

Data-driven design of metal-organic frameworks for wet flue gas CO₂ capture

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Limiting the increase of CO₂ in our atmosphere is one of the largest challenges of our generation¹. Because carbon capture and storage is one of few viable technologies that can mitigate current CO₂ emissions², much effort is focused on developing solid adsorbents that can efficiently capture CO₂ from flue gasses emitted by anthropogenic sources.³ One class of materials that has attracted much research interest in this context are metal organic frameworks (MOFs), where careful combination of organic ligands with metal-ion nodes can in principle give rise to an innumerable number of structurally and chemically distinct nanoporous MOFs. But an important shortcoming is that many MOFs optimized for CO₂/N₂ separation⁴⁻⁷ don't perform well when using realistic flue gas containing water⁸, which competes with CO₂ for the same adsorption sites and thereby causes the materials to lose their selectivity. While flue gasses can be dried, this makes the capture process prohibitively expensive.^{8,9} Here, we show that data mining of a computational screening library of over 300,000 MOFs can identify different classes of strong CO₂ binding sites (adsorbaphores) that endow MOFs with CO₂/N₂ selectivity persisting in wet flue gasses. We subsequently synthesized two water-stable MOFs containing the most hydrophobic adsorbaphore, finding that their carbon capture performance is indeed not affected by water and outperforms

43 **some commercial materials. Further evaluation will require testing of performance in an industrial**
44 **setting, and considering the full capture process (including the targeted CO₂ sink, such as**
45 **geological storage or serving as carbon source for the chemical industry) to identify the optimal**
46 **separation material.**

47 Different strategies have been developed to mitigate the negative effects of water on the CO₂/N₂
48 separation selectivity in MOF materials. For example, for MOFs with open metal sites, these sites
49 can be used to attach amines, taking advantage of the specific amine chemistry that is also used in
50 conventional amine scrubbing.¹⁰⁻¹³ Chanut *et al.*¹⁴ carried out a screening study to investigate
51 whether MOFs, as such, can adsorb CO₂ in the presence of water. Their screening study hints that
52 such MOFs could be de novo designed. In this work, we develop a systematic strategy to tailor make
53 MOFs that can capture carbon from wet flue gasses. Our design methodology is inspired by the
54 rational design of drug molecules, wherein organic molecules that fit well into the binding pocket of
55 a protein are mined from databases of known chemicals.^{15,16} The difference is that in our case the
56 “drug molecule” is known (i.e., CO₂), but not the substrate that binds it optimally (i.e., the MOF).
57 Hence, we generated a library of 325,000 hypothetical MOFs, and screened each material for its
58 CO₂/N₂ selectivity and CO₂ working capacity. The chemical building blocks used in the generation of
59 these materials are sketched in [Extended Data Figs. 1 and 2](#). [Fig. 1a](#) shows that 8,325 hypothetical
60 materials possess a working capacity for CO₂ greater than 2 mmol/g and a CO₂/N₂ selectivity greater
61 than 50, surpassing the performance of zeolite 13x under dry conditions.¹⁷

62 A key component in drug design is to analyze the optimally binding molecules for a common feature
63 or spatial arrangement of atoms of the binding site, which is referred to as the pharmacophore.¹⁵
64 Analogously, we coin the term adsorbaphore to describe the common pore shape and chemistry of a
65 binding site in a MOF that provides optimal interactions to preferentially bind to a particular guest
66 molecule, in this case CO₂. From our top ranked 8,325 materials we identified 106,680 such CO₂
67 binding sites (see [Extended Data Fig. 3](#) for some examples). A similarity analysis of these binding
68 sites resulted in three main classes of adsorbaphore being observed: A1) two parallel aromatic rings
69 with interatomic spacing of approximately 7 Å (31% of all binding sites), A2) metal–oxygen–metal
70 bridges (32%), and A3) open metal sites (21%), see SI for details. Subsequently, we screened the
71 materials possessing these adsorbaphores for their affinity for water. [Fig. 1b](#) shows the Henry
72 coefficient for water in these high performing materials. Analysis of the data shows that the
73 materials with the parallel aromatic rings adsorbaphore (A1) have a low Henry coefficient for H₂O,
74 while the metal-oxygen bridges (A2) and open metal sites (A3) tend to have higher Henry
75 coefficients ([Fig. 1b](#)). A graphical representation of the different adsorbaphores is presented in
76 [Extended Data Fig 4](#). Indeed, comparison of the binding energies, computed at the DFT level, for the
77 adsorbaphore shown in [Fig. 1c](#), indicates a preference for CO₂ (-10.2 kcal/mol) over N₂ and H₂O by
78 2.7 and 1.5 kcal/mol, respectively (see [Extended Data Table 1](#)). The parallel aromatic rings provide a
79 near optimum interaction with all three atoms of CO₂, while for H₂O the lack of hydrogen bonding
80 sites limits its binding energy.

81 The next step is to identify a subclass of MOFs in our library that contains the preferred
82 adsorbaphore. From an experimental point of view, MOFs with the **frz** topology, characterized by
83 tetra-carboxylated organic ligands coordinated to 1D metal – oxygen rods are an attractive starting
84 point. One of these has been synthesized with indium as a metal node giving a structurally stable,
85 non-breathing MOF.¹⁸ In this topology, the metal rods provide an ideal scaffolding to which we can
86 attach our adsorbaphore. By choosing the metal ion we have some flexibility to tune the distance
87 between the aromatic rings. Our calculations predict that if we replace In(III) by Al(III) we approach
88 the ideal adsorbaphore distance of 6.5 – 7.0 Å (see [Extended Data Table 2](#)) which was determined by

89 adjusting the spacing of the aromatic rings incrementally (Extended Data Fig. 5). In addition,
90 aluminum is an attractive choice as it is an abundant metal and it ensures a strong bond with the
91 carboxylate O-atoms of the ligands,¹⁹ which significantly improves the thermal and hydrolytic
92 stability of a MOF.^{20,21}

93 Using our MOF generation algorithm²², we generated a library of 35 isorecticular materials and
94 computed from the mixture isotherms the CO₂/N₂ selectivity in dry and wet flue gasses (Extended
95 Data Figs. 6 and 7). Our calculations show that all our predicted materials maintain an excellent
96 selectivity at low pressures, and in approximately 75% of these materials, the selectivity was not
97 influenced by the presence of water at flue gas conditions. The concept of an adsorbaphore focusses
98 on the design of an adsorption site that optimizes selectivities at low pressure. At higher partial
99 water pressure, water adsorption is dominated by the energetics of hydrogen bond formation.
100 Further analyses showed that the pore shape of the materials that maintain a high CO₂ uptake at
101 high humidity frustrates the formation of these hydrogen bonds. This is illustrated in Figs. 2a,b which
102 compares the water impact on the CO₂ uptake of two materials with the same adsorbaphore but
103 different pore structures (hypothetical MOFs **m8o67** and **m8o71**). Fig. 2a show that **m8o67** is
104 resistant to H₂O flooding; even at a relative humidity of approximately 85% we only see a small
105 effect of H₂O on CO₂ capacity. Conversely, **m8o71** completely loses its CO₂ capacity at 60% relative
106 humidity (Fig. 2b). In Figs. 2c,d we visualize the H-bond network that is formed at 100% relative
107 humidity in both materials. For material **m8o71**, we see a complete H-bond network (Fig. 2d), while
108 for **m8o67** (Fig. 2c) we observe a less extensive network; the benzoate groups separating the
109 adsorbaphores frustrate the formation of a complete H-bonding network.

110 On the basis of these predictions, we synthesized two frz-based MOFs using organic ligands that
111 possess the water-frustrating properties reported above: **Al-PMOF**¹⁹ (**m8o66**) and **Al-PyrMOF**
112 (**m8o67**). These MOFs are based on Al(III) 1-dimensional rods linked by the TCPP (tetrakis-(4-
113 carboxyphenyl)-porphyrin), and TBAPy (1,3,6,8-tetrakis-(*p*-benzoic acid)-pyrene) ligands, respectively
114 (Figs. 3a,b). Fig. 3c,d show no loss of their crystallinity upon activation, as well as exposure to
115 different harsh conditions, including immersion in water for 7 days. Further characterization of both
116 materials (see SI) shows excellent agreement with the predicted cell parameters.

117 By discovering the existence of adsorbaphores in these hypothetical materials, we assume that our
118 *in silico* screening method can correctly predict 1) the structure of a MOF, 2) the adsorption
119 properties, and 3) the nature of the binding sites of CO₂ and H₂O. With **Al-PMOF** and **Al-PyrMOF**, we
120 can test these assumptions. In Fig. 4a, we show that the experimental and predicted CO₂ and N₂
121 adsorption isotherms are in good agreement. The CO₂ binding positions in the adsorbaphore, and
122 the impact of H₂O are more challenging to observe experimentally. The siting of CO₂ was studied
123 using *in-situ* CO₂ loading powder X-ray diffraction. Upon loading, we observed a significant change in
124 the intensity and peak position of the Bragg reflections (see Fig. S2.1). Subsequent Rietveld
125 refinement and Fourier analysis²³ provided us with the preferred locations of CO₂ in the pores of **Al-**
126 **PMOF** shown in Fig. 4b. These results confirm that CO₂ preferentially adsorbs in the adsorbaphore.

127 The effect of water on the siting of CO₂ has been further addressed with solid-state NMR. Under
128 conditions of magic angle spinning, high resolution ¹³C NMR chemical shifts are very sensitive to
129 changes in the chemical environment. The ¹³C NMR spectra of **Al-PyrMOF** and **Al-PMOF** are shown
130 in the Extended Data Fig. 8 where we also assign these peaks to specific atoms on the MOF. The
131 chemical shifts associated with the atoms of the adsorbaphore (see inset) are shown in Fig. 4c as a
132 function of the water concentration. At low water loadings the adsorbaphore atoms experience no
133 change in chemical environment with water loading, and at the highest water loadings there are

134 modest changes in the carbon-13 chemical shifts of only those atoms proximate to the
135 aluminium-coordinated carboxylate groups next to the adsorbaphore (carbons B and F in Fig. 4c).
136 This broadening is consistent with dipolar broadening from proximate water molecules, thus
137 confirming that the adsorbaphore itself is not a preferential adsorption site for H₂O.

138 Our simulations predict that CO₂ adsorbed in the adsorbaphore is insulated from adsorption of
139 water. As the ¹³C NMR spectrum of adsorbed ¹³CO₂ is extremely sensitive to the proximity of water
140 molecules via its chemical shift and line broadening, any disruption of the chemical environment of
141 adsorbed CO₂ by water should be immediately apparent. Fig. 4d shows that the chemical shift of the
142 adsorbed ¹³CO₂ is independent of water content. However, we do see a broadening of the ¹³C NMR
143 line with increasing humidity. If this broadening is due to the proximity of the protons in water, it
144 should disappear if we repeat the experiments with D₂O. Fig. 4d shows it does not. This nicely
145 confirms our simulation results, shown in Fig. 2c, on the limited effect of water on CO₂ adsorption in
146 **Al-PyrMOF**.

147 An important practical test is to evaluate whether these materials can capture CO₂ from wet flue
148 gases. Hence, we determined the capture capacity using a breakthrough experiment for both **Al-**
149 **PMOF** and **Al-PyrMOF** of a mixture of CO₂/N₂ under dry- and humid-conditions (Fig. 4e).²⁴ These
150 results confirm the predictions of the simulations (Extended Data Fig. 7) that for **Al-PMOF** the
151 capture capacity is minimally influenced by humidity in the flue gasses, while for **Al-PyrMOF** we even
152 observe an enhancement of the performance. Furthermore, repeated cycling²⁵ (Fig. 4f) does not
153 result in material degradation or a change in separation performance. It is instructive to compare the
154 performance of our materials with a set of reference materials, which include commercially available
155 ones, such as, zeolite 13X and activated carbon, and a water stable, amino-functionalized MOF, UiO-
156 66-NH₂. For dry flue gasses these materials have a capture capacity between **Al-PyrMOF** and **Al-**
157 **PMOF**, but unlike our MOFs in humid flue gasses the performance reduces significantly. Our
158 materials are not the ones with the highest working capacity,¹⁴ yet it is encouraging to see that in
159 wet flue gasses **Al-PMOF** outperforms commercial materials like zeolite 13X and activated carbon.

160 Although large-scale screening of databases of hypothetical MOFs for various gas separation and
161 storage applications has been reported,²⁶⁻²⁹ we have focused on identifying binding pockets, or
162 structural motifs called adsorbaphores, as synthesis targets rather than on whole materials. This
163 enhances the synthetic viability of the approach, demonstrated by identification of one new material
164 with the targeted adsorbaphore that was synthesized and shown to adsorb CO₂ as predicted. The
165 concept of linking computational screening and synthesis of the corresponding materials through
166 the adsorbaphores should be applicable to other gas separations of increasing complexity.

167

168 REFERENCES AND NOTES

- 169 1 Smit, B., Reimer, J. R., Oldenburg, C. M. & Bourg, I. C. *Introduction to Carbon Capture and*
170 *Sequestration*. (Imperial College Press, 2014).
- 171 2 Bui, M. *et al.* Carbon capture and storage (CCS): the way forward. *Energ Environ Sci* **11**, 1062-
172 1176, doi:10.1039/c7ee02342a (2018).
- 173 3 D'Alessandro, D. M., Smit, B. & Long, J. R. Carbon Dioxide Capture: Prospects for New
174 Materials. *Angew. Chem.-Int. Edit.* **49**, 6058-6082, doi:10.1002/anie.201000431 (2010).
- 175 4 Sumida, K. *et al.* Carbon Dioxide Capture in Metal-Organic Frameworks. *Chemical Reviews*
176 **112**, 724-781, doi:10.1021/cr2003272 (2012).
- 177 5 Furukawa, H., Cordova, K. E., O'Keeffe, M. & Yaghi, O. M. The Chemistry and Applications of
178 Metal-Organic Frameworks. *Science* **341**, 974, doi:10.1126/Science.1230444 (2013).
- 179 6 Huck, J. M. *et al.* Evaluating different classes of porous materials for carbon capture. *Energ*
180 *Environ Sci* **7**, 4136-4146, doi:10.1039/C4EE02636E (2014).
- 181 7 Mason, J. A., Sumida, K., Herm, Z. R., Krishna, R. & Long, J. R. Evaluating metal-organic
182 frameworks for post-combustion carbon dioxide capture via temperature swing adsorption.
183 *Energ Environ Sci* **4**, 3030-3040, doi:10.1039/c1ee01720a (2011).
- 184 8 Li, G. *et al.* Capture of CO₂ from high humidity flue gas by vacuum swing adsorption with
185 zeolite 13X. *Adsorption-Journal of the International Adsorption Society* **14**, 415-422,
186 doi:10.1007/s10450-007-9100-y (2008).
- 187 9 Merel, J., Clausse, M. & Meunier, F. Experimental investigation on CO₂ post-combustion
188 capture by indirect thermal swing adsorption using 13X and 5A zeolites. *Industrial &*
189 *Engineering Chemistry Research* **47**, 209-215, doi:10.1021/ie071012x (2008).
- 190 10 Milner, P. J. *et al.* A Diaminopropane-Appended Metal-Organic Framework Enabling Efficient
191 CO₂ Capture from Coal Flue Gas via a Mixed Adsorption Mechanism. *J. Am. Chem. Soc.* **139**,
192 13541-13553, doi:10.1021/jacs.7b07612 (2017).
- 193 11 McDonald, T. M. *et al.* Cooperative insertion of CO₂ in diamine-appended metal-organic
194 frameworks. *Nature* **519**, 303-308, doi:10.1038/nature14327 (2015).
- 195 12 Faig, R. W. *et al.* The Chemistry of CO₂ Capture in an Amine-Functionalized Metal-Organic
196 Framework under Dry and Humid Conditions. *J. Am. Chem. Soc.* **139**, 12125-12128,
197 doi:10.1021/jacs.7b06382 (2017).
- 198 13 Couck, S. *et al.* An Amine-Functionalized MIL-53 Metal-Organic Framework with Large
199 Separation Power for CO₂ and CH₄. *J. Am. Chem. Soc.* **131**, 6326-+, doi:10.1021/ja900555r
200 (2009).
- 201 14 Chanut, N. *et al.* Screening the Effect of Water Vapour on Gas Adsorption Performance:
202 Application to CO₂ Capture from Flue Gas in Metal-Organic Frameworks. *ChemSusChem* **10**,
203 1543-1553, doi:10.1002/cssc.201601816 (2017).
- 204 15 Wolber, G., Seidel, T., Bendix, F. & Langer, T. Molecule-pharmacophore superpositioning and
205 pattern matching in computational drug design. *Drug Discov Today* **13**, 23-29,
206 doi:10.1016/j.drudis.2007.09.007 (2008).
- 207 16 Sliwoski, G., Kothiwale, S., Meiler, J. & Lowe, E. W. Computational Methods in Drug
208 Discovery. *Pharmacol Rev* **66**, 334-395, doi:10.1124/pr.112.007336 (2014).
- 209 17 Ho, M. T., Allinson, G. W. & Wiley, D. E. Reducing the cost of CO₂ capture from flue gases
210 using pressure swing adsorption. *Industrial & Engineering Chemistry Research* **47**, 4883-
211 4890, doi:10.1021/ie070831e (2008).
- 212 18 Stylianou, K. C. *et al.* A Guest-Responsive Fluorescent 3D Microporous Metal-Organic
213 Framework Derived from a Long-Lifetime Pyrene Core. *J. Am. Chem. Soc.* **132**, 4119-4130,
214 doi:10.1021/ja906041f (2010).
- 215 19 Fateeva, A. *et al.* A Water-Stable Porphyrin-Based Metal-Organic Framework Active for
216 Visible-Light Photocatalysis. *Angew. Chem.-Int. Edit.* **51**, 7440-7444,
217 doi:10.1002/anie.201202471 (2012).

- 218 20 Loiseau, T. *et al.* A rationale for the large breathing of the porous aluminum terephthalate
219 (MIL-53) upon hydration. *Chem.-Eur. J.* **10**, 1373-1382, doi:10.1002/chem.200305413 (2004).
220 21 Reinsch, H. & Stock, N. High-throughput studies of highly porous Al-based MOFs.
221 *Microporous Mesoporous Mat.* **171**, 156-165, doi:10.1016/j.micromeso.2012.12.024 (2013).
222 22 Boyd, P. G. & Woo, T. K. A generalized method for constructing hypothetical nanoporous
223 materials of any net topology from graph theory. *Crystengcomm* **18**, 3777-3792,
224 doi:10.1039/c6ce00407e (2016).
225 23 Carrington, E. J., Vitorica-Yrezabal, I. J. & Brammer, L. Crystallographic studies of gas sorption
226 in metal-organic frameworks. *Acta Crystallographica Section B-Structural Science Crystal*
227 *Engineering and Materials* **70**, 404-422, doi:10.1107/S2052520614009834 (2014).
228 24 Garcia, S. *et al.* Breakthrough adsorption study of a commercial activated carbon for pre-
229 combustion CO₂ capture. *Chemical Engineering Journal* **171**, 549-556,
230 doi:10.1016/j.cej.2011.04.027 (2011).
231 25 Garcia, S., Gil, M. V., Pis, J. J., Rubiera, F. & Pevida, C. Cyclic operation of a fixed-bed pressure
232 and temperature swing process for CO₂ capture: Experimental and statistical analysis. *Int. J.*
233 *Greenh. Gas Control* **12**, 35-43, doi:10.1016/j.ijggc.2012.10.018 (2013).
234 26 Lin, L.-C. *et al.* In silico screening of carbon-capture materials. *Nat. Mater.* **11**, 633-641,
235 doi:10.1038/nmat3336 (2012).
236 27 Wilmer, C. E. *et al.* Large-scale screening of hypothetical metal organic frameworks. *Nat*
237 *Chem* **4**, 83-89, doi:10.1038/nchem.1192 (2012).
238 28 Boyd, P. G., Lee, Y. & Smit, B. Computational development of the nanoporous materials
239 genome. *Nature Materials Review* **2**, 17037, doi:10.1038/natrevmats.2017.37 (2017).
240 29 Yazaydin, A. O. *et al.* Screening of Metal-Organic Frameworks for Carbon Dioxide Capture
241 from Flue Gas Using a Combined Experimental and Modeling Approach. *J. Am. Chem. Soc.*
242 **131**, 18198-+, doi:10.1021/ja9057234 (2009).

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244 **Supplementary Information** is available in the online version of the paper.

245

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247

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267 **Author Contributions** P.G.B., T.K.W., and B.S. developed the MOF generation algorithm, the
268 adsorbaphore identification and analysis, and Monte Carlo simulations, T.D.D. carried out the initial
269 computational screening. S.M.M. carried out the similarity analysis, A.C., C.P.I., and K.C.S.
270 synthesized and characterized the materials. The breakthrough experiments were carried out by
271 E.G., C.P.I., A.C., M.M., J.A.R.N, and S.G. The NMR experiments were carried out by R.B. and J.A.R.
272 The X-ray analysis was carried out by A.G. and P.S. All authors contributed to the analysis of the data
273 and the writing of the article.

274
275 **Competing interests** K.C.S., B.S., A.C., P.G.B., and T.K.W. have filed a patent application (No. 18 168
276 544.7) that relates to water stable polyaromatic MOF materials for CO₂ separation from flue gas and
277 natural gas streams.

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279 **Author Information** Reprint and permission information is available at www.nature.com/reprints.
280 The authors declare competing financial interests: details are available in the online version of the
281 paper. Readers are welcome to comment on the online version of the paper. Correspondence and
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284

285 **Data Availability** The computed data and hypothetical materials that were used in this publication
286 are provided free of charge on the Materials Cloud (DOI: [10.24435/materialscloud:2018.0016/v1](https://doi.org/10.24435/materialscloud:2018.0016/v1)).
287 On this site one can also find an interactive version of [Figs. 1 a](#) and [b](#). Data that are not included in
288 the paper are available upon reasonable request to the authors.

289
290 **Code Availability.** Topology Based Crystal Constructor (ToBasCCo), the python program used to build
291 hypothetical MOFs is hosted on GitHub <https://github.com/peteboyd/tobascco>. The python code
292 that compares common chemical features between fragments is provided on GitHub:
293 <https://github.com/peteboyd/adsorbaphore> and is dependent on a C library called MCQD which
294 performs the maximum clique detection of the chemical graphs. An interface between python and C
295 for this is provided here: https://github.com/peteboyd/mcq_d_api. The Automatic Binding Site
296 Locator (ABSL) program, used to identify CO₂ binding sites in each MOF, is part of a broader python-

297 based code used to facilitate simulations of porous materials called Fully Automated Adsorption
298 Analysis in Porous Solids (FA³PS). This is available on BitBucket:
299 <https://bitbucket.org/tdaff/automation>.

300

301 FIGURE CAPTIONS

302

303 **Fig. 1 | Computational screening of MOFs for strong CO₂ adsorption and selectivity.** **a**, the results
304 from the screening of 325,000 hypothetical MOFs at conditions that mimic post-combustion capture
305 (adsorption at ambient temperature and 1 bar with a molar ratio of 15:85 CO₂/N₂ and regeneration
306 at 363 K and 0.1 bar). The materials in the green box were selected for more refined screening and
307 adsorbaphore identification; the color-coding represents the number of MOFs. **b**, The H₂O affinity of
308 the top performing materials as characterized by the H₂O vs CO₂ Henry coefficients. The color codes
309 represent the three different adsorbaphores found in the top performing structures; A1 – parallel
310 aromatic rings, A2 – metal-oxygen bridges, and A3 – open metal sites. Some materials have both A1
311 and A2 sites. **c**, The parallel aromatic rings adsorbaphore discovered with the feature recognition
312 algorithm.

313

314 **Fig. 2 | Effects of water on different MOFs with the same adsorbaphore.** **a**, and **b**, Simulated
315 adsorption of a ternary mixture of CO₂/N₂/H₂O at 313 K. The partial pressure of CO₂ is held at 0.15
316 bar while the relative humidity increases. The N₂ uptake was negligible and not shown. **c**, and **d**,
317 Visualization of the water loading at 100% relative humidity in (c) hypothetical MOF **m8o67** and **d**,
318 hypothetical MOF **m8o71**. The benzoate groups are represented by grey sticks and water by red and
319 white space filling atoms. Note that in **m8o67** the benzoate groups perpendicular to the plane of the
320 figure prevent H-bond formation across the adsorbaphores.

321

322 **Fig. 3 | Structural representation and stability of [Al-PMOF] and [Al-PyrMOF].** **a**, and **b**, Ball and
323 stick representation of the [Al-PMOF] and [Al-PyrMOF] structures, respectively. The orientation of
324 the tetra-carboxylate ligands around the Al(III) rods results in the generation of the 3D-non
325 interpenetrated structures containing the adsorbaphore (red box). Atom color code: pink: Al; grey:
326 C; blue: N; red: O and pale yellow: H. **c**, and **d**, laboratory PXRD patterns of [Al-PMOF] and [Al-
327 PyrMOF], respectively – black, simulated; red, as made; blue, acetone exchanged; green, activated;
328 sky blue, activated material immersed in liquid water for 7 days, and pink, exposed in controlled
329 vapor atmosphere of nitric acid for 3 hours.

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331 **Fig. 4 | CO₂ adsorption, ¹³C CP-NMR, and breakthrough experiments for [Al-PMOF] and [Al-
332 PyrMOF].** **a**, comparison of experimental (filled) and computational (open) single component
333 adsorption isotherms for CO₂ (squares) and N₂ (circles) adsorption collected on activated [Al-PMOF]
334 (red) and [Al-PyrMOF] (blue) at 313 K. **b**, Rietveld refinement of the XRD data shown in SI revealed
335 that CO₂ binding in [Al-PMOF] occurs between the porphyrin cores – the adsorbaphore, **c**, ¹³C CP-
336 MAS spectrum of [Al-PyrMOF] recorded as a function of relative humidity: linewidth change for each
337 C of the TBAPy ligand. The inset provides labels for each carbon atom in the ligand, **d**, Linewidth vs
338 relative humidity (H₂O) extracted from ¹³C static spectra of ¹³CO₂ loaded in [Al-PyrMOF]. **e**, CO₂
339 capture capacity profiles (in mmol/g) for [Al-PyrMOF] and [Al-PMOF] during breakthrough
340 experiments under dry and humid (85%RH) conditions, with 85/15 v/v of N₂/CO₂ (313 K and 1 bar). **f**,
341 Benchmarking of CO₂ working capacity (in mmol/g) for [Al-PyrMOF] and [Al-PMOF] versus UiO-66-
342 NH₂, activated carbon, and zeolite 13X under dry and humid (85%RH) conditions, with 85/15 v/v of
343 N₂/CO₂ (313 K and 1 bar). For wet flue gasses we studied the performance stability after 3 cycles for
344 reference materials, and after 10 cycles for [Al-PyrMOF] and [Al-PMOF].

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350 **EXTENDED DATA LEGENDS**
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352 **Extended Data Figure 1 | Hypothetical material generation (1).** The organic Secondary Building
353 Units (SBUs) used in the generation of the hypothetical MOF database.

354 **Extended Data Figure 2 | Hypothetical material generation (2).** **a**, Metal SBUs used in the
355 generation of the hypothetical MOF database. **b**, functional groups used to decorate the
356 unfunctionalized hypothetical MOFs in the database. We denote a hypothetical material by **mXoYY**,
357 where X refers to the metal SBU shown in the Extended Data Figure 2(a) and YY to the organic SBU
358 shown in Extended Data Figure 1. Functional groups were decorated on the base hypothetical
359 materials using an internal numbering system. The data is available online at [DOI:
360 [10.24435/materialscloud:2018.0016/v1](https://doi.org/10.24435/materialscloud:2018.0016/v1)].

361 **Extended Data Figure 3 | Examples of Adsorbaphores.** A selection of the most representative
362 adsorbaphores found from visual inspection of the top 50 most frequent adsorbaphores found from
363 the random pairing method described in the SI. There are three major trends in the molecular
364 fragments which can be seen going down the columns of the image, labelled A1, A2 and A3. The
365 chemical features of the fragments increase as one goes across each row. This is accomplished by
366 increasing the minimum number of common atoms allowed during the substructure search, called
367 the Minimum Clique Threshold (MCT). Pictured in each adsorbaphore is a representative contour
368 map of the energy produced from CO₂ binding with the adsorbaphore atoms from each original CO₂
369 binding site. **a-c, A1**: planar aromatic systems where CO₂ binds in between, **d-f, A2**: CO₂ binding near
370 the bridging oxygen of a pillared vanadium SBU, **g-i, A3**: CO₂ bound between open-metal Cr SBUs.

371 **Extended Data Figure 4 | Commonly found adsorbaphores.** **a-c**, commonly found adsorbaphores
372 from the maximum clique detection method. Atom colors: grey – carbon, red – oxygen, green –
373 vanadium, blue – chromium. **d**, Representative adsorbaphore **A1** found in different hypothetical
374 MOFs from the hypothetical database. The adsorbaphore atoms are highlighted green.

375 **Extended Data Figure 5 | Effect of the adsorbaphore spacer.** **a**, plot of the CO₂ adsorption at 0.15
376 bar, 313K in hypothetical MOFs consisting of the **frz** topology, metal node #8 and organic linker #67
377 (m8o67). The interplanar spacing of the adsorbaphore atoms is adjusted re-assembling the structure
378 with larger or smaller Al-O bonds. **b**, graphical representation of the spacing adjustments made to
379 the material.

380 **Extended Data Figure 6 | Hypothetical MOFs built with the frz topology.** These structures contain
381 an Al 1D rod (m8) and the organic ligands 60-82 from Figs. S1 and S2. The spacing between parallel
382 aromatic cores (seen in the centre of each hypothetical MOF) is ~6.7 Å, defining the adsorbaphore
383 site in each material. No functional groups were used to decorate these materials. We refer to
384 synthesized version of m8o66 and m8o67 as **Al-PMOF (Al₂(OH)₂(H₂TCP))** and **AlPyrMOF**
385 **(Al₂(OH)₂(TBAPy))**, respectively.

386 **Extended Data Figure 7 | CO₂ adsorption capacity of a class of frz-based hypothetical MOFs at 0.15**
387 **bar and 313K under 'wet' (85% RH) and 'dry' flue gas conditions.** **a-b**, where the organic ligand is
388 connected to the Al metal ion via 4 benzoate moieties and **c**, where the organic ligand is connected
389 to the Al metal ion via 4 acetylenic carboxylate moieties. The materials are ranked from lowest
390 adsorbaphore density to highest, and number YY on the x-axis correspond to the organic linker
391 number in m8oYY (see Extended Data Fig. 6).

392 **Extended Data Figure 8 | NMR spectra.** ¹³C CP-MAS spectrum of **a, Al-PMOF** and **b, Al-PyrMOF**
393 recorded at 9.39 T with sample spinning at 8 kHz, the contact time for the CP experiment was 2 ms.
394 The alphabets give chemical shift assignment to experimental spectrum.

395 **Extended Data Table 1 | DFT binding energies of gas particles in the adsorbaphore pocket of each**
396 **MOF synthesized in this work**

397 **Extended Data Table 2 | DFT optimized cell parameters of hypothetical MOFs**

398 footnote to the table:

399 The MOFs are built with the **frz** topology and organic linker #67 (m8o67) and various trivalent metal
400 species. The c-axis corresponds to the spacing between aromatic rings in the adsorbaphore.