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The Stability of Metal–Organic Frameworks

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1.1 Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are a recent class of hybrid materials that have attracted considerable attention during the last few decades. Their crystalline structure constructed from the association of inorganic building units connected through complexing organic linkers can be wisely and finely tuned [1, 2], in terms of the chemical nature (metal cations, organic linkers), pore size (micro- or mesoporous), and the shape/type of cavities (cages or channels and triangular, square, or hexagonal, etc.). As a consequence, the versatile and tunable characteristics of MOFs have, nowadays, made them very promising candidates for various applications including gas storage, molecular separation, biomedicine, sensing, catalysis, and so on [3, 4].

Because the particularity of each MOF, for a given property or application, derives from its unique well-defined crystalline chemical structure, its porous framework shall be expected (and mandatory) to be retained without any alteration over the course of a process. In other words, for practical applications, one shall carefully consider the stability as one of the most important requirements to be fulfilled.

In a general manner, and particularly in the field of MOFs, “robustness” or “stability” cannot be considered as an absolute qualification, and one shall consider a predefined set of parameters. These depend on the targeted application where the porous material will be exposed to a given environment (i.e., organic solvents, water, corrosive media, etc.; high temperature and/or compression), at a certain concentration and for a given duration. Consequently, depending on the considered criteria, three main categories of stabilities can be identified: (i) chemical stability, (ii) thermal stability, and (iii) mechanical stability, where,

henceforth, stability of a MOF refers to the resistance of its structure to degradation upon exposure to the operating conditions. Though, it is worthy of note that thermal stability (except in the case of amorphization and melting; see Section 1.3) is closely related to chemical stability because heating may also alter the chemical structure of the MOFs by initiating and/or accelerating the chemical reaction inducing the degradation of the corresponding crystalline framework. This affects mainly the coordination sphere of the metal cation due to the disruption of the coordination bonding between the organic ligand and the inorganic moiety (i.e., hydrolysis, redox activity, etc.), or, sometimes, it can affect the organic linker itself (i.e., decarboxylation, alkyne oxidation, etc.).

Regarding an application of interest, an MOF shall possess one or more types of stabilities. For example, chemical stability is crucial for applications in aqueous media and/or at different pH, such as in molecular separation or drug delivery [5], while both chemical and thermal stabilities are important for catalytic processes performed under harsh conditions as for chemical feedstock and fuel production [6]. Mechanical stability is mainly considered in MOF shaping such as making pellets or other compact forms required in industrial processes [7].

If, at the early stage of MOF exploration, one of the main concerns was to synthesize frameworks possessing the highest surface area and the largest pore volume, more recently considerable efforts have been devoted to the design of highly stable structures, allowing applications under ambient conditions as well as in harsh and corrosive media. This chapter aims at giving a comprehensive overview of the three aforementioned categories of stabilities and their importance in MOFs. Particular attention will be paid to address strategies allowing the synthesis of robust MOFs.

1.2 Chemical Stability

While thousands of different structures of MOFs have been reported to date, relatively, only a limited number have exhibited promising properties under non inert conditions (i.e., outside their mother liquor), in which they can be manipulated without alteration of their porous framework. MOFs consist of divalent cations (M^{2+}) and carboxylate-based linkers are typical fragile materials [8, 9]. For instance, Zn^{2+} terephthalate MOF-5 degrades rapidly in water [8, 10–13], while Cu^{2+} trimesate HKUST-1 degrades over time in water at room temperature [14, 15]. The lack of stability for water is clearly a strong limitation on the use of MOFs not only for practical applications requiring a direct contact with water (e.g., separation processes from flue gas, which may contain considerable amounts of water, or water splitting catalysis [16, 17]), but also for clean applications such as hydrogen storage for fuel cells [18] in which water is itself a product of the reaction or could be a contaminant during the refueling process, for instance. In this context, chemical stability, in general, is one of the most basic criteria one should take into account in order to synthesize an MOF that is resistant to the ambient atmosphere in which water or moisture may be a considerable risk of degradation.

In 2009, Low *et al.* [9] have investigated, through a dual computational and experimental study, the effect of water (and steam) on a series of MOFs. They have highlighted the fact that the probability of the hydrolysis of the metal–ligand bond (involving breaking of coordination bonds and displacement of water (or hydroxide), ligated cations, and ligands) is inversely correlated with the strength of the bond between the metal cation and the organic linker from which the MOF is constructed. To some extent, this correlation can also be applied to all molecules (i.e., phosphate, H₂S, SO_x, NO_x, NH₃, phenolate, etc.) that can potentially compete with the organic linker and break the cation–ligand bond. Hence, regarding the potential competing agent (or reactive species), chemical stability can be subdivided into different categories such as moisture and water stability, stability to acidic or basic media, stability under harsh conditions (e.g., physiological media, in the presence of H₂S or NH₃, etc.), and so on. Accordingly, in order to improve the chemical stability of MOFs, efforts should be devoted to strengthening the interaction between inorganic and organic moieties. An alternative strategy to improve stability may be by preventing or limiting the access of any competing agent to the cation–ligand bond. A series of subfactors that should be considered, such as the redox behavior, the coordination geometry of the cation, the nuclearity and the connectivity of the inorganic building unit, the rigidity of the linker, the presence of open metal sites or defects, the hydrophobic character of the structure, framework catenation, inter- and intramolecular interaction, and so on, are also important to evaluate chemical stability.

Assessing the chemical stability of an MOF is most of the time performed by simply comparing the powder X-ray diffraction (PXRD) patterns of the sample before and after exposing the solid to a given environment. Nevertheless, this method does not give a complete and realistic evaluation of the stability even if the two patterns closely match. Partial degradation can still occur since such PXRD analysis is not quantitative and does not consider what could be released (solution) or the formation of amorphous phases. A complementary and more accurate analysis can be carried out by performing additional inert gas sorption isotherm measurements before and after the treatment. A loss of porosity will clearly reflect any partial degradation of the crystalline framework. Though, no standard methods of chemical stability tests (concentration, exposure time, number of cycles, etc.) or assessments have been established to date. Besides, when evaluating the stability as a function of pH, in most of the cases, verification of the pH of the solution after the addition of the MOF is not performed. Though, in the case of carboxylate-based MOFs, for instance, reporting the chemical stability at high pH values is in most cases inaccurate. In fact, partial degradation of the MOF is likely to occur, inducing partial release of the linker in solution, which in turn leads to a significant decrease in the initial pH of the medium. In addition, most authors indeed do not provide any analysis of the solution or the final solid to prove their assessments (e.g., BET surface measurements, thermal gravimetric analysis, etc.). For these reasons, in the following section, no accurate comparison of the stability of MOFs reported in different studies can be given. Examples discussed in this chapter will only rely on the self-statements of the authors.

The remainder of this section will encompass, in a non-exhaustive manner, the different methods that have been developed in order to enhance the chemical stability of MOFs. Because water stability is a very good indicator of a general chemical stability and a determinant factor for real-world applications, this section will be mainly focusing on MOFs stable in aqueous media (neutral, acidic, and basic pH). However, other types of chemical stabilities will also be discussed [19–22].

1.2.1 Strengthening the Coordination Bond

Since the coordination bond is the elemental part of a MOF, the most intuitive efficient strategy to prevent cation–ligand breaking is to reinforce the interaction between the two components (which is an interaction between a Lewis acid and a Lewis base). Analysis of the stability of different MOFs has clearly shown that the enhancement of the hydrothermal stability of MOFs increased with the charge density of the metal cation in the case of polycarboxylate-based MOFs [9]. For instance, based on quantum mechanical calculations on MOF clusters, the strength of the Zn–O bond in MOF-5 is estimated to be 365 kJ mol^{-1} , whereas the strength of the Al–O bond in MIL-53(Al) is about 520 kJ mol^{-1} . Besides, these calculations have also evaluated the energy for water displacement of linkers in MOF-5 (50 kJ mol^{-1}), which is considerably lower than that in MIL-53(Al) (180 kJ mol^{-1}). Interestingly, it has also been shown that an imidazolate-based MOF, ZIF-8, exhibits one of the best hydrothermal stability among the studied MOFs. Hence, the strengthening of the cation–ligand interaction can be achieved by:

- 1) Using acidic to highly acidic metal cations of higher oxidation states exhibiting a high charge density (which results from the combination of the ionic radius and charge) or high polarizing power
- 2) Using organic linkers bearing highly complexing functional groups, showing high pK_a values (higher than that of carboxylic acids (~ 4.5))
- 3) Combining both cations of high oxidation states and highly complexing ligands.

1.2.1.1 High-Valence Cations and Carboxylate-Based Ligands

As stated earlier, MOFs based on polycarboxylate linkers and divalent metal cations exhibit a very limited chemical stability especially in air moisture or in water. The use of cations of higher oxidation states has, as expected, yielded several MOFs showing drastically enhanced chemical stability.

In general, synthesis reactions involving trivalent cations (or cations of higher oxidation states) with polycarboxylic acid linkers are performed under slightly acidic conditions in the presence of HF [23, 24] or HCl [15] or monocarboxylic acids (known as modulators) [25]. This is done in order to prevent the formation of metal oxides or hydroxides and maintain a sufficient concentration of metal complexes necessary for the formation of hybrid frameworks in solution. In the latter case, the competition between the monotopic and

polytopic carboxylate moieties also allows slowing down of the nucleation process, leading to the formation of larger crystallites [25].

Materials of Institute Lavoisier (MIL) compounds are among the first successful examples of this strategy based on the use of cations of higher degree of oxidation ($>2+$). Different MIL-*n* based on trivalent cations have been reported [26, 27]. They are mainly, but not limited to [28–31], based on two different inorganic building units that are chains of μ_2 -hydroxo corner-shared octahedra $[M(\mu_2\text{-OH})(\text{R-CO}_2)_2]_n$ (where $M = \text{Fe}^{3+}, \text{V}^{3+}, \text{Sc}^{3+}, \text{Al}^{3+}, \text{Ga}^{3+}, \text{and In}^{3+}$; A = anion (F^- , Cl^- , OH^- , etc.); and S = solvent) (Figure 1.1c) and μ_3 -oxo centered trimers $M_3(\mu_3\text{-O})(\text{R-CO}_2)_6A_3S_m$ (Figure 1.1a). It is worthy of note that isostructural MOFs obtained with different trivalent cations do not exhibit similar chemical stabilities, which can drastically drop from one analog to another. This is mainly attributed to the difference in charge density (Z/r^2) between the metal cations such as Al(III) and In(III) [26], the difference in kinetics of ligand exchange (for instance, $2.4 \times 10^{-6} \text{ s}^{-1}$ for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ vs $1.6 \times 10^2 \text{ s}^{-1}$ for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$) [36], or the redox behavior of a cation (for instance, MIL-47(V^{4+}) degrades rapidly in air moisture [37, 38], where isorecticular structures of MIL-53(Al, Cr) are very stable under similar conditions).

Among MIL-*n* compounds, the chain-based MIL-53(Al, Fe) (terephthalate or (1,4-BDC (1,4-benzenedicarboxylate)) ligand) [9, 37–39] (Figure 1.1c,e) and the zeolitic MTN-type MIL-100 (trimesate or (1,3,5-BTC) ligand) [32, 40, 41] based on oxo-trimers (Figure 1.1a,f) have shown very good stability in aqueous media (and at different pH ranging from 2 to 12 for MIL-53). For instance, MIL-100 has been shown to be a successful candidate for applications like dehumidification or separation [42]. In contrast, Fe(III)-dicarboxylate solids MIL-88(Fe) and MIL-101(Fe) exhibit a lower aqueous stability where in some cases they are transformed to denser phases of type MIL-53 or MIL-88 [43]. This clearly highlights the fact that the strength of the cation–ligand interaction is the main, but not the only, parameter in play to target chemically stable MOFs. The nuclearity and the presence of oxo/hydroxo bridges (i.e., 0D vs 1D inorganic building units), the presence of “vulnerable” sites (such as open metal sites), the geometrical constraints, and/or the size of the pore volume are also key parameters to be taken into consideration.

If M(III)-MIL compounds were mostly prepared using di- or tricarboxylate aromatic short size ligands, more recently, few examples based on shorter [44], functionalized [45], or extended linkers [43, 46, 47] have also been reported to show good stability to water [43, 47]. For instance, PCN-333 (Al, Fe), which is an extended version of MIL-100 obtained with 4,4',4''-s-triazine-2,4,6-triyl-tribenzoate (TATB) as a linker, has been claimed to be highly stable in aqueous solutions with pH values ranging from 3 to 9, although these results, as mentioned previously, should be further verified and/or better understood. Besides, tetracarboxylate linkers have also yielded MOFs stable under aqueous conditions. For example, MOFs based on *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) and the Al(III)-chain-based [48] and the Fe(III)-trimer-based PCN-600 [49] have been reported to be stable in water as well as to slightly acidic pH (~ 5) and pH values ranging from 2 to 11, respectively. Moreover, MIL-127(Fe) or

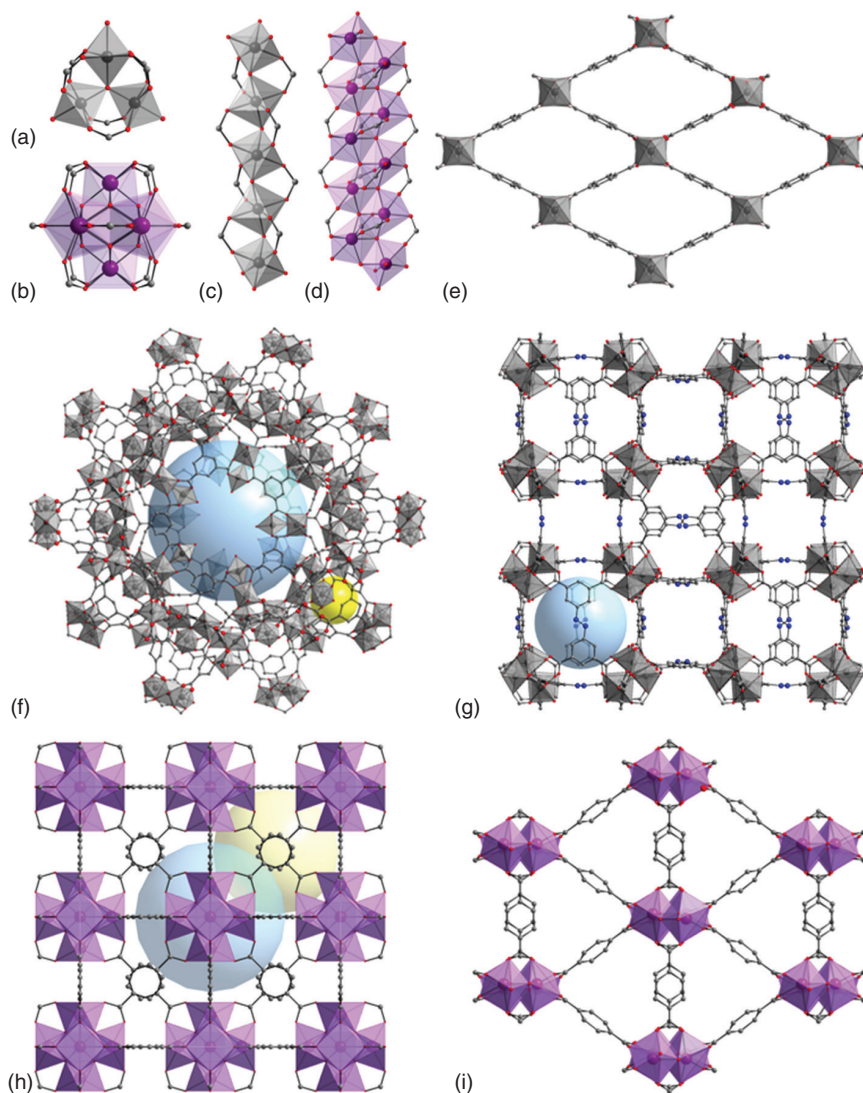


Figure 1.1 Selected M(III and IV)-carboxylate inorganic building units and MOFs. (a) M(III)-oxo-trimer, (b) 12-connected Zr(IV)-hexanuclear oxo-cluster, (c) M(III) chains, and (d) Zr(IV) chains found in MIL-140 (i). Crystalline structures of (e) MIL-53 [23], (f) MIL-100 [32], (g) MIL-127 or soc-MOF [33], (h) UiO-66 [34], and (i) MIL-140A [35]. Color code: M(III) = Fe³⁺, Al³⁺, etc., dark gray; Zr, violet; C, gray; N, blue; O, red. The cages are represented by colored spheres. Hydrogen atoms are not represented for the sake of clarity.

soc-MOF(Fe), based on 3,3',5,5'-azobenzenetetracarboxylate (ABTC) linkers and Fe(III)-trimers (Figure 1.1a,g), has been shown to be, as MIL-100(Fe), hydrothermally resistant [33, 50, 51]. If biomedical applications (under the body fluid conditions) are considered, it appears that tri- and tetravalent cations of polycarboxylate MOFs degrade rapidly (less than 1 day) in phosphate buffer solution

(pH = 7.2 at 37 °C) with slower degradation when it changes from di- to tri- to tetracarboxylate linkers [5].

Incorporation of kinetically inert metal ions such as Cr(III) into the framework backbone could generate MOFs with exceptional chemical stability. Indeed, the very high water stability is attested by Cr(III)-analogs MIL-53 [37, 52], MIL-100 [53, 54], and MIL-101 [24, 42]. However, the direct synthesis of Cr-based MOFs with carboxylate ligands is rather difficult due to the kinetic inertness of Cr(III), which may require the use of hydrofluoric acid (HF) and/or synthesis under hydrothermal conditions. An alternative way to obtain Cr(III)-based MOFs, which seems to be successful, is the postsynthetic metathesis of metal cations from a sacrificial MOF. The best way involves using Fe(III)-based MOFs and exchanging Fe(III) under an inert atmosphere with Cr(II), which will be oxidized later on to Cr(III). This strategy has led to the formation of highly chemically stable MOFs such as PCN-426-Cr(III) [55] and PCN-333-Cr(III) [56]. Both have shown high resistance to water as well as to a broad range of pH for at least 24 h (from 0 to 12 and 0 to 11, respectively).

Rare-earth (RE) trivalent cations generally lead to MOFs exhibiting lower chemical resistance to water. But in some cases RE-based MOFs have shown high chemical stability to water [57–61]. This chemical stability, which in some cases remains in aqueous solution up to pH = 14 [59], is mainly attributed to the use of short hydrophobic linkers that prevent the inorganic cluster from water molecules. For instance, the *fcu*-MOFs $[\text{RE}(\mu_3\text{-OH})_8(1,4\text{-NDC})_6(\text{H}_2\text{O})_6]_n$ (RE = Eu(III), Tb(III), or Y(III); 1,4-NDC = 1,4-naphthalene dicarboxylate) have been shown to be stable in water. Similarly, isorecticular *fcu*-MOFs based on fumarate linkers are stable after exposure to acidic H₂S [62].

In the same line as trivalent cations, tetravalent cations should yield even stronger interactions with the organic ligand and hence an even higher chemical stability. Indeed, it has been established that Ti(IV) MIL-125 [63] based on octameric inorganic units and terephthalate linkers is not only stable in water at room temperature but also (as well as its aminated analog) possesses a good stability in the presence of acidic gasses such as H₂S [64].

A considerable breakthrough in the field of MOFs, not only in terms of structural versatility but also in terms of chemical stability, has been achieved with the discovery of UiO-66, an MOF based on the robust Zr(IV)₆-oxo-cluster and 1,4-BDC ligand [34]. The expansion of structures based on this hexameric oxo-cluster has been supported by the use of modulators [25] (generally, monocarboxylic acids such as formic, acetic, trifluoroacetic, or benzoic acids) that allows control of the reactivity of the highly acidic tetravalent cations and, hence, the crystallization process. Indeed, during the past few years, a large number of MOFs, based on the Zr₆-oxo-cluster (and its Hf analog [65, 66]), have been reported using di-, tri-, or tetrapopic carboxylate ligands showing different topologies and porosity size [67, 68].

The first structure, UiO-66 (Figure 1.1h), presents an *fcu*-topology (with tetrahedral and octahedral cavities) based on the 12-connected Zr₆(μ₃-O)₄(μ₃-OH)₄(R-CO₂)₁₂ oxo-clusters (Figure 1.1b) and the BDC linker. It has been shown to be hydrothermally stable and resistant to the dehydroxylation/hydroxylation process [69]. However its upper analogs UiO-67 and UiO-68 have been found,

more recently, to be unstable under hydrothermal conditions [35, 70]. This evidences again that chemical stability is not only a matter of strong cation–ligand interaction. UiO-66 and its analogs (based on NH_2 –, Br –, and NO_2 –BDC) have also been shown to be stable (or at least to maintain their crystallinity) in aqueous acidic solution (up to $\text{pH} = 1$), but unstable in basic pH solutions (except the NO_2 –BDC analog, which seems, surprisingly, to be (kinetically) stable in 1 M NaOH aqueous solution ($\text{pH} = 13.6$)) [71].

As stated earlier, the use of modulators during the synthesis has contributed to the burgeoning of Zr-MOFs. The use of HCl as an additive, in some cases, led also to an improvement of the crystallinity as it mainly stabilizes Zr^{4+} ions in solution. Though, it has been established that the use of an excess of HCl (and/or monocarboxylate modulators [72, 73]) generally leads to the creation of defects (replacement of polycarboxylate ligands by $\text{OH}/\text{H}_2\text{O}$ species) within the hybrid framework [74, 75]. This may be considered in two different ways, either creating centers of weakness in the frameworks leading to a decrease in stability [76] (which may explain some discrepancy in the chemical stabilities attested from different studies or preparation) or creating more space and open metal sites that may [75, 76], respectively, increase the surface area and/or be of interest for applications such as catalysis, for instance [72, 73].

Various Zr-based MOFs have been obtained and are in general stable in aqueous media from neutral to acidic conditions. A remarkable example of a MOF exhibiting this acidic stability is the sulfated derivative of MOF-808 [77] (based on the trimesate ligand and the 6-connected Zr_6 -oxo-cluster), which was prepared by exposing the parent MOF to aqueous sulfuric acid [78].

Like MOF-808, lower (than 12) connectivity (10, 8, and 6) Zr_6 building units based on di-, tri-, or tetracarboxylate ligands (rigid or flexible small or extended) have also been reported, whereas, for instance, Zr-MOFs constructed from porphyrin tetracarboxylate ligands have demonstrated an unprecedented versatility in terms of topology using the same ligand [68]. Overall, the resulting structures show a relatively good chemical stability to water and acidic pH (~ 1 or 2), at least during a limited time of exposure and at a given concentration [79, 80]. In some cases, this aqueous stability is extended to higher pH (~ 11) [81–85]. However, no systematic study has been reported to evaluate the extent to which the stability at basic pH can be maintained. Similarly, NU-1000 [86] (showing *csq*-topology, octa-connected oxo-cluster, based on tetratopic 1,3,6,8(*p*-benzoate)pyrene linkers) has been shown to possess a very good aqueous stability at pHs ranging from 1 to 11 and to be, like MOF-808, a very good catalyst for the hydrolysis of nerve agents (pH 10) [21, 86, 87].

Compared with Zr_6 -oxo-cluster-based MOFs, particularly UiO-66, the series of pseudo-polymorph Zr oxide chain-based MIL-140 or $\text{ZrO}[\text{O}_2\text{C}-\text{R}-\text{CO}_2]$ ($\text{R} = \text{C}_6\text{H}_4$, C_{10}H_6 , C_{12}H_8 , $\text{C}_{12}\text{N}_2\text{H}_6\text{Cl}_2$) (Figure 1.1d,i), though less porous due to the presence of a denser 1D pore system, are much more hydrophobic and exhibit hydrothermal stability whatever the nature of the organic spacer [35]. This might be explained also through the presence of an infinite Zr oxide chain *versus* isolated Zr_6 -oxo-clusters, which possess a lower hydrolytic stability associated with the hydrolysis of the $\text{Zr}-\text{O}$ bonds [88]. As discussed before, such an increase in stability when transitioning from isolated inorganic building units to

infinite ones has been previously documented for M(III)-terephthalate-based MOFs (see previous text).

1.2.1.2 Low-Valence Cations and Highly Complexing Ligands

The use of organic linkers bearing complexing functional groups with higher pK_a values than carboxylates has also been successfully explored. This phenomenon was rationalized by comparing the pK_a values of the complexing groups: because the cation–ligand interactions are constructed from a Lewis adduct (Lewis acid–Lewis base), the higher the basicity, the stronger the bond and hence the higher the chemical stability. Though, the number of MOFs obtained from this strategy is actually much more limited compared with carboxylate-based MOFs. This is mainly because of the higher chemical reactivity of these ligands (especially when it concerns metal cations of higher (than 2) oxidation states) as well as the lack of their commercial availability.

Among the functional groups bearing high pK_a values, N-rich azole derivatives have been shown to be promising candidates for elaborating chemically stable MOFs. While tetrazole shows very similar pK_a values to those of carboxylic acids, triazole, imidazole, and pyrazole bear much higher pK_a values (13.9, 18.6, and 19.8, respectively) [80]. Indeed, azolate-based MOFs, including zeolitic imidazolate frameworks (ZIFs) [89] and zeolite-like MOFs [90] (ZMOFs, which combine both azolate and carboxylate moieties on the same linker), yield in general moderate to good water-stable MOFs [91–93].

ZIF-8 [93], a porous hydrophobic MOF based on Zn(II)-single nodes and 2-methylimidazolate (Figure 1.2c) ligands, seems to be stable not only under hydrothermal conditions but also to some extent under basic conditions (soaking in 8 M aqueous NaOH at 100 °C). This stability is certainly enhanced due to the presence of methyl groups that makes this MOF rather hydrophobic, which shields the metal centers together with the presence of narrow pore windows (3.4 Å) [97, 98]. Though, it has been shown that the stability of ZIF-8 is only a kinetic phenomenon with a full dissolution in water occurring slowly with time (a few months) [54]. The sodalite-like Ni(BTP) (Figure 1.2d), based on Ni(II)-tetramers (Figure 1.2a) (where BTP = 1,3,5-tris(pyrazolate)benzene), is one of the different azolate MOFs reported by the group of Long [94]. It was found to be stable under extreme conditions such as boiling aqueous solution with pH ranging from 2 to 14. It is worthy of note that the Cu(BTP) analog exhibits a much better chemical stability compared with its carboxylate-based counterparts.

More recently, a series of hydrophobic bis-pyrazolate MOFs (Ni(DP)), based on cubic octanuclear Ni(II) oxo-pyrazolate building units (Figure 1.2b) have been reported and have been proven to be highly chemically stable in water under basic pH conditions [95, 99–101]. They are designated as $[Ni_8(\mu_4-OH)_4(H_2O)_2(L)_6]_n$ (where L is the ditopic linker) and exhibit a *fcu*-topology (as for UiO-66) with octahedral and tetrahedral cages (Figure 1.2e). The use of extended linkers bearing hydrophobic groups allows tuning of water sorption behavior and capturing of harmful volatile organic compounds [95]. More recently, analogs based on benzenedipyrazolate (BDP) derivatives, tailored with defects, have shown selective SO₂ adsorption [101].

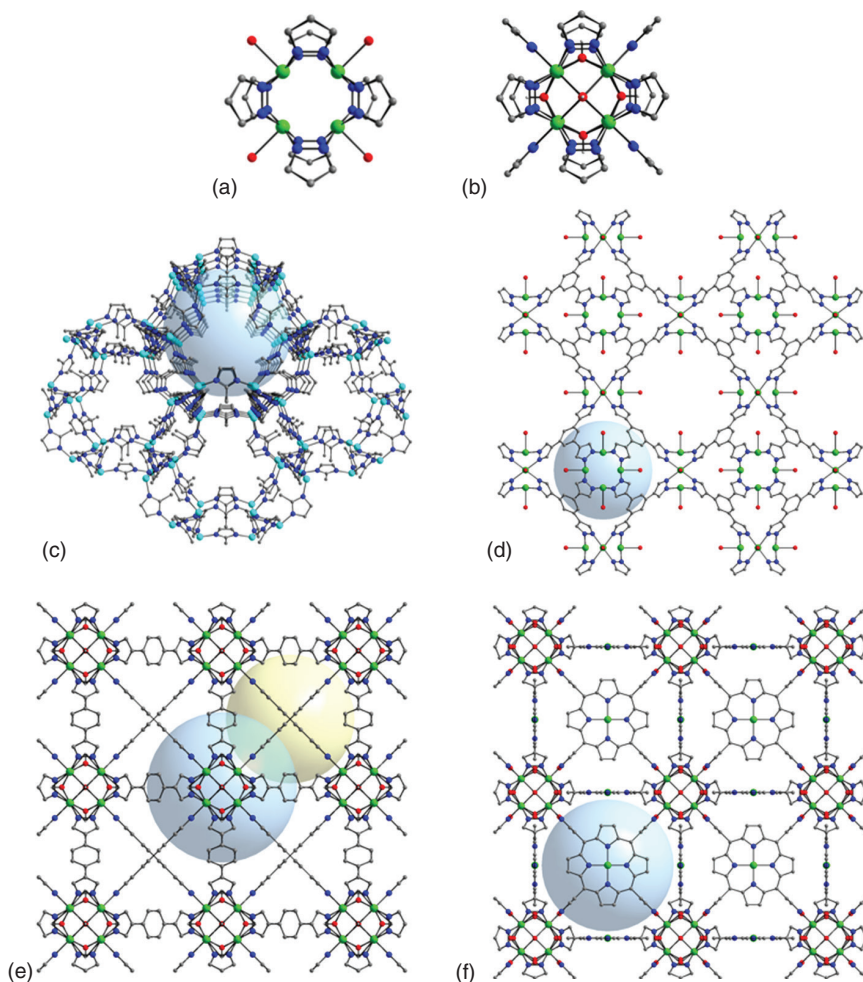


Figure 1.2 Selected M(II)-azolate inorganic building units. Pyrazolate (a) Ni-tetranuclear and (b) Ni-octanuclear building units. Crystalline structures of (c) ZIF-8 [93], (d) Ni(BTP) [94], (e) *fcu*-Ni(DP) [95], and (f) PCN-601 [96]. Color code: Ni, green; Zn, cyan; C, gray; N, blue; O, red. The cages are represented by colored spheres. Hydrogen atoms are not represented for the sake of clarity.

The same octanuclear-oxo-cluster has also yielded a very chemically stable MOF (PCN-601) based on porphyrin-tetrapyrazolate ligands showing an *ftw*-topology made of cubic cages (Figure 1.2f) [96]. Attested by PXRD and sorption measurement, PCN-601 is stable in water and saturated aqueous solution of NaOH up to 100 °C. Thermodynamic and kinetic investigations have shown that the higher crystal field of stabilization energy and the stiffer coordination between Ni₈-oxo-cluster and pyrazolate ligands allow PCN-601 to be resistant to H₂O and OH[−] even under extremely basic conditions. Its extended analog, PCN-602, has also revealed a very good stability for 24 h in water and in saturated

solution of NaOH at room temperature as well as in aqueous solution of anions like fluorides, carbonates, and highly complexing phosphates [102].

M(II)-bistriazolate MOFs of the chain-based honeycomb-type structure have been reported to show relatively good chemical stability. M(II)₂Cl₂(BTDD) (where M = Mn, Co, and Ni and BTDD = bis(1*H*-1,2,3-triazolato[4,5-*b*],[4',5'-*i*]) dibenzo-[1,4]dioxin) have been shown to be sufficiently thermally and chemically stable for the storage and separation of highly corrosive NH₃ [103]. In addition, the Co analog has allowed reversible capture and release of elemental halogens without any significant loss of crystallinity [104].

1.2.1.3 High-Valence Cations and Highly Complexing Ligands

As stated in the aforementioned section, azolates, and particularly pyrazolates, due to their high basicity, have afforded some examples of MOFs showing very high chemical stability in aqueous media. One would assume that combining these complexing ligands with cations of oxidation degree higher than two would give rise to even stronger interaction and, consequently, more chemically stable MOFs. Nevertheless, highly charged cations (*i.e.* M(III), M(IV)) usually hold a strong oxophilic character, which renders the isolation of derived azolate-based MOFs challenging. Indeed, only one single example of a BDP Fe(III) MOF has been reported to date [105]. This solid, with the formula Fe₂(BDP)₃, consists of chains of isolated FeN₆ octahedra connected through the ligands to define triangular channels (Figure 1.3a). Note that this MOF was prepared in anhydrous DMF, probably to avoid the competition with oxygenated ligands such as water. More generally, reacting high-valence cations with highly complexing agents including oxygenated ones (*i.e.*, phosphonates or phenolates) still remains a synthetic challenge because of the very fast coordination process that might occur, leading to the precipitation of amorphous solids or the corresponding metal oxide. Though, very scarce examples of MOFs based on this strategy have been reported.

MIL-91(Ti) is one example of porous MOFs obtained by reacting highly charge cations and highly complexing ligands, namely, *N,N*-piperazinebismethylphosphonates. Its chain-based structure has been shown to be very stable under

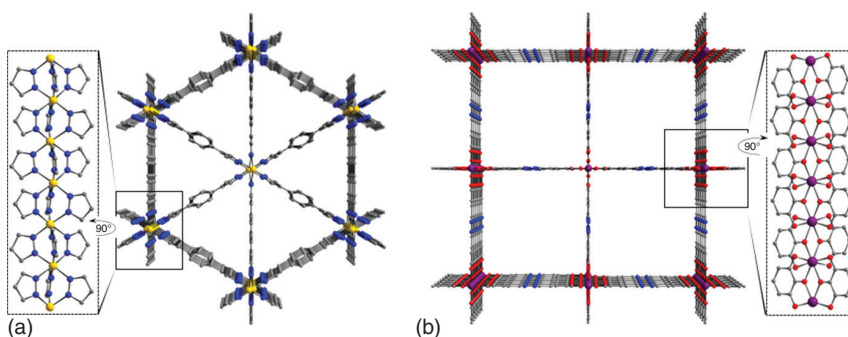


Figure 1.3 Crystalline structures of two highly stable chain-based MOFs: (a) Fe₂(BDP)₃ [105] and (b) MIL-163 [106]. Color code: Fe, yellow; Zr, violet; C, gray; N, blue; O, red. Hydrogen atoms are not represented for the sake of clarity.

hydrothermal conditions [107, 108]. More recently, a Sn(IV)-triphosphate MOF (CALF-28) has been reported and shown to be stable in water at 80 °C with a decrease in surface area only after the first treatment, most probably due to the reorganization of its interpenetrated structure [109]. Though, to date, the still tough challenge of controlling the coordination process in terms of directionality and reactivity prevented the development of a rational design of such compounds.

Moreover, a novel MOF, labeled MIL-163, has been recently obtained following a rational design between Zr(IV) and bis-gallate ligands [110]. Based on the bis-trioxophenyl ligand, the Zr-chain-based structure of MIL-163 (Figure 1.3b) has been shown to be highly resistant not only in boiling water but also noteworthy in a phosphate buffer solution (containing highly complexing phosphate ions) for more than two weeks [106]. This is mainly attributed to the high strength of the Zr–O bonds, associated with the very high pK_a value of the linker, together with μ_3 -oxo and μ_3 -hydroxo bridges between the Zr(IV) units.

1.2.2 Protecting the Coordination Bond

As clearly stated earlier, the key parameter to enhance the chemical stability is to strengthen the interaction between the metal cation and the ligand. One shall also consider a series of additional parameters such as the nuclearity, dimensionality, and connectivity of the inorganic building unit, the topology of the network, the presence of defects and/or open metal sites, and so on, which may reinforce (or not) the chemical stability of the hybrid framework. An alternative strategy is to protect the cation–ligand interaction (which is the weakest point in the structure of a MOF) from the attack of a competing species. This is of great interest when a given topology or molecular arrangement is the key for potential application, but the corresponding MOF shows very limited stability. The metal–ligand bond can be protected by simply creating a shield using bulky groups, preventing any accessibility that might lead to ligand displacement, and/or tuning the hydrophobic character of the porous structure to enhance the water/moisture stability (by maintaining water molecules away from the fragile coordination interaction). The latter can be achieved either by decorating the internal part of the MOF or by coating/embedding the MOF from the outside with a hydrophobic layer.

1.2.2.1 Introducing Bulky and/or Hydrophobic Groups

Several examples of MOFs showing enhanced water/moisture stability due to the presence of bulky and/or hydrophobic moieties have been reported [111–116]. For example, MOFs based on silver and 3,5-bis(trifluoromethyl)-1,2,4-triazolate linkers (FMOF-1 and FMOF-2), which are supposed to exhibit rather weak metal–ligand interactions, have shown resistance upon long-term exposure to boiling water, as revealed by PXRD [117, 118]. Another relevant example is the case of MIL-88B(Fe)-(CF₃)₂ or UiO-66-(CF₃)₂, which exhibits an enhanced hydrothermal stability compared with their bare analogs [45, 119]. Indeed, this is attributed to the presence of dense fluorinated groups that can prevent the water from breaking the coordination bond. Similarly, alkyl group-modified MOF-5

[120] or polymer-based ligands, polyMOFs [121], have shown an improved water stability.

Similarly, phosphonate monoester-based MOFs have also been shown to be more resistant to carboxylate-based MOFs [122, 123]. The presence of one ester group allows phosphonates to possess a carboxylate-like coordination mode but with stronger interaction together with providing a shielding effect.

Introducing bulky groups into the structures of MOFs has also been realized through postsynthetic grafting rather than direct crystallization. This method allows the use of a template MOF structure to render it more stable (in water, most frequently) with a reduction of the initial porosity. A series of enhanced stability MOFs have been modified through this method [124–126]. Furthermore, a series of perfluoroalkane carboxylates with different chain lengths (C1–C9) were attached to the Zr_6 -oxo-cluster of NU-1000, following solvent-assisted ligand incorporation (SALI) [127]. This led to an enhancement of the water stability of the MOF.

1.2.2.2 Coating MOFs with Hydrophobic Matrices

In contrast to the insertion of bulky groups within the crystalline framework, embedding the crystals or the crystalline powder of MOFs with a hydrophobic coating allows to cover the material (mainly) at the outer surface with a protective layer [128]. Indeed this allows the enhancement of the water stability of the MOFs. Moreover another benefit is to avoid any decrease of the inner porous volume of the material. Nonetheless, it is worth mentioning that this technique may only change the kinetics of water diffusion but does not improve the

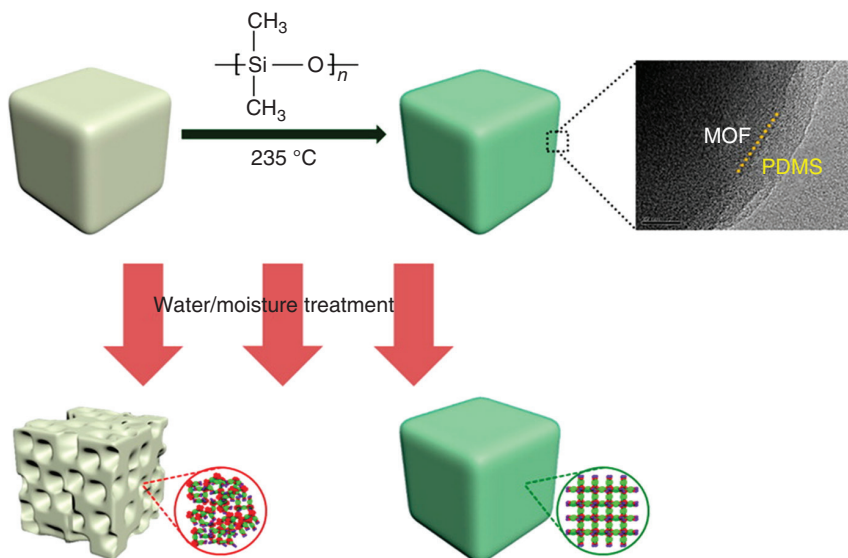


Figure 1.4 Illustration of PDMS coating on the surface of MOFs and the improvement of moisture/water resistance. (Reproduced with permission from Ref. [129]. Copyright 2014 American Chemical Society.)

intrinsic stability of the MOF. Besides, coating a MOF is not a trivial procedure as it needs careful control of the thickness, flexibility, and the hydrophobic character of the protective layer. Albeit it is challenging to balance all these parameters, a polydimethylsiloxane (PDMS) protective layer has been successfully deposited on the surface of HKUST-1 and the more water-sensitive MOF-5 crystals (Figure 1.4). Indeed, this allowed maintaining the morphology and the crystallinity of the crystals even after 3 months in water [129].

Similarly, chemical vapor deposition of hydrophobic perfluorohexane on MOFs has also been proven to be successful, leading to a considerable enhancement of the water stability of HKUST-1 [129]. Coating MOFs with hydrophobic carbonaceous layers has also been achieved using a careful carbon painting technique [130, 131]. This allowed MOF-5 to retain its crystallinity under air moisture up to 2 weeks. Unfortunately, in liquid water, carbon-coated MOF-5 underwent a significant decrease in pore volume.

1.3 Thermal Stability

Thermally stable materials are highly demanded and important in industrial applications. Although more complicated systems with extra cost might be involved, it is still possible to conduct industrial procedures under dried working conditions. In most cases, only the thermal stability of the materials without taking into account the presence of water vapor or liquid water shall be considered. Therefore, here, we will rather focus on the thermal stability than the hydrothermal stability of MOF compounds in this section.

The thermal stability of a MOF compound is usually defined as its ability to avoid irreversible changes in its chemical and physical structures upon heating to a relatively high temperature. During the thermal treatment process, degradation of MOF structures leads to either amorphization [132, 133], melting [134, 135], metal-oxo-cluster dehydration [69], or linker dehydrogenation or graphitization [136, 137]. These phenomena take place progressively during the heating step or only when temperatures above the decomposition limit are reached; this is normally accompanied by the release and/or combustion of the guest molecules as well as breaking of the metal–ligand bonds followed by combustion of the organic spacer.

Current techniques for assessing the thermal stability of a compound are still limited. For most MOF compounds, thermogravimetric analysis (TGA) data are usually provided; this is far from being sufficient. Variable temperature PXRD (VT-PXRD) experiments are a more accurate method of investigating the thermal stability. However, various measurement conditions are considered for each sample (scanning speeds, duration of a certain temperature for collecting data, etc.), which makes comparison of thermal stabilities using this method rather difficult. Besides, VT-PXRD patterns are very often obtained under inert conditions, which do not reflect the real behavior of the framework upon heating in the presence of oxygen and/or moisture. Particular attention should be paid to the details of measurements when the experimental result is reproduced. Therefore, as in the case of the chemical stability study and report, well-accepted

universal standards shall be set up in order to precisely evaluate and compare the thermal stabilities of MOF compounds.

Taking the components of MOF compounds into consideration, their inorganic parts and organic parts as well as the packing modes and fashions of their structures are the most dominant factors to determine thermal stabilities. However, these are usually a consequence of the aforementioned multiple factors, not only relying on one single structural or chemical feature. Thus, it is not easy to predict the thermal stability of a given MOF compound based on well-defined rules as it is the case for chemical stability. Based on the numerous MOF compounds reported, some general experience or tentative “trends” can nevertheless be extracted as follows: note that there will always be exceptions for each parameter due to the poor degree of relationship between the structure, composition, and thermal stability.

Metal species constitutive of MOFs cover a wide range in the periodic table of elements, including transition, main-group, alkali, alkaline-earth, and rare-earth metals. In addition, within the resulting MOF skeleton, these species exist in the form of either single metal sites or metal (oxo)clusters with multinuclearity or even chains or layers. In general, the nature of a metal ion, such as the oxidation state, ion radius, preferred coordination number, and its interaction with a given linker through metal–ligand coordination, plays a significant role in determining the thermal stability of a corresponding MOF compound. Several conclusions can be drawn according to the literature as follows:

- 1) A metal ion at its most stable oxidation state leads to a higher thermal stability compared with cations with multiple oxidation states. For example, Fe(II) is sensitive to oxygen and other oxidative species. It will always be converted into Fe(III) in the presence of oxygen along with a clear color change upon heating, during which the decrease of the crystallinity of the MOF or even the collapse of the framework possibly occurs [138–141]. V(III)-based [142, 143] and Cu(I)-based [144, 145] MOFs also follow the same trend.
- 2) In the case of the most stable oxidation states of metals, the higher the oxidation state, the higher the thermal stability of the MOF. When oxygenated donors are used for the fabrication of MOFs, tri- or tetravalent metal ions, such as Fe(III) [51, 146], Cr(III) [23, 147], Al(III) [148, 149], Ln(III) [150, 151], Zr(IV) [34, 35], Ti(IV) [63, 108], and so on, normally result in higher thermal stabilities than di- and monovalent metals.
- 3) Inorganic secondary building units (SBUs) with higher nuclearity or even infinite subunits possess a better thermal stability compared with MOFs comprised of the same metal ions and similar types of linkers but discrete building units. MOF-74, one of the most well-known divalent metal-based MOFs with infinite metal-oxo chain SBUs, is generally stable up to 300°C (in the absence of oxygen), which outperforms many other MOFs consisting of divalent metals and oxygenated linkers [152, 153]. Another typical example is Ca-SDB, which possesses a 1D chain SBU [154]. This compound was found to maintain its crystallinity up to 500°C, which has been the most thermally stable alkaline-earth metal-based MOF reported so far. In particular, this experience fits well for the MOFs built with high-valence metal ions. For instance, the

MIL-140 series [35] that comprised of infinite Zr–O chains are more stable than their corresponding polymorphs of the UiO-66 structure type constructed from Zr₆-oxo-cluster SBUs [34]. Another example is the Ti₈-oxo-cluster-based MIL-125 [63] compound that is more thermally stable than COK-69 comprising Ti₃-oxo-cluster SBUs [155] or PCN-22 derived from Ti₇-oxo-clusters [156].

The nature of the organic linker is the second main critical parameter for determining the thermal stability of MOF compounds. There are two major types of linkers when classified according to the donor heteroatoms, oxygenated and nitrogenated linkers. They can also be divided into aromatic and aliphatic ones on the basis of their chemical structures. One can note that sometimes a linker molecule can cover some or even all these characters together at the same time, which is usually referred to as a “multifunctional” spacer [157]. In this case, the thermal stability of the corresponding MOF structure becomes extremely unpredictable. Fortunately, most of the reported MOF structures concern only a single type of organic spacer with uniform functional group for coordination or sometimes two types of different organic ligands. Thus from the chemical structure point of view, the impact of the linker on the thermal stability can be estimated as follows:

- 1) Oxygenated linkers contribute to most of the MOF architectures as almost all the metal species can form coordination bonds with oxygen atoms with significantly different strengths. According to the chemical nature of the group to which oxygen atoms are attached, one can classify MOFs into different subgroups, ranging from the most common carboxylate linkers to the less popular sulfate or phosphonate ones, while phenolate groups have only been considered very recently. As a combined result of the strong bond strength and chemical inertness, phosphonate-based and sulfate-based [158–160] MOFs generally tend to display higher thermal stability than those comprising carboxylate and phenolate linkers, which undergo decarboxylation and oxidation, respectively, upon heating. Being different from oxygenated linkers, nitrogen-containing ligands are efficient to build MOF structures based on divalent metal centers rather than with higher-valence metal dots, mostly due to the stronger tendency for coordination of divalent metal ions to nitrogen donors. ZIFs provide convincing support in this case. There is only one type of coordination bond between the nitrogen site and the metal center in the ZIF family, which gives rise in most cases to a very high thermal stability (>500°C) in sharp contrast to the other divalent metal-based MOFs constructed from most oxygenated linkers [91, 161].
- 2) Aromatic moieties are dominantly preferred in organic linker design and selection, not only because of the general robustness of their skeletons for generating accessible porosity within the MOF structures but also because of the resulting higher thermal stability for most of the corresponding MOF materials compared with those assembled from aliphatic linkers. Despite the impressive achievements of flexible MOFs used in molecular separation [162, 163] or bioapplications [164, 165], the use of flexible organic linkers made from aliphatic spacers results in a strong decrease in thermal stability.

For instance, succinic acid, a very cheap natural product with only single C–C bonded C4 skeleton, is one of the earliest aliphatic linkers used in MOF syntheses. Its derived MOFs (Co(II) [166], Ln(III) [167], etc.) consistently display rather low thermal stability (<200 °C). Similarly, the microporous Zr-fumarate compound has a significantly lower thermal resistance than the UiO-66 aromatic-based compounds although they share the same structure type and metal–ligand connectivity [168].

- 3) Structural features, such as framework density, related network topology, interpenetration, presence of defects, and so on, are other parameters that affect the thermal stability. One expects that a denser structure with a minimum porosity might exhibit a better thermal stability. Structural interpenetration or interweaving of networks takes place very often to avoid the formation of large cavities inside most large-pore MOFs, leading to the most energy-favorable construction with the highest structural density, which in turn results in an improved thermal resistance. The fact that the absolute energies of ZIF polymorphs show a tendency to decrease while the structural density increases has been supported by a systematic computational calculation [169]. Recent progress revealed that the introduction of structural defects into MOF structures is also a powerful tool to increase the content of active sites to enhance catalytic activity [170, 171]. However, the presence of such defects is usually accompanied by a decrease in thermal stability depending on the type and ratio of defects [74, 172].

As summarized from the aforementioned trends, an MOF structure that features a short aromatic linker, metal ions with stable oxidation state, strong metal–ligand interaction, and defect-free and dense packing is an ideal candidate for a high thermal stability. Nevertheless, applications of MOF materials do not only need high thermal stability but also require other properties depending on the specific domain of applications. Therefore, the right balance between porosity, functionality, and stability will always be a compromise.

1.4 Mechanical Stability

Looking back to the history of the development of MOFs, major attention has been paid to the generation of as large as possible accessible porosity within the structures, which in turn intrinsically results in the weakening of the mechanical stability. Hence, the investigation of the mechanical stability of MOFs is still at its early stage, and thus, only a limited number of examples could be found in the literature.

It was found initially that some MOFs can lose their crystallinity when the guest molecules are removed. It is mainly due to the capillary force-driven destruction, which is, in our opinion, the most common mechanical stability issue of MOFs. An efficient method to deal with this issue is to use supercritical CO₂ activation, during which the strongly associated guest solvent molecules in the pores can be exchanged with liquid CO₂, leading to zero solvent surface tension and thus zero capillary force [173]. Attaching hydrocarbon or fluorocarbon

to the metal site is an alternative, particularly evidenced for Zr-MOFs with large channels. It does not only limit the hydrogen bonding between inorganic SBU and guest solvent molecules but also reduce the size of the guest water clusters [97, 174]. Noteworthy, the breathing effect is an efficient characteristic to minimize the damage to the capillary force. A few MIL series compounds possess a highly flexible porosity associated with robust frameworks during the removal of guest solvents. Later on, other flexible MOFs with dynamic mechanical stability were reported. COK-69, constructed from Ti_3 -oxo-cluster SBUs and an aliphatic carboxylate linker, represents the first example of a breathing Ti-MOF [155]. DUT-49, a copper dicarboxylate MOF, was found to display a negative gas adsorption behavior, during which the MOF would shrink in order to release the extra inner gas pressure and returns to its normal state [175].

As long as “capillary force-inert” MOFs were reported, such as the breathing MOFs or UiO-66, a major effort has been devoted to study their pressure-induced dynamic behavior. In these studies, several important parameters shall be considered for evaluating and comparing the mechanical resistance of an MOF compound, including the shear modulus (G), Young’s modulus (E), Poisson’s ratio (ν), and the bulk modulus (K). In detail, shear modulus is normally used to describe the response of the material to shear stress, which is a good indicator of the resistance of the MOF to mechanical degradation [176]. Young’s modulus and Poisson’s ratio are parameters for the evaluation of the stiffness and stability of a material upon the loading of stress along the uniaxial and orthogonal directions, respectively. However, these two factors were hardly mentioned in the literature possibly due to the difficulty in collecting experimental data. On the contrary, there are notably more examples of studies on MOFs under pressure in the presence of liquid guest molecules (water, Hg, etc.), in which the bulk modulus was probed frequently, as it describes the response of the material to uniform hydrostatic pressure. MOFs with rigid structures (such as ZIF-8 [7, 177], MOF-5 [178], Cu-BTC [179], and UiO-66 [176]) or flexible frameworks (including MIL-47(V) [180], MIL-53, and its amino group-functionalized derivatives [181–184]) were studied experimentally and theoretically for their mechanical dynamics under pressure in the presence of various types of guest molecules. Noteworthy, the defect-free Hf-UiO-66 compound was predicted to have the highest shear and bulk moduli in all MOFs, which was deduced from the computational investigation [176, 185].

Though limited examples of MOFs have been studied, there are some tendencies that still could be summarized. Generally speaking, dense structures with minimized porosities tend to display better resistance to mechanical loadings. In the MOF component point of view, inorganic subunits with high nuclearity and coordination values, short and rigid linkers, and strong dot-donor interaction prefer to give rise to improved stability under external stress. On the other hand, efficient reduction of the accessible internal porosity in the MOF structure could enhance the stability. Adopting close-packing for the network, replacing long and flexible linkers with short and rigid ones, filling the pores with guest molecules, and making the framework breathe are all effective strategies for limiting the negative effect of the porosities of MOFs.

1.5 Concluding Remarks

With the increased interest in the use of MOFs in real-world applications, considerable efforts have been devoted recently to the elaboration of highly robust and porous structures. In relation to a targeted application, an MOF shall exhibit sufficient chemical, thermal, and/or mechanical stability. Though it is still difficult to achieve the synthesis of porous MOFs showing “ultimate” stability, one should carefully consider the minimum stability requirements for a given application.

Chemical stability has attracted much more attention compared with the thermal and mechanical ones. This allowed establishment of several rational strategies for engineering chemically robust MOFs. Strengthening the cation–ligand interaction is the most prominent strategy. Using highly charged cations (M(III), M(IV), etc.) or highly complexing ligands (azolates, phenolates, etc.) has indeed permitted obtaining a panel of very promising MOFs able to exhibit resistance to aqueous media at different pHs and temperatures and sometimes to very harsh conditions (H_2S , NH_3 , etc.). This strategy starts to show some limitations when combining both cations of high oxidation state and highly complexing ligands. This is certainly due to the difficulty in controlling the crystallization process of these highly reactivity species. The use of modulators during the crystallization is very efficient in the case of carboxylate linkers and M(III, IV) cations, although not 100% of the time sufficient. Another approach that is of great interest is using preformed inorganic building units based on monotopic ligands instead of simple cation salts. Controlled and slow exchange of the monotopic ligand with a polytopic derivative often allows crystallization of extended hybrid porous frameworks [156, 186]. Connecting preformed inorganic units (based on monotopic ligands bearing suitable organic functions) through covalent bonds has also been successful [187, 188].

Thermal and mechanical stabilities have been much less rationalized than chemical stability. However, one can still underline a few important parameters. Thermal stability is closely related to chemical stability since, in general, it derives from the chemical nature of the components of the MOFs. Chemically inert metal cations and ligands such as phosphonates, sulfates, or pyrazolates yield in general high thermal stabilities, while carboxylate and particularly phenolates suffer from decarboxylation and oxidation, respectively, at high temperature. When considering the mechanical stability, one shall avoid very large pores. In such cases, an alternative strategy would be to consider other shaping methods such as embedding particles of MOFs in polymeric binders rather than using mechanical pressure to prepare pellets or membranes of pure MOFs.

Finally, whatever the type of required stability, the robustness of the crystalline structure of MOFs is governed by a complex interplay between the chemical and/or structural parameters that one can, in most cases, tune to achieve a satisfying compromise, although probably not sufficient in all cases for long-term stability under operating conditions. This thus justifies continuing the search for even more stable MOFs and/or developing new process conditions.

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References

- 1 Schoedel, A., Li, M., Li, D., O’Keeffe, M., and Yaghi, O.M. (2016) *Chem. Rev.*, **116**, 12466–12535.
- 2 Stock, N. and Biswas, S. (2012) *Chem. Rev.*, **112**, 933–969.
- 3 Zhou, H.-C., Long, J.R., and Yaghi, O.M. (2012) *Chem. Rev.*, **112**, 673–674.
- 4 “Joe” Zhou, H.-C. and Kitagawa, S. (2014) *Chem. Soc. Rev.*, **43**, 5415–5418.
- 5 Horcajada, P., Chalati, T., Serre, C., Gillet, B., Sebrie, C., Baati, T., Eubank, J.F., Heurtaux, D., Clayette, P., Kreuz, C., Chang, J.-S., Hwang, Y.K., Marsaud, V., Bories, P.-N., Cynober, L., Gil, S., Férey, G., Couvreur, P., and Gref, R. (2010) *Nat. Mater.*, **9**, 172–178.
- 6 Vogt, E.T.C. and Weckhuysen, B.M. (2015) *Chem. Soc. Rev.*, **44**, 7342–7370.
- 7 Chapman, K.W., Halder, G.J., and Chupas, P.J. (2009) *J. Am. Chem. Soc.*, **131**, 17546–17547.
- 8 Greathouse, J.A. and Allendorf, M.D. (2006) *J. Am. Chem. Soc.*, **128**, 10678–10679.
- 9 Low, J.J., Benin, A.I., Jakubczak, P., Abrahamian, J.F., Faheem, S.A., and Willis, R.R. (2009) *J. Am. Chem. Soc.*, **131**, 15834–15842.
- 10 Jasuja, H., Burtch, N.C., Huang, Y.G., Cai, Y., and Walton, K.S. (2013) *Langmuir*, **29**, 633–642.
- 11 Schrock, K., Schroder, F., Heyden, M., Fischer, R.A., and Havenith, M. (2008) *Phys. Chem. Chem. Phys.*, **10**, 4732–4739.
- 12 Kaye, S.S., Dailly, A., Yaghi, O.M., and Long, J.R. (2007) *J. Am. Chem. Soc.*, **129**, 14176–14177.
- 13 Ming, Y., Purewal, J., Yang, J., Xu, C.C., Soltis, R., Warner, J., Veenstra, M., Gaab, M., Muller, U., and Siegel, D.J. (2015) *Langmuir*, **31**, 4988–4995.
- 14 DeCoste, J.B., Peterson, G.W., Schindler, B.J., Killops, K.L., Browe, M.A., and Mahle, J.J. (2013) *J. Mater. Chem. A*, **1**, 11922–11932.
- 15 Wiersum, A.D., Soubeyrand-Lenoir, E., Yang, Q., Moulin, B., Guillerme, V., Yahia, M.B., Bourrelly, S., Vimont, A., Miller, S., Vagner, C., Daturi, M., Clet, G., Serre, C., Maurin, G., and Llewellyn, P.L. (2011) *Chem. Asian. J.*, **6**, 3270–3280.
- 16 Wang, W., Xu, X., Zhou, W., and Shao, Z. (2017) *Adv. Sci.*, 1600371. doi: 10.1002/advs.201600371
- 17 Gomes, S.C., Luz, I., Llabrés i Xamena, F.X., Corma, A., and García, H. (2010) *Angew. Chem. Int. Ed.*, **16**, 11133–11138.
- 18 Ren, Y., Chia, G.H., and Gao, Z. (2013) *Nano Today*, **8**, 577–597.
- 19 Barea, E., Montoro, C., and Navarro, J.A.R. (2014) *Chem. Soc. Rev.*, **43**, 5419–5430.
- 20 DeCoste, J.B. and Peterson, G.W. (2014) *Chem. Rev.*, **114**, 5695–5727.

- 21 Bobbitt, N.S., Mendonca, M.L., Howarth, A.J., Islamoglu, T., Hupp, J.T., Farha, O.K., and Snurr, R.Q. (2017) *Chem. Soc. Rev.*, **46**, 3357–3385.
- 22 Horcajada, P., Gref, R., Baati, T., Allan, P.K., Maurin, G., Couvreur, P., Férey, G., Morris, R.E., and Serre, C. (2012) *Chem. Rev.*, **112**, 1232–1268.
- 23 Serre, C., Millange, F., Thouvenot, C., Nogues, M., Marsolier, G., Louer, D., and Férey, G. (2002) *J. Am. Chem. Soc.*, **124**, 13519–13526.
- 24 Férey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surblé, S., and Margiolaki, I. (2005) *Science*, **309**, 2040–2042.
- 25 Schaate, A., Roy, P., Godt, A., Lippke, J., Waltz, F., Wiebcke, M., and Behrens, P. (2011) *Chem. Eur. J.*, **17**, 6643–6651.
- 26 Devic, T. and Serre, C. (2014) *Chem. Soc. Rev.*, **43**, 6097–6115.
- 27 Serre, C. and Devic, T. (2016) *The Chemistry of Metal–Organic Frameworks*, Wiley-VCH Verlag GmbH & Co, pp. 171–202. doi: 10.1002/9783527693078.ch7.
- 28 Ahnfeldt, T., Guillou, N., Gunzelmann, D., Margiolaki, I., Loiseau, T., Férey, G., Senker, J., and Stock, N. (2009) *Angew. Chem. Int. Ed.*, **48**, 5163–5166.
- 29 Reinsch, H., Feyand, M., Ahnfeldt, T., and Stock, N. (2012) *Dalton Trans.*, **41**, 4164–4171.
- 30 Choi, S.B., Seo, M.J., Cho, M., Kim, Y., Jin, M.K., Jung, D.Y., Choi, J.S., Ahn, W.S., Rowsell, J.L.C., and Kim, J. (2007) *Cryst. Growth Des.*, **7**, 2290–2293.
- 31 Volkringer, C., Popov, D., Loiseau, T., Guillou, N., Férey, G., Haouas, M., Taulelle, F., Mellot-Draznieks, C., Burghammer, M., and Riekel, C. (2007) *Nat. Mater.*, **6**, 760–764.
- 32 Yoon, J.W., Seo, Y.-K., Hwang, Y.K., Chang, J.-S., Leclerc, H., Wuttke, S., Bazin, P., Vimont, A., Daturi, M., Bloch, E., Llewellyn, P.L., Serre, C., Horcajada, P., Grenèche, J.-M., Rodrigues, A.E., and Férey, G. (2010) *Angew. Chem. Int. Ed.*, **49**, 5949–5952.
- 33 Dhakshinamoorthy, A., Alvaro, M., Chevreau, H., Horcajada, P., Devic, T., Serre, C., and Garcia, H. (2012) *Catal. Sci. Technol.*, **2**, 324–330.
- 34 Cavka, J.H., Jakobsen, S., Olsbye, U., Guillou, N., Lamberti, C., Bordiga, S., and Lillerud, K.P. (2008) *J. Am. Chem. Soc.*, **130**, 13850–13851.
- 35 Guillerme, V., Ragon, F., Dan-Hardi, M., Devic, T., Vishnuvarthan, M., Campo, B., Vimont, A., Clet, G., Yang, Q., Maurin, G., Férey, G., Vittadini, A., Gross, S., and Serre, C. (2012) *Angew. Chem. Int. Ed.*, **51**, 9267–9271.
- 36 Helm, L. and Merbach, A.E. (2005) *Chem. Rev.*, **105**, 1923–1960.
- 37 Kang, I.J., Khan, N.A., Haque, E., and Jhung, S.H. (2011) *Chem. Eur. J.*, **17**, 6437–6442.
- 38 Zhao, X., Liu, D., Huang, H., Zhang, W., Yang, Q., and Zhong, C. (2014) *Microporous Mesoporous Mater.*, **185**, 72–78.
- 39 Hu, Y., Dong, X., Nan, J., Jin, W., Ren, X., Xu, N., and Lee, Y.M. (2011) *Chem. Commun.*, **47**, 737–739.
- 40 Cunha, D., Ben Yahia, M., Hall, S., Miller, S.R., Chevreau, H., Elkaim, E., Maurin, G., Horcajada, P., and Serre, C. (2013) *Chem. Mater.*, **25**, 2767–2776.
- 41 Küsgens, P., Rose, M., Senkovska, I., Fröde, H., Henschel, A., Siegle, S., and Kaskel, S. (2009) *Microporous Mesoporous Mater.*, **120**, 325–330.
- 42 Seo, Y.-K., Yoon, J.W., Lee, J.S., Hwang, Y.K., Jun, C.-H., Chang, J.-S., Wuttke, S., Bazin, P., Vimont, A., Daturi, M., Bourrelly, S., Llewellyn, P.L., Horcajada, P., Serre, C., and Férey, G. (2012) *Adv. Mater.*, **24**, 806–810.

- 43 Horcajada, P., Chevreau, H., Heurtaux, D., Benyettou, F., Salles, F., Devic, T., Garcia-Marquez, A., Yu, C., Lavrard, H., Dutson, C.L., Magnier, E., Maurin, G., Elkaim, E., and Serre, C. (2014) *Chem. Commun.*, **50**, 6872–6874.
- 44 Alvarez, E., Guillou, N., Martineau, C., Bueken, B., Van de Voorde, B., Le Guillouzer, C., Fabry, P., Nouar, F., Taulelle, F., de Vos, D., Chang, J.-S., Cho, K.H., Ramsahye, N., Devic, T., Daturi, M., Maurin, G., and Serre, C. (2015) *Angew. Chem. Int. Ed.*, **54**, 3664–3668.
- 45 Devic, T., Horcajada, P., Serre, C., Salles, F., Maurin, G., Moulin, B., Heurtaux, D., Clet, G., Vimont, A., Grenèche, J.-M., Ouay, B.L., Moreau, F., Magnier, E., Filinchuk, Y., Marrot, J., Lavalley, J.-C., Daturi, M., and Férey, G. (2010) *J. Am. Chem. Soc.*, **132**, 1127–1136.
- 46 Halis, S., Reimer, N., Klinkebiel, A., Lüning, U., and Stock, N. (2015) *Microporous Mesoporous Mater.*, **216**, 13–19.
- 47 Feng, D., Liu, T.-F., Su, J., Bosch, M., Wei, Z., Wan, W., Yuan, D., Chen, Y.-P., Wang, X., Wang, K., Lian, X., Gu, Z.-Y., Park, J., Zou, X., and Zhou, H.-C. (2015) *Nat. Commun.*, **6**, 5979.
- 48 Fateeva, A., Chater, P.A., Ireland, C.P., Tahir, A.A., Khimyak, Y.Z., Wiper, P.V., Darwent, J.R., and Rosseinsky, M.J. (2012) *Angew. Chem. Int. Ed.*, **51**, 7440–7444.
- 49 Wang, K., Feng, D., Liu, T.-F., Su, J., Yuan, S., Chen, Y.-P., Bosch, M., Zou, X., and Zhou, H.-C. (2014) *J. Am. Chem. Soc.*, **136**, 13983–13986.
- 50 Wongsakulphasatch, S., Nouar, F., Rodriguez, J., Scott, L., Le Guillouzer, C., Devic, T., Horcajada, P., Grenèche, J.M., Llewellyn, P.L., Vimont, A., Clet, G., Daturi, M., and Serre, C. (2015) *Chem. Commun.*, **51**, 10194–10197.
- 51 Chevreau, H., Permyakova, A., Nouar, F., Fabry, P., Livage, C., Ragon, F., Garcia-Marquez, A., Devic, T., Steunou, N., Serre, C., and Horcajada, P. (2016) *CrystEngComm*, **18**, 4094–4101.
- 52 Millange, F., Serre, C., and Férey, G. (2002) *Chem. Commun.*, 822–823.
- 53 Férey, G., Serre, C., Mellot-Draznieks, C., Millange, F., Surblé, S., Dutour, J., and Margiolaki, I. (2004) *Angew. Chem. Int. Ed.*, **43**, 6296–6301.
- 54 Cychoz, K.A. and Matzger, A.J. (2010) *Langmuir*, **26**, 17198–17202.
- 55 Liu, T.-F., Zou, L., Feng, D., Chen, Y.-P., Fordham, S., Wang, X., Liu, Y., and Zhou, H.-C. (2014) *J. Am. Chem. Soc.*, **136**, 7813–7816.
- 56 Lian, X., Feng, D., Chen, Y.-P., Liu, T.-F., Wang, X., and Zhou, H.-C. (2015) *Chem. Sci.*, **6**, 7044–7048.
- 57 Liang, Y.-T., Yang, G.-P., Liu, B., Yan, Y.-T., Xi, Z.-P., and Wang, Y.-Y. (2015) *Dalton Trans.*, **44**, 13325–13330.
- 58 Surblé, S., Serre, C., Millange, F., Pelle, F., and Férey, G. (2005) *Solid State Sci.*, **7**, 1074–1082.
- 59 Xue, D.-X., Belmabkhout, Y., Shekhah, O., Jiang, H., Adil, K., Cairns, A.J., and Eddaoudi, M. (2015) *J. Am. Chem. Soc.*, **137**, 5034–5040.
- 60 Duan, J., Higuchi, M., Krishna, R., Kiyonaga, T., Tsutsumi, Y., Sato, Y., Kubota, Y., Takata, M., and Kitagawa, S. (2014) *Chem. Sci.*, **5**, 660–666.
- 61 Duan, J., Higuchi, M., Horike, S., Foo, M.L., Rao, K.P., Inubushi, Y., Fukushima, T., and Kitagawa, S. (2013) *Angew. Chem. Int. Ed.*, **23**, 3525–3530.

- 62 Yassine, O., Shekhah, O., Assen, A.H., Belmabkhout, Y., Salama, K.N., and Eddaoudi, M. (2016) *Angew. Chem. Int. Ed.*, **55**, 15879–15883.
- 63 Dan-Hardi, M., Serre, C., Frot, T., Rozes, L., Maurin, G., Sanchez, C., and Férey, G. (2009) *J. Am. Chem. Soc.*, **131**, 10857–10859.
- 64 Vaesen, S., Guillerm, V., Yang, Q., Wiersum, A.D., Marszalek, B., Gil, B., Vimont, A., Daturi, M., Devic, T., Llewellyn, P.L., Serre, C., Maurin, G., and De Weireld, G. (2013) *Chem. Commun.*, **49**, 10082–10084.
- 65 Bon, V., Senkovskyy, V., Senkovska, I., and Kaskel, S. (2012) *Chem. Commun.*, **48**, 8407–8409.
- 66 Bon, V., Senkovska, I., Baburin, I.A., and Kaskel, S. (2013) *Cryst. Growth Des.*, **13**, 1231–1237.
- 67 Lammert, M., Reinsch, H., Murray, C.A., Wharmby, M.T., Terraschke, H., and Stock, N. (2016) *Dalton Trans.*, **45**, 18822–18826.
- 68 Bai, Y., Dou, Y., Xie, L.-H., Rutledge, W., Li, J.-R., and Zhou, H.-C. (2016) *Chem. Soc. Rev.*, **45**, 2327–2367.
- 69 Valenzano, L., Civalleri, B., Chavan, S., Bordiga, S., Nilsen, M.H., Jakobsen, S., Lillerud, K.P., and Lamberti, C. (2011) *Chem. Mater.*, **23**, 1700–1718.
- 70 Mondloch, J.E., Katz, M.J., Planas, N., Semrouni, D., Gagliardi, L., Hupp, J.T., and Farha, O.K. (2014) *Chem. Commun.*, **50**, 8944–8946.
- 71 Kandiah, M., Nilsen, M.H., Usseglio, S., Jakobsen, S., Olsbye, U., Tilset, M., Larabi, C., Quadrelli, E.A., Bonino, F., and Lillerud, K.P. (2010) *Chem. Mater.*, **22**, 6632–6640.
- 72 Vandichel, M., Hajek, J., Vermoortele, F., Waroquier, M., De Vos, D.E., and Van Speybroeck, V. (2015) *CrystEngComm*, **17**, 395–406.
- 73 Vermoortele, F., Bueken, B., Le Bars, G., Van de Voorde, B., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., Van Speybroeck, V., Kirschhock, C., and De Vos, D.E. (2013) *J. Am. Chem. Soc.*, **135**, 11465–11468.
- 74 Shearer, G.C., Chavan, S., Ethiraj, J., Vitillo, J.G., Svelle, S., Olsbye, U., Lamberti, C., Bordiga, S., and Lillerud, K.P. (2014) *Chem. Mater.*, **26**, 4068–4071.
- 75 Katz, M.J., Brown, Z.J., Colon, Y.J., Siu, P.W., Scheidt, K.A., Snurr, R.Q., Hupp, J.T., and Farha, O.K. (2013) *Chem. Commun.*, **49**, 9449–9451.
- 76 Thornton, A.W., Babarao, R., Jain, A., Trousselet, F., and Coudert, F.X. (2016) *Dalton Trans.*, **45**, 4352–4359.
- 77 Furukawa, H., Gándara, F., Zhang, Y.-B., Jiang, J., Queen, W.L., Hudson, M.R., and Yaghi, O.M. (2014) *J. Am. Chem. Soc.*, **136**, 4369–4381.
- 78 Jiang, J., Gándara, F., Zhang, Y.-B., Na, K., Yaghi, O.M., and Klemperer, W.G. (2014) *J. Am. Chem. Soc.*, **136**, 12844–12847.
- 79 Howarth, A.J., Liu, Y., Li, P., Li, Z., Wang, T.C., Hupp, J.T., and Farha, O.K. (2016) *Nat. Rev. Mater.*, **1**, 15018.
- 80 Duan, J., Jin, W., and Kitagawa, S. (2017) *Coord. Chem. Rev.*, **332**, 48–74.
- 81 Feng, D., Chung, W.-C., Wei, Z., Gu, Z.-Y., Jiang, H.-L., Chen, Y.-P., Darensbourg, D.J., and Zhou, H.-C. (2013) *J. Am. Chem. Soc.*, **135**, 17105–17110.
- 82 Jiang, H.-L., Feng, D., Wang, K., Gu, Z.-Y., Wei, Z., Chen, Y.-P., and Zhou, H.-C. (2013) *J. Am. Chem. Soc.*, **135**, 13934–13938.
- 83 Jiang, H.-L., Feng, D., Liu, T.-F., Li, J.-R., and Zhou, H.-C. (2012) *J. Am. Chem. Soc.*, **134**, 14690–14693.

- 84 Liu, T.-F., Feng, D., Chen, Y.-P., Zou, L., Bosch, M., Yuan, S., Wei, Z., Fordham, S., Wang, K., and Zhou, H.-C. (2015) *J. Am. Chem. Soc.*, **137**, 413–419.
- 85 Deibert, B.J. and Li, J. (2014) *Chem. Commun.*, **50**, 9636–9639.
- 86 Mondloch, J.E., Katz, M.J., Isley III, W.C., Ghosh, P., Liao, P., Bury, W., Wagner, G.W., Hall, M.G., DeCoste, J.B., Peterson, G.W., Snurr, R.Q., Cramer, C.J., Hupp, J.T., and Farha, O.K. (2015) *Nat. Mater.*, **14**, 512–516.
- 87 Liu, Y., Howarth, A.J., Vermeulen, N.A., Moon, S.-Y., Hupp, J.T., and Farha, O.K. (2016) *Coord. Chem. Rev.*, **346**, 101–111.
- 88 Schubert, U. (2007) *Acc. Chem. Res.*, **40**, 730–737.
- 89 Wang, B., Cote, A.P., Furukawa, H., O’Keeffe, M., and Yaghi, O.M. (2008) *Nature*, **453**, 207–211.
- 90 Eddaoudi, M., Sava, D.F., Eubank, J.F., Adil, K., and Guillermin, V. (2015) *Chem. Soc. Rev.*, **44**, 228–249.
- 91 Banerjee, R., Phan, A., Wang, B., Knobler, C., Furukawa, H., O’Keeffe, M., and Yaghi, O.M. (2008) *Science*, **319**, 939–943.
- 92 Zhang, J.-P., Zhang, Y.-B., Lin, J.-B., and Chen, X.-M. (2012) *Chem. Rev.*, **112**, 1001–1033.
- 93 Park, K.S., Ni, Z., Côté, A.P., Choi, J.Y., Huang, R., Uribe-Romo, F.J., Chae, H.K., O’Keeffe, M., and Yaghi, O.M. (2006) *Proc. Natl. Acad. Sci. U.S.A.*, **103**, 10186–10191.
- 94 Colombo, V., Galli, S., Choi, H.J., Han, G.D., Maspero, A., Palmisano, G., Masciocchi, N., and Long, J.R. (2011) *Chem. Sci.*, **2**, 1311–1319.
- 95 Padial, N.M., Quartapelle Procopio, E., Montoro, C., López, E., Oltra, J.E., Colombo, V., Maspero, A., Masciocchi, N., Galli, S., Senkovska, I., Kaskel, S., Barea, E., and Navarro, J.A.R. (2013) *Angew. Chem. Int. Ed.*, **52**, 8290–8294.
- 96 Wang, K., Lv, X.-L., Feng, D., Li, J., Chen, S., Sun, J., Song, L., Xie, Y., Li, J.-R., and Zhou, H.-C. (2016) *J. Am. Chem. Soc.*, **138**, 914–919.
- 97 Burtch, N.C., Jasuja, H., and Walton, K.S. (2014) *Chem. Rev.*, **114**, 10575–10612.
- 98 Canivet, J., Fateeva, A., Guo, Y., Coasne, B., and Farrusseng, D. (2014) *Chem. Soc. Rev.*, **43**, 5594–5617.
- 99 Masciocchi, N., Galli, S., Colombo, V., Maspero, A., Palmisano, G., Seyyedi, B., Lamberti, C., and Bordiga, S. (2010) *J. Am. Chem. Soc.*, **132**, 7902–7904.
- 100 Quartapelle Procopio, E., Rojas, S., Padial, N.M., Galli, S., Masciocchi, N., Linares, F., Miguel, D., Oltra, J.E., Navarro, J.A.R., and Barea, E. (2011) *Chem. Commun.*, **47**, 11751–11753.
- 101 Rodríguez-Albelo, L.M., López-Maya, E., Hamad, S., Ruiz-Salvador, A.R., Calero, S., and Navarro, J.A.R. (2017) *Nat. Commun.*, **8**, 14457–14466.
- 102 Lv, X.-L., Wang, K., Wang, B., Su, J., Zou, X., Xie, Y., Li, J.-R., and Zhou, H.-C. (2017) *J. Am. Chem. Soc.*, **139**, 211–217.
- 103 Rieth, A.J., Tulchinsky, Y., and Dincă, M. (2016) *J. Am. Chem. Soc.*, **138**, 9401–9404.
- 104 Tulchinsky, Y., Hendon, C.H., Lomachenko, K.A., Borfecchia, E., Melot, B.C., Hudson, M.R., Tarver, J.D., Korzynski, M.D., Stubbs, A.W., Kagan, J.J., Lamberti, C., Brown, C.M., and Dincă, M. (2017) *J. Am. Chem. Soc.*, **139**, 5992–5997.
- 105 Herm, Z.R., Wiers, B.M., Mason, J.A., van Baten, J.M., Hudson, M.R., Zajdel, P., Brown, C.M., Masciocchi, N., Krishna, R., and Long, J.R. (2013) *Science*, **340**, 960–964.

- 106 Mouchaham, G., Cooper, L., Guillou, N., Martineau, C., Elkaïm, E., Bourrelly, S., Llewellyn, P.L., Allain, C., Clavier, G., Serre, C., and Devic, T. (2015) *Angew. Chem. Int. Ed.*, **54**, 13297–13301.
- 107 Benoit, V., Pillai, R.S., Orsi, A., Normand, P., Jobic, H., Nouar, F., Billemont, P., Bloch, E., Bourrelly, S., Devic, T., Wright, P.A., de Weireld, G., Serre, C., Maurin, G., and Llewellyn, P.L. (2016) *J. Mater. Chem. A*, **4**, 1383–1389.
- 108 Serre, C., Groves, J.A., Lightfoot, P., Slawin, A.M.Z., Wright, P.A., Stock, N., Bein, T., Haouas, M., Taulelle, F., and Férey, G. (2006) *Chem. Mater.*, **18**, 1451–1457.
- 109 Mah, R.K., Lui, M.W., and Shimizu, G.K.H. (2013) *Inorg. Chem.*, **52**, 7311–7313.
- 110 Cooper, L., Guillou, N., Martineau, C., Elkaim, E., Taulelle, F., Serre, C., and Devic, T. (2014) *Eur. J. Inorg. Chem.*, **2014**, 6281–6289.
- 111 Li, T., Chen, D.-L., Sullivan, J.E., Kozłowski, M.T., Johnson, J.K., and Rosi, N.L. (2013) *Chem. Sci.*, **4**, 1746–1755.
- 112 Makal, T.A., Wang, X., and Zhou, H.-C. (2013) *Cryst. Growth Des.*, **13**, 4760–4768.
- 113 Hou, C., Liu, Q., Wang, P., and Sun, W.-Y. (2013) *Microporous Mesoporous Mater.*, **172**, 61–66.
- 114 Liu, H., Zhao, Y., Zhang, Z., Nijem, N., Chabal, Y.J., Zeng, H., and Li, J. (2011) *Adv. Funct. Mater.*, **21**, 4754–4762.
- 115 Ma, D., Li, Y., and Li, Z. (2011) *Chem. Commun.*, **47**, 7377–7379.
- 116 Gu, J.-Z., Lu, W.-G., Jiang, L., Zhou, H.-C., and Lu, T.-B. (2007) *Inorg. Chem.*, **46**, 5835–5837.
- 117 Yang, C., Kaipa, U., Mather, Q.Z., Wang, X., Nesterov, V., Venero, A.F., and Omary, M.A. (2011) *J. Am. Chem. Soc.*, **133**, 18094–18097.
- 118 Serre, C. (2012) *Angew. Chem. Int. Ed.*, **51**, 6048–6050.
- 119 Planchais, A., Devautour-Vinot, S., Salles, F., Ragon, E., Devic, T., Serre, C., and Maurin, G. (2014) *J. Phys. Chem. C*, **118**, 14441–14448.
- 120 Yang, J., Grzech, A., Mulder, F.M., and Dingemans, T.J. (2011) *Chem. Commun.*, **47**, 5244–5246.
- 121 Zhang, Z., Nguyen, H.T.H., Miller, S.A., Ploskonka, A.M., DeCoste, J.B., and Cohen, S.M. (2016) *J. Am. Chem. Soc.*, **138**, 920–925.
- 122 Gelfand, B.S., Lin, J.-B., and Shimizu, G.K.H. (2015) *Inorg. Chem.*, **54**, 1185–1187.
- 123 Iremonger, S.S., Liang, J., Vaidhyanathan, R., Martens, I., Shimizu, G.K.H., Daff, T.D., Aghaji, M.Z., Yeganegi, S., and Woo, T.K. (2011) *J. Am. Chem. Soc.*, **133**, 20048–20051.
- 124 Tanabe, K.K. and Cohen, S.M. (2011) *Chem. Soc. Rev.*, **40**, 498–519.
- 125 Wang, Z. and Cohen, S.M. (2009) *Chem. Soc. Rev.*, **38**, 1315–1329.
- 126 Cohen, S.M. (2012) *Chem. Rev.*, **112**, 970–1000.
- 127 Deria, P., Mondloch, J.E., Tylianakis, E., Ghosh, P., Bury, W., Snurr, R.Q., Hupp, J.T., and Farha, O.K. (2013) *J. Am. Chem. Soc.*, **135**, 16801–16804.
- 128 DeCoste, J.B., Peterson, G.W., Smith, M.W., Stone, C.A., and Willis, C.R. (2012) *J. Am. Chem. Soc.*, **134**, 1486–1489.
- 129 Zhang, W., Hu, Y., Ge, J., Jiang, H.-L., and Yu, S.-H. (2014) *J. Am. Chem. Soc.*, **136**, 16978–16981.

- 130 Yang, S.J. and Park, C.R. (2012) *Adv. Mater.*, **24**, 4010–4013.
- 131 Yang, S.J., Choi, J.Y., Chae, H.K., Cho, J.H., Nahm, K.S., and Park, C.R. (2009) *Chem. Mater.*, **21**, 1893–1897.
- 132 Smedskjaer, M.M., Mauro, J.C., and Yue, Y.Z. (2010) *Phys. Rev. Lett.*, **105**, 4.
- 133 Bennett, T.D., Todorova, T.K., Baxter, E.F., Reid, D.G., Gervais, C., Bueken, B., Van de Voorde, B., De Vos, D., Keen, D.A., and Mellot-Draznieks, C. (2016) *Phys. Chem. Chem. Phys.*, **18**, 2192–2201.
- 134 Umeyama, D., Horike, S., Inukai, M., Itakura, T., and Kitagawa, S. (2015) *J. Am. Chem. Soc.*, **137**, 864–870.
- 135 Bennett, T.D., Yue, Y.Z., Li, P., Qiao, A., Tao, H.Z., Greaves, N.G., Richards, T., Lampronti, G.I., Redfern, S.A.T., Blanc, F., Farha, O.K., Hupp, J.T., Cheetham, A.K., and Keen, D.A. (2016) *J. Am. Chem. Soc.*, **138**, 3484–3492.
- 136 Sun, J.K. and Xu, Q. (2014) *Energy Environ. Sci.*, **7**, 2071–2100.
- 137 Salunkhe, R.R., Kaneti, Y.V., Kim, J., Kim, J.H., and Yamauchi, Y. (2016) *Acc. Chem. Res.*, **49**, 2796–2806.
- 138 Hu, K.L., Kurmoo, M., Wang, Z.M., and Gao, S. (2009) *Chem. Eur. J.*, **15**, 12050–12064.
- 139 Riou-Cavellec, M., Sanselme, M., Nogues, M., Greneche, J.M., and Férey, G. (2002) *Solid State Sci.*, **4**, 619–625.
- 140 Wang, Z.M., Zhang, Y.J., Liu, T., Kurmoo, M., and Gao, S. (2007) *Adv. Funct. Mater.*, **17**, 1523–1536.
- 141 Weber, B., Betz, R., Bauer, W., and Schlamp, S. (2011) *Z. Anorg. Allg. Chem.*, **637**, 102–107.
- 142 Barthelet, K., Marrot, J., Riou, D., and Férey, G. (2002) *Angew. Chem. Int. Ed.*, **41**, 281–284.
- 143 Barthelet, K., Riou, D., Nogues, M., and Férey, G. (2003) *Inorg. Chem.*, **42**, 1739–1743.
- 144 Yu, Y., Zhang, X.M., Ma, J.P., Liu, Q.K., Wang, P., and Dong, Y.B. (2014) *Chem. Commun.*, **50**, 1444–1446.
- 145 Liu, W., Fang, Y., Wei, G.Z., Teat, S.J., Xiong, K.C., Hu, Z.C., Lustig, W.P., and Li, J. (2015) *J. Am. Chem. Soc.*, **137**, 9400–9408.
- 146 Horcajada, P., Serre, C., Maurin, G., Ramsahye, N.A., Balas, F., Vallet-Regi, M., Sebban, M., Taulelle, F., and Férey, G. (2008) *J. Am. Chem. Soc.*, **130**, 6774–6780.
- 147 Serre, C., Millange, F., Devic, T., Audebrand, N., and Van Beek, W. (2006) *Mater. Res. Bull.*, **41**, 1550–1557.
- 148 Loiseau, T., Mellot-Draznieks, C., Muguerra, H., Férey, G., Haouas, M., and Taulelle, F. (2005) *C. R. Chim.*, **8**, 765–772.
- 149 Volkringer, C., Loiseau, T., Devic, T., Férey, G., Popov, D., Burghammer, M., and Riekkel, C. (2010) *CrystEngComm*, **12**, 3225–3228.
- 150 Serre, C. and Férey, G. (2002) *J. Mater. Chem.*, **12**, 3053–3057.
- 151 Serre, C., Millange, F., Marrot, J., and Férey, G. (2002) *Chem. Mater.*, **14**, 2409–2415.
- 152 Rosi, N.L., Kim, J., Eddaoudi, M., Chen, B.L., O’Keeffe, M., and Yaghi, O.M. (2005) *J. Am. Chem. Soc.*, **127**, 1504–1518.
- 153 Wang, L.J., Deng, H.X., Furukawa, H., Gandara, F., Cordova, K.E., Peri, D., and Yaghi, O.M. (2014) *Inorg. Chem.*, **53**, 5881–5883.

- 154 Banerjee, D., Zhang, Z.J., Plonka, A.M., Li, J., and Parise, J.B. (2012) *Cryst. Growth Des.*, **12**, 2162–2165.
- 155 Bueken, B., Vermoortele, F., Vanpoucke, D.E.P., Reinsch, H., Tsou, C.C., Valvekens, P., De Baerdemaeker, T., Ameloot, R., Kirschhock, C.E.A., Van Speybroeck, V., Mayer, J.M., and De Vos, D. (2015) *Angew. Chem. Int. Ed.*, **54**, 13912–13917.
- 156 Yuan, S., Liu, T.F., Feng, D.W., Tian, J., Wang, K.C., Qin, J.S., Zhang, Q., Chen, Y.P., Bosch, M., Zou, L.F., Teat, S.J., Dalgarno, S.J., and Zhou, H.C. (2015) *Chem. Sci.*, **6**, 3926–3930.
- 157 Lin, Z.J., Lu, J., Hong, M.C., and Cao, R. (2014) *Chem. Soc. Rev.*, **43**, 5867–5895.
- 158 Barthelet, K., Merlier, C., Serre, C., Riou-Cavellec, M., Riou, D., and Férey, G. (2002) *J. Mater. Chem.*, **12**, 1132–1137.
- 159 Serre, C. and Férey, G. (2002) *J. Mater. Chem.*, **12**, 2367–2369.
- 160 Shimizu, G.K.H., Vaidhyanathan, R., and Taylor, J.M. (2009) *Chem. Soc. Rev.*, **38**, 1430–1449.
- 161 Huang, X.C., Lin, Y.Y., Zhang, J.P., and Chen, X.M. (2006) *Angew. Chem. Int. Ed.*, **45**, 1557–1559.
- 162 Maji, T.K., Matsuda, R., and Kitagawa, S. (2007) *Nat. Mater.*, **6**, 142–148.
- 163 Tanaka, D., Nakagawa, K., Higuchi, M., Horike, S., Kubota, Y., Kobayashi, L.C., Takata, M., and Kitagawa, S. (2008) *Angew. Chem. Int. Ed.*, **47**, 3914–3918.
- 164 Rabone, J., Yue, Y.F., Chong, S.Y., Stylianou, K.C., Bacsá, J., Bradshaw, D., Darling, G.R., Berry, N.G., Khimyak, Y.Z., Ganin, A.Y., Wiper, P., Claridge, J.B., and Rosseinsky, M.J. (2010) *Science*, **329**, 1053–1057.
- 165 Imaz, I., Rubio-Martinez, M., An, J., Sole-Font, I., Rosi, N.L., and Maspoeh, D. (2011) *Chem. Commun.*, **47**, 7287–7302.
- 166 Livage, C., Egger, C., and Férey, G. (1999) *Chem. Mater.*, **11**, 1546–1550.
- 167 Serpaggi, F. and Férey, G. (1999) *Microporous Mesoporous Mater.*, **32**, 311–318.
- 168 Wissmann, G., Schaate, A., Lilienthal, S., Bremer, I., Schneider, A.M., and Behrens, P. (2012) *Microporous Mesoporous Mater.*, **152**, 64–70.
- 169 Tan, J.C. and Cheetham, A.K. (2011) *Chem. Soc. Rev.*, **40**, 1059–1080.
- 170 Polozij, M., Rubes, M., Cejka, J., and Nachtigall, P. (2014) *ChemCatChem*, **6**, 2821–2824.
- 171 Fang, Z.L., Bueken, B., De Vos, D.E., and Fischer, R.A. (2015) *Angew. Chem. Int. Ed.*, **54**, 7234–7254.
- 172 Shearer, G.C., Chavan, S., Bordiga, S., Svelle, S., Olsbye, U., and Lillerud, K.P. (2016) *Chem. Mater.*, **28**, 3749–3761.
- 173 Farha, O.K. and Hupp, J.T. (2010) *Acc. Chem. Res.*, **43**, 1166–1175.
- 174 Deria, P., Chung, Y.G., Snurr, R.Q., Hupp, J.T., and Farha, O.K. (2015) *Chem. Sci.*, **6**, 5172–5176.
- 175 Krause, S., Bon, V., Senkovska, I., Stoeck, U., Wallacher, D., Tobbens, D.M., Zander, S., Pillai, R.S., Maurin, G., Coudert, F.X., and Kaskel, S. (2016) *Nature*, **532**, 348–352.
- 176 Wu, H., Yildirim, T., and Zhou, W. (2013) *J. Phys. Chem. Lett.*, **4**, 925–930.
- 177 Moggach, S.A., Bennett, T.D., and Cheetham, A.K. (2009) *Angew. Chem. Int. Ed.*, **48**, 7087–7089.
- 178 Graham, A.J., Allan, D.R., Muszkiewicz, A., Morrison, C.A., and Moggach, S.A. (2011) *Angew. Chem. Int. Ed.*, **50**, 11138–11141.

- 179 Chapman, K.W., Halder, G.J., and Chupas, P.J. (2008) *J. Am. Chem. Soc.*, **130**, 10524–10526.
- 180 Yot, P.G., Ma, Q.T., Haines, J., Yang, Q.Y., Ghoufi, A., Devic, T., Serre, C., Dmitriev, V., Férey, G., Zhong, C.L., and Maurin, G. (2012) *Chem. Sci.*, **3**, 1100–1104.
- 181 Ghoufi, A., Subercaze, A., Ma, Q., Yot, P.G., Ke, Y., Puente-Orench, I., Devic, T., Guillerme, V., Zhong, C., Serre, C., Férey, G., and Maurin, G. (2012) *J. Phys. Chem. C*, **116**, 13289–13295.
- 182 Ma, Q.T., Yang, Q.Y., Ghoufi, A., Férey, G., Zhong, C.L., and Maurin, G. (2012) *Dalton Trans.*, **41**, 3915–3919.
- 183 Yot, P.G., Vanduyfhuys, L., Alvarez, E., Rodriguez, J., Itie, J.P., Fabry, P., Guillou, N., Devic, T., Beurroies, I., Llewellyn, P.L., Van Speybroeck, V., Serre, C., and Maurin, G. (2016) *Chem. Sci.*, **7**, 446–450.
- 184 Yot, P.G., Yang, K., Guillerme, V., Ragon, F., Dmitriev, V., Parisiades, P., Elkaim, E., Devic, T., Horcajada, P., Serre, C., Stock, N., Mowat, J.P.S., Wright, P.A., Férey, G., and Maurin, G. (2016) *Eur. J. Inorg. Chem.*, **27**, 4424–4429.
- 185 Kuc, A., Enyashin, A., and Seifert, G. (2007) *J. Phys. Chem. B*, **111**, 8179–8186.
- 186 Guillerme, V., Gross, S., Serre, C., Devic, T., Bauer, M., and Férey, G. (2010) *Chem. Commun.*, **46**, 767–769.
- 187 Nguyen, H.L., Gándara, F., Furukawa, H., Doan, T.L.H., Cordova, K.E., and Yaghi, O.M. (2016) *J. Am. Chem. Soc.*, **138**, 4330–4333.
- 188 Elsaidi, S.K., Mohamed, M.H., Loring, J.S., McGrail, B.P., and Thallapally, P.K. (2016) *ACS Appl. Mater. Interfaces*, **8**, 28424–28427.