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1 A Robust Ultra-microporous Cationic Aluminium-  
2 based Metal-Organic Framework with a Flexible  
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16

17 **KEYWORDS:** Metal-Organic Framework, Cationic MOF, Three-dimensional electron  
18 diffraction, Hydrolytically Stable, Environment-friendly Synthesis, CO<sub>2</sub> Capture.

19 **ABSTRACT:** Al-based cationic metal-organic frameworks (MOFs) are uncommon. Here, we  
20 report a cationic Al-MOF, MIP-213(Al) ([Al<sub>18</sub>(μ<sub>2</sub>-OH)<sub>24</sub>(OH<sub>2</sub>)<sub>12</sub>(mdip)<sub>6</sub>]6Cl·6H<sub>2</sub>O) constructed  
21 from flexible tetra-carboxylate ligand (5,5'-Methylenediisophthalic acid; H<sub>4</sub>mdip). Its crystal  
22 structure was determined by the combination of three-dimensional electron diffraction (3DED)  
23 and high-resolution powder X-ray diffraction. The structure is built from infinite corner-sharing  
24 chains of AlO<sub>4</sub>(OH)<sub>2</sub> and AlO<sub>2</sub>(OH)<sub>3</sub>(H<sub>2</sub>O) octahedra forming an 18-membered rings honeycomb  
25 lattice, similar to that of MIL-96(Al), a scarce Al-polycarboxylate defective MOF. Despite sharing  
26 these structural similarities, MIP-213(Al), unlike MIL-96(Al), lacks the isolated μ<sub>3</sub>-oxo-bridged  
27 Al-clusters. This leads to an ordered defective cationic framework whose charge is balanced by  
28 Cl<sup>-</sup> sandwiched between two Al-trimers at the corner of the honeycomb, showing strong interaction  
29 with terminal H<sub>2</sub>O coordinated to the Al-trimers. The overall structure is endowed by a narrow  
30 quasi-1D channel of dimension ~4.7 Å. The Cl<sup>-</sup> in the framework restrains the accessibility of the  
31 channels, while the MOF selectively adsorbs CO<sub>2</sub> over nitrogen and possesses high hydrolytic  
32 stability.

### 33 **Introduction.**

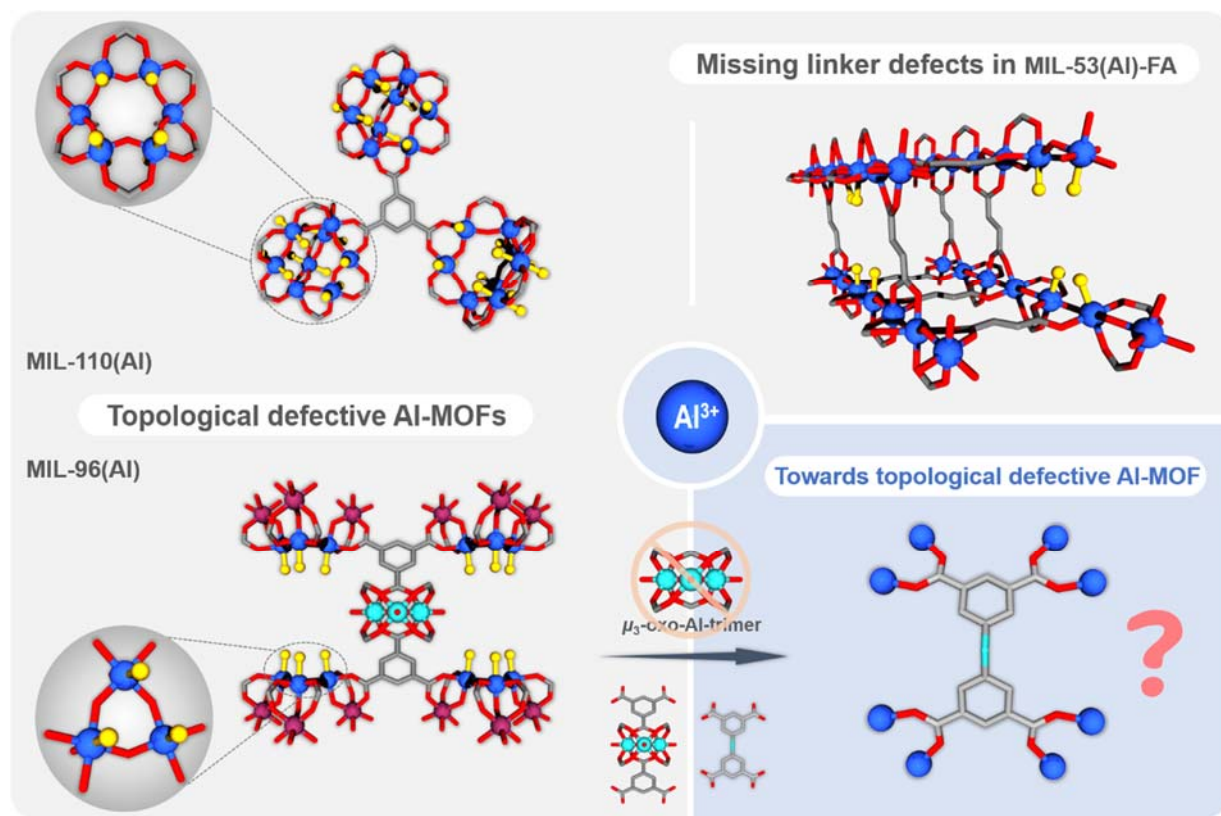
34 Metal-Organic frameworks (MOFs) constructed from inorganic nodes (metal ions,  
35 clusters, chains, layers, etc.) linked via organic linkers have emerged as a new class of porous  
36 solids. Owing to their ordered porous structure, highly tunable pore size, shape and composition,  
37 they have been proposed for a wide range of potential applications such as separation,<sup>1-8</sup> gas  
38 storage,<sup>9-10</sup> catalysis,<sup>11-13</sup> heat reallocation,<sup>14-15</sup> water harvesting,<sup>16</sup> biomedicine<sup>17-18</sup> etc. Among

39 different classes of MOFs reported so far, trivalent (Al, Cr, Fe) and tetravalent (Ti, Zr, Hf, Ce)  
40 metal polycarboxylate MOFs are considered as the most promising candidates due to their high  
41 hydrolytic stability compared to different divalent metal carboxylate MOFs.<sup>19-23</sup>

42 Defects in MOFs, that break the systematic arrangements of the atoms or motifs within the  
43 crystal of the parent framework, has become an important additional tool for tuning their  
44 properties. These are mainly related to the organic moieties but can also concern the inorganic  
45 building units. In the case of ligand defects, one can distinguish (i) topological defects where  
46 usually no bridging ligands are expected as per the topological requirement; and (ii) missing  
47 linkers where normally a topologically needed ligand is absent in the structure. In both cases, the  
48 absence of bridging ligand can be compensated by the coordination of solvents, modulators or  
49 other labile ligands. Thus, both the defects create some potential coordination vacancies around  
50 the adjacent metal/clusters and thereby drastically change the properties of the solids. Very  
51 recently, defective MOFs have attracted tremendous attention due to their unique properties  
52 compared to the non-defective MOFs.<sup>24-26</sup> Via engineering the defects, and hence the potentially  
53 uncoordinated sites, one can provide novel opportunities in adsorption,<sup>26, 27</sup> catalysis,<sup>28</sup> optical,<sup>29</sup>  
54 magnetic,<sup>29</sup> and conducting properties,<sup>27</sup> etc. Indeed, defect engineered M<sup>IV</sup>-MOFs enabled  
55 enhanced properties compared to the respective non-defective analogues, such as in catalysis,  
56 <sup>30,31,32</sup> pollutant or organic dye removal, <sup>33, 34</sup> heat allocation, <sup>35</sup> and adsorption <sup>26, 27, 36, 37</sup>. More  
57 importantly, ligand defect has a significant impact on Lewis and Bronsted acidities<sup>38</sup> of the solids  
58 giving rise to unique binding/active and/or molecular imprinted sites.<sup>28</sup> The proton conductivity of  
59 the MOFs could also be tuned eventually boosted via grafting of acidic species to the defect sites.<sup>39</sup>  
60 <sup>40</sup> It is quite common to observe defects in case of a tetravalent metal-based MOFs such as  
61 Zr/Hf/Ce based MOFs. Although these defective MOFs, particularly the Zr-based ones, show very

62 promising properties, controlling the defects onto the SBUs is not a trivial task especially when  
63 synthesized in large scale in the presence of a modulator. Similar to Zr/Hf based MOFs, very few  
64 Ti based defective MOFs could also be observed.<sup>41,42</sup> When it turns to the case of trivalent metals-  
65 based MOFs such as those based on Fe<sup>III</sup>, several defective Fe-MOFs has been observed  
66 particularly when the MOFs are derived from the Fe-based trimeric oxo/hydroxo clusters.<sup>43, 44</sup>  
67 Interestingly, in the case of Al-MOFs, there exist only very few examples of defective MOFs.<sup>45</sup>  
68 The reason for this is that the chemistry of Al MOFs can be quite complex to control leading often  
69 to different polymorphs. Besides, in most of the cases, the structures are built from Al-hydroxo  
70 chains where it is more challenging to introduce defects (Fig. 1). In contrast, the latter are, in  
71 general, more frequently observed in the case of oxo/hydroxo-cluster-based MOFs, although very  
72 scarce in the case of Al-MOFs. For instance, Al-trimesates such as MIL-96(Al) and MIL-110(Al)  
73 exhibit topological defects leading to the presence of terminal hydroxyl groups and water  
74 molecules.<sup>46,47</sup> Indeed, MIL-96(Al) comprises oxo-centered Al-trimers that are coordinated to  
75 bridging trimesates, as well as another 18-member 2D hexagonal secondary building unit made  
76 from infinite chains of AlO<sub>4</sub>(OH)<sub>2</sub> and AlO<sub>2</sub>(OH)<sub>4</sub> octahedra (arranged in a trimeric fashion). The  
77 structure contains terminals water molecules as well as terminal hydroxyl groups which potentially  
78 act as open metal sites (OMS) or coordinatively unsaturated sites, that might be also used as  
79 grafting sites for active metal ions or nanoparticles. These hydroxyls groups could also be replaced  
80 by other anions (such as chloride, fluoride, nitrate or acetate depending on the reactants used in  
81 the synthesis) as well. Despite such a possibility, it has not been exploited except in the case of  
82 fluoride.<sup>48</sup> Due to its highly functional active sites (terminal water and OH groups), this MOF has  
83 been explored for several applications such as CO<sub>2</sub> capture,<sup>49, 50</sup> catalytic dye degradation,<sup>51</sup> liquid  
84 phase absorption of *p*-hydroxybenzoic acid,<sup>51</sup> fluoride removal from water<sup>48</sup>, etc. Series of Al-

85 MOFs derived from di/tri/tetra-carboxylate linkers have been reported to date. However, reports  
86 on Al-polycarboxylate MOFs to be either cationic and/or defective remain still extremely rare.<sup>46,47</sup>  
87 For example, the typical dicarboxylates such as terephthalate (1,4-BDC),<sup>52</sup> isophthalate (1,3-  
88 BDC),<sup>53</sup> fumarate (FA)<sup>54</sup> and their derivatives led to rigid or flexible frameworks without any  
89 topological defect. Only missing linker defects have been reported such as in the case of MIL-53-  
90 FA associated with the presence of Lewis acid sites.<sup>54</sup> In case of tricarboxylates, although few  
91 trimesate MOFs exhibited structural defects, the use of benzene-1, 3, 5-tribenzoate (BTB)<sup>55</sup> does  
92 not lead to any structural defect. Similarly, different tetra carboxylates such as 1,2,4,5 benzene  
93 tetracarboxylate (BTcC),<sup>56, 57</sup> 1,2,4,5-tetrakis-(4-carboxylatophenyl)-benzene (TCPB),<sup>58</sup>  
94 tetrakis(4-carboxyphenyl) porphyrin (TCPP),<sup>59</sup> 1,3,6,8-tetrakis (*p*-benzoic acid) pyrene  
95 (TBAPy),<sup>59</sup> biphenyl tetra carboxylate (BPTC),<sup>60</sup> led only to rigid or flexible framework without  
96 any topological defect. In most cases, one can conclude that when the use of rigid linkers is  
97 considered, one ends up with rigid/flexible MOFs without any topological defects, albeit scarce  
98 exceptions. Therefore, the idea here was to explore the use of flexible linker for the construction  
99 of topologically defective Al-MOFs inspired by MIL-96(Al) structure.



100

101 **Fig. 1: Al-defective MOFs.** Examples of Al-MOFs showing topological defects and missing  
 102 linkers as well as our new proposed synthesis strategy to generate a topologically defective MOF  
 103 inspired by MIL-96(Al) structure.

104 In this regard, herein we investigated the flexible tetracarboxylic acid linker (5, 5'-  
 105 Methylene-diisophthalic acid; H<sub>4</sub>mdip; Supplementary Fig. 1) for the construction of new Al-  
 106 MOFs. After screening a wide range of synthesis conditions (solvent, pH, temperature, metal  
 107 sources, etc.), we finally obtained a new ultra-microporous MOF having a general formula  
 108  $[Al_{18}(\mu_2-OH)_{24}(OH_2)_{12}(mdip)_6]6Cl \cdot 6H_2O$  denominated as MIP-213(Al), cationic in nature (MIP  
 109 stands for Materials from Institute of Porous Materials of Paris). Its crystalline structure was  
 110 determined using a combination of three-dimensional electron diffraction (3DED) and high-  
 111 resolution Powder X-ray diffraction (HRPXRD). The MOF exhibits a hexagonal structure very

112 similar to MIL-96(Al) framework as a consequence of similar inorganic secondary building unit  
113 (SBU) built from the infinite chains of  $\text{AlO}_4(\text{OH})_2$  and  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})$  octahedra forming a  
114 honeycomb lattice based on 18-membered rings, without, however, the isolated oxo-centered Al-  
115 trimers in the case of MIP-213(Al). Consequently, MIP-213(Al) possesses chloride ions which are  
116 sandwiched between two topologically defective Al-trimers present at the corner of the  
117 honeycomb. Due to the presence of these anions, the pores along [1 0 0] become inaccessible for  
118 nitrogen at 77K. To assess the potential of this MOF for adsorption of small gas molecules, and as  
119 this compound possesses very high hydrolytic stability of interest for real applications, we have  
120 explored the selective adsorption of  $\text{CO}_2$  over  $\text{N}_2$  at room temperature, taking into account the  
121 promises of MIL-96(Al) for the  $\text{CO}_2$  capture.<sup>45</sup>

122

## 123 **Results and Discussion.**

124 MIP-213(Al) was synthesized under ambient pressure conditions employing green  
125 solvents. In a typical synthesis, H<sub>4</sub>mdip linker was dissolved in equivalent amount of 2M NaOH  
126 and added to  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  dispersed in a mixture of benzyl alcohol which was preheated to 180°C.  
127 The mixture was then refluxed at 200°C overnight. After cooling the mixture to room temperature,  
128 the solid off-white powder was isolated via filtration followed by washing with water, ethanol and  
129 drying the sample at 80°C. The dried solid product was characterized using PXRD,  
130 thermogravimetric analysis (TGA), FTIR and other advanced characterization methods  
131 (Supplementary Figs. 2-7).

## 132 **Structural Characterization and Analysis**



133           Because of the small size of the obtained crystallites (ca.100-300 nm, Supplementary Figs.  
134 8-9), we have first attempted to solve the structure from HRPXRD methods. The indexing of the  
135 HRPXRD pattern revealed that the material crystallizes in a hexagonal crystal system with space  
136 group  $P6_3/mmc$  ( $N^\circ 194$ ). However, our initial crystal structure determination from the HRPXRD  
137 data was not successful. In addition, our attempts to grow single crystals yielded above the  
138 submicronic scale, even under solvothermal conditions, were not successful (Supplementary Figs.  
139 8-9), ruling out the structure determination from single crystal X-ray diffraction even under a  
140 microfocus synchrotron source. We then considered the assistance of single crystal electron  
141 diffraction technique known as 3DED<sup>61, 62</sup> which allows obtaining structure solution from tiny  
142 crystals. The continuous rotation electron diffraction (cRED)<sup>63</sup> data has been collected using the  
143 instrumental conditions detailed in supporting information (Section: material and methods). The  
144 temperature of the sample in the TEM was decreased to 95 K using a cryo-transfer holder, to  
145 enhance the stability of the MOF under the electron beam. Two datasets (collected in less than 20  
146 seconds) were selected to be merged into a single dataset with an improved combination of  
147 resolution and completeness.

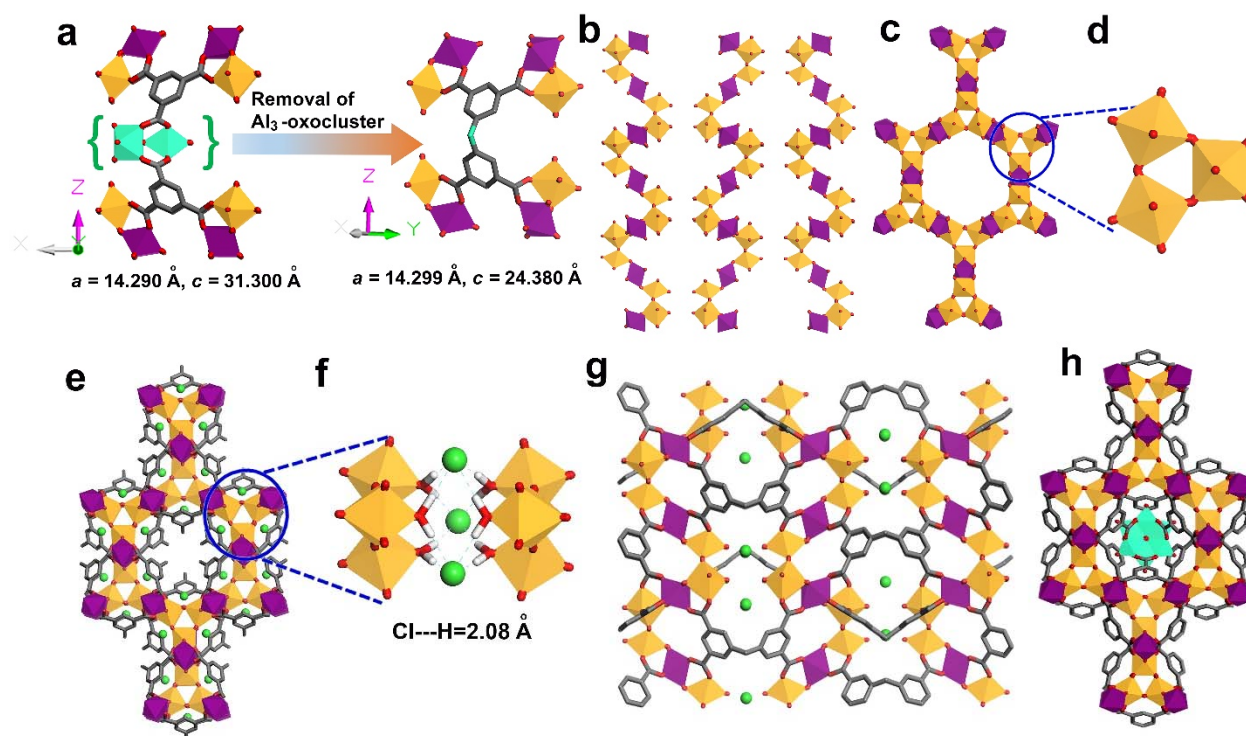
148           The structure solution step gives a 3D density map with well-identified positions for all  
149 non-hydrogen atoms (Supplementary Fig. 11). Actually, only a strong residual density present in  
150 the voids of the structure seemed to us more difficult to attribute with certainty and was initially  
151 thought to be free water molecules. Nonetheless, the presence of water molecules did not match  
152 with the observation made from the TGA data (Supplementary Fig. 6) and, therefore, we had to  
153 consider other possibilities for the inclusion of solvent molecules to the voids of this framework.  
154 STEM imaging of the MOF's particles combined with EDX spectroscopy provides a map of the  
155 elemental distribution and indicates the presence of chloride ions homogeneously in the sample

156 (Supplementary Fig. 11). The presence of this halide arises from the salt  $\text{AlCl}_3$  used as a precursor  
157 for the MOF synthesis. From the initial density map obtained from 3DED data after the structure  
158 solution step (Supplementary Fig. 11a), replacing water molecules with  $\text{Cl}^-$  ions is in good  
159 agreement with the highest residual intensity (Supplementary Fig. 12). While the 3DED data were  
160 of good quality to provide a structural model, the kinematical refinement convergences to high  $R$   
161 factors ( $R(\text{obs}) = 33.25\%$ ,  $wR(\text{obs}) = 33.15$ ) which prevented from any finer structural analysis.  
162 The obtained model was thus confirmed using a Rietveld refinement against the laboratory  
163 HRPXRD data (Supplementary Fig. 12 and Supplementary Data 1), where satisfying  $R$  factors  
164 were obtained ( $R_{\text{Bragg}} = 13.1\%$ ,  $R_{\text{F}} = 9.01\%$ ). The inclusion of the  $\text{Cl}^-$  to the voids of the framework  
165 resulted in a better match between the experimental and calculated diffraction patterns compared  
166 to inclusion of water molecules.

167 The crystal structure of MIP-213(Al) ( $P6_3/mmc$  with  $a = 14.2995(3)$  Å) shows strong  
168 similarities with the structure of MIL-96(Al) ( $P6_3/mmc$  with  $a = 14.290$  Å). Only, the  $c$  parameters  
169 of both crystal structures differ ( $31.300(6)$  versus  $24.3801(10)$  Å for MIL-96(Al) and MIP-  
170 213(Al), respectively) in agreement with the change of the framework connectivity along  $[0\ 0\ 1]$ .  
171 From the geometrical considerations, the exclusion of the  $\mu_3$ -oxo-centered isolated Al-trimers from  
172 the structure of MIL-96(Al) and the “merging” of its two isophthalate linkers along  $[0\ 0\ 1]$  into one  
173 5,5'-methylenediisophthalate are, as expected by replacing trimesate by  $\text{mdip}^{4-}$  linker, at the origin  
174 of the framework model of MIP-213(Al) (Fig. 2a).

175 The crystal structure analysis reveals that this MOF is built from the infinite chains of  
176  $\text{AlO}_4(\text{OH})_2$  and  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})$  octahedra forming a honeycomb lattice based on 18-membered  
177 rings which is very similar to the SBU present in MIL-96(Al) (Fig. 2). These SBU layers get  
178 connected by the tetracarboxylate linkers ( $\text{mdip}^{4-}$ ) and thereby generate the three-dimensional

179 framework (Fig. 2e). The 3D framework consists of narrow hexagonal channels of dimension  $\sim 4.7$   
 180  $\text{\AA}$  along  $[0\ 0\ 1]$  (Fig. 2e), which are interconnected with another narrow channels present along  $[1$   
 181  $0\ 0]$ .

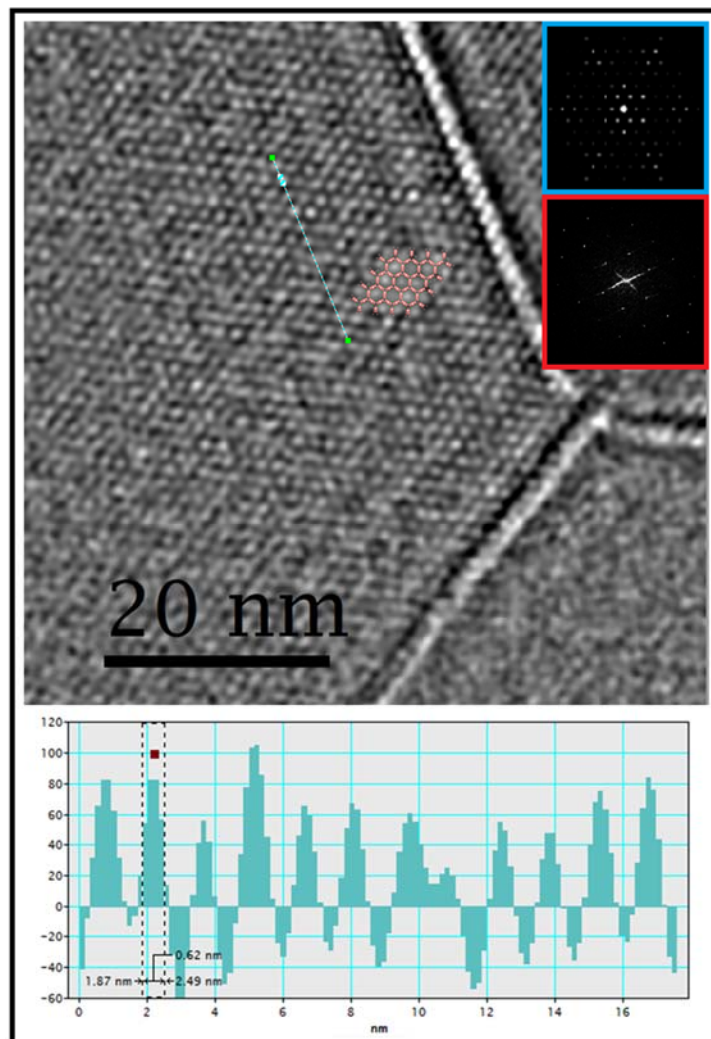


182

183 **Fig. 2: Depiction of the crystal structure of MIP-213(Al) and the structural similarities with**  
 184 **MIL-96(Al).** (a) The geometrical similarities of the framework structures of MIL-96(Al) and MIP-  
 185 213(Al). (b) Secondary building unit, the infinite chains of  $\text{AlO}_4(\text{OH})_2$  and  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})$   
 186 octahedra present in MIP-213(Al). (c) Inorganic SBU along  $[0\ 0\ 1]$  showing the infinite chains of  
 187  $\text{AlO}_4(\text{OH})_2$  and  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})$  octahedra forming an 18-membered hexagonal honeycomb  
 188 layer. (d) Al-trimers present in the corner of the hexagonal honeycomb layers. (e) 3D view of the  
 189 crystal structure of MIP-213(Al) along  $[0\ 0\ 1]$ , showing the narrow corrugated hexagonal channel.  
 190 (f) Zoom-in view at the corners of the hexagonal honeycomb showing the exact position of the  
 191 chloride ions with typical  $\text{Cl}\dots\text{H}$  interaction. (g) 3D view of the crystal structure along  $[1\ 0\ 0]$ . (h)

192 3D view of the crystal structure of MIL-96(Al) along [0 0 1]. Color code:  $\text{AlO}_4(\text{OH})_2$  polyhedra,  
193  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})$  polyhedra, carbon, oxygen and chloride atoms are in purple, orange, grey, red,  
194 and light-green, respectively ( $\mu_3$ -oxo-centered Al-trimers presented by the cyan polyhedral;  
195 hydrogen atoms are omitted for clarity).

196 According to the crystallographic structure, this framework shall be positively charged.  
197 The extra positive charge of the framework is here balanced by the presence of chloride counter  
198 ions which are typically positioned between two Al-trimers present at the corner of the honeycomb  
199 as presented in Fig. 2e and 2f. Interestingly, these chloride ions are having strong interaction with  
200 the terminal water molecules connected to the Al centers of the Al-trimers with a typical Cl...H  
201 distance of  $\sim 2.08$  Å (Fig. 2f). Due to the presence of the chloride ions the channels/cages along [1  
202 0 0] become very restricted for gas molecules to enter the channel (Fig. 2g), although such ultra-  
203 microporous windows might, as shown previously in the case of MFU-4 for instance, be accessible  
204 under specific conditions.<sup>64</sup> However, the hexagonal channels along the [0 0 1] are quite accessible  
205 to the gas molecules. Furthermore, the presence of channels of hexagonal symmetry was directly  
206 observed in real space using low-dose HRTEM imaging, from which the unit cell parameters  
207 (Supplementary Table 3) and the diameters of the channel are extracted, and the values  
208 corroborated well with those from the initial structural model from 3DED data (Fig. 3). The  
209 diameter of the channels calculated from the profile line is around 0.6 nm. The full width at half  
210 maximum (FWHM) of each peak is defined as the diameter of the corresponding channel (bright  
211 spot in the image; Fig. 3).



212  
 213 **Fig. 3: Low dose HRTEM image of MIP-213(Al).** Filtered HRTEM image of MIL-213(Al)  
 214 oriented along the [0 0 1] axis. The structural model exhibiting the hexagonal channels along the  
 215 *c* axis is superposed on the image. The insets are the FFT (red), the simulated electron diffraction  
 216 pattern (blue), generated from the ED model using the Crystdiff software.<sup>65</sup>  
 217

218 A comparative structural analysis shows very high topological similarities between the MIP-  
 219 213(Al) and MIL-96(Al) (Fig. 2h and Supplementary Fig. 13). Both frameworks are built from the  
 220 same 18-member hexagonal honeycomb layers from the infinite chains of  $\text{AlO}_4(\text{OH})_2$  and  
 221  $\text{AlO}_2(\text{OH})_3(\text{H}_2\text{O})/\text{AlO}_2(\text{OH})_4$  octahedra (Supplementary Fig. 13). The main difference between  
 222 MIL-96(Al) and MIP-213(Al) is the absence of the  $\mu_3$ -oxo-centered isolated Al-trimers in the later

223 one. In the case of MIL-96(Al), if one removes the carboxylate groups connected to the isolated  
224 oxo-centered Al-trimers leading to an isophthalate, that accounts to one-half of the mdip<sup>4+</sup> linker,  
225 then the generated SBU layer is the same as the SBU layer present in MIP-213(Al) (Supplementary  
226 Fig. 13a-13d). Subsequently, in the case of the MIL-96(Al), these SBU layers are connected to  
227 each other via the third arm of the trimesate linker connecting the isolated Al-trimers  
228 (Supplementary Fig. 13g) whereas in the case of MIP-213(Al) the SBU layers are connected via  
229 the methylene carbon of the mdip<sup>4+</sup> linker thereby generating the 3D framework (Supplementary  
230 Fig. 13h). The SBU layers are separated by a larger distance (O...O distance between the layers =  
231 6.57 Å) compared to that observed in the case of MIP-213(Al) (O...O distance between the layers  
232 = 3.20 Å) (Supplementary Fig. 13). Another important difference is that MIL-96(Al) is neutral and  
233 contains terminal water/hydroxy ligands which are connected to the Al centers of the Al-trimers  
234 present at the corner of the hexagonal honeycomb layer. In MIP-213(Al) the framework exhibits  
235 a positive charge that is balanced by the chloride ions present in between the Al-trimers from two  
236 different layers (Supplementary Fig. 13j and 1e, 1f) while all the oxygen atoms connected to the  
237 Al-trimers at the corner of the hexagonal honeycomb are from the water molecules. Thus MIP-  
238 213(Al) possesses a hexagonal corrugated narrow channel along [0 0 1]. Nevertheless, in case of  
239 MIL-96(Al) this hexagonal channel is blocked by the isolated  $\mu_3$ -oxo centered Al-trimers  
240 (Supplementary Fig. 13i). Despite being cationic in nature, this framework is highly thermally  
241 stable under oxygen atmosphere as observed from the variable temperature PXRD and TGA  
242 measurement (Supplementary Figs. 5-6). This can be supported by the fact that the chloride  
243 counter ions do not easily leave the structure due to a strong interaction with the terminal water  
244 molecules. Overall, although the structures of MIP-213 and MIL-96 are obtained from 2 different  
245 ligands (pure organic for the former, and metalo-ligand for the latter), they are structurally quite

246 well related thanks to the 18-membered hexagonal honeycomb layer SBU at the origin of both  
247 MOFs, with specific chemical features for each.

### 248 **Solid State NMR Studies**

249 Furthermore, for a deeper structural understanding solid state NMR has been considered  
250 with  $^1\text{H}$  and  $^{13}\text{C}$  NMR to provide information on the linker's structure whereas  $^{27}\text{Al}$  NMR is  
251 expected to shed light on the metal ions configurations. Supplementary figure 14 shows the  $^1\text{H}/^{13}\text{C}$   
252 two-dimensional correlation spectra evidencing the various proton and carbon environment and  
253 their connectivity. On the carbon side, intensities found around 130 ppm are assigned to the  
254 aromatic carbons (C4, C5, C14, C15) while some additional resonances found around 170 ppm  
255 and 40 ppm correspond to the carboxylates (C3) and methylene bridge (C17) carbons, respectively.  
256 To confirm this assignment, first principle calculations of NMR parameters were performed on the  
257 structure with proton positions optimized. The results are given in Supplementary Table 4 and  
258 show very reasonable agreement with the experimental spectrum (Supplementary Fig. 15).  
259 Additional resonances observed around 120 ppm and 60 ppm belongs to residual solvents (benzyl  
260 alcohol). Non-protonated carbons C3, C5 and C14 are further evidenced by their marked  
261 dependence to the contact time in the CPMAS experiments (Supplementary Fig. 16). This provides  
262 the full assignment of the six inequivalent carbons as shown in Supplementary Table 4. On the  
263 proton side, the 2D HETCOR along with the DFT calculations allows us to propose the assignment  
264 of the six inequivalent protons as shown in supplementary Fig. 17. The  $^1\text{H}$  signals absent from the  
265  $^1\text{H}$  HETCOR projection correspond to the non-carbonated protons  $\mu_2\text{-OH}$  (H13 and H19) and  
266 structural  $\text{H}_2\text{O}$  (H7), which are found, respectively, at around 2 ppm and 7 ppm, (Supplementary  
267 Fig. 18) in good agreement with the DFT calculation (Supplementary Table 4). An additional  
268 resonance is needed around 5 ppm and assigned to residual benzyl alcohol as it correlates in the

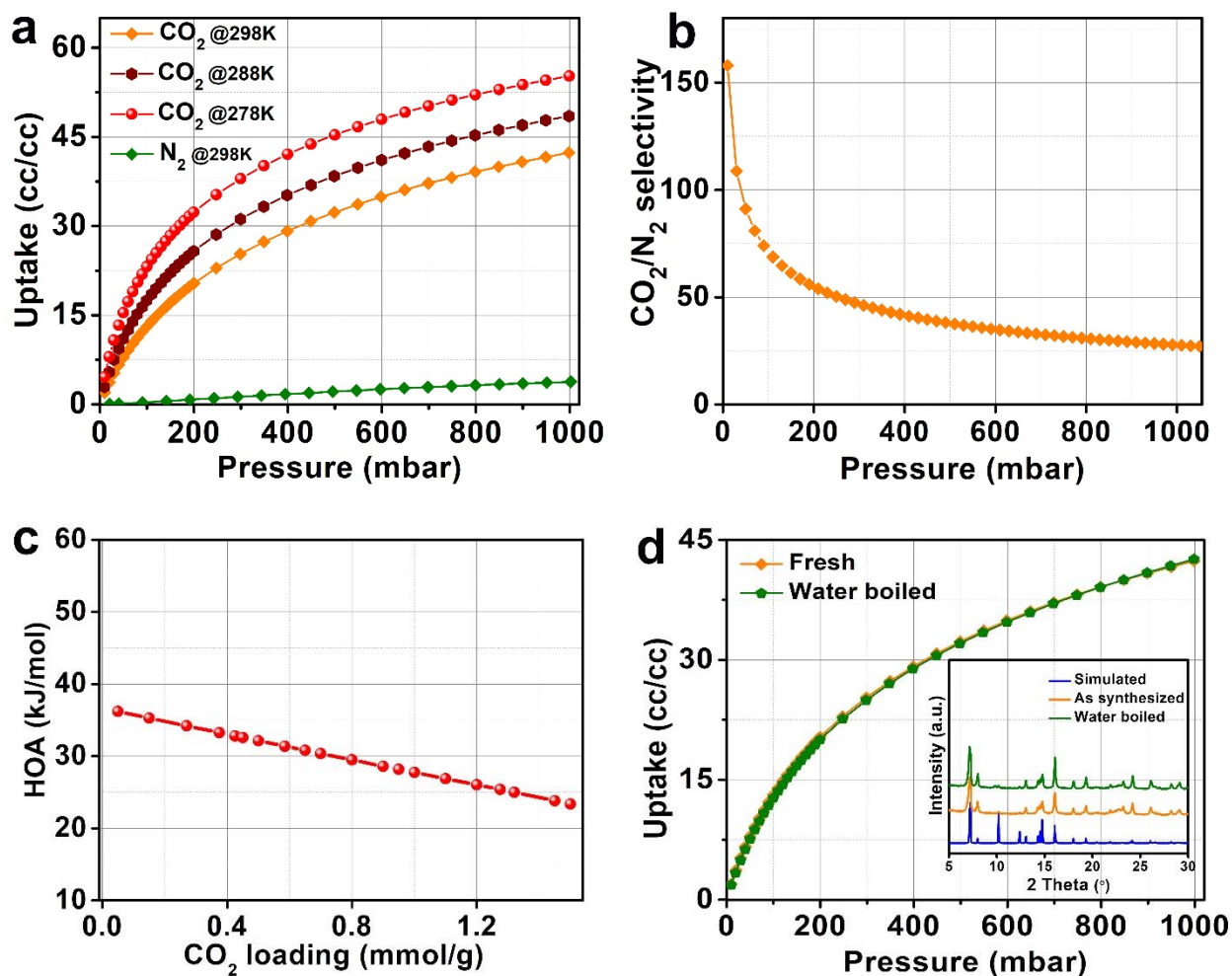
269  $^{13}\text{C}\{^1\text{H}\}$  HETCOR to the carbon site assigned above to this residual solvent. Overall, the full  
270 assignment of the  $^{13}\text{C}$  and  $^1\text{H}$  spectra confirm the structural model of the linkers derived in the  
271 preceding sections. The  $^{27}\text{Al}$  spectra shown a complex lineshape resulting from overlapping sites  
272 partially resolved in an MQMAS experiments (Supplementary Figs. 19-20), showing 3  
273 components with distribution of NMR parameters and, hence, distribution of structural  
274 environments. This 2D experiment can be satisfactorily simulated with 1 site presenting a strong  
275 quadrupolar coupling constant ( $C_Q \sim 7.3$  MHz) and 2 with rather small ones ( $C_Q \sim 2.5$  MHz). The  
276 crystal structure predicts only two inequivalent aluminum sites (Al8 and Al9) and the DFT  
277 calculation shows that they possess contrasted  $C_Q$ s:  $C_Q(\text{Al8}) = 8.65$  MHz and  $C_Q(\text{Al9}) = 1.24$  MHz,  
278 allowing to assign the site with  $C_Q \sim 7.3$  MHz to Al8 of the form  $\text{Al}(\text{OAl})_2(\text{OC})_4$ . For the Al9 site  
279 of the form  $\text{Al}(\text{OAl})_3(\text{OC})_2(\text{H}_2\text{O})$ , we expect a smaller  $C_Q$ , but two sharp resonances are observed  
280 experimentally. A double-quantum 2Q-filtered experiment (Supplementary Fig. 21) which selects  
281 aluminum with close-by proximities, does remove the sharp line in the middle of the spectrum,  
282 this one being therefore attributed to an isolated aluminum arising from an impurity. The full  
283 2Q/1Q experiment also evidences Al9/Al9 and Al9/Al8 proximities, and absence of Al8/Al8  
284 proximities, in full agreement with the crystal structure. This allows an attribution of the two  
285 resonances corresponding to the two inequivalent aluminum sites expected from the  
286 aforementioned structure and confirms the validity of the structure derived above.

## 287 **Gas Sorption Analysis**

288 As established from the structural investigation, the material possesses microporous  
289 channels. The permanent porosity of this MOF was established from the  $\text{N}_2$  sorption at 77 K  
290 (Supplementary Fig. 22). The material does not adsorb much  $\text{N}_2$  even at 77 K (saturation uptake  
291  $\sim 1.0$  mmol $\text{g}^{-1}$ ) with a calculated BET surface area of 60  $\text{m}^2\text{g}^{-1}$ , which is much lower compared to



292 the one of MIL-96(Al) ( $>600 \text{ m}^2\text{g}^{-1}$ ). This can be explained in the case of MIP-213(Al), by the fact  
293 that the channels along [1 0 0] are inaccessible to  $\text{N}_2$  due to the presence of the chloride ions right  
294 at the center of the channels (details on ion exchange attempts are available in the Supplementary  
295 Information). Although, in case of MIP-213 the channel along the [0 0 1] are open but the small  
296 channel diameter restricts the  $\text{N}_2$  molecule to diffuse. Considering the ultra-micropores present in  
297 MIP-213(Al), we further tested the  $\text{CO}_2$  capture properties of this MOF at room temperature (Fig.  
298 4 and Supplementary Data 2). Interestingly at 298K the material selectively adsorbs  $\text{CO}_2$  over  $\text{N}_2$   
299 ( $\text{CO}_2$  uptake = 17.5 cc/cc at 0.15 bar against 3.8 cc/cc for  $\text{N}_2$  at 298K and 1 Bar). Such a lower  
300  $\text{CO}_2$  uptake of MIP-213(Al) compared to MIL-96(Al) was expected because of the presence of  
301 narrow channels partially occupied by the chloride ions in MIP-213(Al). An IAST prediction from  
302 the single component isotherms yielded a  $\text{CO}_2/\text{N}_2$  selectivity of 60 (Fig. 4b and Supplementary  
303 Fig. 23) at 0.15 bar which is quite good in a view of post-combustion carbon capture applications.  
304 In fact, the selectivity value is slightly higher than some of the Al, Sc and Zr based microporous  
305 MOFs such as MIL-96(Al) (S= 40), ScBDC (S=40), UiO-66(Zr) (S=12), UiO-66(Zr)\_BTeC  
306 (S=30), UiO-66(Zr)\_NH<sub>2</sub> (S=37) but comparable/slightly less than some of the microporous Al/Ti  
307 MOFs such as MIL-91(Al) (S=68), MIL-91(Ti) (S=150), MIL-69(Al) (S=120).<sup>49,66</sup>



308

309 **Fig. 4: CO<sub>2</sub> and N<sub>2</sub> sorption data of MIP-213(Al) showing its selective CO<sub>2</sub> capture**  
 310 **property and high hydrolytic stability.** (a) CO<sub>2</sub> and N<sub>2</sub> isotherms on MIP-213(Al) collected at  
 311 different temperatures. (b) CO<sub>2</sub>/N<sub>2</sub> selectivity predicted using IAST model employing a nominal  
 312 composition of 15CO<sub>2</sub>:85N<sub>2</sub>. (c) HOA plot derived from a virial calculation employing CO<sub>2</sub>  
 313 isotherm at 3 different temperatures (278, 288 and 298 K). (d) A comparative 298 K CO<sub>2</sub> isotherm  
 314 of the fresh sample and water boiled sample showing the hydrolytic stability of the MOF. The inset  
 315 shows the PXRD patterns (Cu K $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) of the fresh and water boiled sample.

316 Furthermore, a virial analysis of the CO<sub>2</sub> isotherms at 273, 283 and 298 K yielded a zero coverage  
 317 heat of adsorption (HOA) of 37 kJmol<sup>-1</sup> (Fig. 4c and Supplementary Fig. 24). The water sorption

318 isotherm at 298 K shows a clear type I isotherm indicating very strong interactions between the  
319 water molecules and the framework at low pressure (Supplementary Fig. 25). This is in good  
320 agreement with the structural model. One of the most important properties of MOFs to be  
321 implemented in any potential industrial applications is the robustness under humid atmosphere or  
322 the hydrolytic stability of the MOF.<sup>67</sup> Considering this we have subjected this MOF for stability  
323 tests under boiling water conditions. Interestingly, there was no sign of structural or chemical  
324 degradation even after 24 hours of boiling as evidenced from the PXRD data (Fig. 4d) as well as  
325 CO<sub>2</sub> adsorption isotherm on the water boiled sample, which further confirms the hydrolytic  
326 stability or robustness of this MOF (Fig. 4d).

327 In conclusion, based on a fine structural analysis and a “merging” strategy when replacing  
328 tricarboxylate by a flexible tetracarboxylate linker, we have developed a rare example of cationic  
329 Al-based MOF with topological defective sites. The structure elucidation from both 3DED and  
330 HRPXRD data for this MOF was complemented by low-dose HRTEM imaging and EDX chemical  
331 mapping. The MOF is built from the infinite chains of AlO<sub>4</sub>(OH)<sub>2</sub> and AlO<sub>2</sub>(OH)<sub>4</sub> octahedra which  
332 form 18-membered hexagonal honeycomb layers, similar to those present in MIL-96(Al).  
333 Although both MOFs share similar SBU, they strongly differ in some other chemical aspects.  
334 Unlike MIL-96(Al), MIP-213(Al) does not contain isolated  $\mu_3$ -oxo-centered Al-trimers leading to  
335 an overall cationic framework, where chloride ions balance the extra positive charge in the  
336 framework. Although the presence of these chloride ions in the framework makes this solid less  
337 porous (at least to N<sub>2</sub> at 77 K) compared to MIL-96(Al), this MOF still selectively adsorb CO<sub>2</sub>  
338 over N<sub>2</sub> with a selectivity of 60 at 0.15 bar and 298 K. Moreover, the reported MOF possess high  
339 hydrolytic stability and could be applied for many other applications utilizing the  
340 defective/cationic nature and/or Lewis acidity. Considering the challenge of developing Al MOFs

341 with controlled defects, this study will pave the way for the design of new Al-based defective  
342 MOFs for versatile applications in near future.

### 343 **Methods.**

#### 344 **Synthesis of MIP-213(Al).**

##### 345 **Milligram-scale synthesis:**

346 MIP-213(Al) was synthesized in a typical ambient pressure reflux synthesis method employing  
347  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_4\text{mdip}$  linker, water, benzyl alcohol and NaOH. In a typical synthesis, 0.723g of  
348  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (3 mmol) was dispersed in 18 ml of Benzyl alcohol and the mixture was heated to 180  
349 °C. To this a solution of  $\text{H}_4\text{mdip}$  0.345g (1 mmol) in 2ml of 2M NaOH was added under continuous  
350 stirring. Additional 8 ml distilled water was added to the mixture. The reaction mixture was then  
351 refluxed at 200 °C for 16 hours. After cooling the reaction to room temperature, the off-white  
352 powder was filtered and washed with 20 ml of water and 10 ml of ethanol. The final product was  
353 then air dried (yield = 440 mg). The powder product was then characterized using PXRD, IR, TGA  
354 and adsorption analysis. The synthesis can be done in a different scale as per the requirement.

##### 355 **Gram-scale synthesis:**

356 In a typical synthesis, 7.23g of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (30 mmol) was dispersed in 180 ml of Benzyl alcohol  
357 and the mixture was heated to 180 °C. To this a solution of  $\text{H}_4\text{mdip}$  3.45g (10 mmol) in 20ml of  
358 2M NaOH was added under continuous stirring. Additional 80 ml distilled water was added to the  
359 mixture. The reaction mixture was then refluxed at 200°C for 16 hours. After cooling the reaction  
360 to room temperature, the off-white powder was filtered and washed with 100ml of water and 60  
361 ml of ethanol. The final product was then air dried (yield = 4.66 g).

362 **Note:** The synthesis temperature could be reduced up to 160 °C but with longer synthesis time (up  
363 to 48h).

364 **Characterization of MIP-213(Al).**

365 **The crystal structure determination and refinement from HRPXRD:**

366 The unit cell parameters and the space group of MIP-213(Al) have been indexed using the program  
367 EXPO2014.<sup>68</sup> Although accurate cell parameters and the space group were determined from the  
368 indexing of the powder pattern, crystal structure determination was not successful (*See supporting*  
369 *information for more details*). The refinement using the Rietveld method was based on the model  
370 from 3DED using Fullprof.<sup>69</sup> The refinement of the powder X-ray diffraction data required the  
371 inclusion of benzyl alcohol solvent in the large cavities.

372 **cRED data collection and structure determination:**

373 The cRED data were collected on a JEOL F200 cold-FEG operated at 200 kV, equipped with a  
374 GATAN RIO16 camera. A series of 2D electron diffraction patterns are acquired while  
375 continuously rotating the crystal using the Digital Micrograph plugin insteadMatic.<sup>70</sup> The  
376 diameter of the parallel beam was set to 300 nm obtained by inserting a 10  $\mu\text{m}$  condenser aperture.  
377 The sample was cooled down to a lower temperature (95K) in the TEM using a Gatan Elsa<sup>TM</sup> cryo-  
378 transfer tomography holder, to reduce the electron beam damage.

379 Several cRED datasets were recorded and processed using PETS 2.<sup>71</sup> Two cRED datasets  
380 (Supplementary Table 1) collected on isolated crystals were kept to obtain the result presented  
381 here. These two datasets were merged in order to obtain a data completeness of 95.3% for a 0.71  
382 Å resolution. The structure was solved using SUPERFLIP program (charge flipping method)<sup>72</sup> and  
383 refined using JANA2020<sup>73</sup> using electron scattering factors. The density maps (electrostatic  
384 potential map in Supplementary Figure 11 and difference Fourier maps in Supplementary Figure  
385 12) are visualized using VESTA.<sup>74</sup> A summary of the data collection and structure refinement are  
386 given in Supplementary Table 2.

387 **Low-dose high-resolution transmission electron microscopy:**

388 Low-dose HRTEM data were collected on the FEI Titan 80-300 E-TEM microscope equipped  
389 with the Gatan K2 direct-detection electron counting camera (DDEC), operated at 300 kV. An  
390 electron dose rate of  $8 \text{ e}^- \text{Å}^{-2}$  is used. The “HRTEM filter” was used to apply a Wiener filter,  
391 followed by the Average Background Subtraction Filter (ABSF). The details to calculate the  
392 channel diameter is provided in the supporting information.

393 **High-resolution scanning transmission microscopy:**

394 High-resolution scanning transmission microscopy images (HRSTEM) were acquired on a FEI  
395 Titan Themis microscope 200 corrected for spherical aberrations on the probe, operating at 200  
396 kV, equipped with a Ceta 16M hybrid camera from ThermoFischer Scientific capable of working  
397 under low-dose conditions.

398 **Solid state NMR:**

399  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$  spectra were obtained on a Bruker Avance III 17.6 T spectrometer operating at  
400 750.0 MHz using magic angle spinning at 30 kHz. Direct spectra were obtained using a Hahn echo  
401 sequence with radiofrequency fields. Direct  $^{13}\text{C}$  NMR spectra were obtain using a CPMAS  
402 experiment.  $^{27}\text{Al}$  was obtained using a quantitative pulse at  $\nu_{\text{rf}}(^{27}\text{Al}) = 50 \text{ kHz}$ , and a recycle delay  
403 of 0.3 s based on estimated T1 measurements done by saturation-recovery experiments. 2Q/1Q  
404  $^{27}\text{Al}$ - $^{27}\text{Al}$  correlation was used with a  $R2_1^2$  recoupling (*A detailed procedure is provided in the*  
405 *supporting information*).

406

407 **ASSOCIATED CONTENT**

408 **Data Availability**

409 Supporting information contains all the synthetic and experimental details as well as  
410 Supplementary methods (PXRD, N<sub>2</sub>, CO<sub>2</sub> and water sorption, TGA, FTIR, etc.) and data. This  
411 material is available free of charge from <https://www.nature.com/commschem/> or from the authors  
412 on request. The crystallographic structure reported in this study has been deposited at the  
413 Cambridge Crystallographic Data Centre (CCDC), under deposition number 2246502. CIF can be  
414 obtained free of charge from The Cambridge Crystallographic Data Centre or directly downloaded  
415 from the editor webpage as Supplementary Data 1. IAST and related numerical source data are  
416 available as Supplementary Data 2.

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421

### 422 **Author Contributions**

423 The manuscript was written through the contributions of all authors. All authors have given  
424 approval to the final version of the manuscript. SN performed towards the synthesis,  
425 characterization and CO<sub>2</sub> capture studies of the material. AM, ID, GP, PB and CS contributed  
426 towards the structure solution. IC and PF contributed towards the NMR experiments and analyzed  
427 the data. GM and CS supervised the work and contributed towards the overall concept.

### 428 **Notes**

429 The authors declare no competing interest.

430

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439

440 **REFERENCES**

- 441 (1) Barea, E., Montoro, C., & Navarro, J. A. R. Toxic gas removal – metal–organic frameworks  
442 for the capture and degradation of toxic gases and vapours. *Chem. Soc. Rev.*, **43**, 5419-5430  
443 (2014).
- 444 (2) Woellner, M. *et al.* Adsorption and Detection of Hazardous Trace Gases by Metal–Organic  
445 Frameworks. *Adv. Mater.* **30**, 1704679 (2018).
- 446 (3) Han, X., Yang, S., & Schröder, M. Porous metal–organic frameworks as emerging sorbents  
447 for clean air. *Nat. Rev. Chem.* **3**, 108-118 (2019).
- 448 (4) Carter, J. H. *et al.* Exceptional Adsorption and Binding of Sulfur Dioxide in a Robust  
449 Zirconium-Based Metal–Organic Framework. *J. Am. Chem. Soc.* **140**, 15564-15567 (2018).
- 450 (5) Tchalala, M. R. *et al.* Fluorinated MOF platform for selective removal and sensing of SO<sub>2</sub> from  
451 flue gas and air. *Nat. Commun.* **10**, 1328; 10.1038/s41467-019-09157-2 (2019).



- 452 (6) Zhang, Z., Yao, Z. -Z., Xiang, S. & Chen, B. Perspective of microporous metal–organic  
453 frameworks for CO<sub>2</sub> capture and separation. *Energy Environ. Sci.* **7**, 2868-2899 (2014).
- 454 (7) Zhao, X., Wang, Y., Li, D. S., Bu, X. & Feng, P. Metal–Organic Frameworks for Separation.  
455 *Adv. Mater.* **30**, 1705189 (2018).
- 456 (8) Kumar, A., *et al.* Direct Air Capture of CO<sub>2</sub> by Physisorbent Materials. *Angew. Chem. Int. Ed.*  
457 **54**, 14372-14377 (2015).
- 458 (9) Mason, J. A., Veenstra, M. & Long, J. R. Evaluating metal–organic frameworks for natural  
459 gas storage. *Chem. Sci.* **5**, 32-51 (2014).
- 460 (10) Li, B., Wen, H. M., Zhou, W. & Chen, B. Porous Metal–Organic Frameworks for Gas  
461 Storage and Separation: What, How, and Why?. *J. Phys. Chem. Lett.* **5**, 3468-3479 (2014).
- 462 (11) Pascanu, V., Miera, G. G., Inge, A. K. & Martín-Matute, B. Metal–Organic Frameworks  
463 as Catalysts for Organic Synthesis: A Critical Perspective. *J. Am. Chem. Soc.* **141**, 7223-7234  
464 (2019).
- 465 (12) Kornienko, N. *et al.* Metal–Organic Frameworks for Electrocatalytic Reduction of Carbon  
466 Dioxide. *J. Am. Chem. Soc.* **137**, 14129-14135 (2015).
- 467 (13) Zheng, F., Zhang, Z., Zhang, C. & Chen, W. Advanced Electrocatalysts Based on  
468 Metal–Organic Frameworks. *ACS Omega* **5**, 2495-2502 (2020).
- 469 (14) Lenzen, D. *et al.* A metal-organic framework for efficient water-based ultra-low-  
470 temperature-driven cooling. *Nat. Commun.* **10**, 3025; 10.1038/s41467-019-10960-0 (2019).

- 471 (15) Wang, S. *et al.* A robust large-pore zirconium carboxylate metal–organic framework for  
472 energy-efficient water-sorption-driven refrigeration. *Nat. Energy* **3**, 985-993; 10.1038/s41560-  
473 018-0261-6 (2018).
- 474 (16) Kim, H. *et al.* Water harvesting from air with metal-organic frameworks powered by  
475 natural sunlight. *Science*, **356**, 430-434 (2017).
- 476 (17) McKinlay, A. C. *et al.* BioMOFs: Metal–Organic Frameworks for Biological and Medical  
477 Applications. *Angew. Chem. Int. Ed.* **49**, 6260-6266 (2010).
- 478 (18) Pinto, R. V. *et al.* Tuning Cellular Biological Functions Through the Controlled Release of  
479 NO from a Porous Ti-MOF. *Angew. Chem. Int. Ed.* **59**, 5135-5143 (2020).
- 480 (19) Serre, C. *et al.* Very Large Breathing Effect in the First Nanoporous Chromium (III)-Based  
481 Solids: MIL-53 or CrIII(OH)·{O<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–CO<sub>2</sub>}·{HO<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–CO<sub>2</sub>H}<sub>x</sub>·H<sub>2</sub>O<sub>y</sub>. *J. Am. Chem.*  
482 *Soc.* **124**, 13519-13526 (2002).
- 483 (20) Férey, G. *et al.* A Chromium Terephthalate-Based Solid with Unusually Large Pore  
484 Volumes and Surface Area. *Science* **309**, 2040-2042 (2005).
- 485 (21) Abtab, S. M. T. *et al.* Reticular Chemistry in Action: A Hydrolytically Stable MOF  
486 Capturing Twice Its Weight in Adsorbed Water. *Chem* **4**, 94-105 (2018).
- 487 (22) Dai, S., Nouar, F., Zhang, S., Tissot, A. & Serre, C. One-Step Room-Temperature  
488 Synthesis of Metal (IV) Carboxylate Metal-Organic Frameworks. *Angew. Chem.* **133**, 4328-  
489 4334 (2021).

- 490 (23) Mouchaham, G. *et al.* Metal-Organic Frameworks and Water: ‘From Old Enemies to  
491 Friends’. *Trends in Chemistry* **2**, 910 (2020).
- 492 (24) Ren, J. *et al.* Structural defects in metal–organic frameworks (MOFs): Formation, detection  
493 and control towards practices of interests. *Coord. Chem. Rev.* **349**, 169-197 (2017).
- 494 (25) Sholl, D. S. & Lively, R. P. Defects in Metal-Organic Frameworks: Challenge or  
495 Opportunity?. *J. Phys. Chem. Lett.* **6**, 3437-3444 (2015).
- 496 (26) Thornton, A. W., Babarao, R., Jain, A., Trouselet, F. & Coudert, F.-X. Defects in metal-  
497 organic frameworks: a compromise between adsorption and stability? *Dalton Trans.* **45**, 4352-  
498 4359 (2016).
- 499 (27) Dissegna, S., Epp, K., Heinz, W. R., Kieslich, G. & Fischer, R. A. Defective Metal-Organic  
500 Frameworks. *Adv. Mater.* **30**, 1704501 (2018).
- 501 (28) García-Baldoví, A. *et al.* Active site imprinting on Ti oxocluster metal–organic  
502 frameworks for photocatalytic hydrogen release from formic acid. *Energy Environ. Sci.* **16**,  
503 167-177 (2023).
- 504 (29) Xiang, W., Zhang, Y., Chen, Y., Liu, C. J. & Tu, X. Synthesis, characterization and  
505 application of defective metal-organic frameworks: current status and perspectives. *J. Mater.*  
506 *Chem. A*, **8**, 21526-21546 (2020).
- 507 (30) Fu, Q. *et al.* Defect-engineered MOF-808 with highly exposed Zr sites as highly efficient  
508 catalysts for catalytic transfer hydrogenation of furfural. *Fuel* **327**, 125085 (2022).

- 509 (31) Rimoldi, M. *et al.* Catalytic Zirconium/Hafnium-Based Metal-Organic Frameworks. *ACS*  
510 *Catal.* **7**, 997-1014 (2017).
- 511 (32) Liu, X., Hu, C., Wu, J., Cui, P. & Wei, F. Defective NH<sub>2</sub>-UiO-66 (Zr) effectively  
512 converting CO<sub>2</sub> into cyclic carbonate under ambient pressure, solvent-free and co-catalyst-free  
513 conditions. *Chin. J. Chem. Eng.* **43**, 222-229 (2022).
- 514 (33) Yuan, N., Gong, X., Sun, W. & Yu, C. Advanced applications of Zr-based MOFs in the  
515 removal of water pollutants. *Chemosphere* **267**, 128863 (2021).
- 516 (34) Liu, B., Liu, M., Xie, Z., Li, Y. & Zhang, A. Performance of defective Zr-MOFs for the  
517 adsorption of anionic dyes. *J. Mater. Sci.* **57**, 5438-5455 (2022).
- 518 (35) Cho, K. H. *et al.* Defective Zr-Fumarate MOFs Enable High-Efficiency Adsorption Heat  
519 Allocations. *ACS Appl. Mater. Interfaces* **13**, 1723-1734 (2021).
- 520 (36) Yoskamtorn, T. *et al.* Responses of Defect-Rich Zr-Based Metal–Organic Frameworks  
521 toward NH<sub>3</sub> Adsorption. *J. Am. Chem. Soc.* **143**, 3205-3218 (2021).
- 522 (37) Lin, S., Zhao, Y. & Yun, Y. S. Highly Effective Removal of Nonsteroidal Anti-  
523 inflammatory Pharmaceuticals from Water by Zr(IV)-Based Metal-Organic Framework:  
524 Adsorption Performance and Mechanisms. *ACS Appl. Mater. Interfaces*, **10**, 28076-28085  
525 (2018).
- 526 (38) Taddei, M. When defects turn into virtues: The curious case of zirconium-based metal-  
527 organic frameworks. *Coord. Chem. Rev.* **343**, 1-24 (2017).

- 528 (39) Chena, X. & Li, G. Proton conductive Zr-based MOFs. *Inorg. Chem. Front.* **7**, 3765-3784  
529 (2020).
- 530 (40) Basu, O., Mukhopadhyay, S., Laha, S., Das, S. K. Defect Engineering in a Metal-Organic  
531 Framework System to Achieve Super-Protonic Conductivity. *Chem. Mater.* **34**, 6734-6743  
532 (2022).
- 533 (41) Wang, S. *et al.* A phase transformable ultrastable titanium-carboxylate framework for  
534 photoconduction. *Nat. Commun.* **9**, 1660; 10.1038/s41467-018-04034-w (2018).
- 535 (42) Wang, S. *et al.* Toward a Rational Design of Titanium Metal-Organic Frameworks. *Matter*  
536 **2**, 440-450 (2020).
- 537 (43) Duan, T., Jiang, H., Wu, W., Lin, D., Yang, K. Defective iron based metal-organic  
538 frameworks derived from zero-valent iron for highly efficient fenton-like catalysis, *J. Hazard.*  
539 *Mater.* **445**, 130426 (2023).
- 540 (44) Feng, D. *et al.* Kinetically tuned dimensional augmentation as a versatile synthetic route  
541 towards robust metal-organic frameworks. *Nat Commun.* **5**, 5723 (2014).
- 542 (45) Shan, Y., Zhang, G., Shi, Y. & Pang, H. Synthesis and catalytic application of defective  
543 MOF materials. *Cell Reports Physical Science* **4**, 101301 (2023)
- 544 (46) Loiseau, T. *et al.* MIL-96, a Porous Aluminum Trimesate 3D Structure Constructed from  
545 a Hexagonal Network of 18-Membered Rings and  $\mu_3$ -Oxo-Centered Trinuclear Units. *J. Am.*  
546 *Chem. Soc.* **128**, 10223-10230 (2006).

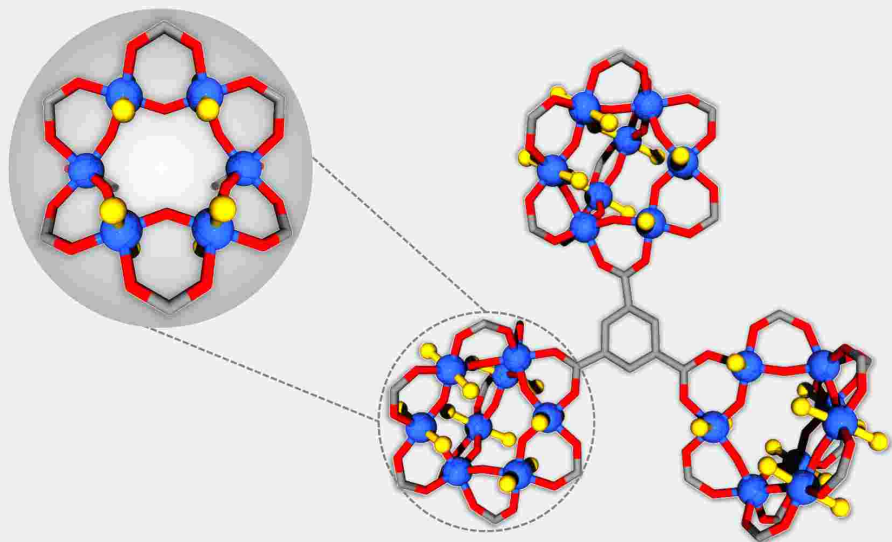
- 547 (47) Volkringer, C. *et al.* A microdiffraction set-up for nanoporous metal–organic-framework-  
548 type solids. *Nat. Mater.* **6**, 760-764 (2007).
- 549 (48) Wang, X. *et al.* Synthesis and Study of an Efficient Metal-Organic Framework Adsorbent  
550 (MIL-96(Al)) for Fluoride Removal from Water. *J. Nanomater.* **2019**, Article ID 3128179;  
551 10.1155/2019/3128179 (2019).
- 552 (49) Benoit, V. *et al.* A promising metal–organic framework (MOF), MIL-96(Al), for CO<sub>2</sub>  
553 separation under humid conditions. *J. Mater. Chem. A* **6**, 2081-2090 (2018).
- 554 (50) Benzaqui, M. *et al.* Revisiting the Aluminum Trimesate-Based MOF (MIL-96): From  
555 Structure Determination to the Processing of Mixed Matrix Membranes for CO<sub>2</sub> Capture.  
556 *Chem. Mater.* **29**, 10326-10338 (2017).
- 557 (51) Rizwan, M. *et al.* Cascade applications of robust MIL-96 metal organic frameworks in  
558 environmental remediation: Proof of concept. *Chem. Eng. J.* **341**, 262-271 (2018).
- 559 (52) Loiseau, T. *et al.* A Rationale for the Large Breathing of the Porous Aluminum  
560 Terephthalate (MIL-53) Upon Hydration. *Chem. Eur. J.* **10**, 1373-1382 (2004).
- 561 (53) Reinsch, H. *et al.* Structures, Sorption Characteristics, and Nonlinear Optical Properties of  
562 a New Series of Highly Stable Aluminum MOFs. *Chem. Mater.* **25**, 17-26 (2013).
- 563 (54) Alvarez, E. *et al.* The structure of the aluminum fumarate metal-organic framework A520,  
564 *Angew. Chem. Int. Ed.* **54**, 3664 -3668 (2015).
- 565 (55) Reinsch, H. *et al.* A new aluminium-based microporous metal-organic framework:  
566 Al(BTB) (BTB = 1,3,5-benzenetrisbenzoate), *Micro. Meso. Mater.* **157**, 50-55 (2012).

- 567 (56) Volkringer, C. *et al.* Occurrence of Uncommon Infinite Chains Consisting of Edge-Sharing  
568 Octahedra in a Porous Metal Organic Framework-Type Aluminum Pyromellitate  
569  $\text{Al}_4(\text{OH})_8[\text{C}_{10}\text{O}_8\text{H}_2]$  (MIL-120): Synthesis, Structure, and Gas Sorption Properties. *Chem.*  
570 *Mater.* **21**, 5783 (2009).
- 571 (57) Volkringer, C. *et al.* Structural Transitions and Flexibility during Dehydration-Rehydration  
572 Process in the MOF-type Aluminum Pyromellitate  $\text{Al}_2(\text{OH})_2[\text{C}_{10}\text{O}_8\text{H}_2]$  (MIL-118). *Cryst.*  
573 *Growth Des.* **9**, 2927 (2009).
- 574 (58) Krüger, M. *et al.*  $[\text{Al}_2(\text{OH})_2(\text{TCPB})]$  – An Al-MOF based on a tetratopic linker molecule.  
575 *Micro. Meso. Mater.* **216**, 27e35 (2015).
- 576 (59) Boyd, P. G. *et al.* Data-driven design of metal-organic frameworks for wet flue gas  $\text{CO}_2$   
577 capture. *Nature* **576**, 253-256 (2019).
- 578 (60) Yang, S. *et al.* Selectivity and direct visualization of carbon dioxide and sulfur dioxide in  
579 a decorated porous host. *Nat. Chem.* **4**, 887-894 (2012).
- 580 (61) Huang, Z., Svensson, E., Jian, G., KenInge, L. & Zou, X. 3D electron diffraction as an  
581 important technique for structure elucidation of metal-organic frameworks and covalent  
582 organic frameworks. *Coord. Chem. Rev.* **427**, 213583 (2021).
- 583 (62) Gemmi, M. *et al.* 3D Electron Diffraction: The Nanocrystallography Revolution. *ACS*  
584 *Cent. Sci.* **5**, 1315-1329 (2019).
- 585 (63) Nederlof, I., Genderen, E. V., Li, Y.-W. & Abrahams, J. P. A Medipix quantum area  
586 detector allows rotation electron diffraction data collection from submicrometre three-  
587 dimensional protein crystals. *Acta Crystallogr. D Biol. Crystallogr.* **69**, 1223-1230 (2013).

- 588 (64) Teufel, J. *et al.* MFU-4 – A Metal-Organic Framework for Highly Effective H<sub>2</sub>/D<sub>2</sub>  
589 Separation. *Adv. Mater.* **25**, 635-639 (2013).
- 590 (65) Wan, W. & Zou, X. *CrystDiff*. DOI 10.5281/zenodo.2545681 (2019).  
591
- 592 (66) Benoit, V. *et al.* MIL-91(Ti), a small pore metal-organic framework which fulfils several  
593 criteria: an upscaled green synthesis, excellent water stability, high CO<sub>2</sub> selectivity and fast  
594 CO<sub>2</sub> transport. *J. Mater. Chem. A.* **4**, 1383-1389 (2016).
- 595 (67) Gelfand, B. S. & Shimizu, G. K. H. Parameterizing and grading hydrolytic stability in  
596 metal-organic frameworks. *Dalton Trans.* **45**, 3668-3678 (2016).
- 597 (68) Altomare, A. *et al.* EXPO2013: a kit of tools for phasing crystal structures from powder  
598 data. *J. Appl. Cryst.* **46**, 1231-1235 (2013).
- 599 (69) Rodriguez-Carvajal, J. Recent advances in magnetic structure determination neutron  
600 powder diffraction. *Physica B*, **192**, 55-69 (1993).
- 601 (70) Roslova, M. *et al.* InsteaDMatic: towards cross-platform automated continuous rotation  
602 electron diffraction. *J. Appl. Crystallogr.* **53**, 1217-1224 (2020).
- 603 (71) Palatinus, L. *et al.* Specifics of the data processing of precession electron diffraction  
604 tomography data and their implementation in the program PETS2.0. *Acta Crystallogr. Sect. B*  
605 **75**, 512-522 (2019).
- 606 (72) Palatinus, L. & Chapuis, G. SUPERFLIP – a computer program for the solution of crystal  
607 structures by charge flipping in arbitrary dimensions. *J. Appl. Crystallogr.* **40**, 786-790 (2007).



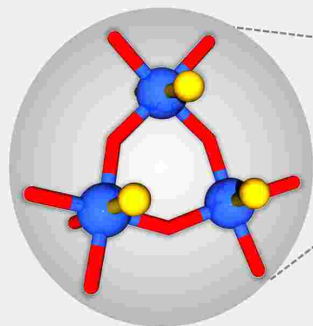
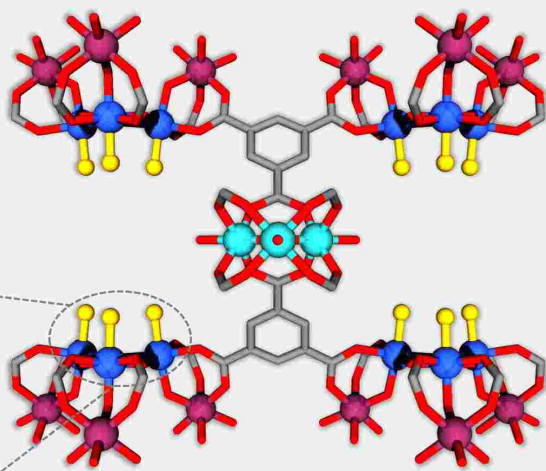
- 608 (73) Petříček, V. Dušek, M. & Palatinus, L. Crystallographic Computing System JANA2006:  
609 General features. *Zeitschrift für Krist. - Cryst. Mater.* **229**, 345 (2014).
- 610 (74) Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal,  
611 volumetric and morphology data. *J. Appl. Crystallogr.* **44**, 1272-1276 (2011).



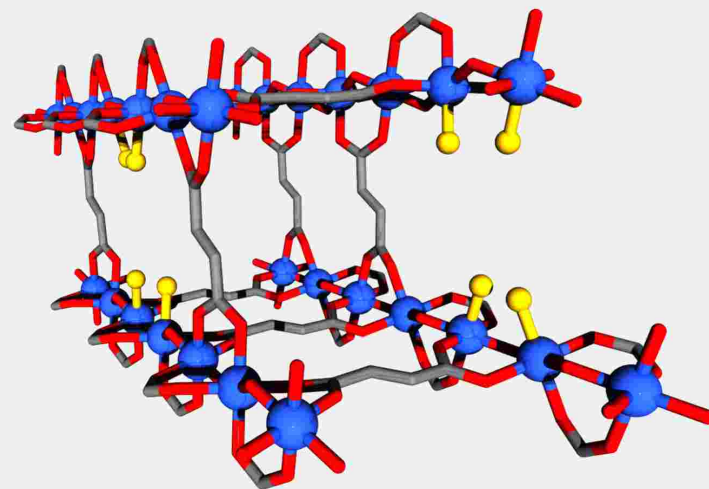
MIL-110(AI)

Topological defective Al-MOFs

MIL-96(AI)



Missing linker defects in MIL-53(AI)-FA



Towards topological defective Al-MOF

