

Electronic supplementary information (ESI)

Mixed-motif interpenetration and cross-linking of high-connectivity networks lead to robust and porous metal-organic frameworks with high gas uptake capacities

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Material and Methods: All solvents were purchased from Fisher or TCI and used without further purification. Thermogravimetric analysis (TGA) was performed in air using a Shimadzu TGA-50 equipped with a platinum pan and heated at a rate of 3 °C per minute. Single-crystal X-ray diffraction and Powder X-ray diffraction (PXRD) patterns were collected on a Bruker SMART APEX II diffractometer using Cu radiation. The PXRD patterns were processed with the APEX 2 package using PILOT plug-in. Nitrogen and hydrogen adsorption experiments were performed with Autosorb-1C from Quantachrome, Inc. The methanetetra-(biphenyl-p-carboxylic acid) ligand (**H₄L**) was synthesized using the literature procedure.¹

Procedures for crystal growth:

Synthesis of [Zn₄(L**)(**H₂L**)₂]·12DEF·40H₂O (**1**):** A mixture of **H₄L** (1 mg, 0.00125 mmol) and Zn(NO₃)₂·6H₂O (2 mg, 0.00672 mmol) was dissolved in DEF (1 mL) and H₂O (0.1 mL) in a screw capped vial. After addition of 1 μL HCl (3M, aq.), the vial was capped and placed in an oven at 80 °C for five days. Colorless block crystals (0.5 mg, 37%) were obtained after filtration.

Synthesis of [Co₅(L**)(**HL**)₂]·15DMF·37H₂O (**2**):** A mixture of **H₄L** (2.5 mg, 0.003175 mmol) and Co(NO₃)₂·6H₂O (8 mg, 0.0275 mmol) was dissolved in DMF (1 mL) in a screw capped vial. After addition of 5 μL of HCl (3M, aq.), the vial was capped and placed in an oven at 80°C for five days. Needle shaped crystals (1.8 mg, 46%) were obtained after filtration.

X-ray Structure Determination

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based

X-ray diffractometer system equipped with Cu –target X-ray tube and operated at 1600 watts. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. All of the structures were solved by direct methods and refined to convergence by least squares method on F^2 using the SHELXTL software suit. All non-hydrogen atoms are refined anisotropically. SQUEEZE subroutine of the PLATON software suit was applied to remove the scattering from the highly disordered solvent molecules. The resulting new HKL4 files were used to further refine the structures. Datasets for **1** and **2** were collected to $2\theta = 101^\circ$ and 71° respectively.

Table S1. Crystal data and structure refinements for **1** and **2**

MOF	1 (Framework)	2 (Framework)
Empirical formula	C ₁₅₉ H ₁₀₀ O ₂₄ Zn ₄	C ₁₅₉ H ₁₀₀ O ₂₅ Co ₅
Formula weight	2556.08	2604.24
Temperature	100(2) K	100(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system, space group	Monoclinic, P21	Monoclinic, P21
Unit cell dimensions	a = 20.6536(3) Å	a = 19.3772(8) Å
	b = 33.4974(5) Å	b = 34.3744(10) Å
	c = 20.7926(3) Å	c = 20.7308(7) Å
	$\alpha = \gamma = 90^\circ$	$\alpha = \gamma = 90^\circ$
	$\beta = 118.6190(10)^\circ$	$\beta = 115.432(2)^\circ$
Volume	12627.7(3) Å ³	12470.3(8) Å ³
Z, Calculated density	2, 0.672 Mg/m ³	2, 0.694 Mg/m ³

Absorption coefficient	0.740 mm ⁻¹	2.869 mm ⁻¹
F(000)	2534	2578
Crystal size	0.2 x 0.2 x 0.2 mm	0.10 x 0.1 x 0.1 mm
Theta range for data collection	2.42 to 55.19 deg.	2.36 to 42.08 deg.
Limiting indices	-21<=h<=21, -33<=k<=35, -22<=l<=21	-12<=h<=16, -29<=k<=29, -18<=l<=17
Reflections collected / unique	27767/20758 [R(int) = 0.0512]	14527 / 9315 [R(int) = 0.0585]
Completeness to theta =	99.0%	99.0 %
Max. and min. transmission	0.8660 and 0.8660	0.7624 and 0.7624
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	27767 / 195 / 747	14527 / 200 / 765
Goodness-of-fit on F ²	1.320	0.813
Final R indices [I>2sigma(I)]	R1 = 0.0868, wR2 = 0.2131	R1 = 0.0602, wR2 = 0.1493
R indices (all data)	R1 = 0.1038, wR2 = 0.2226	R1 = 0.0912, wR2 = 0.1655
Absolute structure parameter	0.04(3)	0.006(4)
Largest diff. peak and hole	1.168 and -2.950 e.A ⁻³	0.337 and -0.615 e.A ⁻³

^aR(F) = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^bRW(F²) = $[\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

Quantitative determination of solvent molecules in 1 and 2: Sample of **1** and **2** were treated in exactly the same way for both ¹H NMR and TGA experiments. Fresh crystals were harvested by quick filtration, and briefly dried on filter paper under air. The sample was then

loaded into screw-capped vial or the sample tray in TGA. To the weighted sample in the crew-capped vial, 0.75 mL CD₃OD was added. 5 or 3 µL mesitylene (Mes) was then added as an internal standard. After soaking overnight, the ¹H NMR spectrum was taken on a 400 MHz Burker NMR spectrometer. The organic solvent inside the crystals is DEF or DMF which has been exchanged by CD₃OD, and its exact amount was determined by calibrating against the internal standard. The total amounts of the solvents were obtained by TGA, the amount of water molecules was calculated by subtracting DEF/DMF from the total solvent amount.

1:

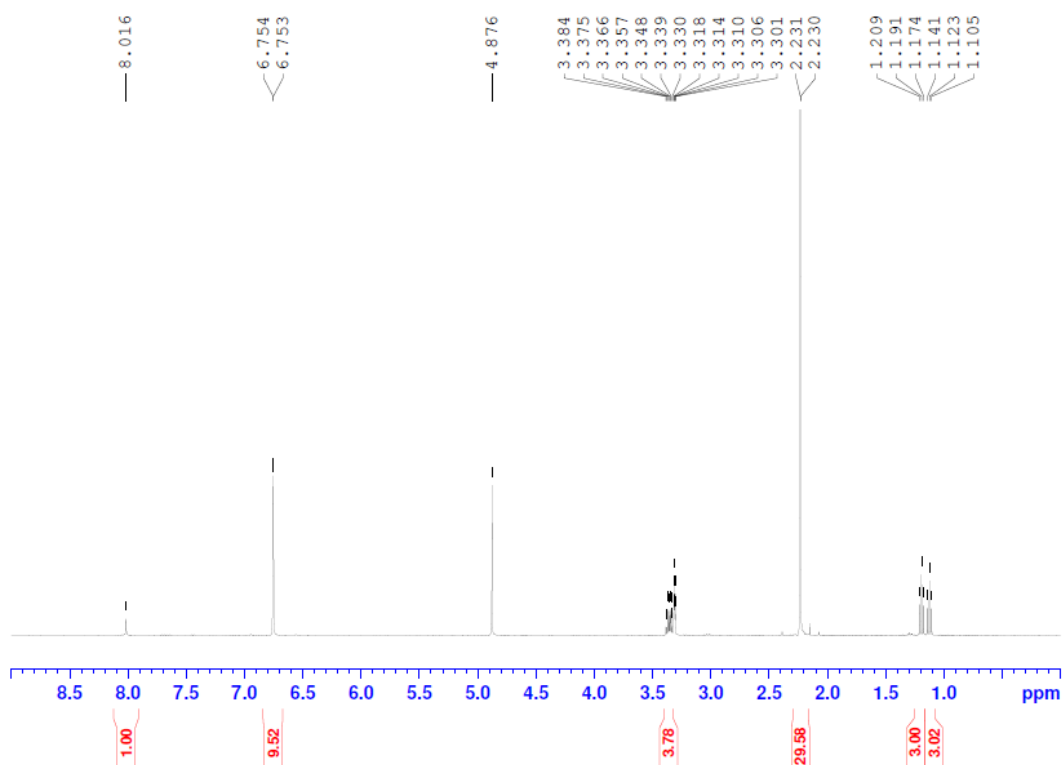


Figure S1. ¹H NMR spectroscopic determination of solvent content in **1**; mesitylene was added as an internal standard.

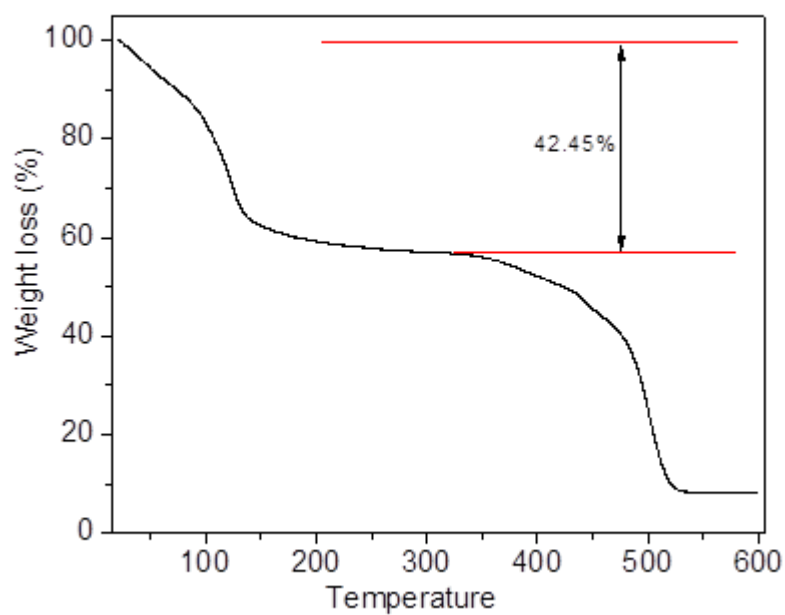


Figure S2. TGA cure for fresh crystals of **1**.

W_{crystal} (mg)	4.30
$W_{\text{mesitylene}}$ (mg)	4.34
W_{DEF} (mg) (From NMR)	1.15
$W_{\text{DEF}}\%$	26.74
$W_{\text{DEF}+\text{H}_2\text{O}}\%$ (From TGA)	42.45
$W_{\text{H}_2\text{O}}\%$	15.72
Formula: $[\text{Zn}_4(\text{L})(\text{H}_2\text{L})_2] \cdot 12\text{DEF} \cdot 40\text{H}_2\text{O}$	

2:

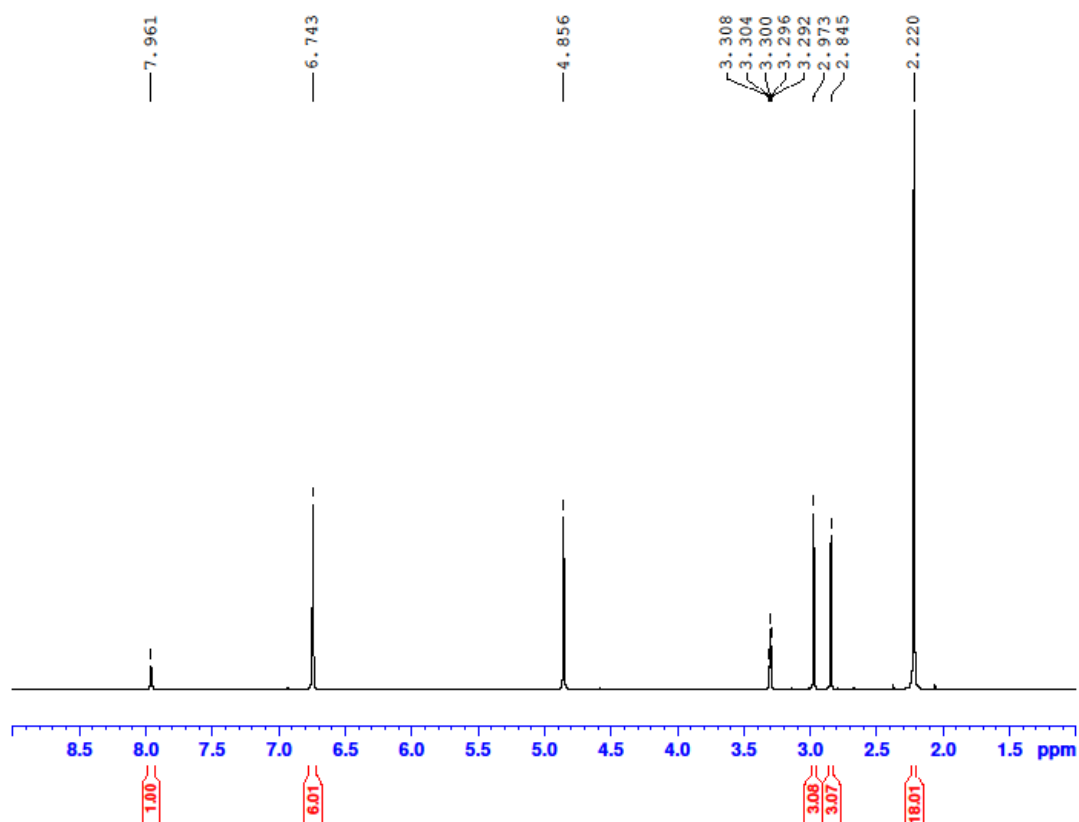


Figure S3. ^1H NMR spectroscopic determination of solvent content in **2**; mesitylene was added as an internal standard.

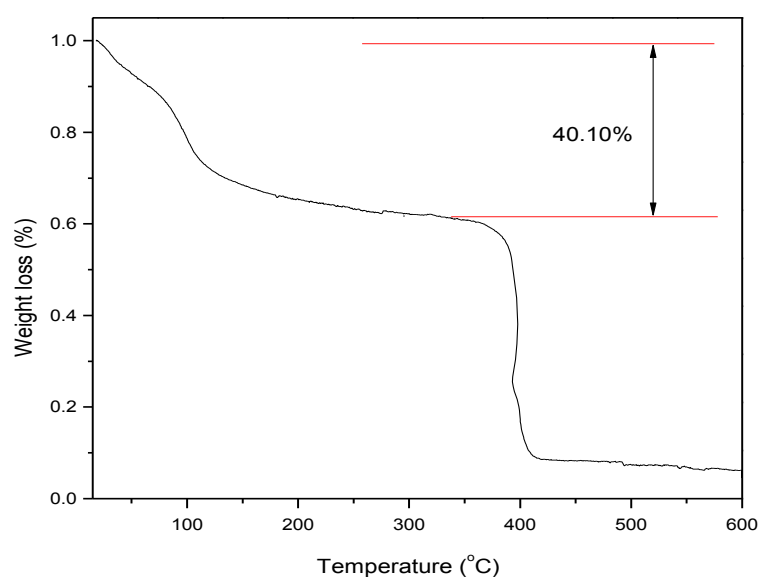
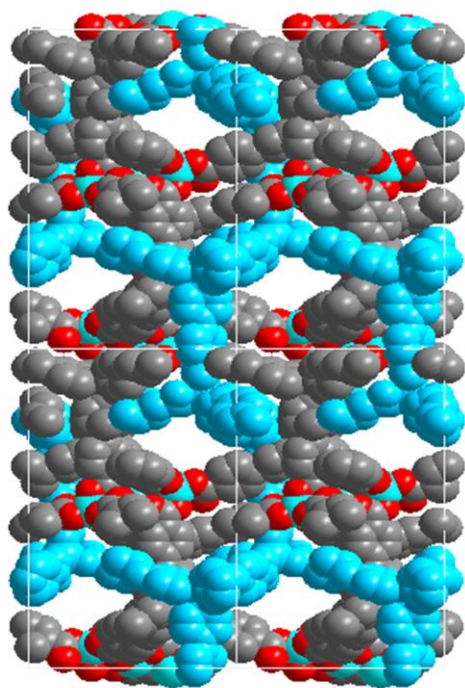


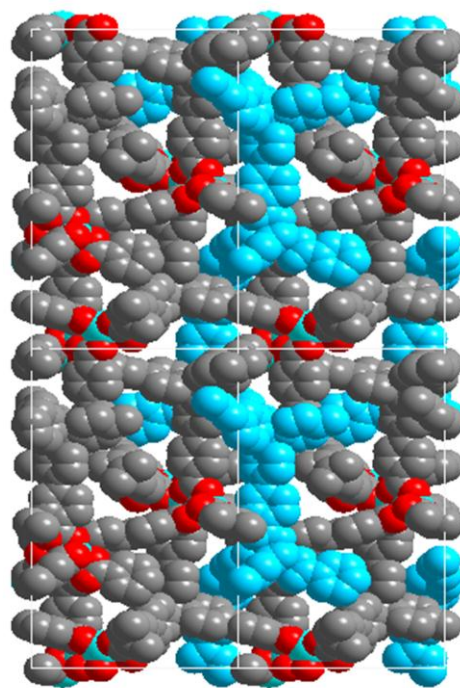
Figure S4. TGA curve for fresh crystals of **2**

W_{crystal} (mg)	3.14
$W_{\text{mesitylene}}$ (mg)	2.60
W_{DMF} (mg) (From NMR)	0.79
$W_{\text{DMF}}\%$	25.11
$W_{\text{DEF+H}_2\text{O}}\%$ (From TGA)	40.10
$W_{\text{H}_2\text{O}}\%$	14.99
Formula: $[\text{Co}_5(\text{L})(\text{HL})_2] \cdot 15\text{DMF} \cdot 37\text{H}_2\text{O}$	

a)



b)



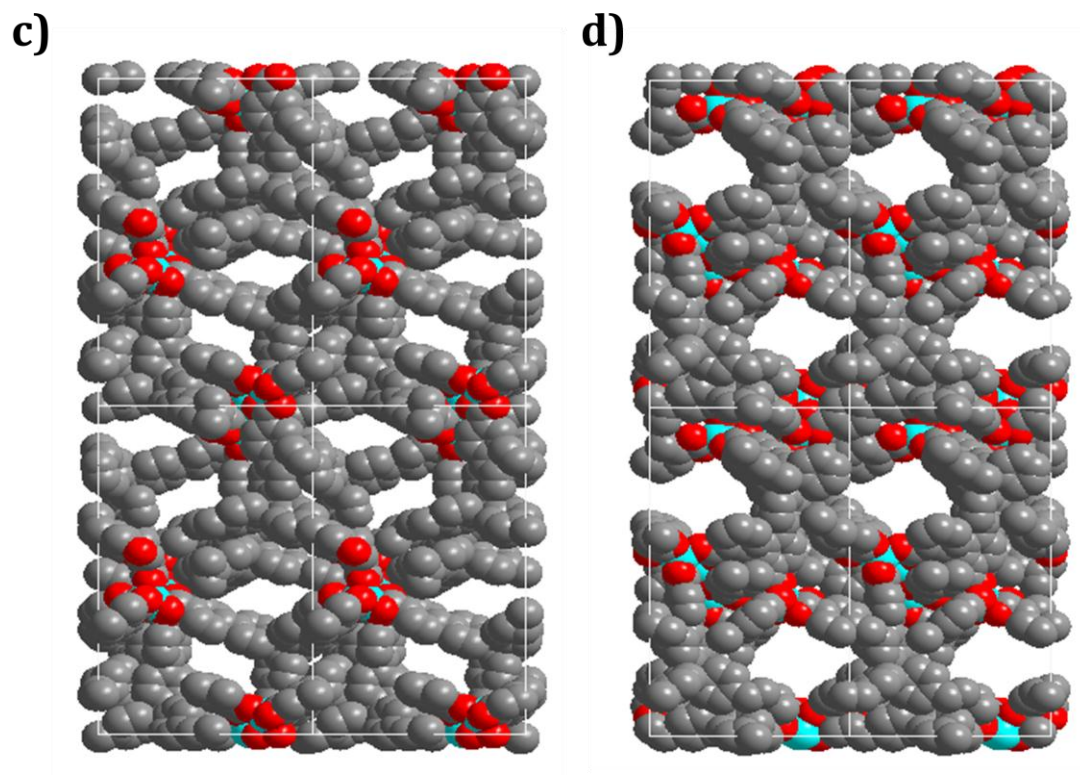


Figure S5. Space-filling model of **1** along the *a* axis (a) and the *b* axis (b) and of **2** along the *a* axis (c) and the *b* axis (d). Hydrogen atoms and guest molecules are omitted for clarity.

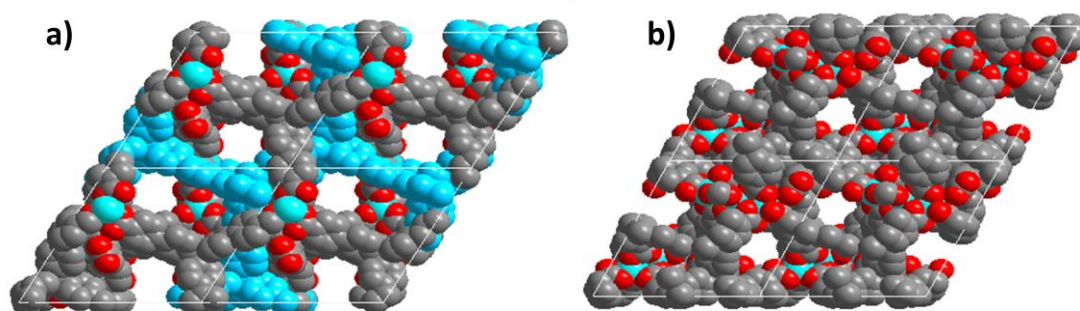


Figure S6. Space-filling model of **1** (a) and **2** (b) as viewed along the *b* axis. Hydrogen atoms and guest molecules are omitted for clarity.

Powder X-ray diffraction (PXRD) results:

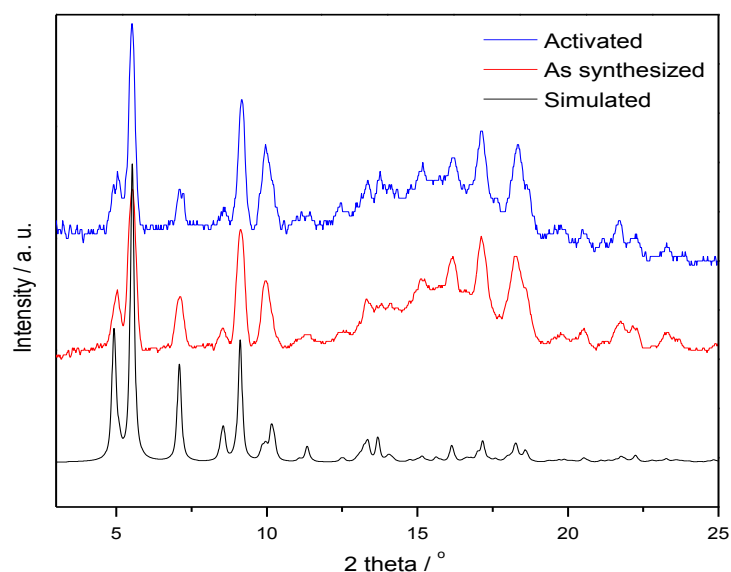


Figure S7. Powder X-ray diffraction patterns of as synthesized crystals of **1**, **1** after activation, and calculated PXRD pattern of **1**.

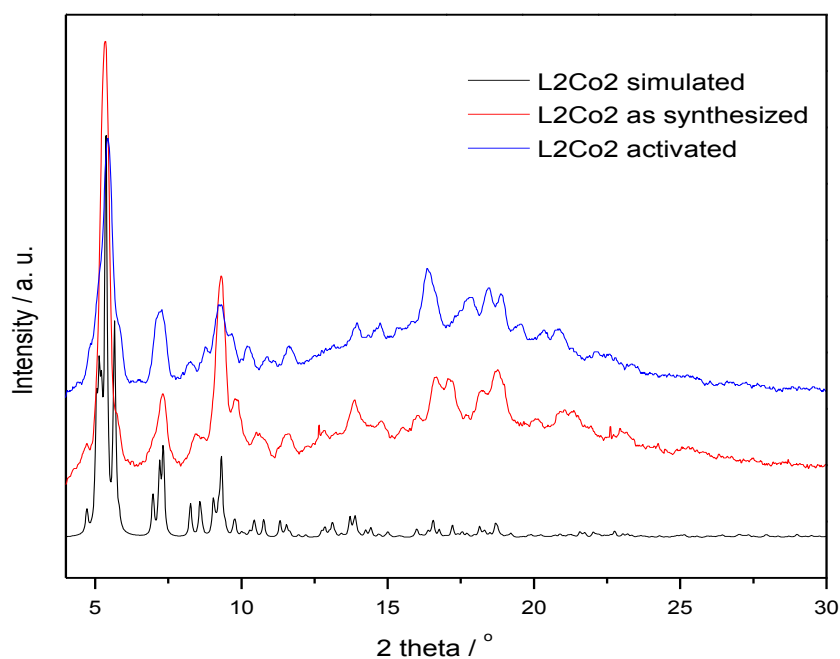


Figure S8. Powder X-ray diffraction patterns of as synthesized crystals of **2**, **2** after activation, and calculated PXRD pattern of **2**.

Analysis of sorption isotherms:

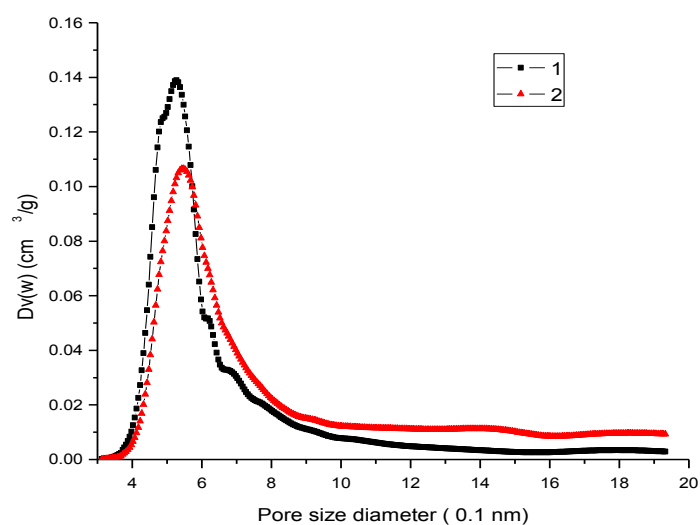


Figure S9. Pore size distribution for **1** (black) and **2** (red)

Table 2 Gas uptake data of **1** and **2**

MOF	gas	Temp.	amount of gas adsorb		Surface Area (m ² /g)	
			cm ³ /g (STP)	mmol/g	wt% BET	Langmuir
1	N ₂	77K	345.45	15.42	1284	1588
	H ₂	77K	229.98	10.27	2.07	
	CO ₂	273K	101.74	4.54		
		298K	63.06	2.82		
2	N ₂	77K	262.00	11.70	965	1051
	H ₂	77K	149.76	6.69	1.35	
	CO ₂	273K	75.99	3.39		
		298K	50.31	2.25		

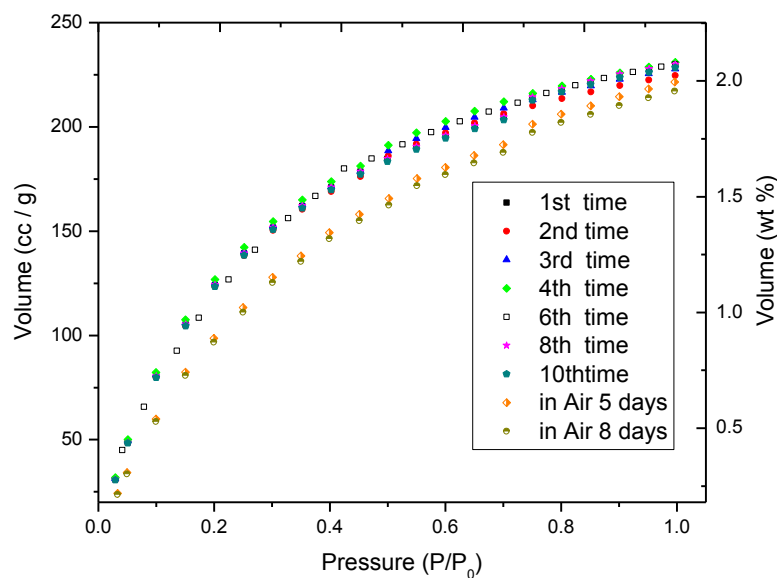


Figure S10. Repeated runs of H₂ adsorption isotherms of **1** at 77 K.

Analysis of isosteric adsorption enthalpy:

The isosteric heat of adsorption Q_{st} was determined by Virial Method (equation 1) from CO₂ adsorption isotherms at 293 K and 298 K,

$$\ln(p) = \ln(n) + 1/T \sum_{i=0}^m a_i n^i + \sum_{j=0}^n b_j n^j \quad (1)$$

Where p is the pressure expressed in mbar, n is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using equation (2). Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

$$Q_{st} = -R \sum_{i=0}^m a_i n^i$$

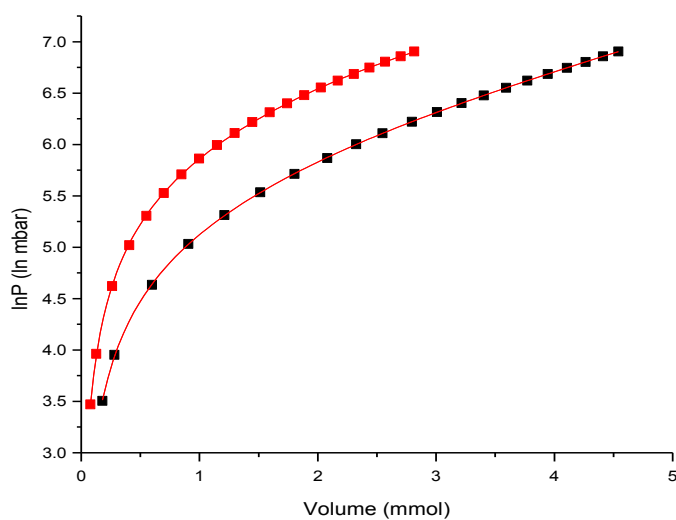


Figure S11. Virial expression fitting graphs for CO₂ adsorption data for **2** at 273K (black) and 298K (red). Fitting error = 0.011, $R^2 = 0.99994$.

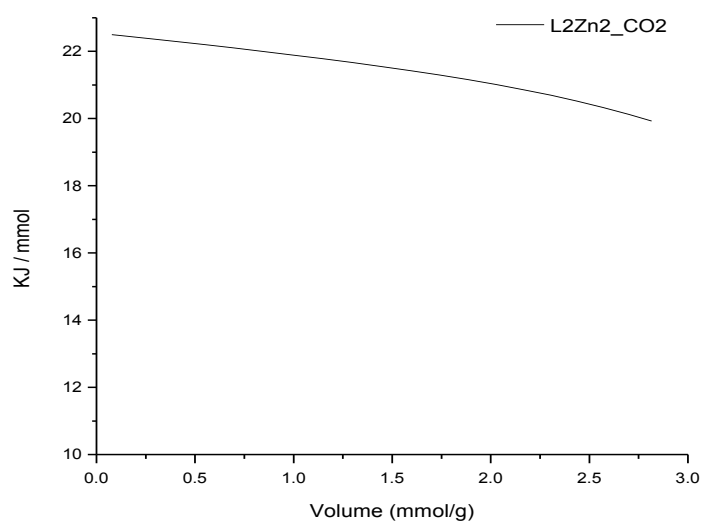


Figure S12. Isothermic heat of CO₂ adsorption for **1**.

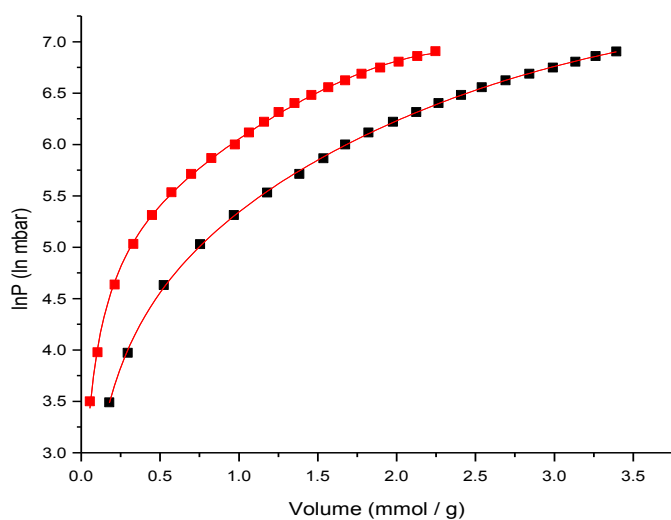


Figure S13. Virial expression fitting graphs for CO₂ adsorption data for **2** at 273K (black) and 298K (red). Fitting error = 0.029, $R^2 = 0.9990$.

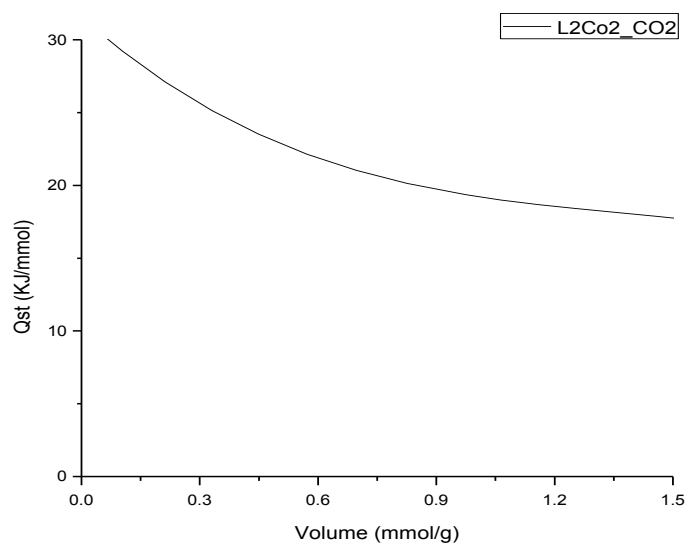


Figure S14. Isostatic heat of CO₂ adsorption for **2**.

Reference:

1. L. Ma, A. Jin, Z. Xie and W. Lin, *Angew. Chem. Int. Ed.*, 2009, **48**, 9905-9908.