

Inter-Ligand Cross-Links Determine Secondary Building Unit Formation in OligoMOFs

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SUPPORTING INFORMATION

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A. Materials

Reagents and solvents were procured from standard chemical vendors and used without further purification.

B. Methods

Powder X-Ray Diffraction. Powder X-Ray Diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer equipped with a LynxEye detector under ambient conditions. The Cu K α ($\lambda = 1.5418 \text{ \AA}$) X-ray source was operated at 40 kV and 40 mA in Bragg-Brentano geometry. Each pattern was collected in the 2θ range of 4° to 40° , with a step size of 0.02° and a scan speed of 0.4 seconds per step. Profile fitting and refinement of PXRD patterns was carried out using the GSAS-II package (Toby, B. H., & Von Dreele, R. B., *J. Appl. Cryst.*, **2013**, 46, 544-549).

Chemical Stability Tests. Activated MOF samples (15 mg) were immersed in 5 mL of organic solvent (MeOH, MeCN, CHCl_3 and CH_2Cl_2) and water for durations of 1 day and 7 days, followed by PXRD data collection.

SEM Imaging. Prior to SEM experiments, samples were soaked in DMF and CHCl_3 which was replaced three times. Samples were dispersed in CHCl_3 using a vortex mixer and deposited onto a Si wafer over conductive carbon tape on a sample holder. Samples were coated using Ir sputter coating for 60 seconds. Imaging was carried out using a FEI Apreo SEM instrument using a 5-10 kV energy source under vacuum.

NMR Spectroscopy. NMR spectra were collected using a JEOL spectrometer operated at 400 MHz. Chemical shifts are reported in parts per million (ppm) referenced to the d_6 -DMSO solvent peak.

TGA Analysis. TGA experiments were conducted using activated MOF samples placed in a 90 μL ceramic crucible. Samples were analyzed on a TA Instruments Discovery TGA 5500 using a temperature range of 30-550 $^\circ\text{C}$, scanning at 10 $^\circ\text{C}/\text{min}$ under nitrogen flow (100 cm^3/min).

FTIR Spectroscopy. Infrared spectra were collected on activated MOF samples using a Bruker Alpha-P ATR FTIR spectrometer with 32 scans collected at a resolution of 4 cm^{-1} .

Gas Sorption. Prior to gas sorption experiments, samples were soaked in CHCl_3 which was replaced three times and decanted after centrifugation. Samples were surface dried using filter paper and then activated under high vacuum at 120 $^\circ\text{C}$ for 8 hours using a Micromeritics Smart VacPrep degasser. Gas sorption was carried out using a Micromeritics Tristar II Plus sorption analyser using N_2 gas (UHP grade, Matheson Gas Products) at 77 K, as well as CO_2 (99.9% Bone Dry, Airgas) at 195 K. The temperature was maintained over the duration of each experiment using liquid nitrogen in a 3 L Dewar flask (77 K), a dry ice-acetone mixture in a 3 L Dewar flask (195 K). For the CO_2 195 K isotherm of $[\text{Zn}_2(\text{octyl}(\text{bdc})_2)(\text{bpy})]$, equilibration intervals were reduced to 10 s from 15 s to enable completion of the experiment before sample warming occurred. Surface areas were determined using the BETSI

program (Osterrieth, J. W., Rampersad, J., Madden, D., et al. *Adv. Mater.* **2022**, *34* (27), 2201502). Pore size distributions were calculated using the Horvath-Kawazoe module as implemented in the Microactive software suite (Micromeritics Inc., GA).

C. Ligand Synthesis

The syntheses of 2,2'-(hexane-1,6-diylbis(oxy))diterephthalic acid (hexyl(bdc)₂), 2,2'-(heptane-1,7-diylbis(oxy))diterephthalic acid (heptyl(bdc)₂), and 2,2'-(octane-1,7-diylbis(oxy))diterephthalic acid (octyl(bdc)₂) were carried out as per Dodson *et al.* (Dodson, R. A., Park, J., Kim, J., Cliffe, M. J. & Cohen, S. M., *Inorg. Chem.* **2022**, *61* (31), 12284-12292).

D. MOF Synthesis

MOF-508 Synthesis

This procedure was adapted from Chen *et al.* (Chen, B., Liang, C., Yang, J., Contreras, D. S., Clancy, Y. L., Lobkovsky, E. B., Yaghi, O. M. & Dai, S., *Angew. Chem. Int. Ed.*, **2006**, *45*, 1390-1393). Zn(NO₃)₂·6 H₂O (73 mg, 0.23 mmol), 4,4'-bipyridine (bpy, 18 mg, 0.11 mmol) and H₂bdc (39 mg, 0.23 mmol) were dissolved in 10 mL of dimethylformamide (DMF) and 10 mL of EtOH in a 6-dram vial. The vial was placed in an oven preheated to 90 °C for 24 h. After cooling, the solid product was washed 3x with DMF and 3x with hexane, and dried in air. Yield: 79 mg, 88 %.

[Zn₂(hexyl(bdc)₂)(bpy)] synthesis

This procedure was adapted from Zhang *et al.* (Zhang, Z., Nguyen, H. T. H., Miller, S. A., Ploskonka, A. M., DeCoste, J. B., & Cohen, S. M., *J. Am. Chem. Soc.* **2016**, *138* (3), 920-925). Zn(NO₃)₂·6 H₂O (104 mg, 0.35 mmol), 4,4'-bipyridine (bpy, 54 mg, 0.35 mmol) and hexyl(bdc)₂ (78 mg, 0.35 mmol) were dissolved in 4 mL of dimethylformamide (DMF) and 0.2 mL of EtOH in a 6-dram vial. The vial was placed in an oven preheated to 85 °C for 48 h. After cooling, the solid product was washed 3x with DMF and 3x with chloroform, and stored under chloroform. Yield: 34 mg, 75 %.

[Zn₂(heptyl(bdc)₂)(bpy)] synthesis

This procedure was adapted from Zhang *et al.* (Zhang, Z., Nguyen, H. T. H., Miller, S. A., Ploskonka, A. M., DeCoste, J. B., & Cohen, S. M., *J. Am. Chem. Soc.* **2016**, *138* (3), 920-925). Zn(NO₃)₂·6 H₂O (104 mg, 0.35 mmol), 4,4'-bipyridine (bpy, 54 mg, 0.35 mmol) and heptyl(bdc)₂ (81 mg, 0.35 mmol) were dissolved in 4 mL of dimethylformamide (DMF) and 0.2 mL of EtOH in a 6-dram vial. The vial was placed in an oven preheated to 85 °C for 48 h. After cooling, the solid product was washed 3x with DMF and 3x with chloroform, and stored under chloroform. Yield: 36 mg, 78 %.

[Zn₂(octyl(bdc)₂)(bpy)] synthesis

This procedure was adapted from Zhang *et al.* (Zhang, Z., Nguyen, H. T. H., Miller, S. A., Ploskonka, A. M., DeCoste, J. B., & Cohen, S. M., *J. Am. Chem. Soc.* **2016**, *138* (3), 920-925). Zn(NO₃)₂·6 H₂O (104 mg, 0.35 mmol), 4,4'-bipyridine (bpy, 54 mg, 0.35 mmol) and octyl(bdc)₂ (83 mg,

0.35 mmol) were dissolved in 4 mL of dimethylformamide (DMF) and 0.2 mL of EtOH in a 6-dram vial. The vial was placed in an oven preheated to 85 °C for 48 h. After cooling, the solid product was washed 3x with DMF and 3x with chloroform, and stored under chloroform. Yield: 38 mg, 82 %.

E. Supplementary Tables

Table S1. Summary of attempted crystallisation conditions. Reagent and solvent quantities are as per the synthetic procedures in Section D.

Solvent	Temp. (°C)	Time (h)	Modulator	Ligand		
				Hexyl(bdc) ₂	Heptyl(bdc) ₂	Octyl(bdc) ₂
DMF	120	24	-	Microcrystalline, [Zn ₂ (hexyl(bdc) ₂)(bpy)] pcu	Microcrystalline, [Zn ₂ (heptyl(bdc) ₂)(bpy)] honeycomb-like	Microcrystalline, [Zn ₂ (octyl(bdc) ₂)(bpy)] honeycomb-like
DEF	120	24	-	Microcrystalline, [Zn ₂ (hexyl(bdc) ₂)(bpy)] pcu	Microcrystalline, [Zn ₂ (heptyl(bdc) ₂)(bpy)] honeycomb-like	Microcrystalline, [Zn ₂ (octyl(bdc) ₂)(bpy)] honeycomb-like
DMF:MeOH (19:1)	105	24	-	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase
DMF:MeOH (19:1)	105	24	-	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase
DMF:EtOH (19:1)	105	24	-	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase
DMF:EtOH (19:1)	105	24	-	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase	Agglomerated, indeterminate phase
DMF:H ₂ O (19:1)	105	24	-	Amorphous	Amorphous	Amorphous
DMF:H ₂ O (19:1)	105	24	-	Amorphous	Amorphous	Amorphous
DMF	120	72	HNO ₃ (50 μL)	Block single crystals, OligoIRMOF-1	Block single crystals, OligoIRMOF-1	Polycrystalline, OligoIRMOF-1
DEF	120	72	HNO ₃ (50 μL)	Polycrystalline, OligoIRMOF-1	Polycrystalline, OligoIRMOF-1	Polycrystalline, OligoIRMOF-1

Table S2. Summary of PXRD refinement parameters.

Compound	Reference structure	Space Group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	R _{wp} (%)
[Zn ₂ (hexyl(bdc) ₂)(bpy)]	ECIWUJ04 (pcu <i>lp</i>)	<i>P2</i> ₁ / <i>c</i>	14.027	10.786	22.031	90	90.269	90	10.85
[Zn ₂ (heptyl(bdc) ₂)(bpy)]	EVOTIT	<i>R</i> -3 <i>c</i>	53.988	53.988	17.433	90	90	120	11.32
[Zn ₂ (octyl(bdc) ₂)(bpy)]	EVOTIT	<i>R</i> -3 <i>c</i>	54.617	54.617	17.453	90	90	120	10.10

Table S3. Summary of ligand ratios determined by digestion ¹H NMR.

Compound	bpy ligands per bdc ²⁻ unit
MOF-508	0.49
[Zn ₂ (hexyl(bdc) ₂)(bpy)]	0.52
[Zn ₂ (heptyl(bdc) ₂)(bpy)]	0.49
[Zn ₂ (octyl(bdc) ₂)(bpy)]	0.48

Table S4. Summary of TGA decomposition temperatures.

Compound	TGA decomposition temperature (°C)
MOF-508	354
[Zn ₂ (hexyl(bdc) ₂)(bpy)]	354
[Zn ₂ (heptyl(bdc) ₂)(bpy)]	359
[Zn ₂ (octyl(bdc) ₂)(bpy)]	370

Table S5. Summary of pore properties calculated from 195 K CO₂ isotherms.

Compound	Saturation Uptake (cm ³ /g STP)	Pore Volume (cm ³ /g)	BET Surface Area (m ² /g)	Peak HK Pore Width (Å)
MOF-508*	188	0.344	-	-
[Zn ₂ (hexyl(bdc) ₂)(bpy)]	94	0.171	245 ±3.5	7.1
[Zn ₂ (heptyl(bdc) ₂)(bpy)]	204	0.372	794 ±40	12.7
[Zn ₂ (octyl(bdc) ₂)(bpy)]	112	0.204	303 ±26	10.0

*Flexible isotherm does not permit BET or HK treatment.

F. Supplementary Figures

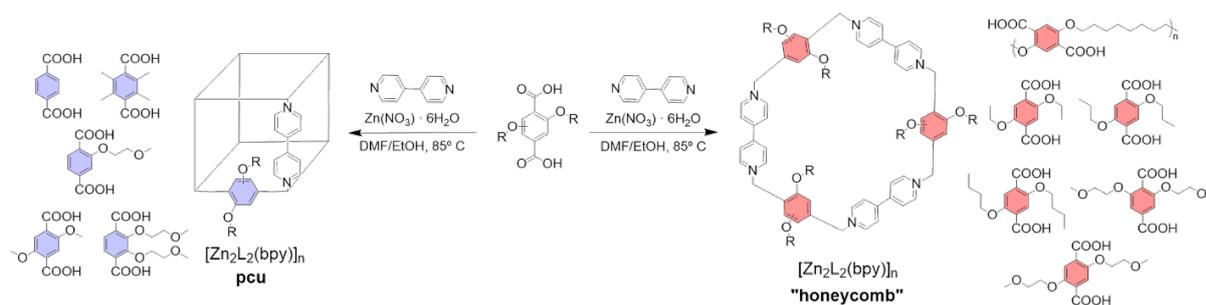


Figure S1. Schematic summarizing reported examples of adoption of **pcu** or honeycomb-like network topologies by various bdc^{2-} -based ligands in combination with $Zn(NO_3)_2 \cdot 6H_2O$ and bpy .

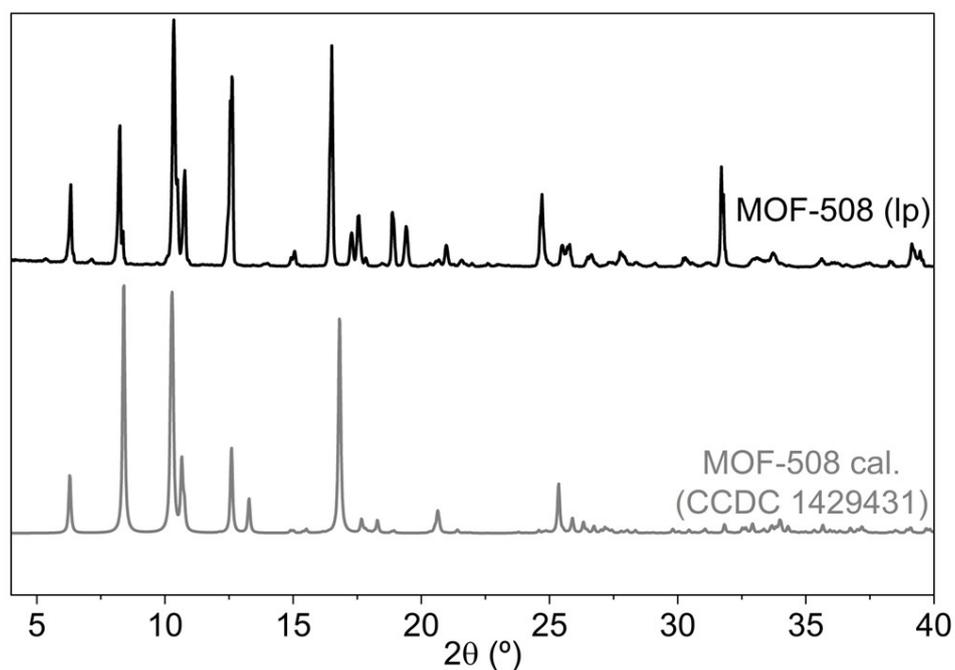


Figure S2. PXRD pattern of as-synthesized MOF-508 (DMF-loaded) (black) compared to the PXRD pattern calculated for the reference MOF-508 phase (ECIWUJ01, gray).

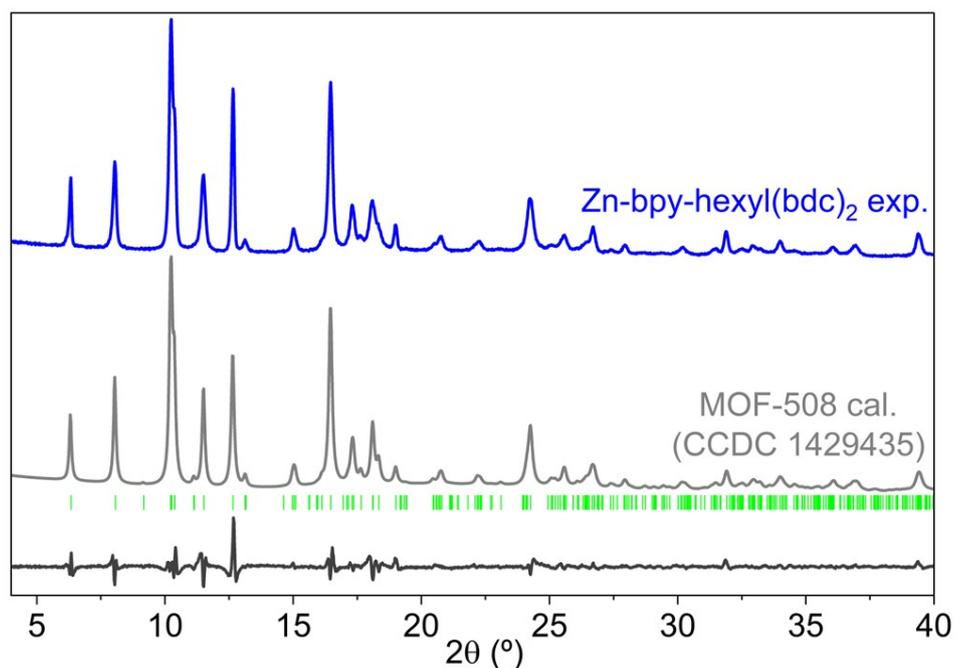


Figure S3. The PXRD pattern of as-synthesized $[\text{Zn}_2(\text{hexyl}(\text{bdc})_2(\text{bpy}))]$ (blue) compared to the PXRD pattern calculated for the reference phase (ECIWUJ04, gray), with the reflection positions (green), and the difference plot (dark gray).

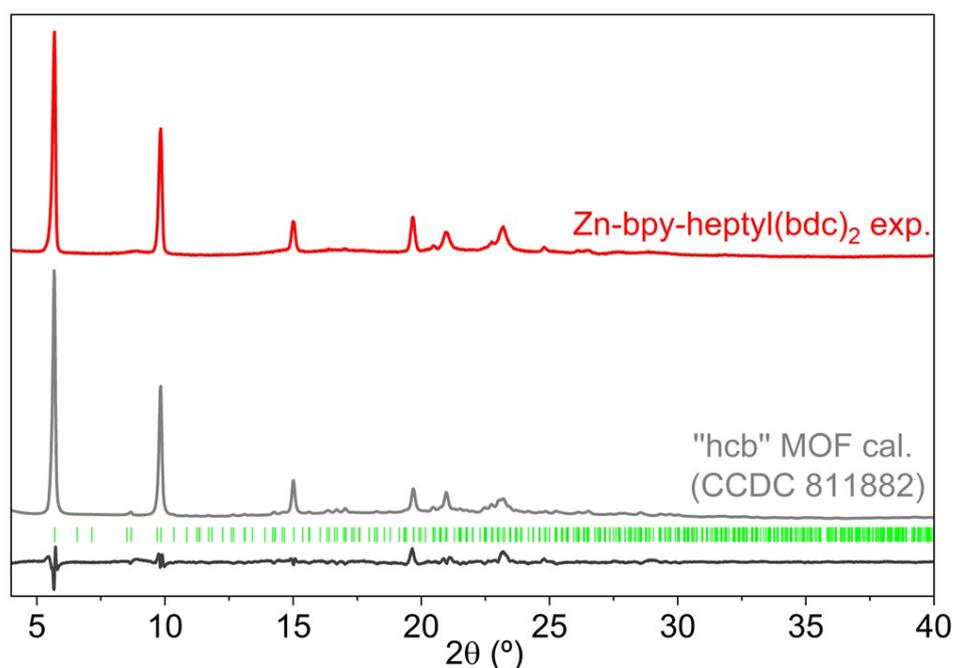


Figure S4. PXRD pattern of as-synthesized $[\text{Zn}_2(\text{heptyl}(\text{bdc})_2(\text{bpy}))]$ (red) compared to PXRD patterns calculated for reported phase, with the reflections (green), and the difference (dark gray).

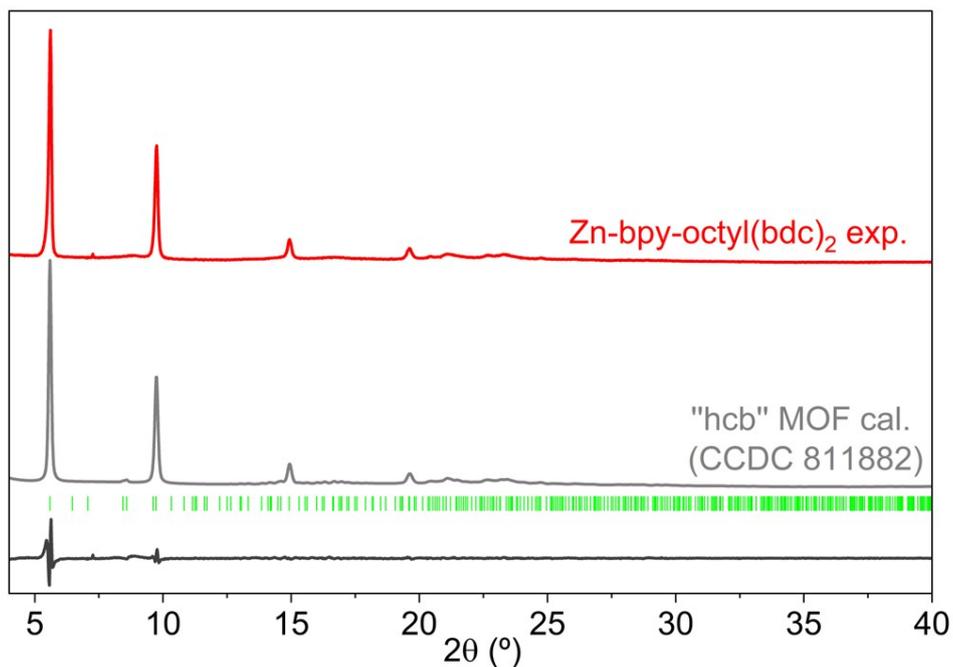


Figure S5. PXRd pattern of as-synthesized $[Zn_2(octyl(bdc)_2)(bpy)]$ (red) compared to PXRd patterns calculated for reported phase, with the reflections (green), and the difference (dark gray).

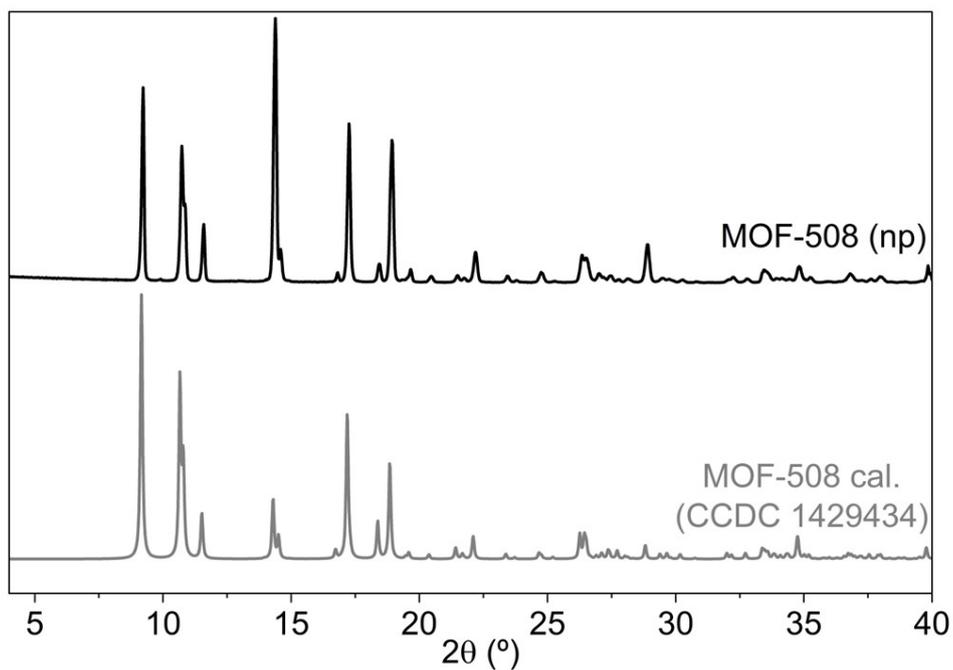


Figure S6. Experimental PXRd pattern of activated MOF-508 (*np*, black) compared to the calculated PXRd pattern of activated MOF-508 (ECIWUJ03, gray).

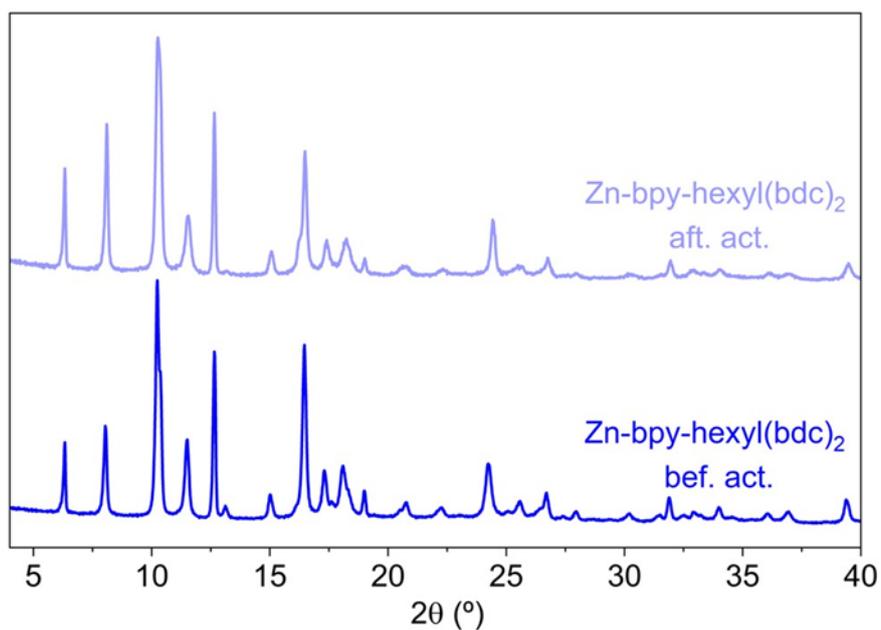


Figure S7. PXRD pattern of activated [Zn₂(hexyl(bdc)₂)(bpy)] compared to as-synthesized [Zn₂(hexyl(bdc)₂)(bpy)].

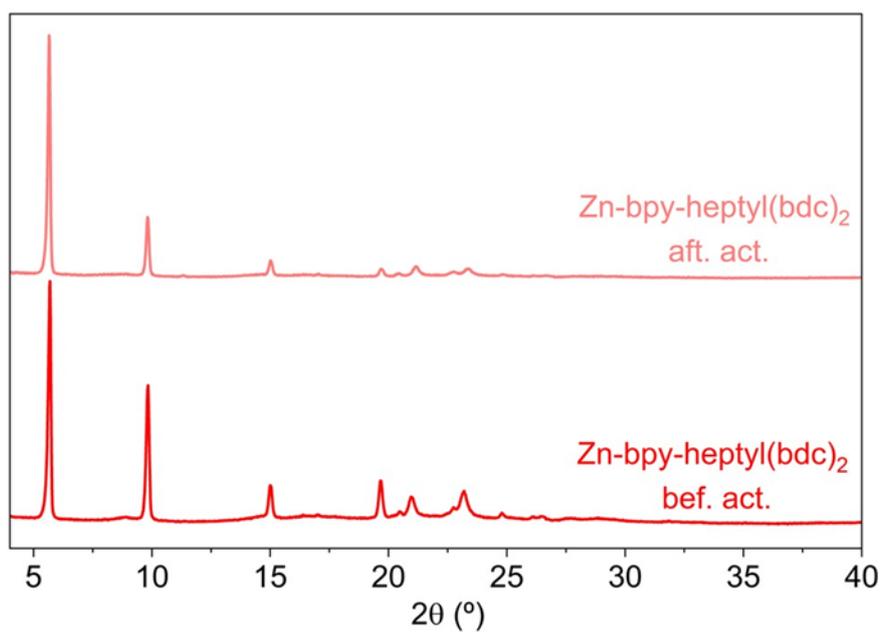


Figure S8. PXRD pattern of activated [Zn₂(heptyl(bdc)₂)(bpy)] compared to as-synthesized [Zn₂(heptyl(bdc)₂)(bpy)].

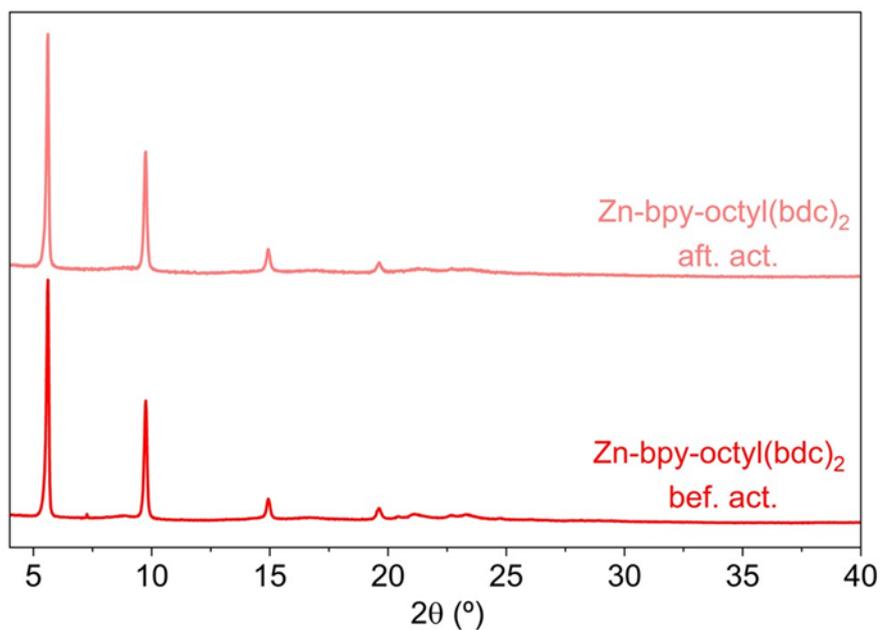


Figure S9. PXRD pattern of activated $[\text{Zn}_2(\text{octyl}(\text{bdc})_2)(\text{bpy})]$ compared to as-synthesized $[\text{Zn}_2(\text{octyl}(\text{bdc})_2)(\text{bpy})]$.

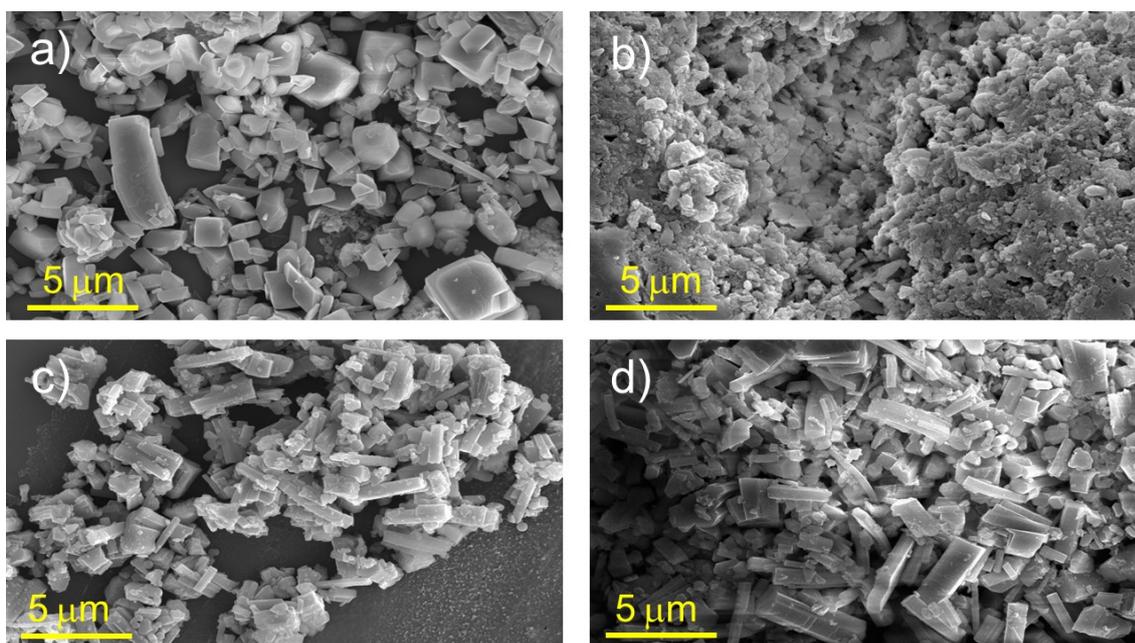


Figure S10. SEM micrographs of: (a) as synthesized MOF-508, (b) as synthesized $[\text{Zn}_2(\text{hexyl}(\text{bdc})_2)(\text{bpy})]$, (c) $[\text{Zn}_2(\text{heptyl}(\text{bdc})_2)(\text{bpy})]$, (d) $[\text{Zn}_2(\text{octyl}(\text{bdc})_2)(\text{bpy})]$.

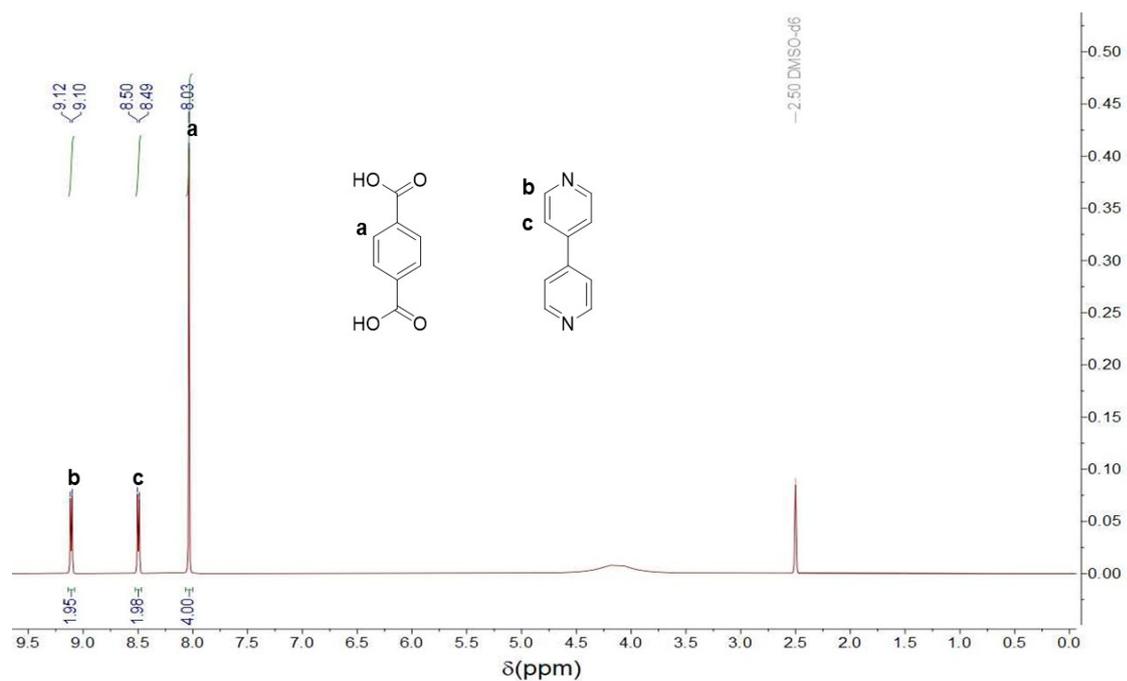


Figure S11. ^1H NMR spectrum of digested MOF-508.

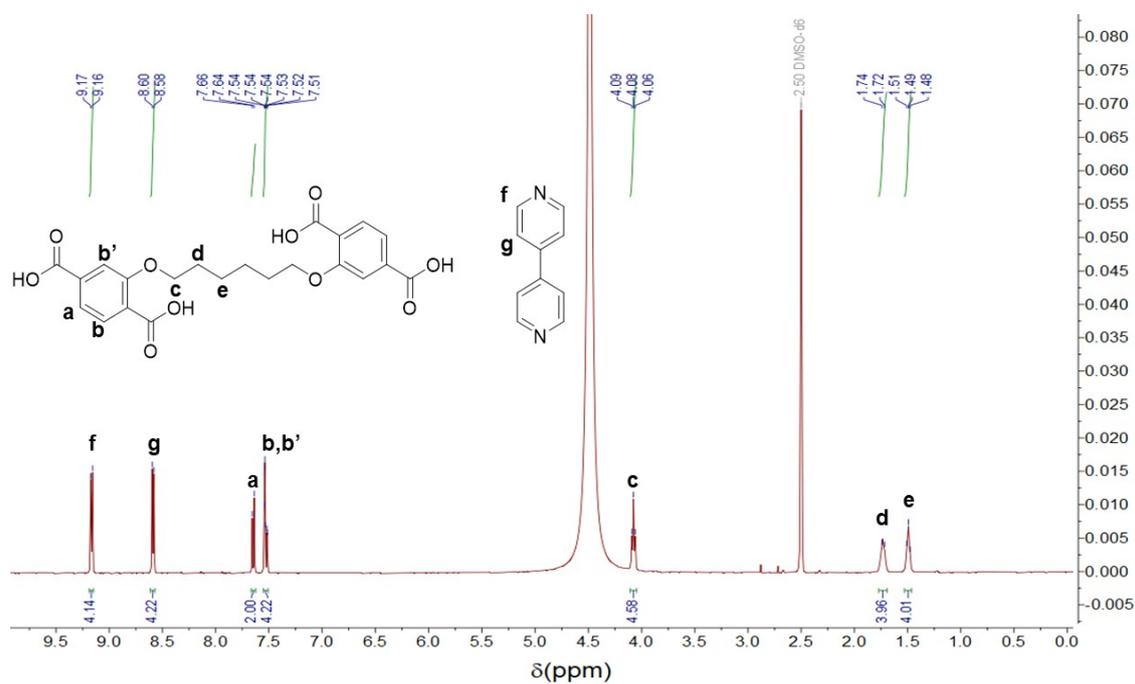


Figure S12. ^1H NMR spectrum of digested $[\text{Zn}_2(\text{hexyl}(\text{bdc})_2)(\text{bpy})]$.

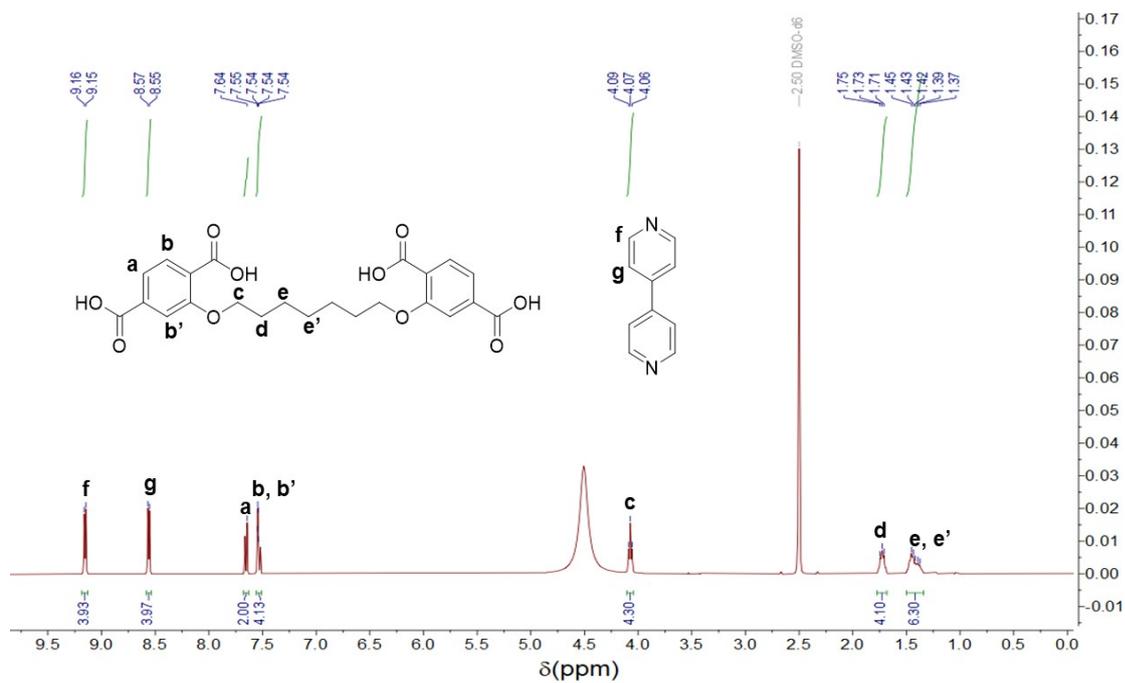


Figure S13. ^1H NMR spectrum of digested $[\text{Zn}_2(\text{heptyl}(\text{bdc})_2)(\text{bpy})]$.

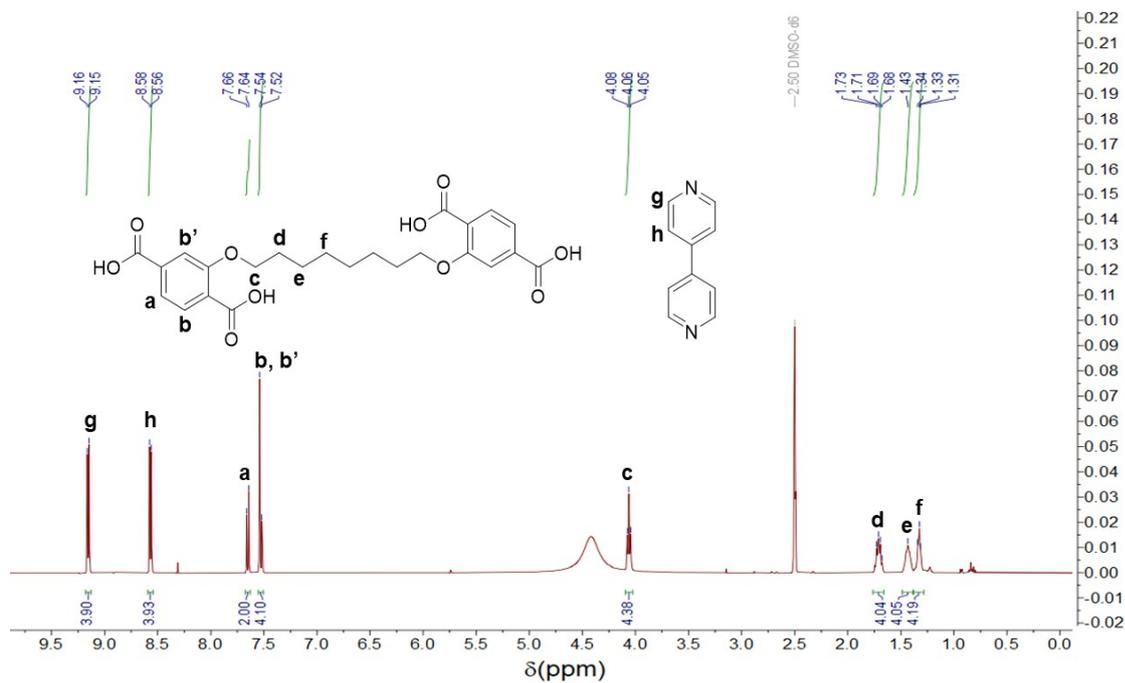


Figure S14. ^1H NMR spectrum of digested $[\text{Zn}_2(\text{octyl}(\text{bdc})_2)(\text{bpy})]$.

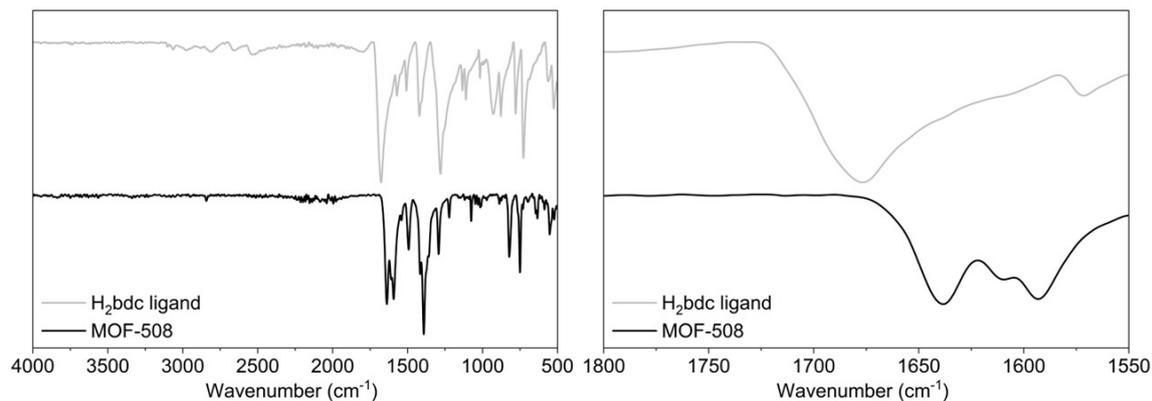


Figure S15. FTIR spectrum of activated MOF-508 compared to the H₂bdc ligand; (a) full spectrum, (b) enlarged view of the region from 1800-1550 cm⁻¹.

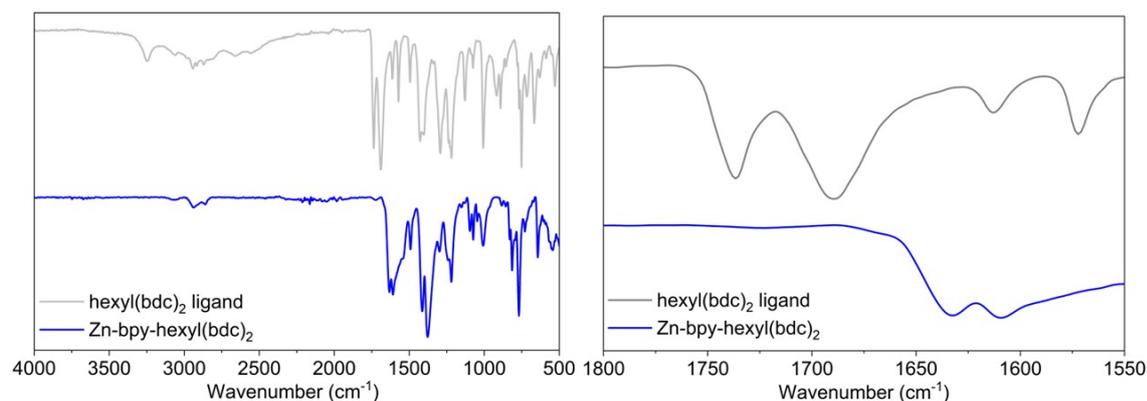


Figure S16. FTIR spectrum of activated [Zn₂(hexyl(bdc)₂)(bpy)] compared to the hexyl(bdc)₂ ligand; (a) full spectrum, (b) enlarged view of the region from 1800-1550 cm⁻¹.

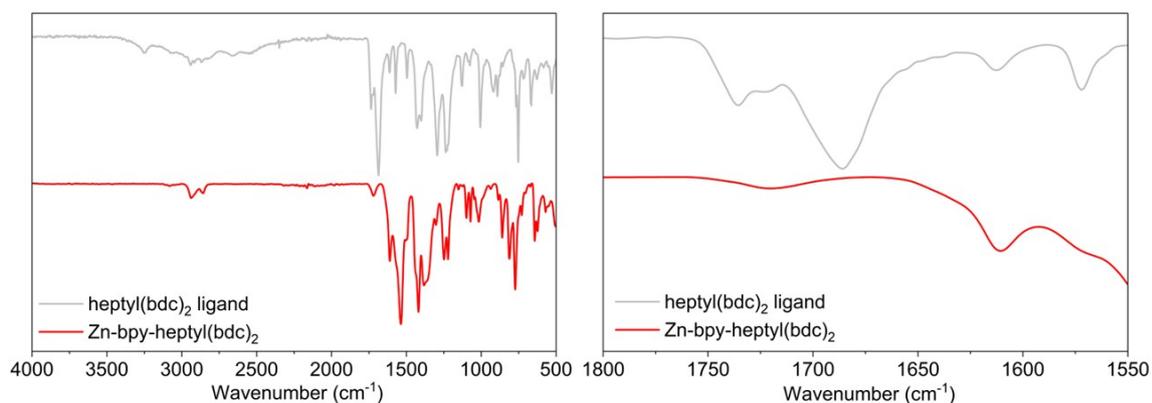


Figure S17. FTIR spectrum of activated [Zn₂(heptyl(bdc)₂)(bpy)] compared to the heptyl(bdc)₂ ligand; (a) full spectrum, (b) enlarged view of the region from 1800-1550 cm⁻¹.

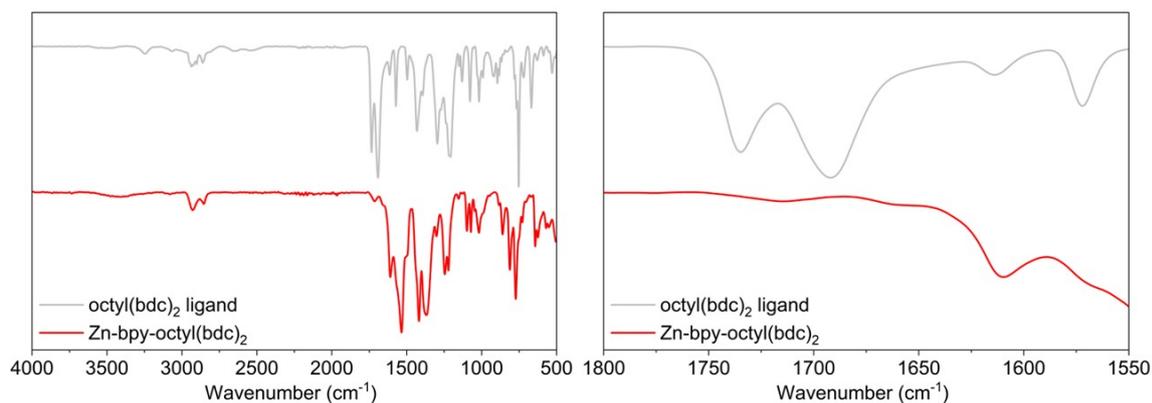


Figure S18. FTIR spectrum of activated $[Zn_2(octyl(bdc)_2)(bpy)]$ compared to the $octyl(bdc)_2$ ligand; (a) full spectrum, (b) enlarged view of the region from $1800-1550\text{ cm}^{-1}$.

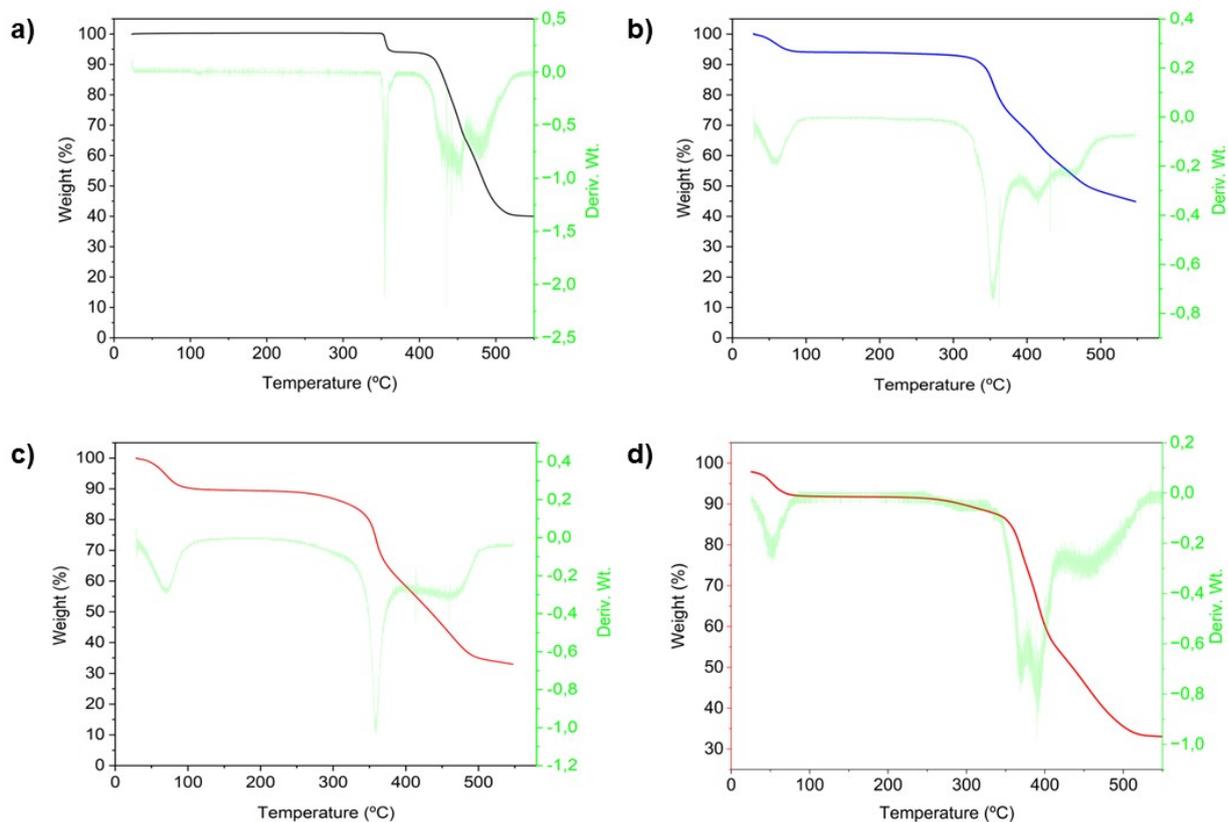


Figure S19. TGA curve and the first derivative of weight % with respect to temperature (blue) of: (a) MOF-508 (black), (b) $[Zn_2(hexyl(bdc)_2)(bpy)]$ (blue), (c) $[Zn_2(heptyl(bdc)_2)(bpy)]$ (red), (d) $[Zn_2(octyl(bdc)_2)(bpy)]$ (red).

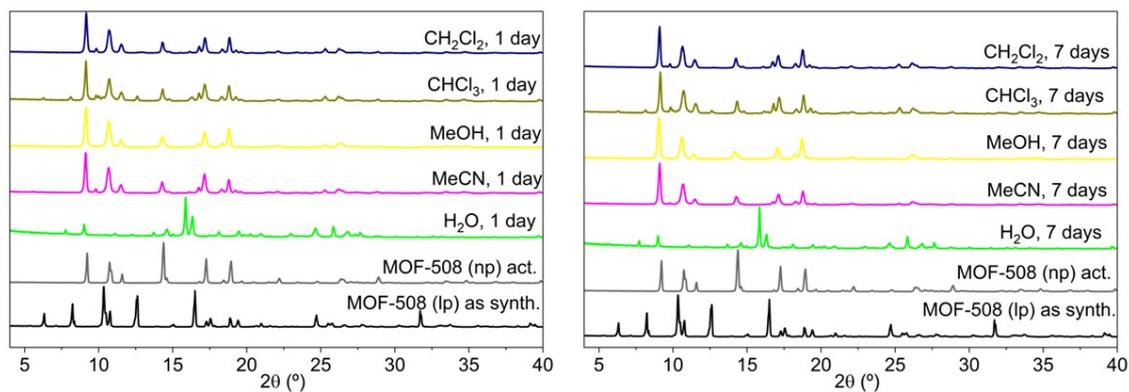


Figure S20. PXRD patterns of MOF-508 after soaking in various solvents for 1 day (left) and 7 days (right) respectively.

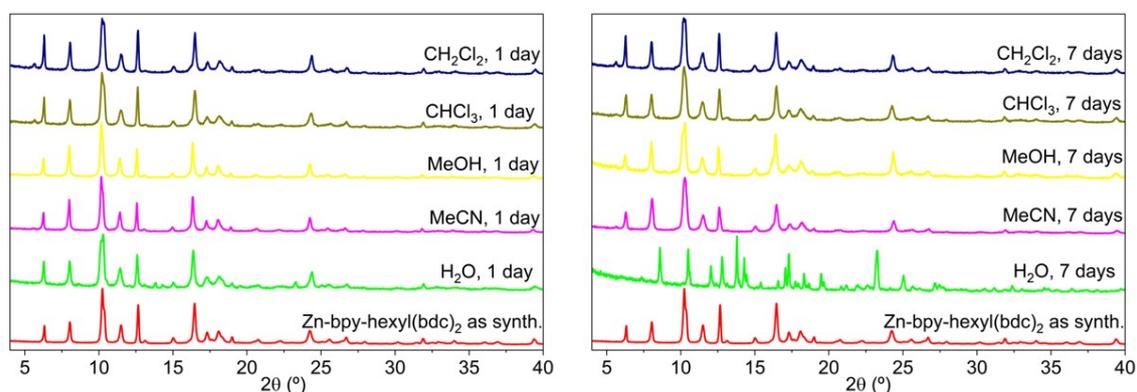


Figure S21. PXRD patterns of $[Zn_2(\text{hexyl}(\text{bdc})_2)(\text{bpy})]$ after soaking in various solvents for 1 day (left) and 7 days (right) respectively.

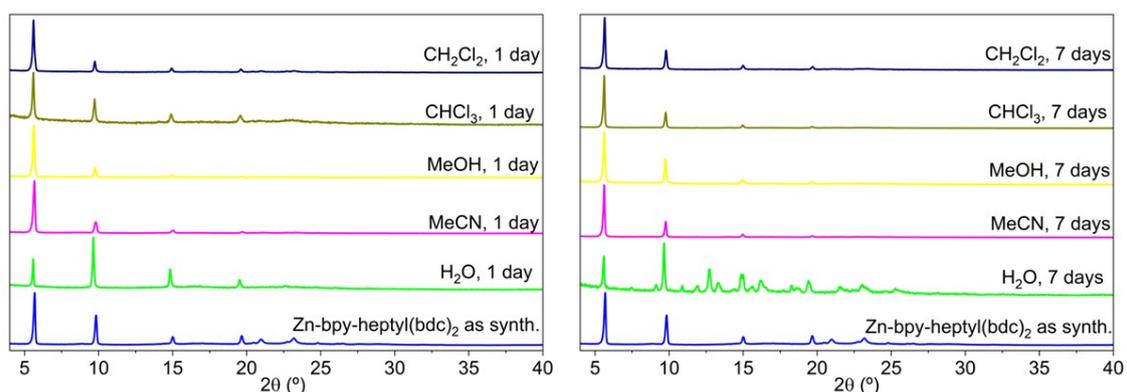


Figure S22. PXRD patterns of $[Zn_2(\text{heptyl}(\text{bdc})_2)(\text{bpy})]$ after soaking in various solvents for 1 day (left) and 7 days (right) respectively.

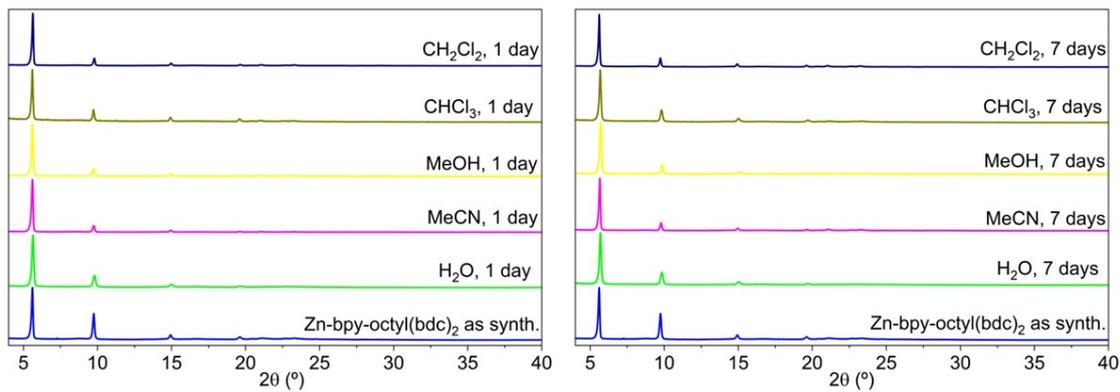


Figure S23. PXRD patterns of $[Zn_2(octyl(bdc)_2)(bpy)]$ after soaking in various solvents for 1 day (left) and 7 days (right) respectively.

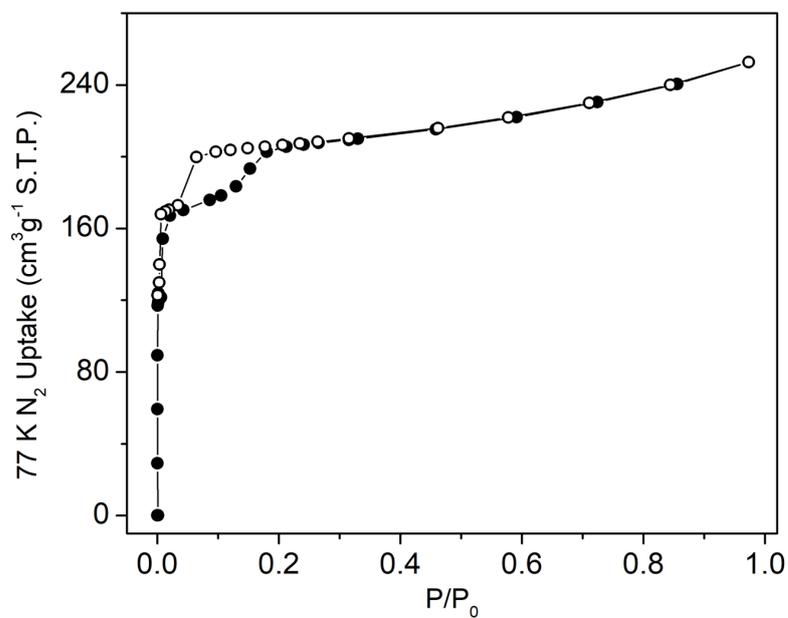


Figure S24. N_2 sorption isotherm (77 K) of MOF-508 (adsorption: closed symbols, desorption: closed symbols).

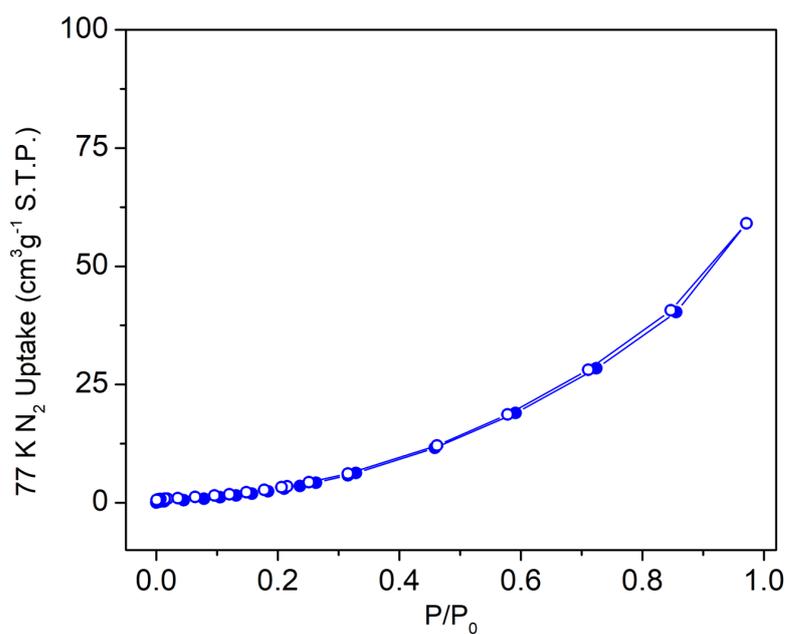


Figure S25. N₂ sorption isotherm (77 K) of [Zn₂(hexyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).

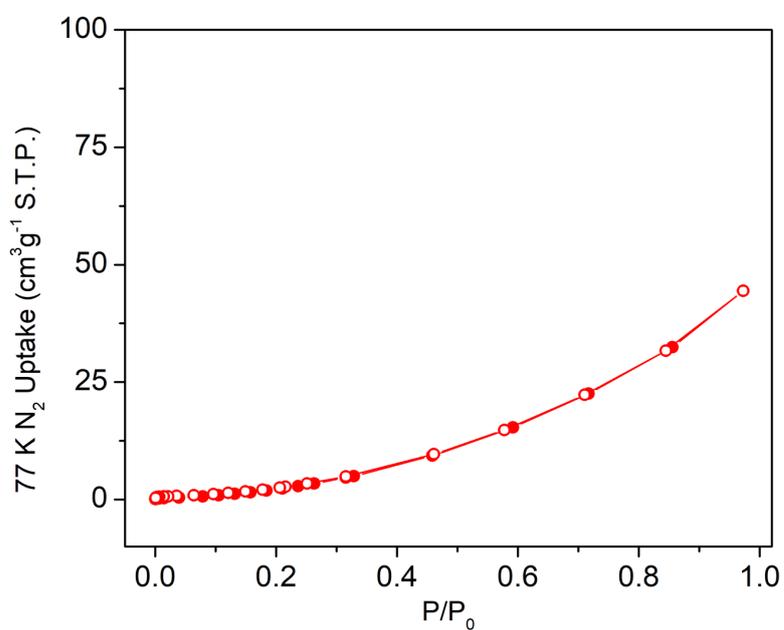


Figure S26. N₂ sorption isotherm (77 K) of [Zn₂(heptyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).

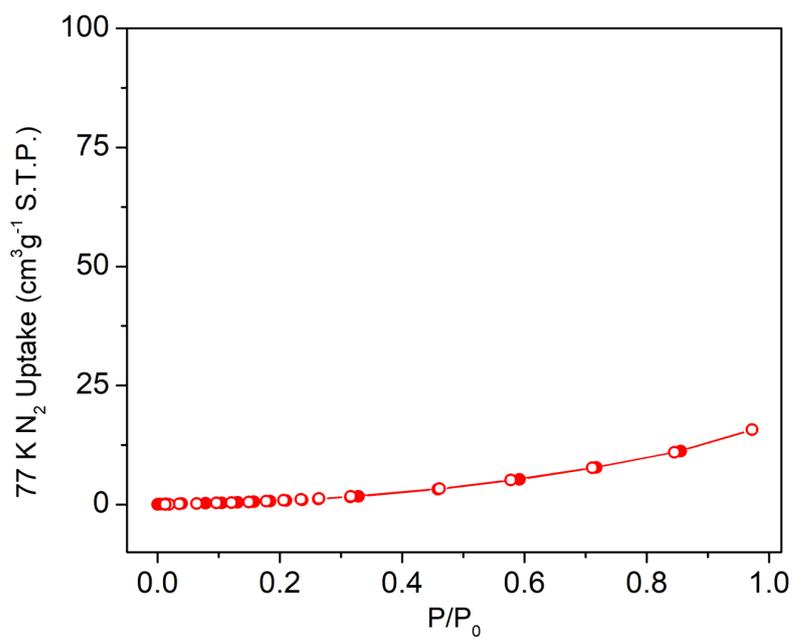


Figure S27. N₂ sorption isotherm (77 K) of [Zn₂(octyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).

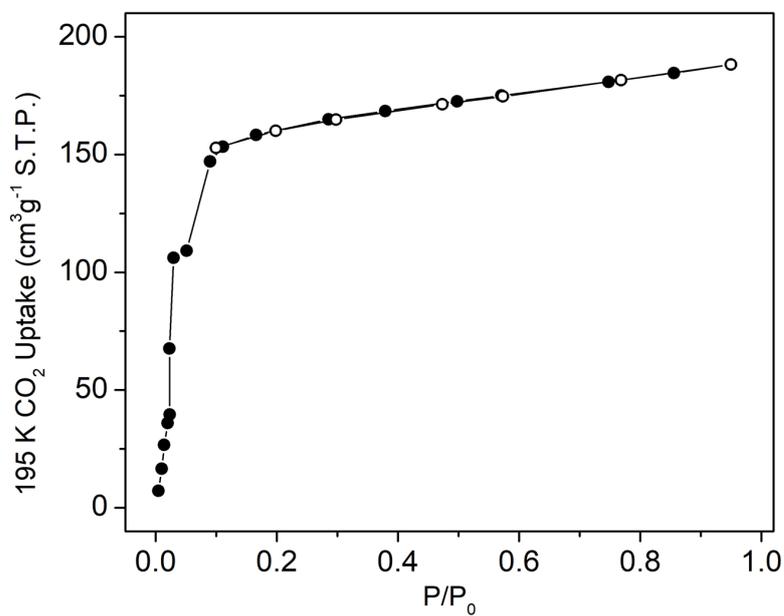


Figure S28. 195 K CO₂ sorption isotherm of MOF-508 (adsorption: closed symbols, desorption: closed symbols).

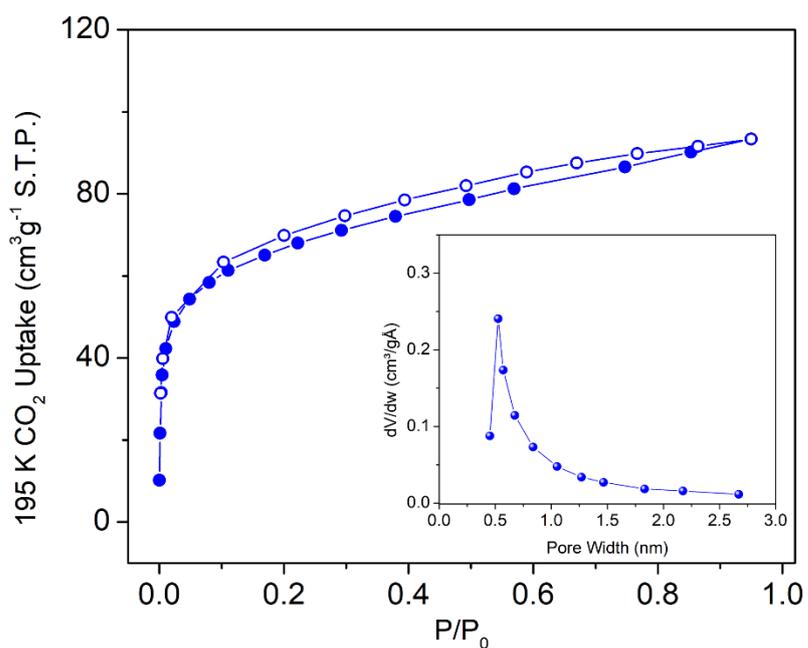


Figure S29. CO₂ sorption isotherm (195 K) and HK pore size distribution (inset) of [Zn₂(hexyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).

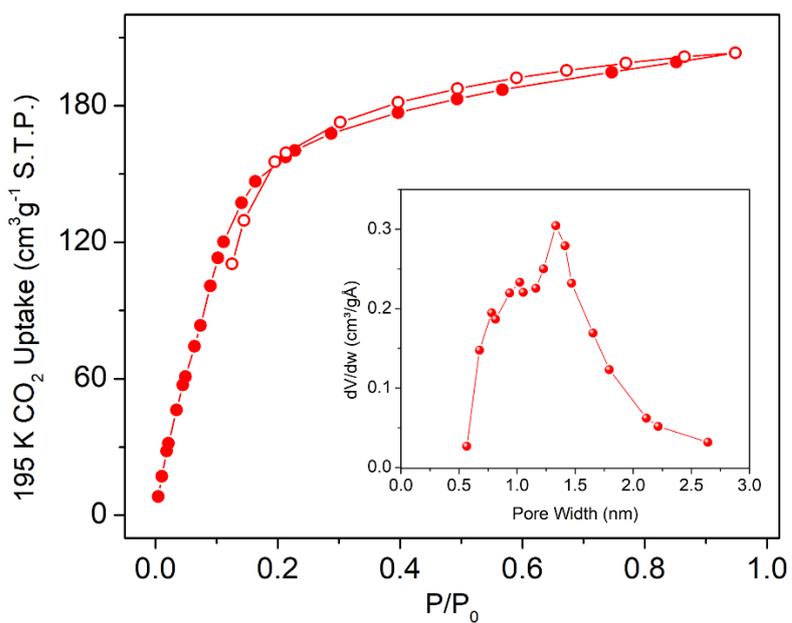


Figure S30. CO₂ sorption isotherm (195 K) and HK pore size distribution (inset) of [Zn₂(heptyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).

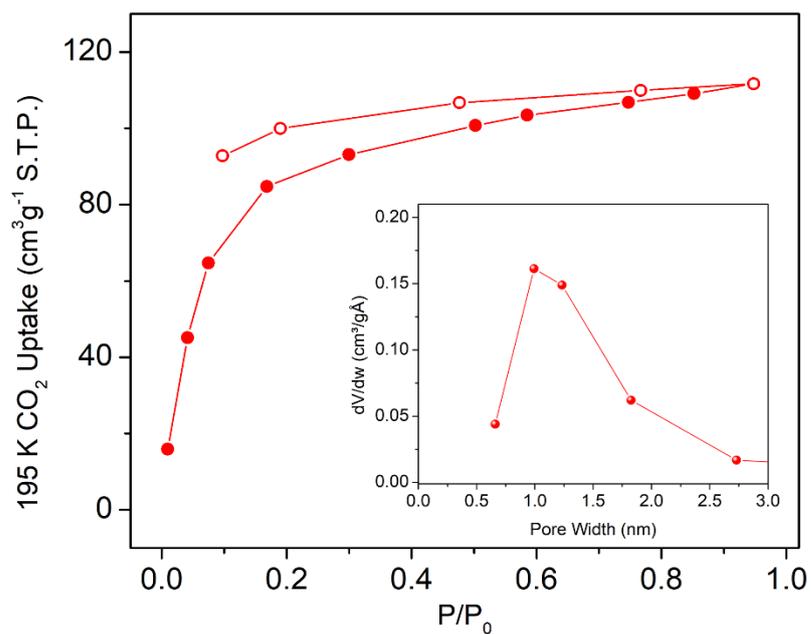


Figure S31. CO₂ sorption isotherm (195 K) and HK pore size distribution (inset) of [Zn₂(octyl(bdc)₂)(bpy)] (adsorption: closed symbols, desorption: closed symbols).