

## Activation of metal–organic framework materials†

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Crystalline metal–organic frameworks (MOFs) have emerged as a highly desirable class of solid-state materials. Some of their most attractive features include exceptionally high porosities as well as surface areas. A key aspect to the realization of high porosity is the removal of guest molecules from the framework while still maintaining its structural integrity (*i.e.*, “activation”). This contribution highlights the strategies utilized to date for activating MOFs, including: (i) conventional heating and vacuum; (ii) solvent-exchange; (iii) supercritical CO<sub>2</sub> (scCO<sub>2</sub>) exchange; (iv) freeze-drying; and (v) chemical treatment.

## Introduction

Metal–organic frameworks (MOFs) constitute an important and rapidly growing class of solid-state compounds. MOFs are composed of inorganic nodes (metal ions or clusters) and organic linkers that are interconnected by coordination bonds of moderate strength.<sup>1–3</sup> From a functional materials perspective, some of the most attractive features of MOFs are: (i) their crystalline nature, allowing unambiguous structural determination, which, in turn, has allowed predictive materials discovery,<sup>4,5</sup> (ii) their chemical and structural diversity, and (iii) their permanent porosity, uniformly nanostructured cavities, and, to date, surface areas exceeding those of all known porous materials (exceeding *ca.* 7000 m<sup>2</sup> g<sup>−1</sup> experimentally and 14 000 m<sup>2</sup> g<sup>−1</sup> computationally).<sup>6,7</sup>

Given these exceptional properties, MOFs are being investigated for a number of potential applications including gas storage<sup>8,9</sup> and separation,<sup>10</sup> chemical catalysis,<sup>11,12</sup> sensing,<sup>13</sup> ion-exchange<sup>14</sup> and conductivity,<sup>15</sup> drug delivery,<sup>16</sup> biomedical imaging,<sup>17</sup> and light harvesting.<sup>18–20</sup> Highly desirable are the permanent porosities and large internal surface areas exhibited by many MOFs (*vide infra*) which can be of paramount importance for successful implementation of many potential applications (*e.g.*, gas storage and gas phase catalysis). Significant challenges exist in the synthesis of MOFs with permanent porosity as well as tuneable pore structure and volume; preparation of phase-pure, non-catenated, and “activated” MOFs has been particularly troublesome, especially in the high surface area regime.<sup>21</sup>

Phase-pure MOF materials are often obtained *via* synthetic optimization that is laborious and cumbersome. High-throughput syntheses can alleviate some of these efforts,<sup>22</sup>

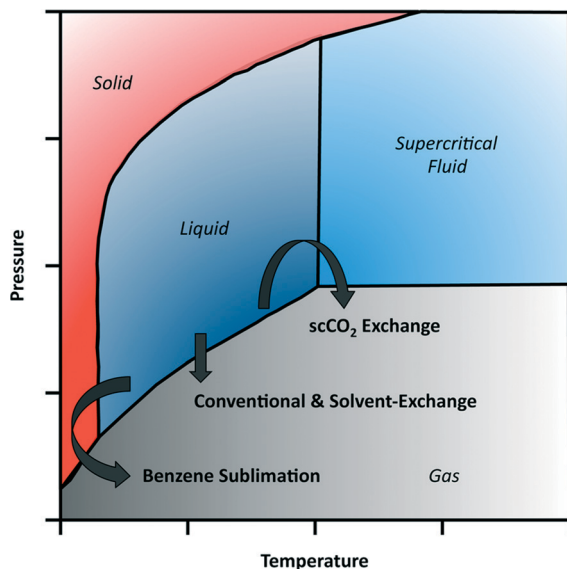
yet more rational purification protocols are desirable.<sup>21,23</sup> Farha *et al.* demonstrated that density separation, utilizing mixed organic solvent systems, is broadly applicable for the purification of MOFs.<sup>24</sup> Density separation was utilized to separate mixtures of MOF phases, mixtures of MOFs containing single and multiple ligands (*e.g.*, in pillared paddlewheel structures), and catenated and non-catenated phases.<sup>24</sup> Controlling catenation—the interpenetration or interweaving of two or more identical networks—has also been extensively investigated.<sup>25</sup> Concentration,<sup>26</sup> temperature,<sup>27</sup> templating strategies (utilizing solvents or other molecules),<sup>28,29</sup> liquid-phase epitaxy,<sup>30</sup> ligand design<sup>31</sup> as well as judicious consideration of framework topology,<sup>6,32</sup> and solvent-assisted linker exchange (SALE)<sup>33</sup> have all been utilized to control catenation.

The final step *en route* to MOFs exhibiting permanent porosity is “activation”, or the removal of guest molecules (solvent or other chemicals used during the synthesis) from the MOF without compromising its structural integrity and hence porosity.<sup>21</sup> Robson noted the significance of this challenge in a seminal contribution, proposing that “despite Nature’s abhorrence of a vacuum it may be possible to devise rods (linkers) with sufficient rigidity to support the existence of solids with relatively huge empty cavities”.<sup>34</sup> This “abhorrence of a vacuum” is exacerbated when the cavities are filled with high boiling point solvents such as *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide (DEF), or dimethyl sulfoxide (DMSO) that are required as a part of the MOF synthesis. Significant capillary forces, and hence surface tension, can be created (see Fig. 1) during activation, which in turn can yield fully or partially collapsed frameworks. In many instances, the experimentally observed surface areas and pore volumes are significantly lower than those predicted from simulations based on single-crystal structures and often incomplete activation is invoked to explain the observed data.

Hence, an important question and therefore focus of the present contribution is, what are the most effective and general

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† Electronic supplementary information (ESI) available: A full table of all studies utilizing scCO<sub>2</sub> activation to date. See DOI: 10.1039/c3ce41232f

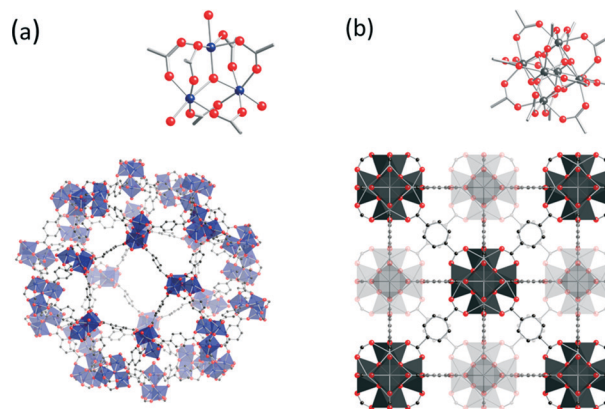


**Fig. 1** An illustrative phase diagram of the physical phenomena encountered for conventional and solvent-exchange activation,  $\text{scCO}_2$  exchange, and benzene freeze-drying.

**strategies for removing (i.e., activating) guest molecules from MOFs with increasing porosity and surface area?** Herein we outline five strategies that have been effective for activating MOFs: (i) conventional heating and vacuum; (ii) solvent-exchange; (iii) **supercritical  $\text{CO}_2$  ( $\text{scCO}_2$ )** processing; (iv) freeze-drying; and (v) chemical treatment. Fig. 1 illustrates the physical phenomenon that each activation strategy utilizes and these will be discussed further throughout this highlight. This contribution is not intended to be an exhaustive review of the literature, but rather a highlight of what we perceive to be some of the most important advances in activating MOFs. Our hope is that it helps future researchers who encounter some of the struggles associated with the activation of MOFs.

### Conventional activation

Conventional activation is the removal of solvent and/or other guest molecules by simple heat and vacuum treatment. This is carried out in a manner analogous to the strategies commonly used to activate zeolites and carbons. Two successful examples utilizing conventional activation include Cr-MIL-101 ( $[\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3]$ , Fig. 2a)<sup>35</sup> and UIO-66 ( $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{bdc})_{12}]$ , Fig. 2b)<sup>36</sup> which have surface areas of  $4100 \text{ m}^2 \text{ g}^{-1}$  and  $1070 \text{ m}^2 \text{ g}^{-1}$  respectively (bdc = benzene dicarboxylate). Both Cr-MIL-101 and UIO-66 exhibit exceptional thermal and chemical stability that render them stable to conventional activation protocols. Unfortunately, conventional activation has found minimal utility for accessing the full porosity of many other MOFs. Indeed this was an early challenge for the field—one however, that has largely been overcome—with many researchers noting the worst case scenario of complete loss of crystallinity and lack of porosity upon activation.<sup>37–39</sup> The reason for this is quite clear: as the sample passes through the liquid-to-gas phase



**Fig. 2** Molecular representations of the small cage of Cr-MIL-101 (a) and UIO-66 (b). Cr atoms are shown in dark blue, Zr atoms are shown in grey, oxygen and fluorine atoms in red, carbon atoms in black, and hydrogen atoms have been omitted for clarity.

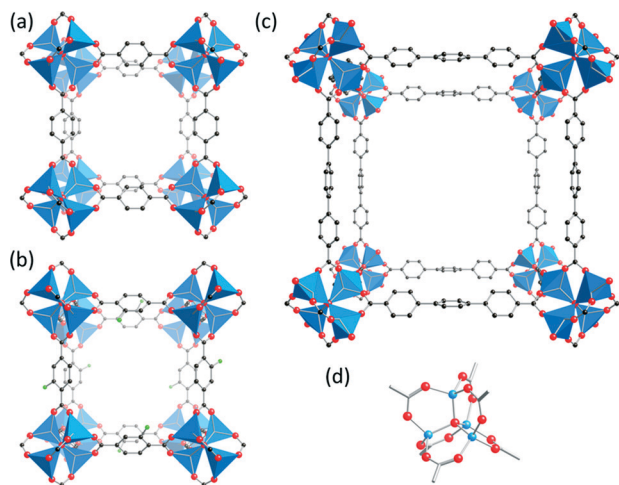
boundary (see Fig. 1), significant surface tension and capillary forces are created that cannot be offset by the moderate coordination bond strengths in many MOFs. Clearly additional activation strategies needed to be developed to fully access the large internal surface areas and porosities of most MOF materials.

### Activation by solvent-exchange

One alternative and effective activation strategy is to exchange the high-boiling point solvent (*e.g.*, DMF), required for synthesis, for a lower boiling point solvent (*e.g.*,  $\text{CHCl}_3$ ) followed by more mild activation under vacuum, a process often referred to as solvent-exchange. Lower boiling-point solvents have weaker intermolecular interactions and hence minimize surface tension and capillary forces during the activation process. Li *et al.* were apparently the first to demonstrate that solvent-exchange could be effectively used to enhance the activation of MOFs.<sup>40</sup> The iconic framework, MOF-5 (IRMOF-1,  $[\text{Zn}_4\text{O}(\text{bdc})_3]$ , Fig. 3a), was synthesized in DMF–chlorobenzene. The structure could be maintained and subsequently activated after exchanging the DMF–chlorobenzene for  $\text{CHCl}_3$ . The result is a microporous solid with a Langmuir surface area of  $2900 \text{ m}^2 \text{ g}^{-1}$ .<sup>40</sup> A more detailed analysis of two isorecticular MOFs (IRMOFs) was done by Nelson *et al.*<sup>41</sup> Utilizing conventional activation, IRMOF-3 (Fig. 3b) showed a BET surface area of  $10 \text{ m}^2 \text{ g}^{-1}$  while no  $\text{N}_2$  uptake was observed for IRMOF-16 (Fig. 3c). By exchanging DMF for  $\text{CHCl}_3$  the surface areas were increased to  $1800 \text{ m}^2 \text{ g}^{-1}$  for IRMOF-3 and  $470 \text{ m}^2 \text{ g}^{-1}$  for IRMOF-16. While impressive, even higher surface areas were expected for IRMOF-3 and IRMOF-16 (*vide infra*). Thus while solvent-exchange has been widely and successfully utilized, in some instances it still leads to materials exhibiting porosities lower than those predicted from single-crystal structures.

### Activation by $\text{scCO}_2$

**The use of  $\text{scCO}_2$  is a relatively new strategy for activating MOFs that is proving to be quite general (*vide infra*).**<sup>41</sup>  $\text{scCO}_2$



**Fig. 3** Molecular representations of (a) MOF-5, (b) IRMOF-3, (c) IRMOF-16 and (d) the  $Zn_4O$  node for MOF-5, IRMOF-3, 16. Zn atoms are shown in blue, O atoms are shown in red, C atoms are shown in black, and H atoms are not shown for clarity.

is “green” and non-toxic in nature, cost competitive, and scalable, making it a highly attractive candidate for the activation of MOF materials.<sup>42,43</sup> Activation by  $scCO_2$  builds on the conventional solvent-exchange process, as solvents such as EtOH (or other solvents miscible in liquid  $CO_2$  and compatible with the instrument can also be used) are exchanged for liquid  $CO_2$  at high pressure (*i.e.*,  $>73$  atm) over the course of hours. Next, the sample is brought above the supercritical temperature of  $CO_2$  (*i.e.*,  $31$  °C); the result is a framework occupied by  $scCO_2$ . Finally, the  $scCO_2$  apparatus is slowly vented while holding the temperature above the critical point. The key conceptual advance is going directly to the gas-phase from the supercritical phase, thereby avoiding the liquid-to-gas phase transition and its associated capillary forces (Fig. 1). In addition,  $scCO_2$  activation likely diminishes particle-to-particle aggregation.<sup>41,44</sup>

The initial demonstration on the use of  $scCO_2$  for activating MOFs was reported by Nelson, *et al.*;<sup>41</sup>  $scCO_2$  had been extensively used previously to activate other porous materials such as aerogels.<sup>54</sup> Four MOFs were studied, each containing  $Zn_4O$  nodes and dicarboxylate linkers. IRMOF-3 (Fig. 3b) exhibited a BET surface area of  $2850$   $m^2$   $g^{-1}$  representing a

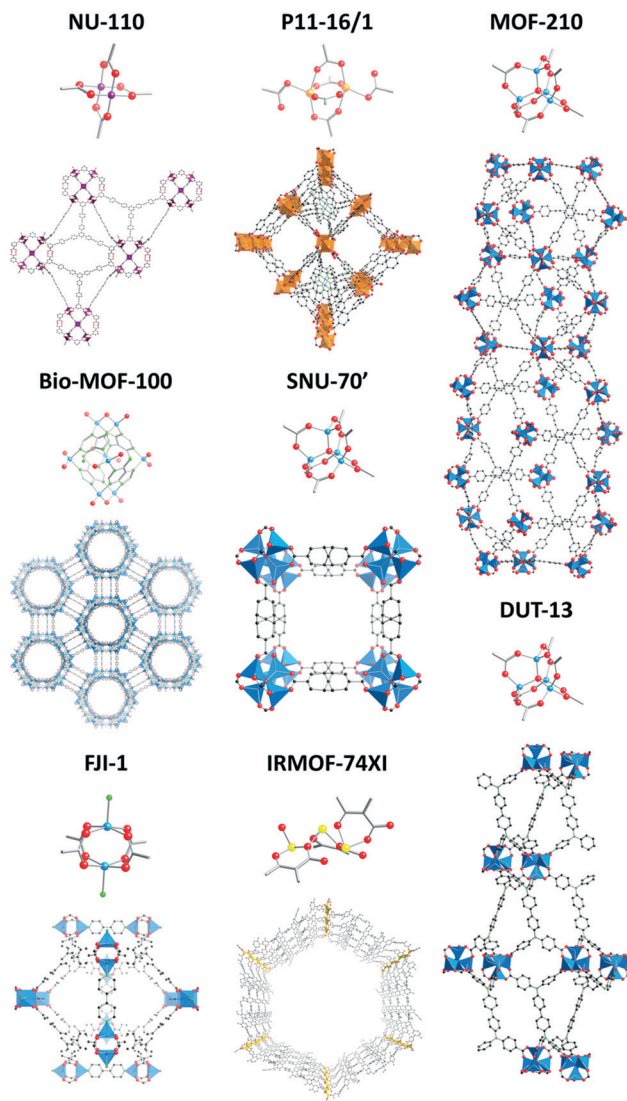
285-fold increase over conventional activation and a 1.6-fold increase over conventional solvent-exchange. As the framework is extended, IRMOF-16 (Fig. 3c) showed a BET surface area of  $1910$   $m^2$   $g^{-1}$ , which is a 4-fold increase over the material obtained by conventional solvent-exchange. (Nelson *et al.* could not obtain a BET surface area for IRMOF-16 by conventional activation.) While  $scCO_2$  activation is not always effective,<sup>55–57</sup> we have had continued success within our laboratories.<sup>4,6,58–63</sup>

Other researchers around the world have also effectively utilized the  $scCO_2$  strategy to activate a wide variety of MOFs.<sup>45–53,55–57,64–101</sup> We suspect this effectiveness, along with its low cost and scalability are important factors driving the use of  $scCO_2$  as an activation strategy. Table 1 and Fig. 4 illustrate some of the more impressive examples from around the world (a full catalogue is provided as ESI† for the interested reader). Collectively these materials represent some of the most porous MOFs known, including MOFs exhibiting: (i) the largest known surface areas;<sup>6</sup> (ii) the highest known pore volumes;<sup>6,97</sup> (iii) extreme pore and aperture sizes,<sup>52</sup> (iv) encapsulated reactive species;<sup>53</sup> and (v) dynamic structural behavior.<sup>85</sup> Clearly  $scCO_2$  activation is becoming an integral part of MOF preparation.

Very recently, Koh *et al.* introduced the concept of “flowing”  $scCO_2$  activation.<sup>102</sup> Here the sample is placed in a column and  $scCO_2$  flows through the sample (*vs.* static delivery and exchange cycling in conventional  $scCO_2$  activation) and effectively exchanges the guest solvent molecules. One important advance of the flowing  $scCO_2$  technique is that MOFs containing solvents such as DMF can be activated without exchange. We note however, that direct exchange of DMF for  $CO_2$  is also possible (in principle) in the static/exchange  $scCO_2$  strategy described by Nelson *et al.*<sup>41</sup> (DMF is miscible in liquid  $CO_2$ .<sup>103</sup>) In that earlier study, EtOH was used as an intermediate solvent because of the susceptibility of some instrument components to damage by DMF.<sup>41</sup> Certainly different designs and/or engineering strategies can be utilized to improve upon the static/exchange  $scCO_2$  technique (in fact  $scCO_2$  extraction is often “a semi-batch process in which  $CO_2$  flows in a continuous mode”<sup>43</sup>), yet the fundamental science is identical. Nonetheless, flowing  $scCO_2$  has been shown to be capable of effectively activating otherwise delicate MOFs.<sup>48,84,98</sup>

**Table 1** Selected MOFs and some of their relevant material characteristics enabled by  $scCO_2$  activation. Values are reported as they appear in the original contributions

MOF	University	BET SA ( $m^2$ $g^{-1}$ )	Pore volume ( $cm^3$ $g^{-1}$ )	Ref.
NU-110	Northwestern University	7140	4.40	6
MOF-210	UCLA	6240	3.60	45
SNU-70'	Seoul National University	5290	2.17	46
$Co_6(btb)_4(bp)_3$	Ulsan National Institute of Science & Technology	5200	2.10	47
UMCM-9	University of Michigan	4970	1.80	48
bio-MOF-100	University of Pittsburgh	4300	4.30	49
FJI-1	Fujian Institute of Research	4043	1.43	50
DUT-13	Dresden University of Technology	2532	1.98	51
IRMOF-74XI	UCLA	1760	3.41	52
P11-16/1	University of South Florida	1009	—	53

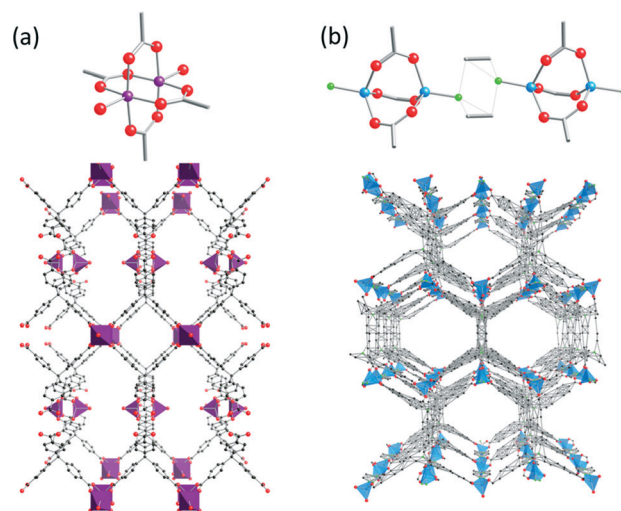


**Fig. 4** Molecular-scale representations of some interesting MOFs activated by  $\text{scCO}_2$ . Zn atoms are shown in blue, Cu atoms are shown in purple, Cd atoms in orange, Mg atoms in yellow, oxygen and fluorine atoms in red, carbon atoms in black, nitrogen atoms in green, and hydrogens have been omitted for clarity.

### Activation by freeze-drying

Activation by benzene freeze-drying is a newly developed technique for activating MOFs.<sup>67</sup> To utilize this technique, the MOF must be exchanged with and left in benzene. The sample is then frozen at 0 °C and brought back to room temperature several times. Upon the final freeze cycle, the sample is placed under vacuum at a temperature and pressure below the solvent's triple point. Finally, as the sample is warmed under reduced pressure, the benzene sublimates (*i.e.*, a direct solid-to-gas phase transition) and therefore avoids the liquid-to-gas phase transition and its associated capillary forces (Fig. 1).

Ma *et al.* demonstrated that benzene freeze-drying could be utilized to activate two isorecticular Cu paddlewheel based MOFs ( $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2]$ ) which are shown in Fig. 5.<sup>67</sup> Significant increases in BET surface areas were observed for both

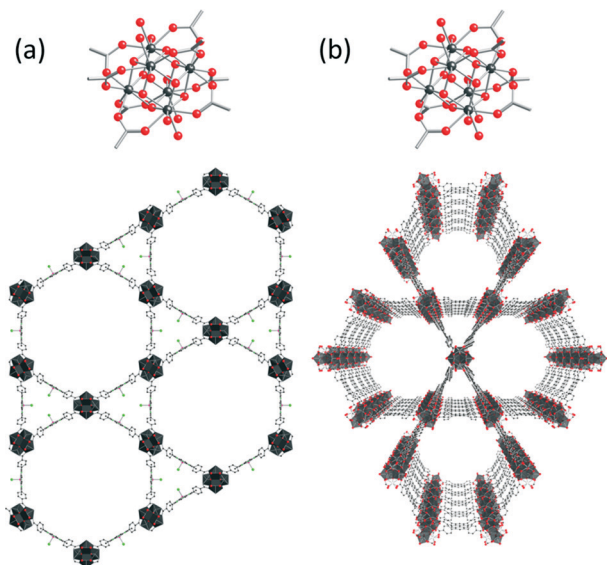


**Fig. 5** Two Cu paddlewheel based MOFs activated by freeze-drying. Cu atoms are shown in blue, O atoms are shown in red, C atoms are shown in black, and H atoms are not shown for clarity.

Cu paddlewheel based MOFs *vs.* conventional solvent-exchange. Interestingly, the powder X-ray diffraction pattern of the pristine (solvent soaked) sample is different from that of the freeze-dried sample. Ma *et al.* interpreted this change as a breathing phenomenon, however one might also speculate that the innocence of the technique is of concern. Other solvents can also be utilized for freeze-drying: He *et al.* recently demonstrated that cyclohexane could be substituted for benzene.<sup>104</sup> (This is an important practical result, as benzene is a carcinogen but cyclohexane is not.) Conventional solvent exchange yielded a material (FIR-3, Fig. 5) displaying a BET surface area of  $24 \text{ m}^2 \text{ g}^{-1}$ , while cyclohexane freeze-drying yielded a material with  $497 \text{ m}^2 \text{ g}^{-1}$ . If freeze-drying proves to be more general, we suspect that it will also become a widely used MOF activation technique.

### Activation by chemical treatment

In some instances a chemical treatment is needed to activate the MOF. One set of examples comes from the increasingly popular class of MOFs constructed from  $\text{Zr}_6$ -based nodes.<sup>36,105–107</sup> These materials have attracted interest, in part, because of their exceptional stability in aqueous environments, including highly acidic aqueous solutions. Often a large excess of acid (*e.g.*, benzoic acid) is utilized to help modulate the nucleation and growth kinetics of the MOF during synthesis. Subsequently, that acid is removed either by rigorous washing or by chemical treatment. Feng *et al.* noticed for a tetracarboxylate-porphyrin-containing MOF, PCN-222 (Fig. 6a; also known as MOF-545<sup>105</sup>) that treatment in concentrated HCl (and subsequent activation under vacuum and heat) led to a significant increase in the pore volume of the material.<sup>106</sup> However, the precise action of the HCl was not elucidated. For a similar tetracarboxylated-pyrene- and  $\text{Zr}_6$ -containing MOF (NU-1000,



**Fig. 6** Molecular-scale representations of PCN-222 (MOF-545) (a), and NU-1000 (b). Zr atoms are shown in grey, Fe atoms in pink, O in red, N and Cl in green, C in black, and H atoms are not shown for clarity.

Fig. 6b), Mondloch *et al.* found that HCl cleaves the coordinated benzoate ion from the  $Zr_6$  node.<sup>107</sup> This effectively opens up mesoporosity in this intriguing class of MOFs. Note that ionic species, in contrast to neutral species, cannot be driven from a cavity or a coordination site of an evacuated MOF simply by heating, since isolated ions lack volatility. Thus, in cases where molecules such as benzoic acid are present during synthesis (for modulation or other reasons), and where they are subsequently ligated as ions, chemical treatment may need to be considered for effective activation of the MOF.

## Conclusions

The activation of MOFs is an evolving and important topic of research. Five primary strategies have emerged: conventional activation, solvent-exchange,  $scCO_2$  activation, freeze-drying, and chemical activation. Often multiple strategies need to be considered to find conditions for optimal activation; yet, in most instances, it appears that permanent porosity can now be obtained. Each of the strategies has served to facilitate significant advances in functional MOF chemistry. **However, utilization of  $scCO_2$  processing for MOF activation has enabled the porosities of evacuated MOFs to reach previously unseen levels and has helped established MOFs as one of the most porous class of materials known to date.**

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