appears to be of potential interest for photo-related applications upon irradiation in the visible range (see below).

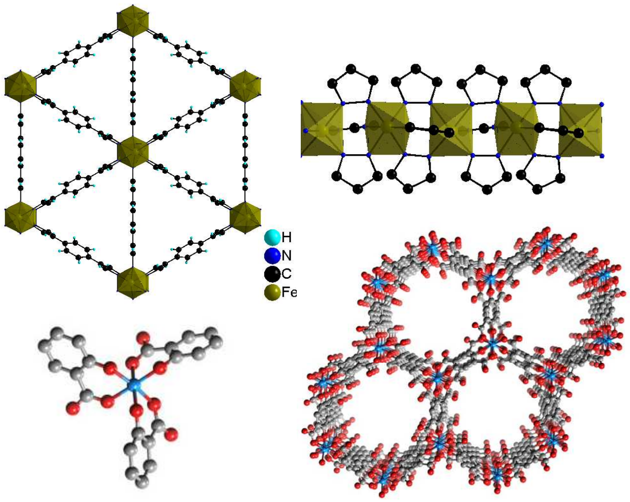

Figure 11 Top: structure of $Fe_2(BDP)_3$ (top) and NTU-9 (bottom). Both the whole structure and the inorganic unit are shown.

Stability issues

Thermal stability

The thermal stability of MOFs is related to both the nature of inorganic sub-unit and the constitutive linker. Under air atmosphere, in the absence of moisture, the thermal stability typically ranges from 150 up to 500°C with a few MOFs, such as a few metal diphosphonates, being stable to even higher temperatures.[64, 168]

More specifically, though there is no doubt that the presence of organic moieties is the main limiting parameter for the thermal stability of MOFs, which will always be inferior to those of inorganic porous solids (zeolites, mesoporous silica…) or carbons, other parameters are also in play. For a given structure, i.e. such as the metal(III) terephthalate MIL-53(Al, Cr, Fe),[16, 64, 66] the nature of the metal plays a drastic role in the temperature at which the structure decomposes under air atmosphere to produce the corresponding metal oxide. Indeed, the order of stability increases when turning from Fe, Cr to Al with a much higher stability, up to 550°C, for the Al form, respectively. At first sight, this could be related to the strength of the metal-ligand bond with average M-O bond distances ranging from 1.95 Å (Fe), 1.93 Å (Cr) and 1.87 Å Al. However, Jhung et al. explained it through the chemical stability of the isotypic MOFs, as a function of the differences in terms of inertness (or decreasing lability) of the central metal ions.[169]

If one now compares the stability under air for a given metal and linker, i.e. considering metal terephthalate polymorphs or pseudo-polymorphs such as MIL-101(Cr)[9] (~230°C) or MIL-88B(Cr)[170] (~250°C) (trimers) vs. MIL-53(Cr)[16] (~330°C) (chains), or UiO-66(Zr)[7] (400°C) (hexamers) vs. MIL-140A(Zr)[161] (450°C) (chains), it appears that infinite SBUs result in a slightly higher thermal stability.

Finally, as of yet/up to now, no fundamental study has looked at such phenomenon in enough depth to be able explain these discrepancies.

Chemical stability

As stated above, most MOFs suffer from a poor chemical stability. Metal(II) carboxylates typically degrade fairly rapidly under air moisture or in water at low to medium temperature (<100°C). For instance, the rapid degradation of the Zn^{2+} terephthalate MOF-5 is notorious[171] while the topical porous Cu^{2+} trimesate CuBTC or HKUST-1 degrades over time in water at room temperature.[28, 172] This lack of hydrothermal stability is clearly a strong limitation for the use of most MOFs for some separation processes,[173] or for liquid phase catalysis such as the production of hydrogen from water splitting.[174] Analysis of the stability of MOFs as a function of temperature under variable humidity rate has indeed shown that for a given linker, increasing the charge of the metal leads on the whole to an enhancement of the hydrothermal stability of the resulting MOF (Figure 12).[18] As a consequence, even if systematic studies of the stability of MOFs in the presence of water are still very scarce, one can reasonably argue that metal(III or IV) polycarboxylate solids usually bear/present a higher water resistance than their metal(II) counterparts, although significant differences are noticeable as a function of other parameters such as hydrophilicity, pore size, redox behavior etc…

Our own experience has revealed that metal(III) trimer-polycarboxylate based MOFs offer a distribution of water stability. As mentioned above, trimer dicarboxylate trivalent MOFs tend to transform into the more stable chain based MIL-53 structure type solids. As a consequence, MIL-88(Fe) dicarboxylate solids are clearly less moisture stable than the tricarboxylate MIL-100(Fe) which bears an interesting hydrothermal stability suitable for several applications of interest such as dehumidification or separation.[175] Mesoporous MIL-101(Fe) solids nevertheless suffer from a lower aqueous stability,[176] and in some cases are transformed into denser phases of structure type MIL-53 or MIL-88 when dispersed into strongly polar liquids.[106]

Changing the nature of the metal, for a given structure, often drastically modifies the water stability of the resulting MOF. Two extreme cases are those of chromium(III) or vanadium(III) compared to iron(III) or aluminum(III). To our knowledge, chromium(III) polycarboxylate MOFs are hydrothermally stable[19, 175] while vanadium(III) polycarboxylate solids degrade more or less rapidly upon exposure to water.[111]

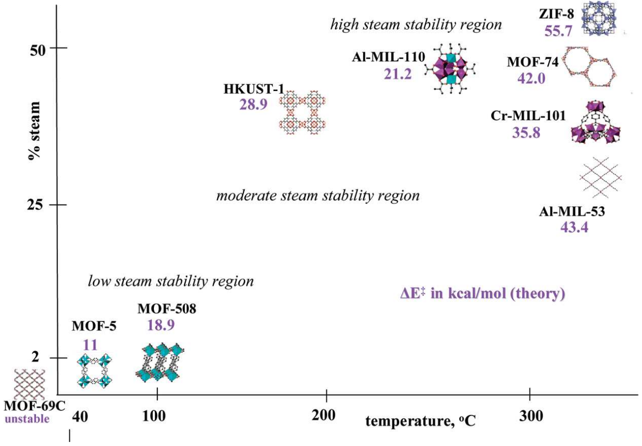

Figure 12 Steam stability map of several MOFs (taken from reference [18]).

For chromium, this is attributed to the very slow kinetics of ligand exchange (for instance, 2.4 x 10^{-6} s^{-1} for $Cr(H_2O)_6^{3+}$ versus 1.6 x 10^2 s^{-1} for $Fe(H_2O)_6^{3+}$)[177] which probably renders these solids more stable with regards to water. For vanadium(III), ligand exchange constants are of the same order of magnitude as for Al^{3+} or Fe^{3+} cations; therefore here what probably plays a role is its redox behaviour. Indeed, vanadium(IV) carboxylate MOFs, such as the metal terephthalate MIL-47 or $V^{4+}O(O_2C\text{-}C_6H_4\text{-}CO_2)$, degrade rapidly under air moisture, this degradation is associated with a change in colour from brown to green and is probably related to a partial reduction of vanadium(IV) into vanadium(III).[72]

In the field of metal(IV) MOFs, the stability towards water has been slightly documented for Zr MOFs. UiO-66(Zr) has been shown to be hydrothermally stable and resistant to a dehydroxylation/hydroxylation process.[7] (However)It has been found recently that its upper analogues, built up from larger dicarboxylate linkers, are not as hydrothermally resistant, evidencing that stability is not only a matter of metal-ligand bond.[161, 178] On the other hand, the series of pseudo-polymorphs

MIL-140s or $ZrO[O_2C\text{-}R\text{-}CO_2]$ ($R=C_6H_4$, $C_{10}H_6$, $C_{12}H_8$, $C_{12}N_2H_6Cl_2$), albeit less porous due to the presence of a denser 1D pore system, offers a higher hydrothermal stability whatever the spacer used (Figure 13).

This might be explained through the presence of an infinite Zr oxide chain vs the isolated $Zr_6O_4(OH)_4$ oxoclusters of the UiO structures, which possess a lower hydrolytic stability associated with the hydrolysis of the Zr-O bonds.[141] As discussed before, such an increase in stability when turning from isolated SBU to infinite ones has been previously documented for metal(III) terephthalate based MOFs.

Finally, the use of alternative, non-aqueous solvents or a mixture of solvents for the preparation of new MOFs might also give rise to stability issues (=problems with stability). For instance, in the case of Al polycarboxylates prepared in alcohols, as mentioned earlier, alcoholate moieties are often found in the final structure instead of hydroxyl bridges for example. These groups are prone to hydrolysis and hence can act as weak points, favouring the degradation of the solids.

The stability under various acidic or basic conditions is of interest for liquid phase applications such as catalysis, separation or drug delivery. Studies relating the pH dependence to the stability of MOFs are even more scarce than those focused on the water stability.[164, 179] It has been shown that metal(III) polycarboxylates degrade in phosphate buffer medium (pH=7.4), with the degradation time depending on the ligand constitutive of the MOF.[176] It should be noted that the highly water stable UiO-66(Zr) also degrades rapidly in PBS medium probably as a consequence of the rapid formation of Zr oxide or phosphate.[180]

Although, the high stability of UiO-66(Zr) under basic conditions has previously been reported [181] no analysis of the solution was provided to show whether a partial dissolution of the solid had occurred and if the final solution pH had decreased over the course of the stability test.

For metal(II) cations, it seems that the replacement of carboxylate linkers by azolates is a fruitful method for strongly enhancing the chemical stability of MOFs. The ZIF-8, a porous hydrophobic Zn imidazolate MOF seems to be stable not only under hydrothermal conditions but also to some extent under basic conditions while the porous Ni(BTP), a nickel pyrazolate MOF, would be more stable still going from acidic to basic conditions even at 100°C for a prolonged period of time. Matzger et al. have however revealed that in the case of ZIF-8, the stability is only a kinetics phenomenon and that a dissolution in water occurs after a few months. Replacing the carboxylic groups with pKa ranging from 3.5 to 5.5 by complexing groups (pyrazolates, phenolates...) whose pKa are much higher, (higher than 10 especially) would strongly strengthen the metal-ligand bond making the MOF less sensitive to changes in pH. One would argue that replacing metal(II) by metal(III or IV) cations when forming azolate based MOFs would further increase the chemical stability of MOFs. Indeed, the first porous metal(III) pyrazolate MOF (see above) reported by Long et al., presents a high chemical stability.[165] Nevertheless, out of the synthesis challenges raised, parameters other than pKa might be considered, such as the higher oxophilic character of these higher valence cations which could impact on the stability towards water.

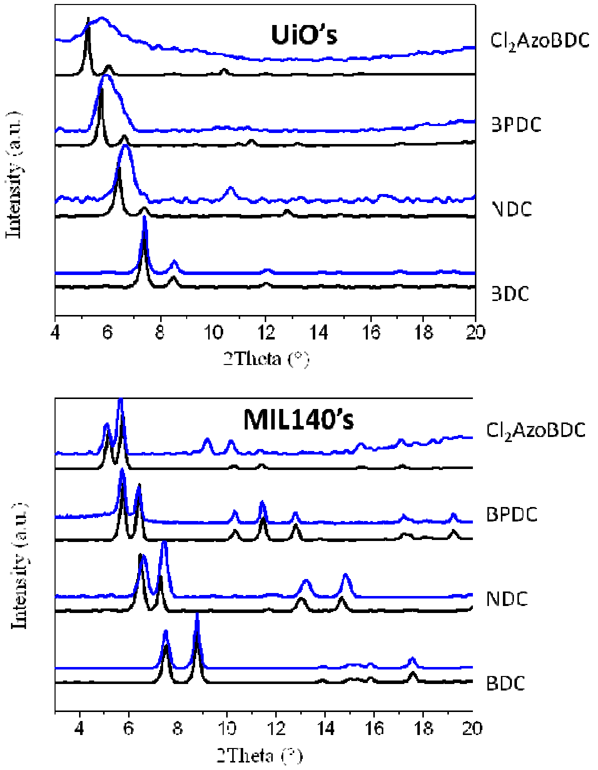

Figure 13 XRPD analysis (λ_{Cu}~1.5406 Å) of the comparative stability of UiO-66s and MIL-140s series of Zr dicarboxylate in water after night exposure; (a) as-synthesised (black); (b) at 100°C (in blue).

Studies relating the exposure of MOFs to the presence of other cations have shown that the highly stable ZIF-8 is stable when exposed to metal(I) cations only and starts to degrade when exposed in aqueous solution to other divalent cations, and is fully transformed into other phases when trivalent cations are present (In, Al) (Figure 14).[182] This is clearly in agreement with the fact that from a thermodynamical point of view, the stability of the metal-ligand bond increases with the charge of the cation.

Exposure to corrosive gases such as H_2S has also been documented recently and shows that metal(III or IV) dicarboxylate (M = Cr, Al, V) consisting of chains of octahedra are more stable than those built up from trimers of octahedra,[183] while it was shown that ZIF-8 or MIL-53(Fe) rapidly form metal(II) sulfide.[184] This indicates that it is not only the charge which plays a role, (with once again a better stability for high valence cations), but also the redox behaviour or the relative stability of the M-O bond with regards to the M-S one.

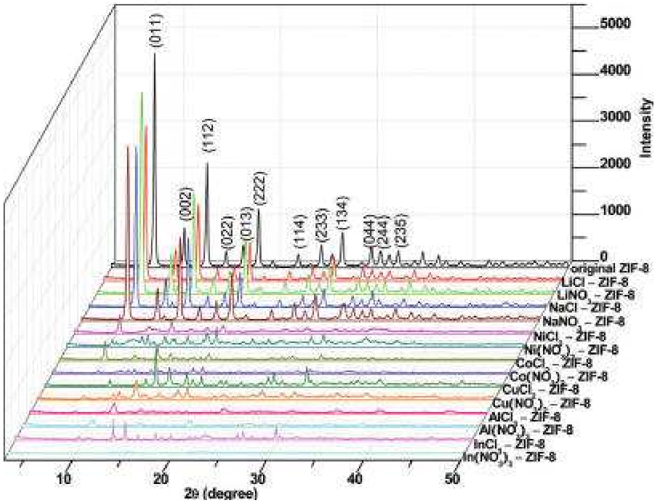

Figure 14 Impact of cation exposure on the crystallinity of ZIF-8 (taken from reference [182]).

Properties

This section does not intend to cover all the properties of high valence metal based MOFs, but rather to focus on those specifically associated with these cations. In this respect, the conventional sorption properties and applications in storage, separation and release are not discussed, neither is structural flexibility,[99] although few archetypical flexible MOFs (MIL-53, MIL-88) are built up from M^{3+} cations.

Comparative acidity

Most M^{3+} based MOFs exhibiting well defined Lewis acid sites are built up from trimers of MO_6 octahedra (see Figure 6). In these trimers, two thirds of the terminal ligands (solvent molecules) can in principle be eliminated to give rise to accessible cationic sites, which will then play a critical role in the sorptive and catalytic properties of the material. Such trimers can be found in the MIL-88 and MIL-100 series.

The Lewis acid character of MIL-100(Cr) was first probed/investigated by following *in situ* the adsorption of CO by infrared spectroscopy.[185] Once the solid is heated above 100°C, vibration bands characteristic of the coordination of CO to Cr^{3+} start to appear, eventually reaching the amount expected theoretically (ie two CO per trimer). On the other hand, for MIL-101(Cr), only one third of the theoretical value was reached, indicating that most of the sites are poisoned by other species (eg carboxylates).[186] The adsorption of indole in a series of MIL-100 (M = Cr, Al, V, Fe) was investigated by De Vos et al. [187] Infrared spectroscopy indicated the appearance of coordinated indole species in all cases, while the initial enthalpy of adsorption followed the order V > Cr > Fe > Al. Nevertheless, such values do not simply derive from the strength of indole-cation interaction but also depend on the poisoning of metallic sites, and cannot therefore be read as a direct measurement of the acidity of the cations. This Lewis acid character was further used to post-synthetically graft organic moieties, such as alcohols,[185] linear[188] and chiral[189] amines onto MIL-100(Cr) and MIL-101(Cr). For alcohols, such treatment leads to the transformation of the Lewis acid character to a Brönsted one, whose acidic strength depends on the nature of the alcohol.[190]

Lewis acid sites were also detected by *in situ* infrared spectroscopy in the Zr based MOFs belonging to the UiO[28, 181] and MIL-140[161] series. In these cases, the acidity arises from randomly distributed structural defects rather than well defined accessible metal sites, probably associated with a slight sub-stoichiometry of ligands (in the case of UiO-66, 11 carboxylate per Zr_6 units instead of 12[181]). In fact, by introducing trifluoroacetic acid (H_2TFA) and hydrochloric acid into the reaction medium, De Vos et al. were able to tune the amount of defect in UiO-66.[191] Thermal treatment of the as-synthesized solid, in which terephthalates were partially replaced by TFA, led to the appearance of up to two Lewis acid sites per Zr_6 unit.

As mentioned in the first section, M^{3+} and M^{4+} cations are prone to forming MOFs whoch incorporate inorganic hydroxyl groups, that can potentially act as Brönsted acid sites. For MIL-53(Cr), μ_2-OH groups were found to present a very weak acidic character, lower than that of silanol groups on silica.[192, 193] The introduction of various functional groups on the terephthalate linkers in a series of MIL-53(Fe) solids was shown to modify the acidic strength: the more electron withdrawing the functional group (eg. -CF_3), the higher the acidity.[76] In the case of UiO-66, μ_3-OH were also found to be of low Brönsted acidity, with a strength similar to that of hydroxyl groups on zirconia.[28] Although weak, the acidity of the OH groups was exploited in order to post-synthetically graft molecular complexes onto the surface of the pores. Upon the reaction of MIL-53(Al) with 1,1'-ferrocenediyl-dimethylsilane, ferrocene moieties were bound to the framework through the formation of O-Si bonds.[194] In the same vein, OH groups present in UiO-67 were reacted with $Au(PMe_3)$ to afford O-Au-P linkages.[195]

Catalysis

The Lewis acidity of a few M^{3+} and M^{4+} based MOFs was exploited for heterogeneous catalysis. MIL-101(Cr) was shown to be active as a convenient catalyst for oxidation reactions, such as the oxidation of arylsufides with H_2O_2,[196] or tetralin[197] and cyclohexane with O_2.[198] Monge et al. have also demonstrated the activity of various Sc[123, 199] and In[200, 201] based solids, for example in the acetalization of carbonyl compounds. In these cases, the cations are 6 coordinated with non labile ligands only, the activity is thus either associated with the presence of defects or with a transitory increase of the coordination number, which is quite realistic for such large cations.

Iron(III) based MOFs, and especially MIL-100(Fe), were also considered to be promising catalysts, eg. for the isomerization of α-pinene oxide[202] and oxidation reactions.[203] MIL-100(Fe) was found to be highly efficient for the Friedel-Craft benzylation of benzylchloride to diphenylmethane, whilst the redox inert MIL-100(Cr) analogue remained almost inactive.[110] The high activity of the Fe^{3+} based solid was therefore attributed to the combination of a Lewis acidity and a redox activity (see below). Vanadium based solids of the MIL-47 type were investigated in various catalytic oxidation processes, such as the conversion of methane to acetic acid[204] or the oxidation of cyclohexene.[83, 205, 206] An in depth characterization of the mechanism highlighted that in this solid, which exhibits only saturated V^{IV} sites, the catalytic reaction requires the formation of structural defects associated with the breaking of carboxylate-V bonds.[83, 205, 206]

Lewis acid defects in the UiO-66 series were also investigated/explored for catalytic purposes. For various reactions, it was shown for the first time that the catalytic activity can be modulated by a careful control of the number of defects. [191, 207] Using a series of functionalized UiO-66 and the conversion of citronellal as a test reaction, De Vos et al. also proved that the activity can be tuned by/via/through electronic effects. Using both electron withdrawing and donating groups, they showed that the relative reaction rate linearly depends on the *m*-Hammett constant of the functional group, [208] paving the way to a rationale control of the catalytic activity.

Very recently, Ivanchikova et al. also succeed in the H_2O_2 based oxidation of phenols using MIL-125s solids; in these cases, the active materials were not the MOFs but their degradation products.[209]

Although not as widely explored, the use of the weak Brönsted acidity of the μ_2-OH groups within the MIL-53 series was also proposed for catalytic purposes. IR spectroscopy showed that the μ_2-OH groups are more acidic in the Ga than in the Al analogue, leading to an enhanced catalytic activity for the alkylation of aromatics.[210]

The good chemical stability usually associated with M^{3+} and M^{4+} based MOFs (see above) also make them suitable candidates for heterogeneous catalysis based on organic functional groups with Brönsted acid or base character.

As a case example, MIL-101(Cr)[211] and a Zr-based MOF[212] bearing -SO_3H groups were both considered for hydrolysis of glucose and transesterification reactions. On the other hand the amine-grafted MIL-53(Al)-NH_2 was considered for base catalysis. This compound presented only a limited catalytic activity for the Knoevenagel condensation, lower than that of the IRMOF-3 solid, which might be the consequence of diffusion limitations in this 1-D pore, flexible solid.[213] Higher activities were indeed found with MIL-101(Al)-NH_2[214] and MIL-101(Cr) grafted with diamines.[215]

More interestingly, solids bearing both Lewis acid sites (Cr^{3+}, Zr^{4+}) and Brönsted basic sites (NH_2) were used for tandem catalysis, such as cross-aldol condensation (with UiO-66-NH_2)[216] and Meinwald rearrangement - Knoevenagel condensation (with MIL-101(Al)-NH_2). [217] Taking into account the number of functional groups which can be introduced (either by direct synthesis or post-synthetic modification (PSM)) in MOFs, such an approach could lead to solids with optimized (catalytic) activities for complex, or even multi-step reactions.

Redox activity

Although a few trivalent and tetravalent cations are inert towards redox processes under mild conditions (Al, Ga, Sc, In, Zr), Fe (Fe^{3+}/Fe^{2+}), Ti (Ti^{4+}/Ti^{3+}) and V ($V^{5+}/V^{4+}/V^{3+}$) present accessible reduced or oxidized states.

As already mentioned in the 'carboxylate' section, the specificity of vanadium thus does not rely on its specific SBU, but on its redox activity. This property was mainly investigated and exploited in the MIL-47(V^{4+}) / MIL-53(V^{3+}) solid. Whereas this compound is initially synthesized in its V^{III} form (formula V(OH)(BDC)•$(guest)_x$, activation under air gives rise to the V^{IV} form (VO(BDC)).[6] The oxidation is thus associated with the departure of a proton, leading to the transformation from the $[V^{3+}(\mu_2\text{-OH})]$ to the $[V^{IV}(\mu_2\text{-O})]_n$ chain. This form is rigid, and thus/therefore exhibits a very limited variation of the structure upon adsorption.[218] Nevertheless, a careful control of the activation procedure allowed the preparation of the activated V^{3+} form (VOH(BDC)), presenting a breathing behaviour similar to that of other members of the MIL-53 series.[72] This redox process was exploited to insert reducing species within the pores of MIL-47: starting from the V^{4+} form, cobaltocenium[219, 220] and Cu^+ species[221] were incorporated into the pores of MIL-47 through a redox-driven process. Interestingly, the mixed valence V^{4+}/V^{3+} MIL-47 was shown to present a significantly higher electronic conductivity than the pure V^{3+} and V^{4+} counterparts.[72]

As Fe^{3+} and Fe^{2+} can adopt similar coordination spheres, Fe based MOFs are also suitable for reversible redox based processes. As detailed earlier, in MIL-100(Fe) each cation contains a terminal ligand, either neutral (solvent, 2/3) or anionic (OH^- or F^-, 1/3). Activation at 150°C leads to the departure of coordinated solvent molecules and the apparition of accessible Fe^{3+} sites, however increasing the temperature to 250°C under vacuum leads to the departure of bound anions concomitantly/simultaneously with the partial reduction of Fe^{3+} to Fe^{2+}. While the Fe^{3+} based solid separates propene from propane only moderately well, the reduced form shows a higher separation factor.[222] The Fe^{2+} sites were found, as expected, to be less acidic than the Fe^{3+} sites,[223] and the stronger interaction of propene with Fe^{2+} than with Fe^{3+} sites was attributed to electron back-donation effects. Similarly, it is possible to play on the different hard/soft character of the Fe^{3+} and Fe^{2+} cations in order to tune the sorption properties: while the Fe^{3+} based MIL-100 adsorbs indole (N) selectively over thiophene (S) derivatives, this selectivity decreases for the reduced form, in agreement with the softer character of sulfur towards that of nitrogen.[224] The CPO-27(Fe) solid, which is initially an Fe^{2+} carboxyphenolate based MOF, was shown to oxidize in the presence of dioxygen.[225] While this phenomenon is reversible at low temperature and associated with the direct binding of one molecule of O_2 per Fe centre, it becomes irreversible at ambient temperature, ultimately leading to the decomposition of the framework.

Chain based Fe^{3+} MOFs were also considered for use as positive electrodes for Li-ion batteries. For MIL-53(Fe), up to 0.6 Li/Fe were reversibly inserted within the structure, this insertion is associated with the reduction of Fe^{3+} to Fe^{2+} at around 3 V vs. Li^+/Li,[65] while in the case of MIL-68(Fe) only about 0.35 Li/Fe were reversibly introduced.[73] As MIL-68(Fe) presents larger pores, the limitation of capacity is not related to pore filling issues, but is rather an intrinsic property of the inorganic sub-unit. Indeed, theoretical calculations indicate that the introduction of 0.5 Li/Fe leads to a stabilized, localized mixed valence Fe^{3+}/Fe^{2+} state,[226] while further reduction leads to an irreversible structural transformation.

Photoactivity

Among the various high valence transition metal cations, it is known that their metal oxides, in their highest oxidation states, exhibit semiconducting properties. [227] This is particularly the case with cations such as Ti^{4+} or Zr^{4+}, V^{5+}, Nb^{5+}, Mo^{6+} or W^{6+}. The most widly studied case/example for photocatalysis is TiO_2, particularly for its low cost, large abundance, high efficiency, low toxicity and its adequate photostability. Although other metal oxides are also wide band gap semiconductors, their properties as active materials are not as well known.As mentioned previuosly, the number of porous or open framework Ti-MOFs is still very low, they are mainly phosphonate (MIL-22, MIL-91),[14, 42] carboxylate (MIL-125 and MIL-125-NH_2)[8, 138] and phenolate[167] based MOFs. The first analysis of the photoactive properties of high valence based Ti-MOFs was carried out on a sample of the porous MIL-125.[8] It was shown that under UV irradiation, in the absence of oxygen, a partial reduction of the Ti oxocluster occurred concommitly/ simultaneously with the oxidation of alcohol into aldehyde (Figure 15). It is worthy of note that, this phenomenon was fully reversible with no impact over the stability of the framework.

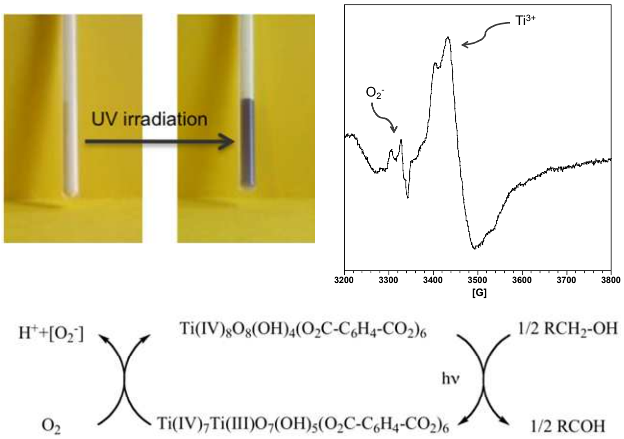

Figure 15 top left : view of the partial reduction of MIL-125(Ti) under UV irradiation in the presence of alcohol under inert atmosphere. Top right : EPR spectra of irradiated MIL-125 irradiated MIL-125 sample at 75 K in air atmosphere. Bottom : proposed scheme of the reduction/oxidation mechanism.

This report was the starting point for a still growing series of studies based on MIL-125 or its derivatives (see Table 1). Li et al. reported the use of MIL-125-NH_2 as a photocatalyst with visible-light-induced activity for CO_2 reduction; [139] they used light-driven water splitting to make the reduction more attractive. Horiouchi et al. also used MIL-125-NH_2 to achieve visible-light-promoted photocatalytic hydrogen production. [228] In parallel, Garcia et al. confirmed the ability of MIL-125-NH_2 to undergo photoinduced charge separation. [229]

Table 1 optical band gaps of different Ti-MOFs.

MOF	MIL-125	MIL-125-NH_2^+	MIL-125-NH_2-10% BDC$(NH_2)_2$	NTU-9
Optical bandgap (eV)	3.6	2.6	1.3	1.74

Recently, Walsh et al. succeeded in tuning the optical response of MIL-125-NH_2 through an experimental-modelling ligand replacement strategy, [230] a substitution of 10 % of the BDC-NH_2 linker by its diamino analogue, led to a reduction of the optical band-gap from 2.6 eV (MIL-125-NH_2) down to 1.3 eV (10 % substituted material) (see Table 1). This was related to the effect of the amino groups and their strong electron-donating effect. An alternative approach was reported by Gascon and coworkers based on the PSM of MIL-125-NH_2 using dye-like molecular fragments. The new material, denoted methyl red MIL-125 exhibited an absorption in thevisible light range with enhanced photocatalytic oxidation activity under visible light illumination.[231] More recently, a new concept was proposed through the use of an open-framework Ti carboxyphenolate, denoted NTU-9 (see above).[167] In this later case, the reduction of the optical bandgap (Table 2) is not related to the reduction of the ligand-centered HOMO-LUMO gap, but to ligand to metal charge transfer. This leads to a photocatalytic activity for the degradation of organic dyes in aqueous solutions under visible light irradiation (> 420 nm).

Several studies have also dealt with the photoactive properties of porous Zr carboxylate based MOFs with the UiO-66 structure type. Garcia et al. showed a similar optical band gap reduction and red shift for the UiO-66-NH_2 derivative, thus confirming the role of the amino group in tuning the optical response in MOFs.[232] Lin et al. used the PSM of functionalized derivatives of UiO-67 through the inclusion of specific metal complexes known for their photocatalytic properties (eg. Ir complexes).[176]

Iron(III) oxides are known to be of interest as visible light photocatalysts due to their small band gap however their high (electron–hole) recombination rate renders them inefficient.[233] This issue was recently overcome through the use of porous iron(III) MOFs based on small discrete oxocentered trimers of iron(III) octahedra.[234] These solids showed a remarkable ability to degrade organic dyes in aqueous solution under visible light irradiation (350 up to 850 nm) with no apparent degradation of the MOF framework.

Finally, if all these results based on rather chemically robust Ti^{4+}, Zr^{4+} or Fe^{3+} cations based MOFs pave the way for the design of new photoactive catalysts, future improvements are still required and will rely not only on the discovery of new robust MOFs through the engineering of the metal-ligand bonds but also on the use of other cations of interest (Mo^{6+}, W^{6+}…).

Conclusion/outlooks

Despite the high interest thanks/owing to their increased stability and sometimes unique properties, MOFs based on trivalent,tetravalent, 3p or transition metal cations are still scarce. Some effort has been focused recently on developping both new synthetic and characterization methods (in order) to foster /enable the phase discovery of such classes of MOF.

Firstly, several recent studies have highlighted suitable synthetic alternatives for increasing the degree of control over their chemistries in solution. One can cite the use of inhibitors.[28] In the case of zirconium salts and polycarboxylic acids, excess of monocarboxylic acid triggers the formation of molecular Zr^{4+} oxo-aceto complexes instead of the polycarboxylate equivalent clusters which slows down the crystallisation of the MOF. Then, either single crystals or nanoparticles can be obtained by tuning the monocarboxylic acid to metal ratio, amongst other parameters.

Another method to control the crystallisation would be to adjust the pH.[151] In the absence of linkers, playing on the acidity is a way to tune the degree of inorganic condensation and thus the charge density of the SBU. When exposed to the linker, this redefines the equilibrium in solution and leads to the formation of hybrid complexes. For instance, MOFs built up from oxoclusters, trimers or hexamers, are in competition with those made up of infinite chains of metal polyhedra and it is not fully understood what controls their formation, even if molecular inorganic SBUs based MOFs might be kinetically favored in most cases.

Another route consists in using predefined secondary building units. It was indeed shown that iron(III) acetates (trimers) or Zr methacrylates oxoclusters (hexamers) could be used at low temperature as precursors to form MOFs of either MIL-88(Fe) or UiO-66(Zr) type structures, respectively. In the field of high valence cations, there are other molecular hybrid clusters which could lead to new MOFs. Among them, one could point out octameric SBUs such as the titanium(IV) carboxylate oxocluster or iron(III) carboxylate oxohydroxo cluster,[136] reminiscent of the SBU from MIL-125(Ti) or CAU-1(Al).

In order to speed-up the process of phase discovery, high throughput methodology is of interest and this strategy was used successfully for the Fe^{3+} aminoterephthalate system to isolate the various polymorphs MIL-53, MIL-88 and MIL-101.[107] One can assume that the use of such a technique is highly complementary with the study of the chemistry in solution.

Secondly, new methods for characterising the structure of hybrid solids have also recently been implemented which strongly participated to/aided the structure solution for series of MOFs obtained only as crystalline powders. One could cite the use computer modelling in the case of series of isoreticular solids (MIL-88s, MIL-140s…) or series of functionalized MOFs bearing various functional groups (MIL-53, MIL-88, MIL-140...).[9, 26, 76, 100, 161, 235, 236] This process starts with an initial crystal structure, with the experimental cell parameters for a given linker, and then uses a ligand replacement strategy combined with energy minimization to provide structural models, which as a result strongly decreases the sometimes highly time consuming process of structure solution and/or allows a structural analysis of often poorly crystalline materials.

Development of new characterization methods has also shown to be very effective for solving structures of powdered MOFs. Firstly, a synchrotron microdiffraction set-up was used for the structure solutions of very small single crystals, i.e. down to a few microns. This was successfully applied to series of highly porous MOFs such as the porous Al^{3+} trimesate MIL-110,[131] or the rigid Fe^{3+} dicarboxylate MIL-126.[237] Another possibility involves the use of automated tomography and electron diffraction to propose a structural model for MOFs whose crystal size is down to the few hundred nanometer scale,[238] as recently demonstrated with a Bi^{3+} based MOF.[239]

Finally, despite the recent and very useful progress of characterization methods and the empirical use of additives to control crystallisation, one has to admit that little is still known about the chemistry in solution for a given combination of metal precursor / linker / solvent. This time-consuming domain, explored first in the 60's but then later neglected, probably needs to be reconsidered if one aims to reach a higher degree of prediction and/or design of new hybrid architectures. *In situ* techniques such as Energy Dispersive X-ray diffraction, *in situ* NMR or EXAFS have been used for decades to probe the crystallization of metalophosphates, zeolites, and have been recently implemented for MOFs.[240]

One can assume that the further development of this fascinating MOF chemistry will strongly rely on an increased combination of synthetic and characterization efforts in the near future. This is certainly often far more difficult than working with divalent cations, but is mandatory in order to produce MOFs with enhanced stability, truly applicable in real applications.

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Notes and references

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