Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Selective CO_2 adsorption in water-stable alkaline-earth based metal-organic frameworks

Yiwen Tang,[a] Andreas Kourtellaris,[b] Anastasios J. Tasiopoulos,[b] Simon J. Teat,[c] David Dubbeldam,[a] Gadi Rothenberg,[a] Stefania Tanase*[a]

a. Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.

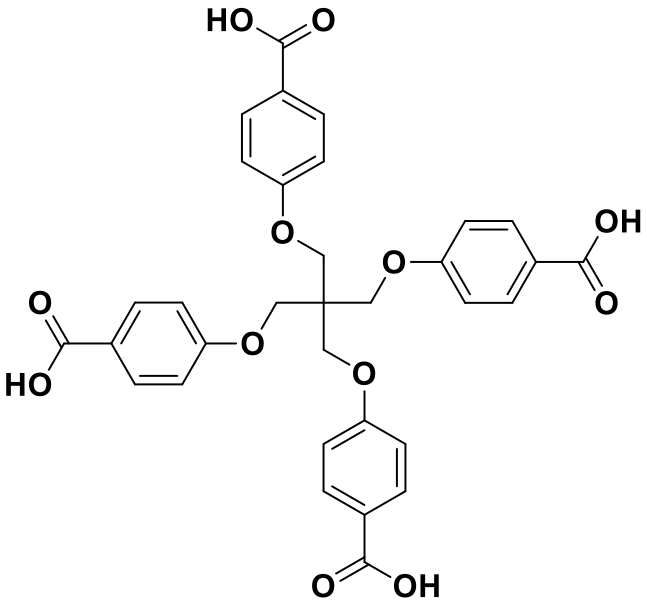
b. Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus.

c. Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

*To whom correspondence should be addressed.

E-mail: s.grecea@uva.nl

S1 Scheme of H_4L Ligand



Scheme S1. Schematic representation of the H_4L ligand structure.

S2 X-ray Structure Analysis

Table S1. Crystal Data and Refinement Information for Complexes.

Complexes	**1**	**2**	**3**	**4**
Formula	$C_{41}H_{42}Mg_2N_2O_{15}$	$C_{78}H_{75}Ca_4N_3O_{27}$	$C_{86}H_{97}Ca_4N_5O_{31}$	$C_{84}H_{84}Sr_4N_6O_{30}$
Formula weight	851.38	1646.73	1857.00	2008.05
Space group	P_{bca}	P_{bca}	$C222_1$	P-1
a (Å)	12.5932 (2)	22.398 (2)	11.1690 (6)	14.287 (5)
b (Å)	18.4157 (4)	30.468 (2)	24.2978 (13)	19.257 (5)
C (Å)	33.2641 (6)	26.820 (2)	33.4201 (18)	19.522 (5)
α (°)	90	90	90	65.213 (5)
β (°)	90	90	90	73.212 (5)
γ (°)	90	90	90	75.976 (5)
Volume ($Å^3$)	7714.4 (2)	18303 (2)	9069.6 (8)	4623 (2)
Z	8	8	4	2
Dx (g/cm^3)	1.466	1.195	1.360	1.447
μ (mm^{-1})	1.228	2.666	0.402	2.376
Reflections Collected	28310	41341	64501	31939
Reflections Unique	6881	16258	10562	16259
R_1[a] [$I > 2\sigma(I)$]	0.0568	0.0952	0.0459	0.0505
wR_2[b]	0.1603	0.2932	0.1222	0.1414

[a]$R_1 = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, [b]$wR_2 = \{\Sigma[w(|Fo|^2 - |Fc|^2)^2] / \Sigma[w(|Fo|^4)]\}^{1/2}$

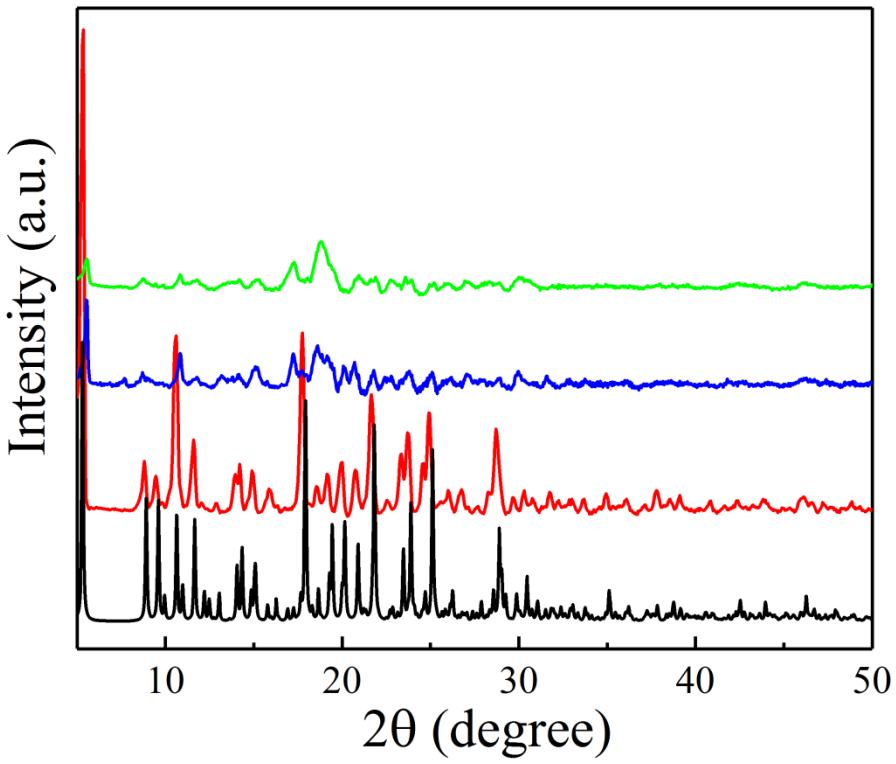


Fig. S1 PXRD patterns of the simulated **1** (black), as-synthesized **1** (red), activated **1** (blue) and compound **1** exposed at 98% relative humidity after 12h (green), respectively.

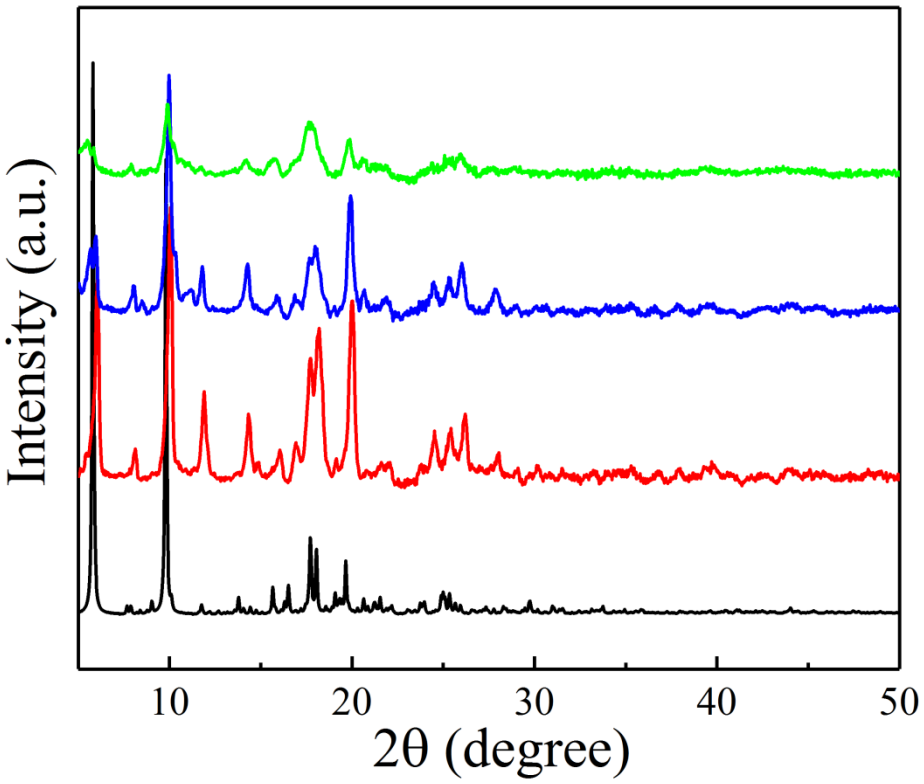


Fig. S2 PXRD patterns of the simulated **2** (black), as-synthesized **2** (red), activated **2** (blue) and compound **2** exposed at 98% relative humidity after 96h (green), respectively.

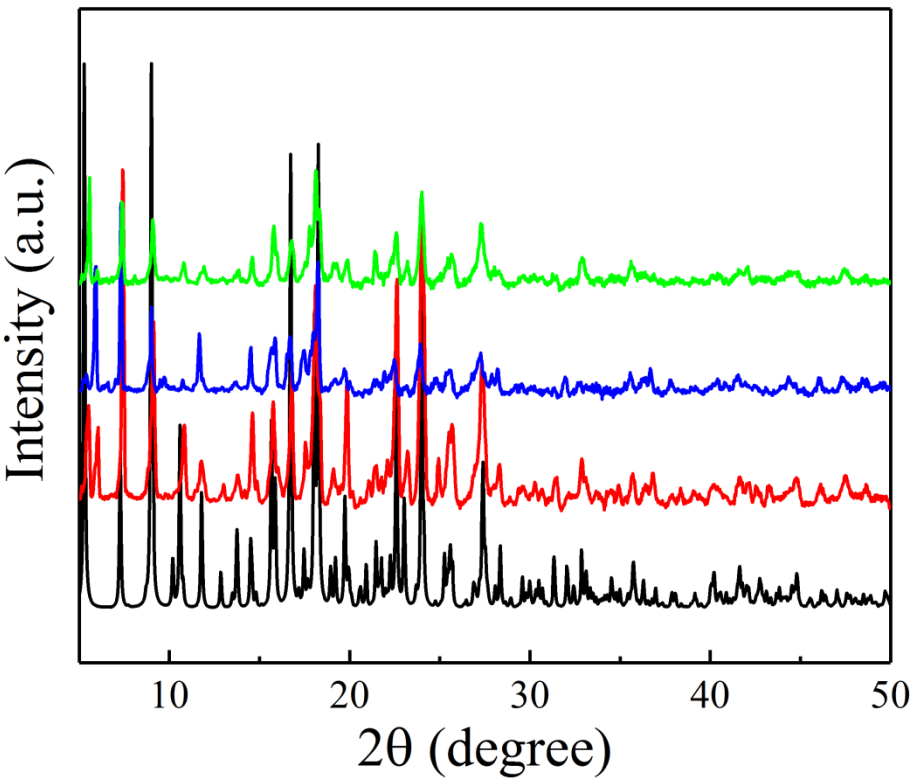


Fig. S3 PXRD patterns of the simulated **3** (black), as-synthesized **3** (red), activated **3** (blue) and compound **3** exposed at 98% relative humidity after 96h (green), respectively.

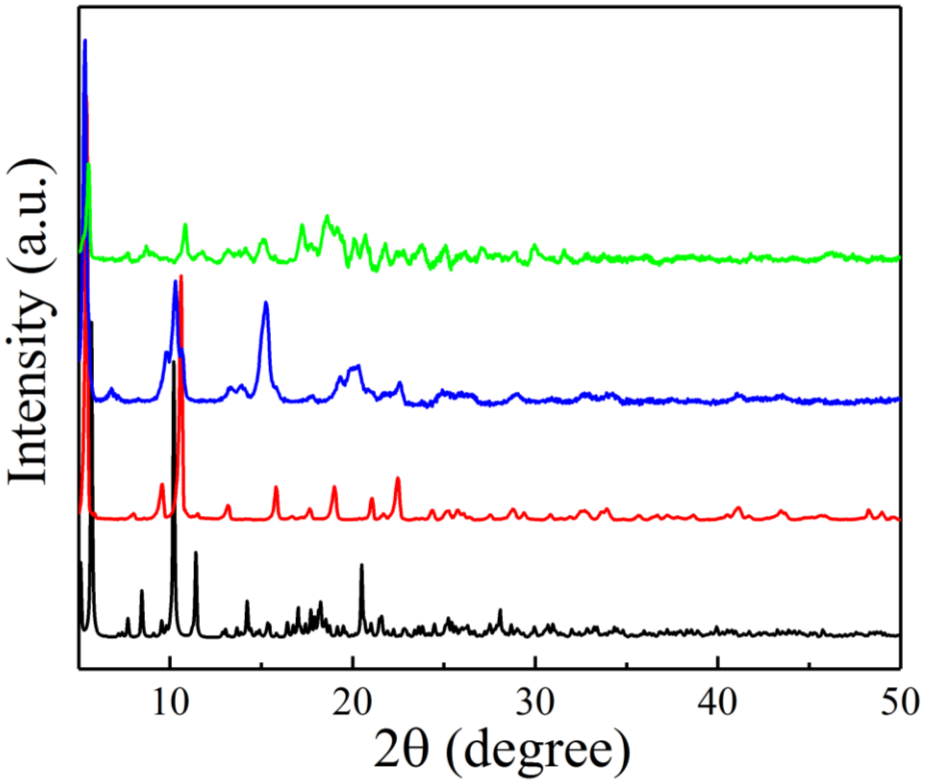


Fig. S4 PXRD patterns of the simulated **4** (black), as-synthesized **4** (red), activated **4** (blue) and compound **4** exposed at 98% relative humidity after 12h (green), respectively.

S3 Thermal Stability

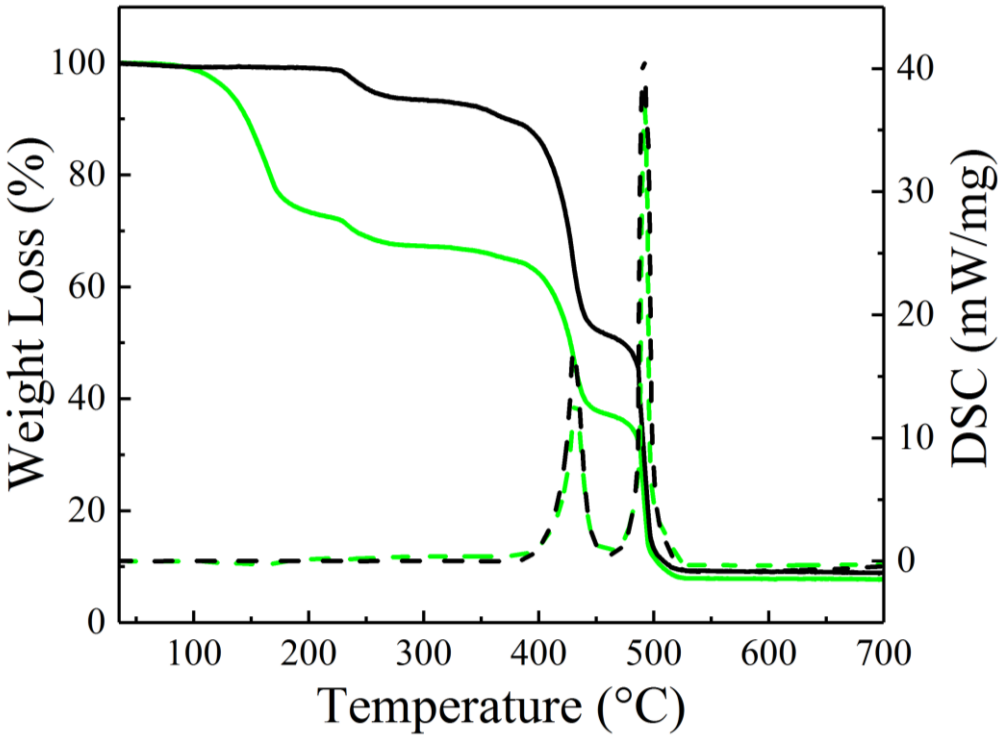


Fig. S5 TGA (solid line) and DSC (dash line) analysis of the as-synthesized **1** (green) and the activated **1** (black).

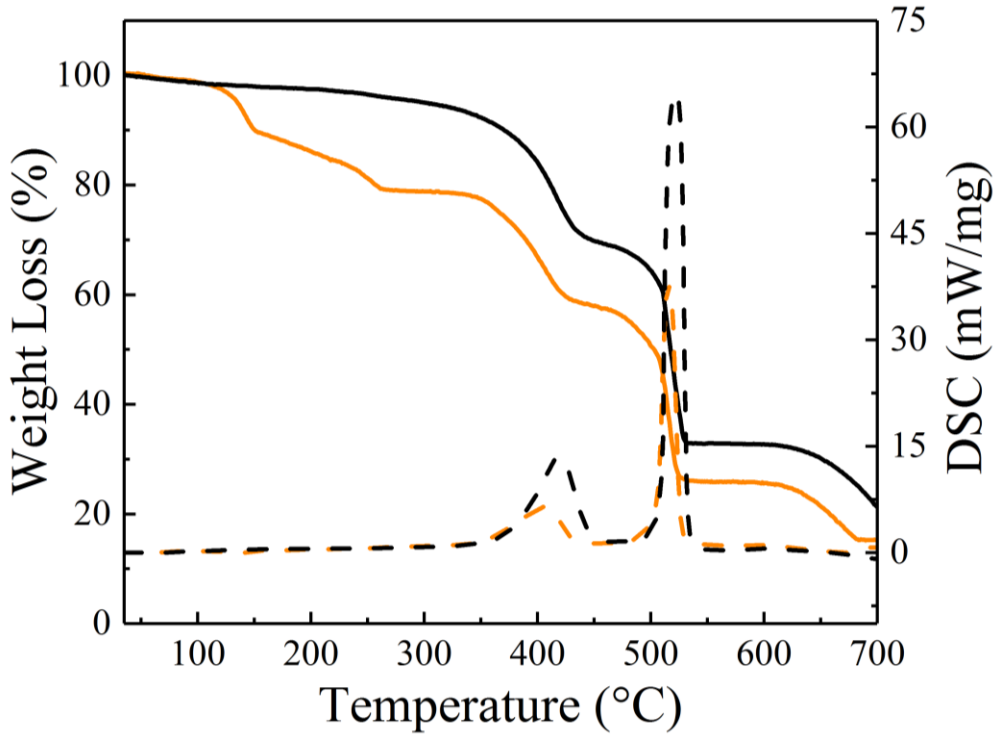


Fig. S6 TGA (solid line) and DSC (dash line) analysis of the as-synthesized **2** (orange) and the activated **2** (black).

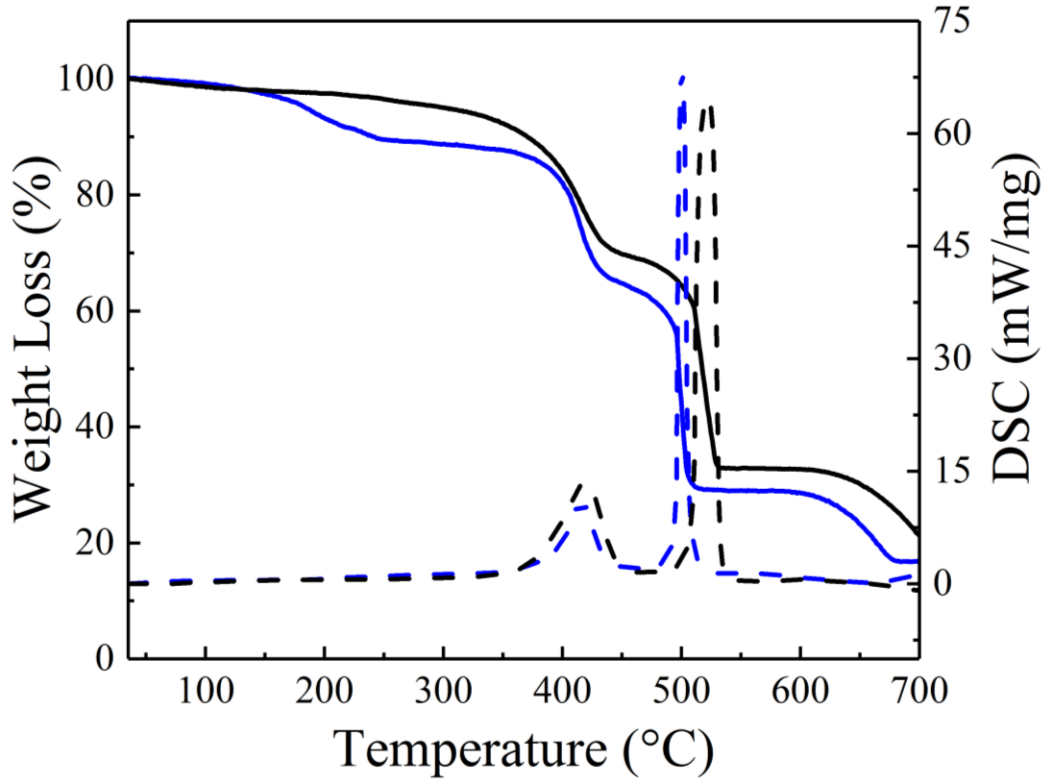


Fig. S7 TGA (solid line) and DSC (dash line) analysis of the as-synthesized **3** (blue) and the activated **3** (black).

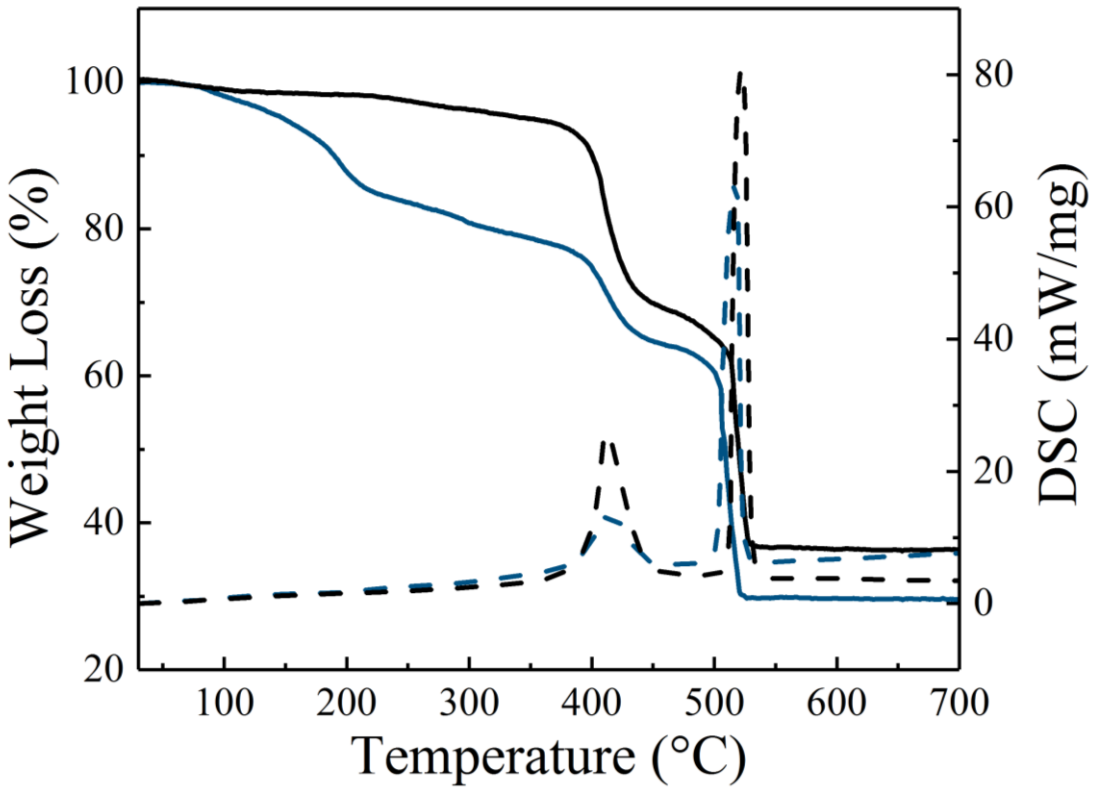


Fig. S8 TGA (solid line) and DSC (dash line) analysis of the as-synthesized **4** (dark blue) and the activated **4** (black).

Table S2. Elemental Analysis of the Activated Alkaline-Earth Based MOFs

	1	**2**	**3**	**4**
C% (calc.)	59.75	57.06	55.63	50.21
C% (exp.)	58.24	57.60	55.45	49.66
N% (calc.)	1.00	0.95	1.75	0.85
N% (exp.)	1.24	0.52	1.29	1.07
H% (calc.)	3.77	3.87	4.38	3.33
H% (exp.)	4.72	4.21	3.92	3.76

S4 Gas Adsorption

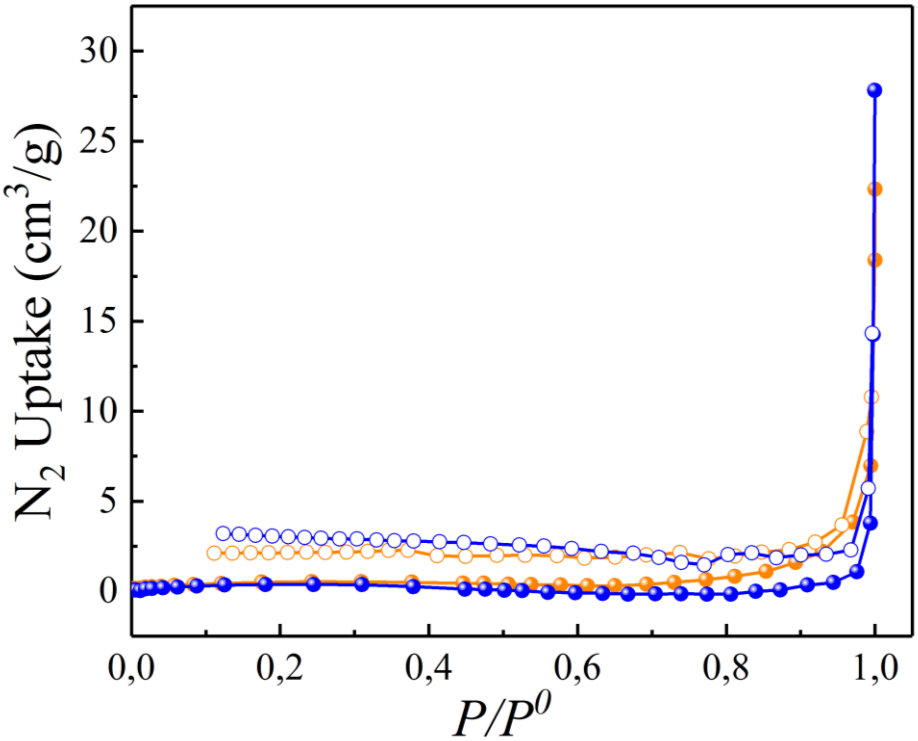


Fig. S9 N_2 uptake of the alkaline-earth metal-based MOFs **2** (orange) and **3** (blue) at 77 K. (Closed symbols correspond to the adsorption and the open symbols to the desorption). Adsorption isotherms of compounds **1** and **4** are not shown here for clarity and both of them do not show the N_2 uptake at 77 K.

S5 IAST Adsorption Selectivity Calculation

IAST (ideal adsorption solution theory) is applied to predict mixed-gas adsorption isotherms from single-component adsorption isotherms.[1,2]

The experimental CO_2 adsorption isotherm data measured at 273 K for compounds **2** and **3** are fitted well with the BET equation:

$$n_i^o(P) = M \frac{K_A P}{(1 - K_B P)(1 - K_B P + K_A P)}$$

Here, P is the pressure of the bulk gas equilibrium with the adsorbed phase (bar), M is the adsorbed amount per mass of adsorbent (mol/kg; M=39.252 and 24.066 for compounds **2** and **3**, respectively), K_A is the Langmuir constant for the first layer of the adsorbate molecules in direct contact with the surface, and K_B is the constant for the second and higher layers of adsorbate molecules (K_A=2.330 and 3.165 for **2** and **3**; K_B=0.336 and 0.281 for **2** and **3**, respectively). The fitted data are then applied to predict binary CO_2/N_2 adsorption with IAST.

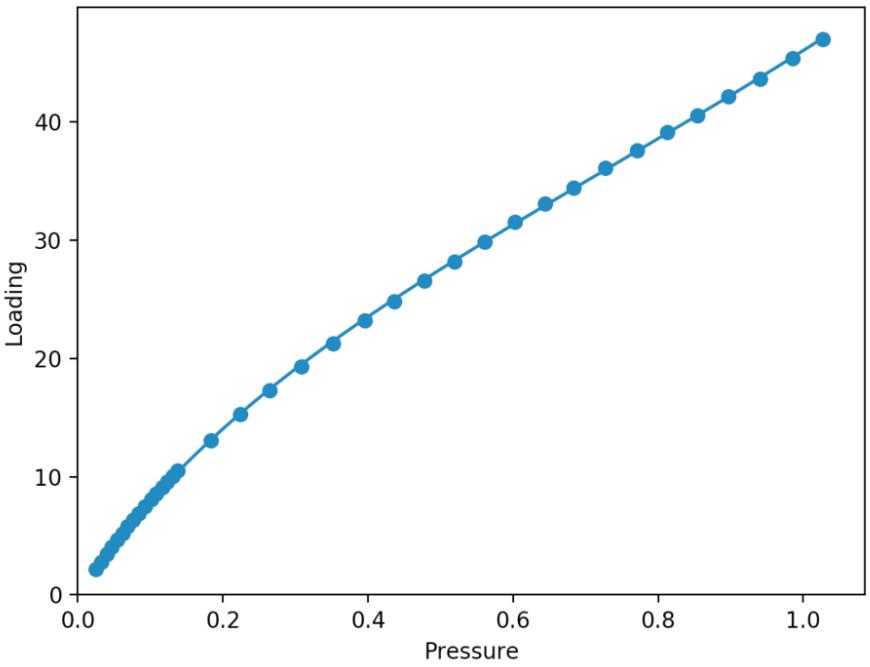


Fig. S10 CO_2 adsorption isotherm of compound **2** along with the BET model fit (Unit: Pressure in bar; Loading in $cm^3 \cdot g^{-1}$).

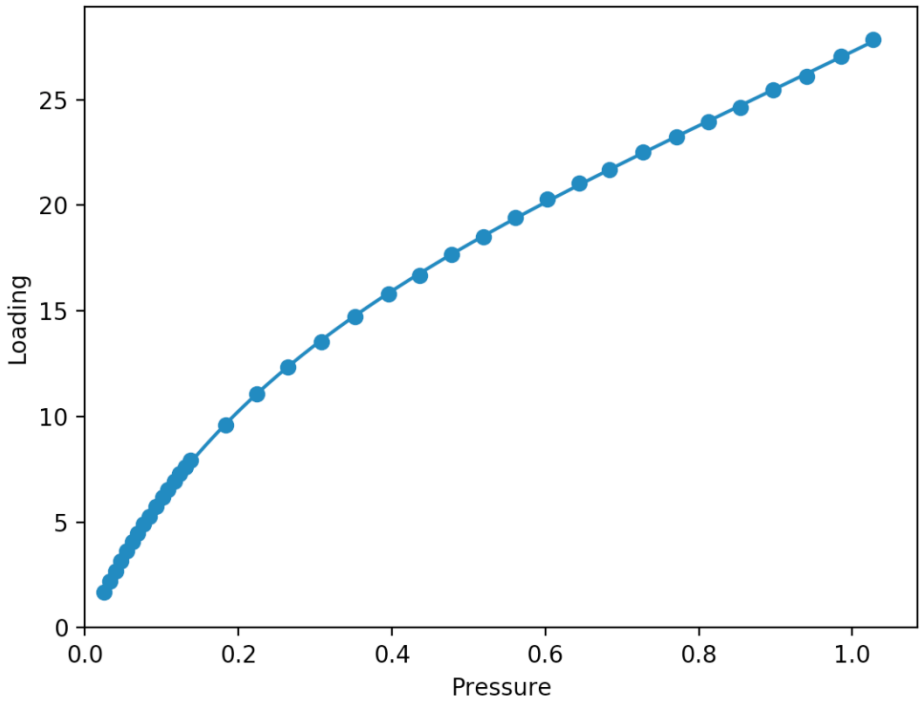


Fig. S11 CO_2 adsorption isotherm of compound **3** along with the BET model fit (Unit: Pressure in bar; Loading in $cm^3 \cdot g^{-1}$).

The experimental N_2 adsorption isotherm data measured at 273 K for compound **2** is fitted well with the *Henry's law* equation:

$$n_i^o(P) = K_H P$$

Here, P is the pressure of the bulk gas equilibrium with the adsorbed phase (bar), K_H is the Henry coefficient (K_H=2.241). The fitted data are then applied to predict binary CO_2/N_2 adsorption with IAST.

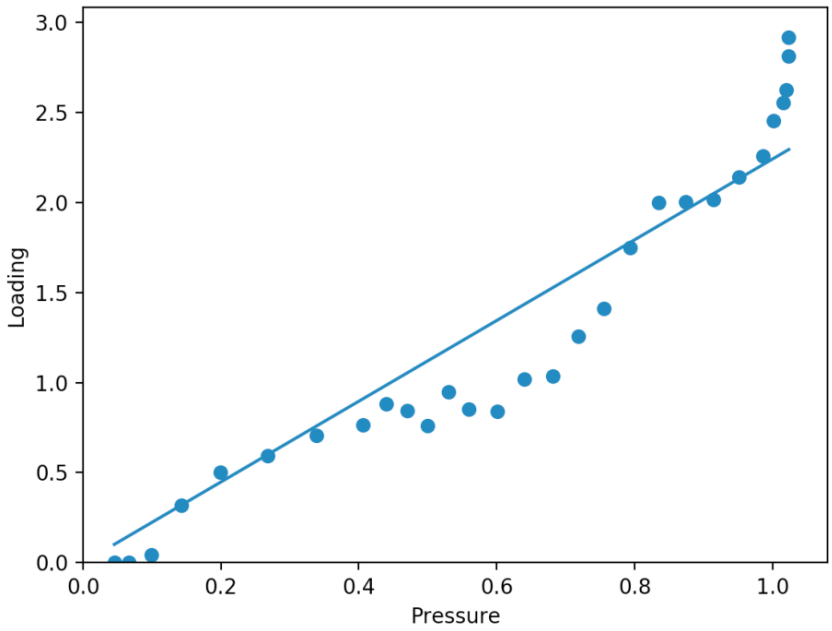


Fig. S12 N_2 adsorption isotherm of compound **2** along with the *Henry's law* model fit (Unit: Pressure in bar; Loading in $cm^3 \cdot g^{-1}$).

The experimental N_2 adsorption isotherm data measured at 273 K for compound **3** is hard to fit any models within IAST method, so we choose the numerical interpolation for this one and added an artifical point 10.0, 16.0 and 16.0 after that for all pressures. The fitted data are then applied to predict binary CO_2/N_2 adsorption with IAST.

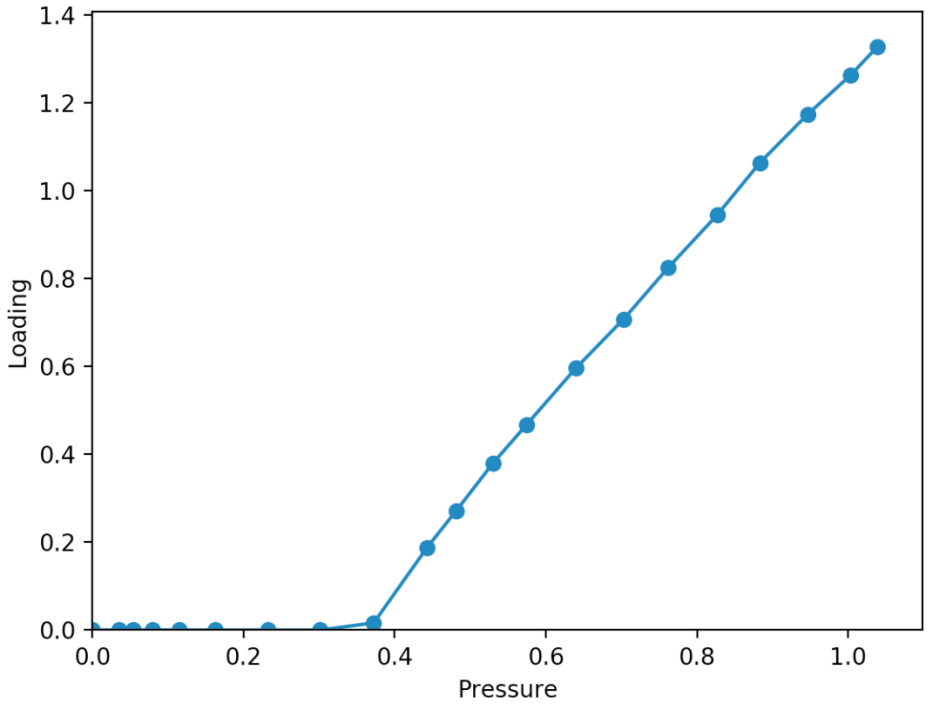


Fig. S13 N_2 adsorption isotherm of compound **3** along with the numerical interpolation method (Unit: Pressure in bar; Loading in $cm^3 \cdot g^{-1}$).

.

The adsorption selectivity of CO_2 over N_2 in a binary mixture is defined as:

$$S_{CO_2/N_2} = \frac{x_{CO_2}/y_{CO_2}}{x_{N_2}/y_{N_2}}$$

Here, x and y are the mole fractions of CO_2 and N_2 in the adsorbed and gas phases, respectively.

References

[1] A. L. Myers and J. M. Prausnitz, *AIChE. J.*, **1965**, 11, 121-127.

[2] C. Simon, B. Smit, M. Haranczyk. (2016) pyIAST: Ideal Adsorbed Solution Theory (IAST) Python Package. *Computer Physics Communications*. 200, pp.364-380.