

*Supporting Information for:*

**Mixing Ligands to Enhance Gas Uptake in PolyMOFs**

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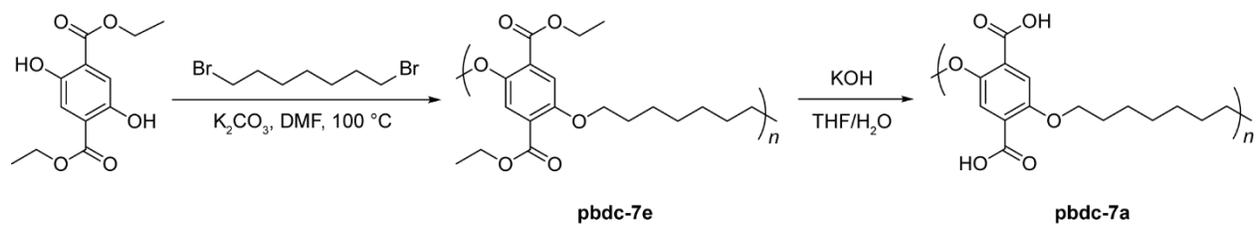
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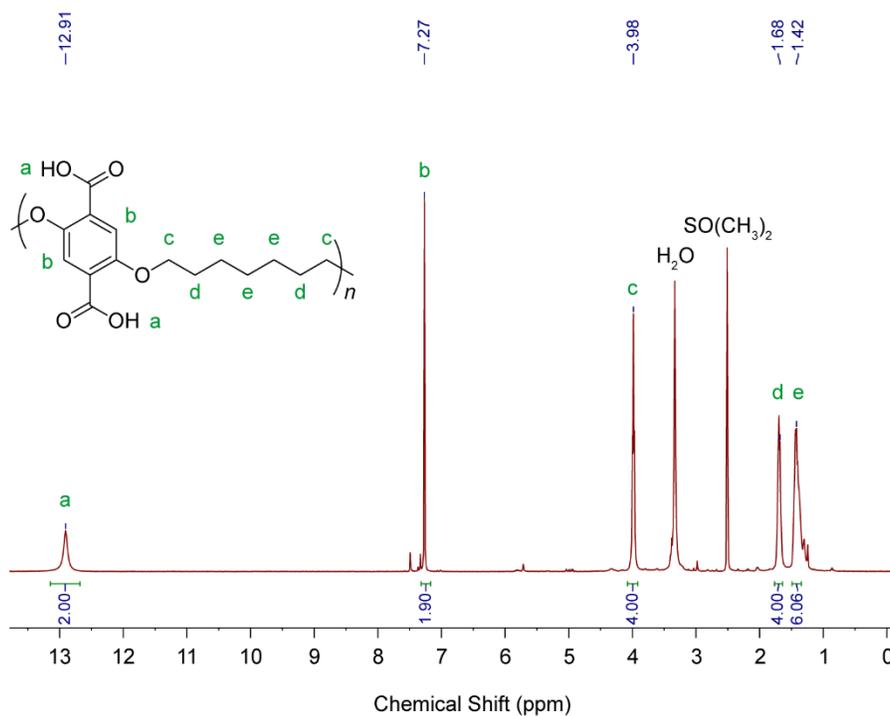
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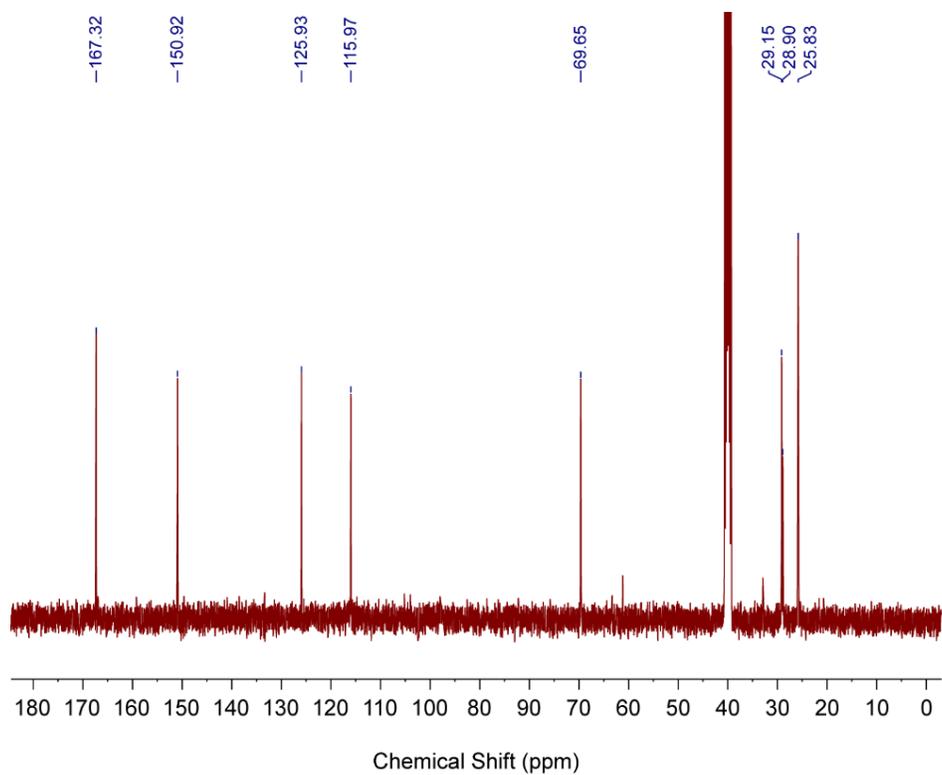
## 1. Supplementary Figures Cited in Main Text



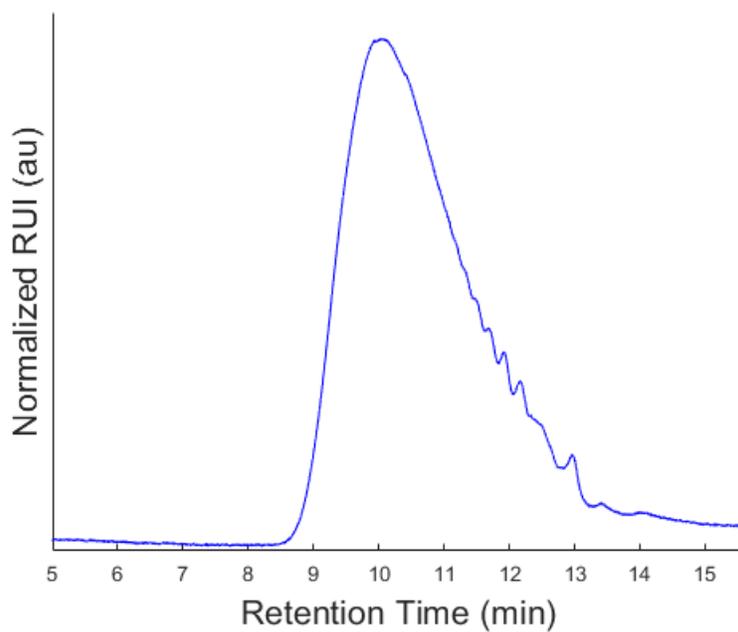
**Scheme S1.** Synthesis of polymer ligand **pbdc-7a**.



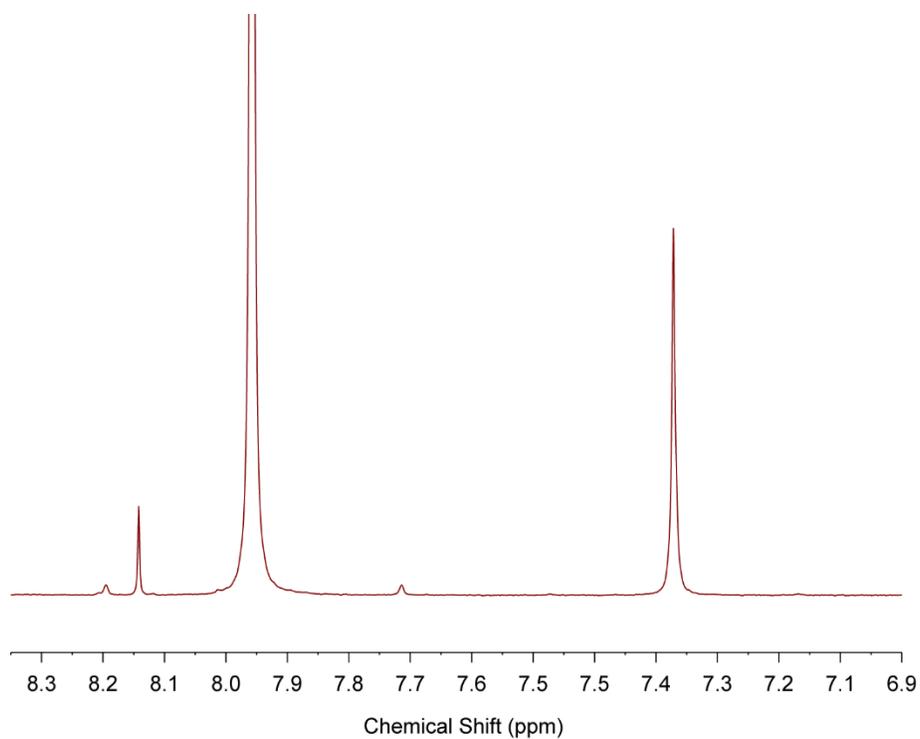
**Figure S1.**  $^1\text{H}$  NMR spectrum of **pbdc-7a** digested in  $\text{DMSO-}d_6$ .



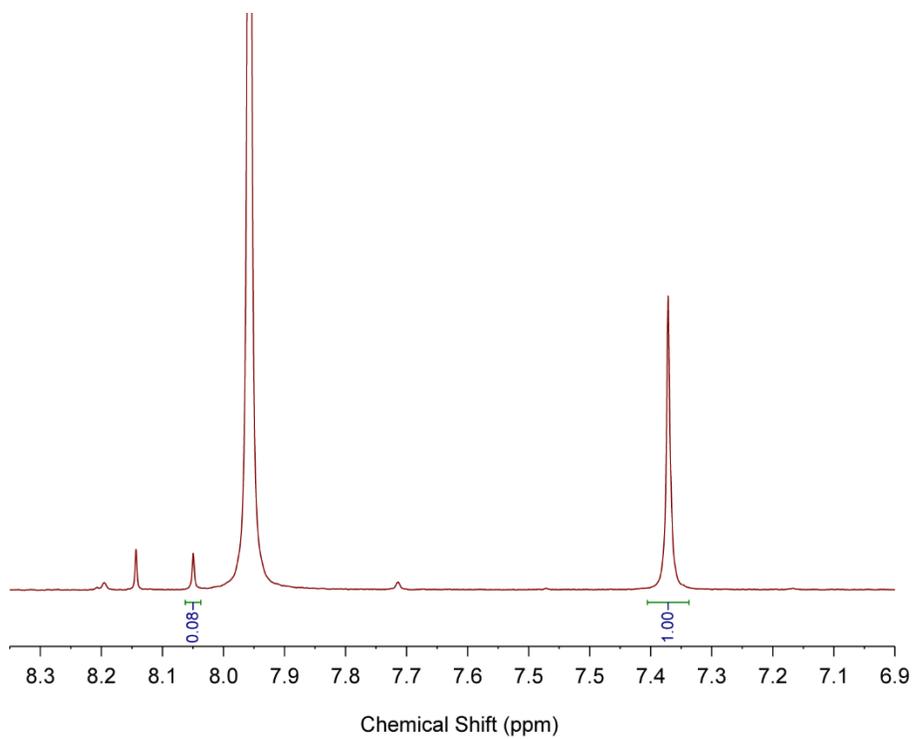
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **pbdc-7a** in  $\text{DMSO-}d_6$ .



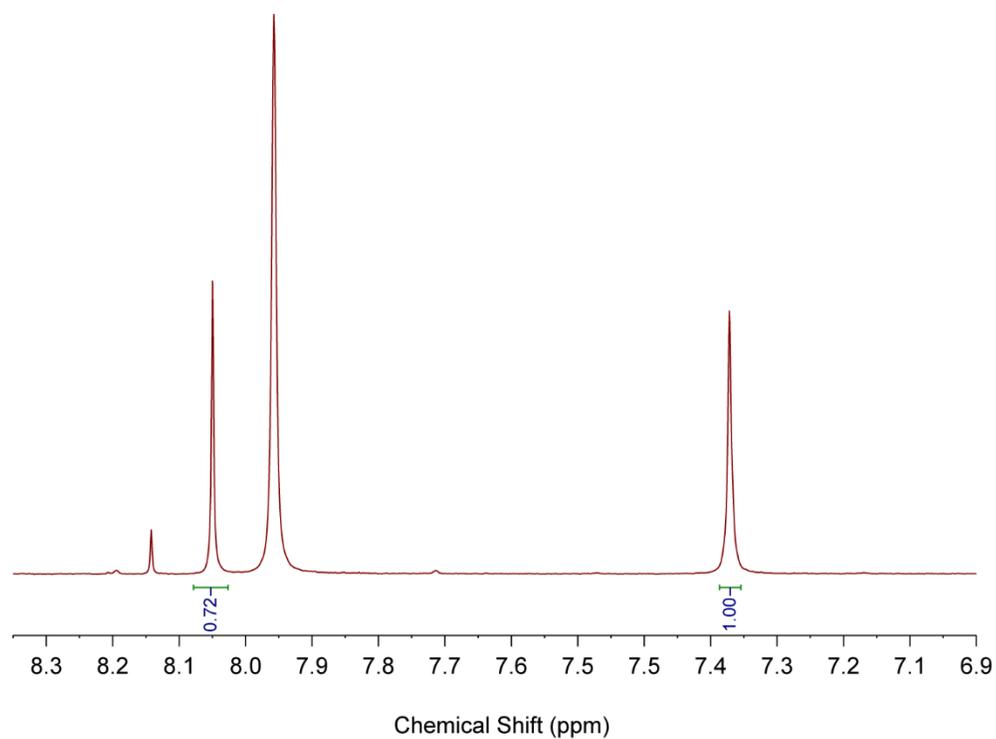
**Figure S3.** GPC traces for **pbdc-7e** in  $\text{CHCl}_3$ .



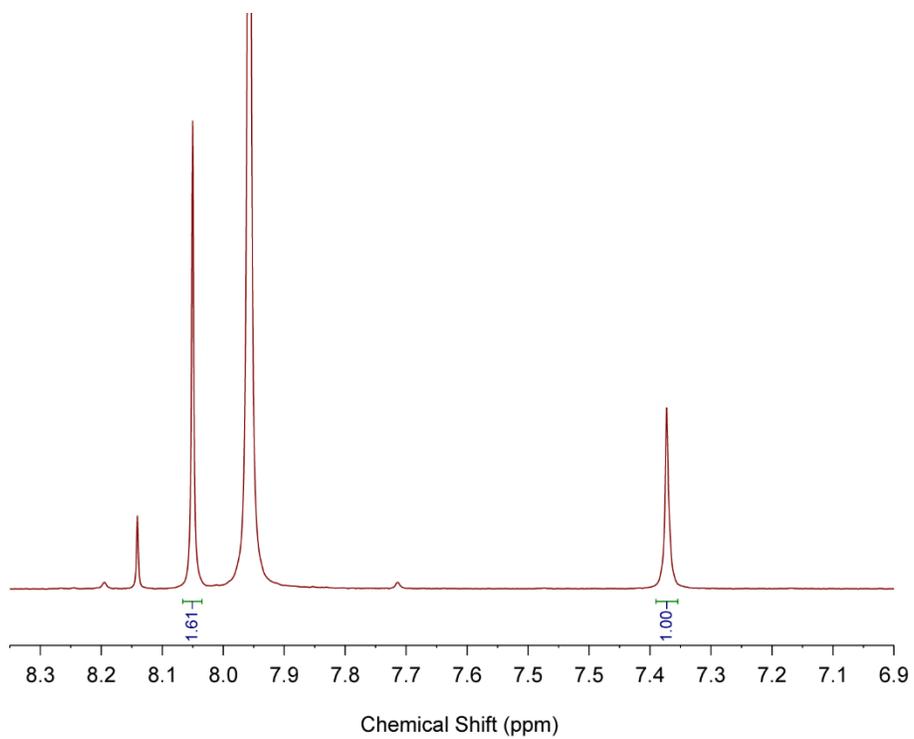
**Figure S4.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-0eq** digested in DCI/DMSO- $d_6$ .



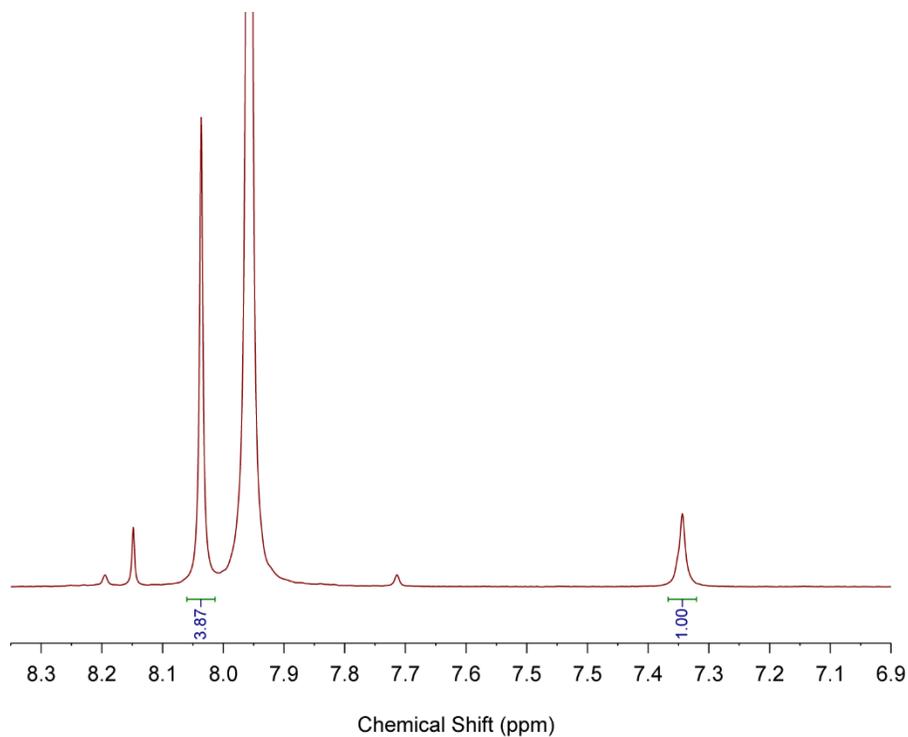
**Figure S5.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-0.1eq** digested in DCI/DMSO- $d_6$ .



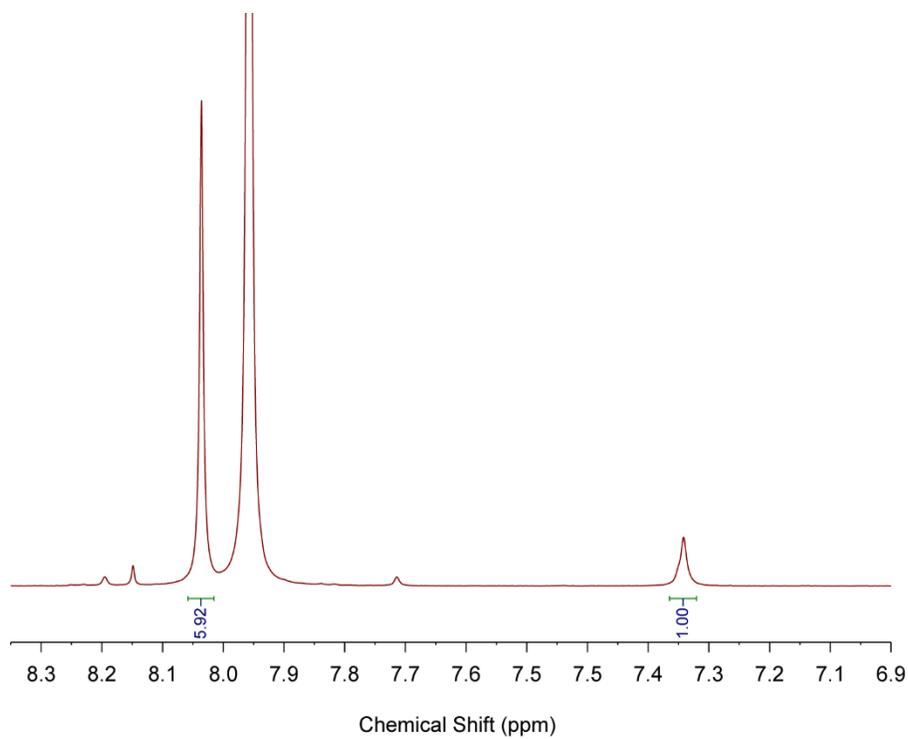
**Figure S6.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-0.5eq** digested in DCI/DMSO- $d_6$ .



**Figure S7.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-1eq** digested in DCI/DMSO- $d_6$ .



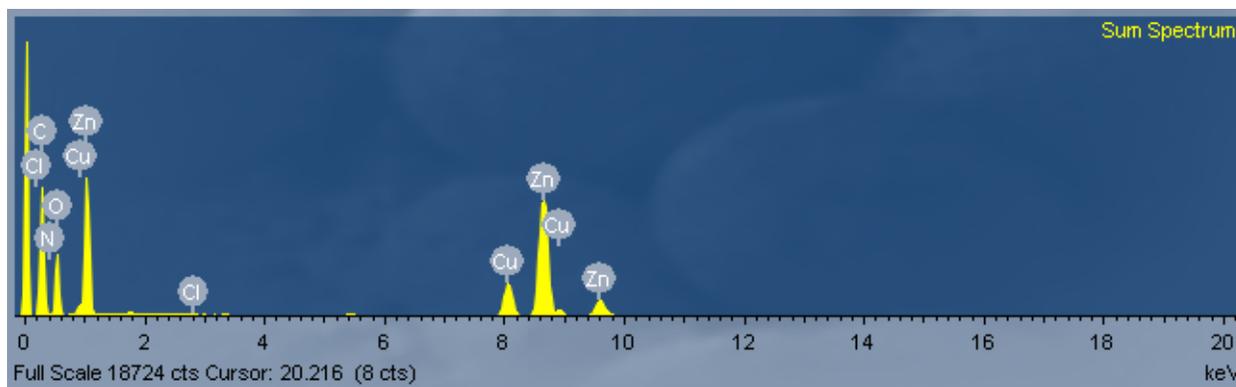
**Figure S8.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-2eq** digested in DCI/DMSO- $d_6$ .



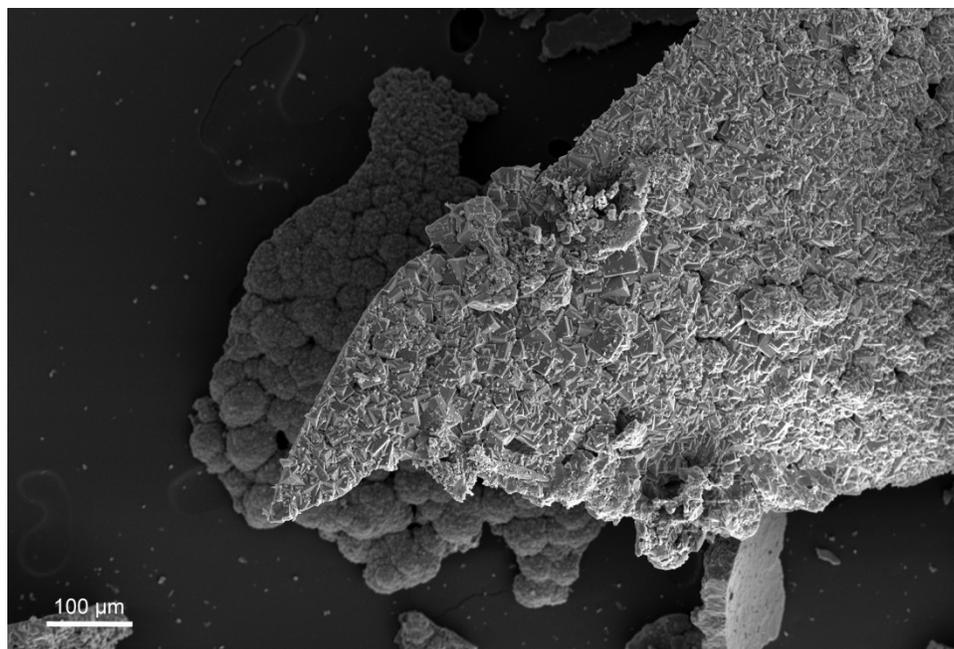
**Figure S9.**  $^1\text{H}$  NMR spectrum of **Zn-pbdc-7a-3eq** digested in DCI/DMSO- $d_6$ .

Equivalents of free H <sub>2</sub> bdc per polymer-bound H <sub>2</sub> bdc	Free H <sub>2</sub> bdc per polymer-bound H <sub>2</sub> bdc (from <sup>1</sup> H NMR integration)	Percent Difference of Incorporation from Reaction Stoichiometry
0 eq	0	N/A
0.1 eq	0.04	60%
0.5 eq	0.38	24%
1 eq	0.80	20%
2 eq	1.85	7.5%
3 eq	2.91	3%

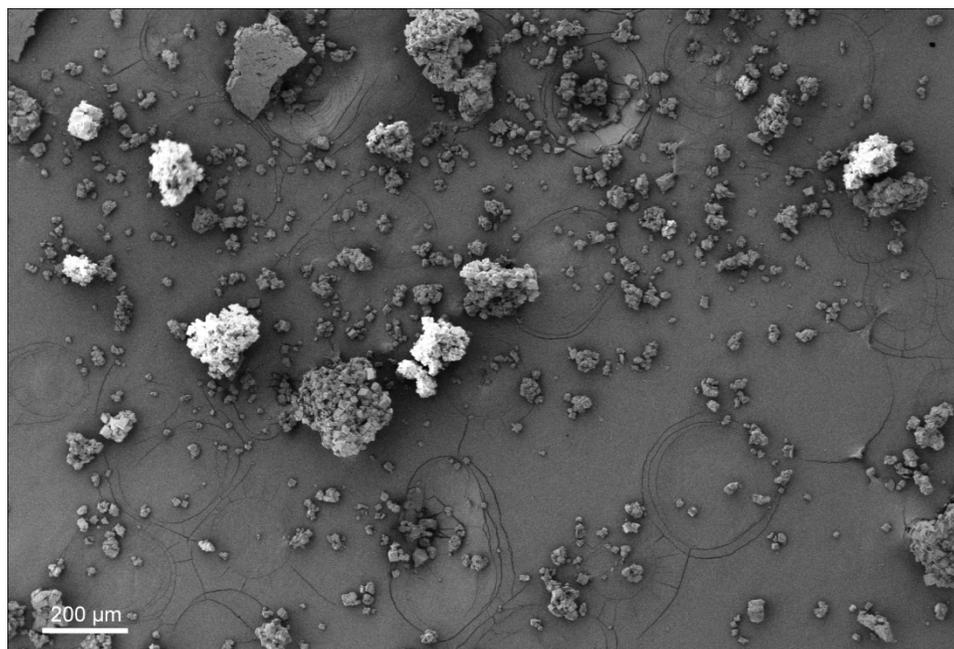
**Table S1.** Free H<sub>2</sub>bdc to polymer-bound H<sub>2</sub>bdc ratios



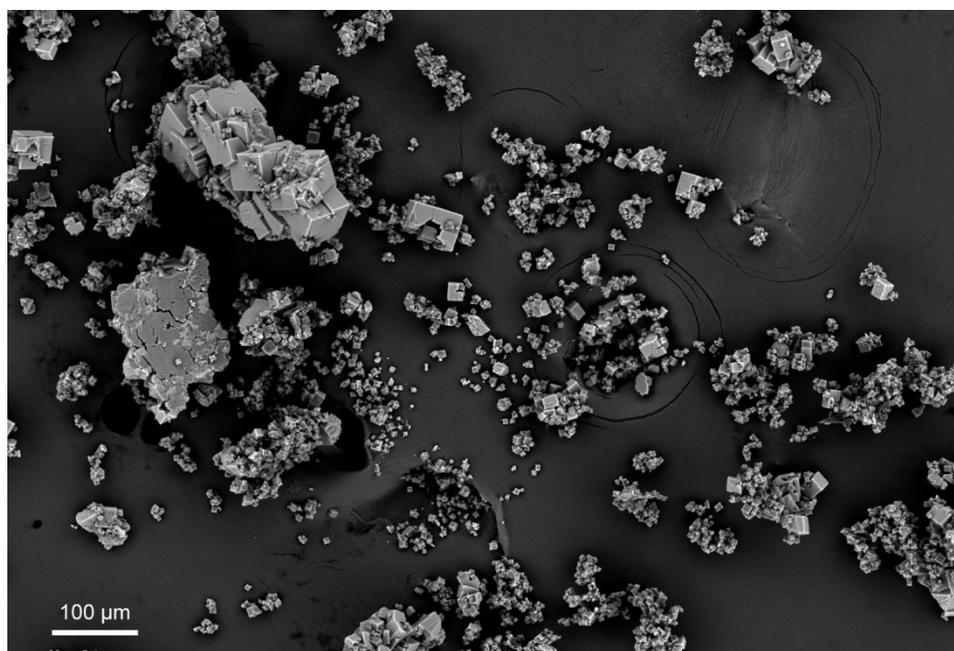
**Figure S10.** EDX sum spectrum of Zn-pbdc-7a-2eq-NH<sub>2</sub>.



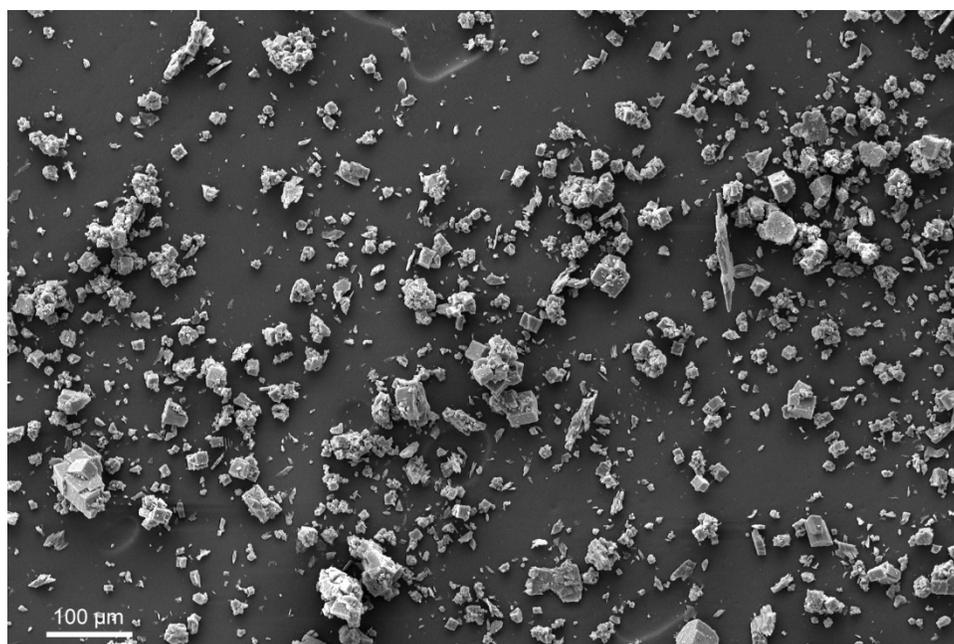
**Figure S11.** SEM image of Zn-pbdc-7a-0eq.



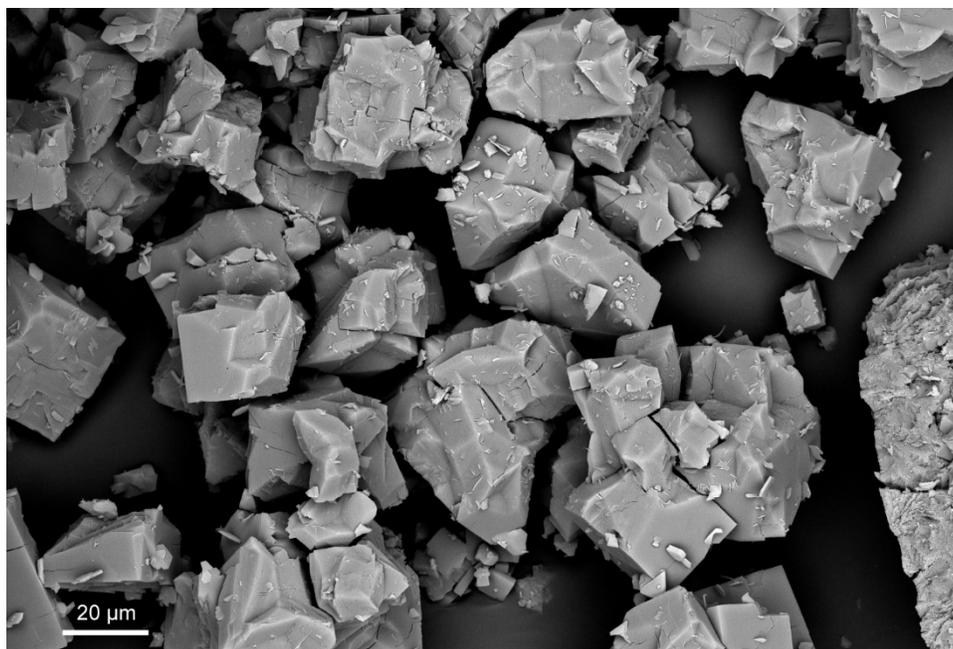
**Figure S12.** SEM image of Zn-pbdc-7a-1eq.



**Figure S13.** SEM image of Zn-pbdc-7a-3eq.



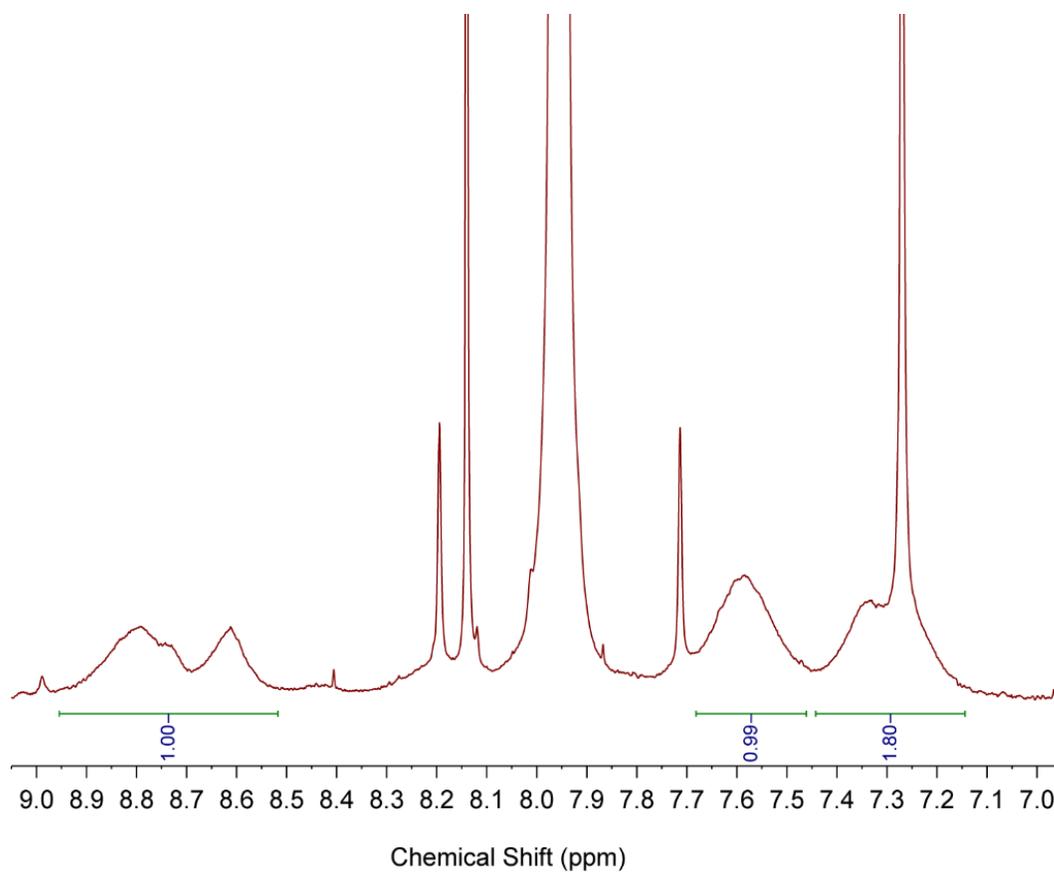
**Figure S14.** SEM image of Zn-pbdc-7a-15eq.



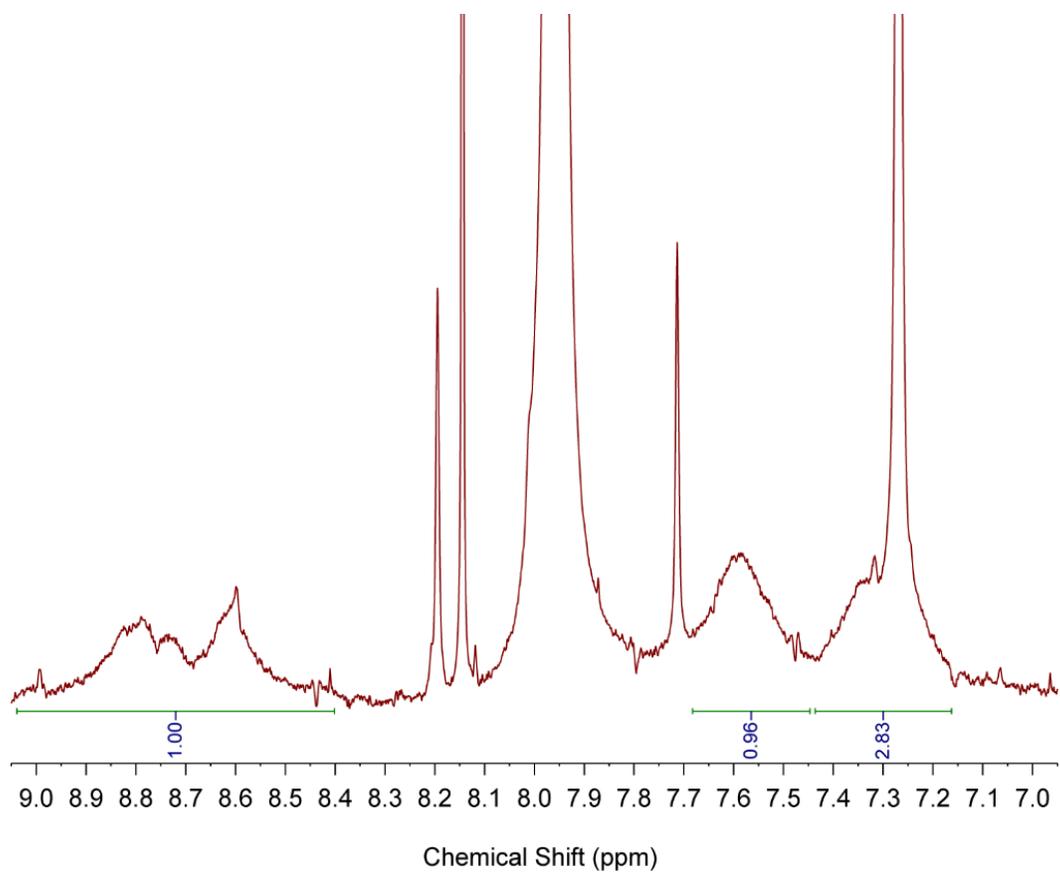
**Figure S15.** SEM image of **Zn-pbdc-7a-30eq.**

Equivalents of H <sub>2</sub> bdc Added	0	1	3	15	30
Stoichiometric Formula of MOF	ZnO <sub>4</sub> (pbdc) <sub>3</sub>	ZnO <sub>4</sub> (bdc) <sub>1.5</sub> (pbdc) <sub>1.5</sub>	ZnO <sub>4</sub> (bdc) <sub>2.25</sub> (pbdc) <sub>0.75</sub>	ZnO <sub>4</sub> (bdc) <sub>2.81</sub> (pbdc) <sub>0.19</sub>	ZnO <sub>4</sub> (bdc) <sub>2.90</sub> (pbdc) <sub>0.10</sub>
PolyMOF Molar Mass	1011.38	816.38	718.88	645.76	633.96
Ratio of MOF-5 Molar Mass to PolyMOF Molar Mass	0.61	0.76	0.86	0.96	0.98
Measured BET Surface Area (cm <sup>3</sup> /g)	1011	1287	1359	1356	562
Mass-Corrected BET Surface Area (cm <sup>3</sup> /g)	1646	1691	1572	1409	573

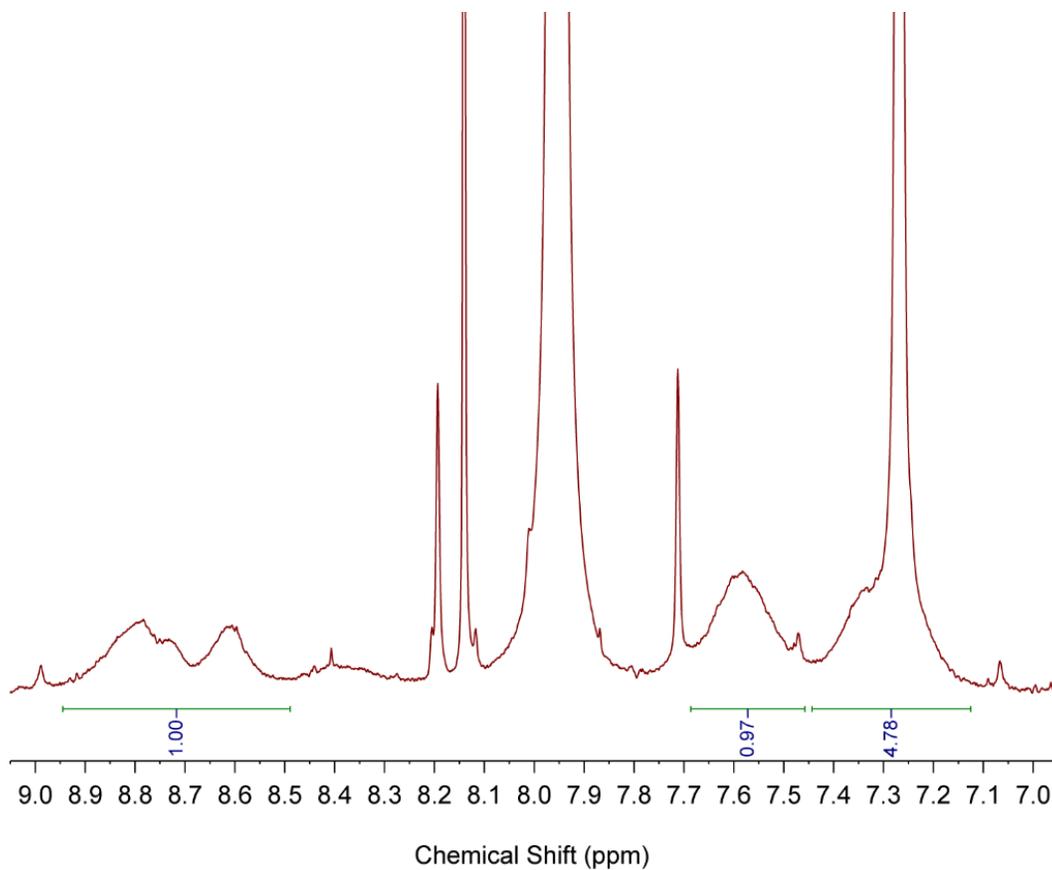
**Table S2.** Mass correction of mixed ligand polyMOF BET surface areas.



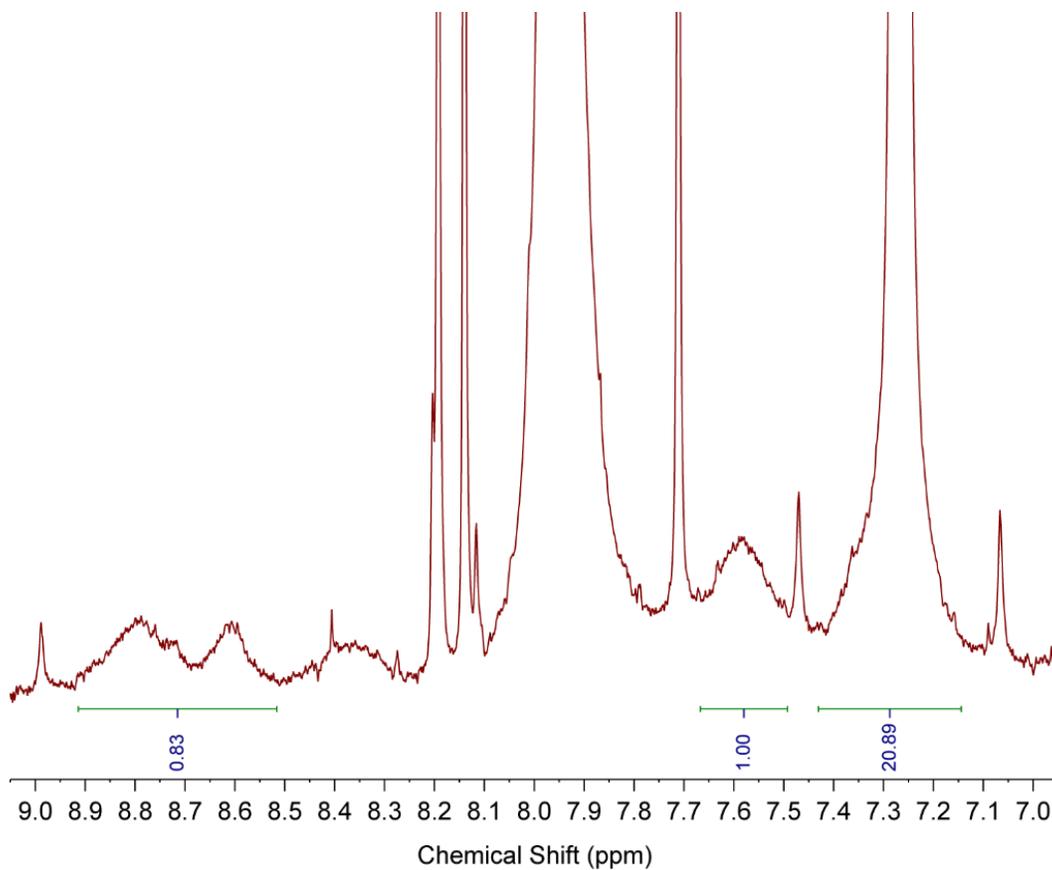
**Figure S16.** <sup>1</sup>H NMR spectrum of **MTV-polyMOF-5\_1\_2** digested in DCI/DMSO-*d*<sub>6</sub>. (*Note:* the aryl-H peak of **pbdc-7a** (2H) at 7.25 ppm overlaps an aryl-H peak of **pabdc-0a** (1H). The integration includes both. The other two integrate peaks both correspond to aryl-H peaks of **pabdc-0a** (1H).



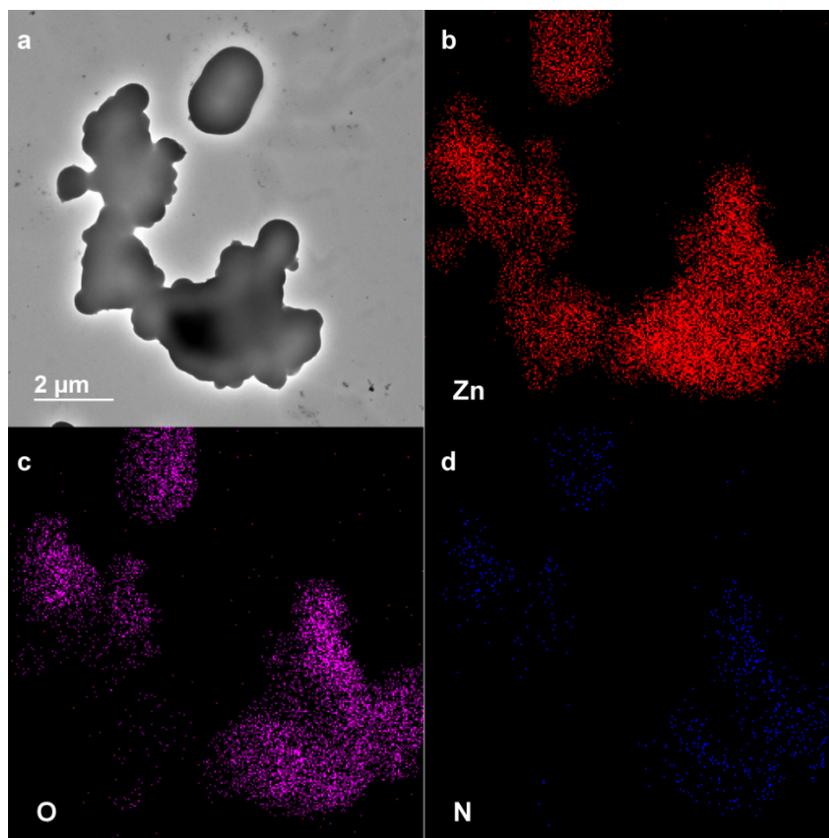
**Figure S17.**  $^1\text{H}$  NMR spectrum of **MTV-polyMOF-5\_1\_1** digested in DCI/DMSO- $d_6$ . (Note: the aryl-H peak of **pbdc-7a** (2H) at 7.25 ppm overlaps an aryl-H peak of **pabdc-0a** (1H). The integration includes both. The other two integrate peaks both correspond to aryl-H peaks of **pabdc-0a** (1H).



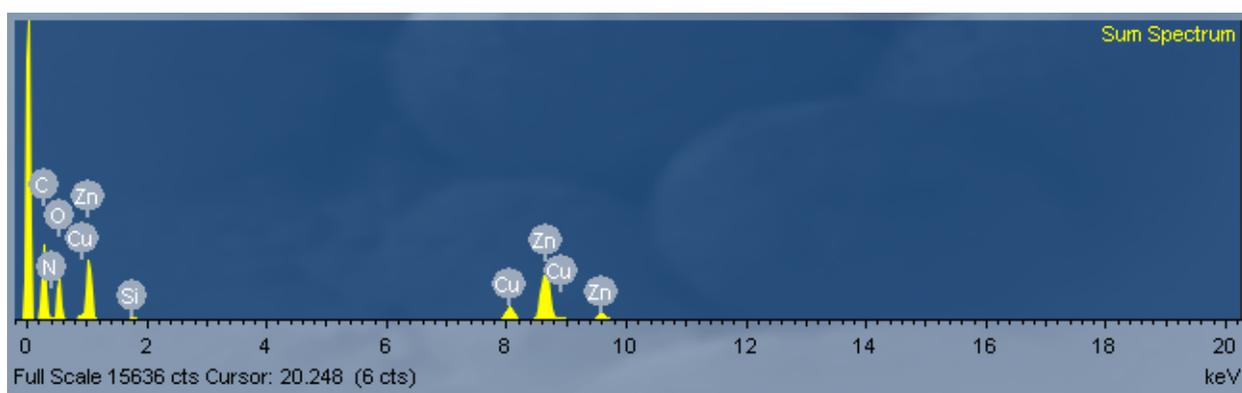
**Figure S18.** <sup>1</sup>H NMR spectrum of **MTV-polyMOF-5\_2\_1** digested in DCI/DMSO-*d*<sub>6</sub>. (Note: the aryl-H peak of **pbdc-7a** (2H) at 7.25 ppm overlaps an aryl-H peak of **pabdc-0a** (1H). The integration includes both. The other two integrate peaks both correspond to aryl-H peaks of **pabdc-0a** (1H).



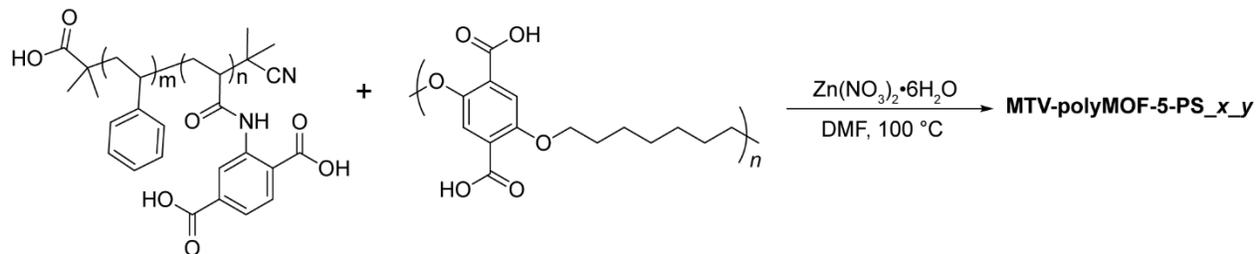
**Figure S19.**  $^1\text{H}$  NMR spectrum of **MTV-polyMOF-5\_10\_1** digested in DCI/DMSO- $d_6$ . (Note: the aryl-H peak of **pbdc-7a** (2H) at 7.25 ppm overlaps an aryl-H peak of **pabdc-0a** (1H). The integration includes both. The other two integrate peaks both correspond to aryl-H peaks of **pabdc-0a** (1H).



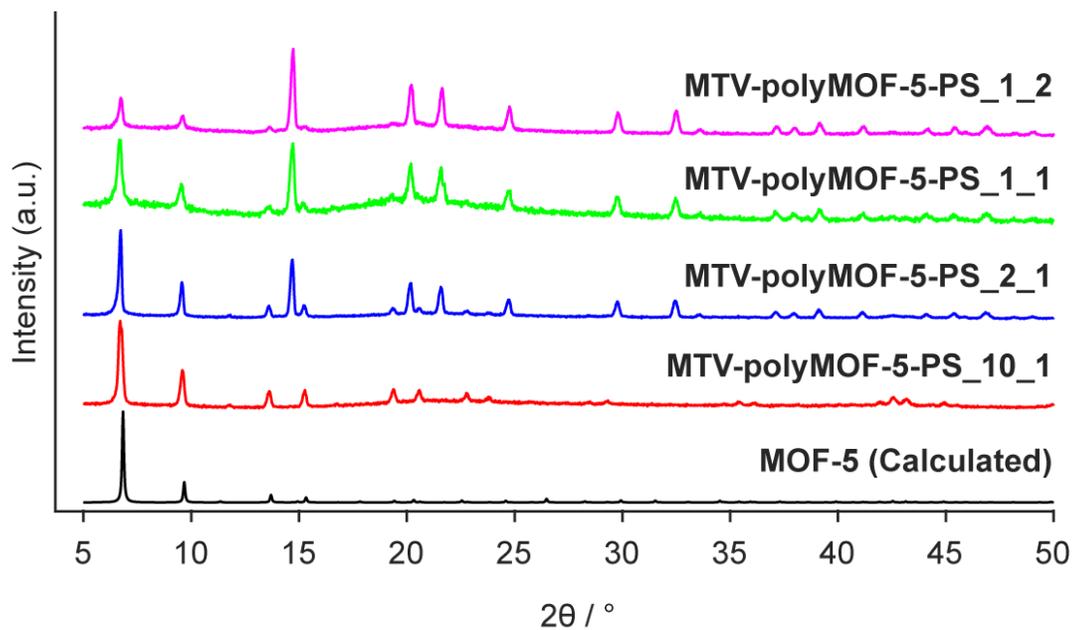
**Figure S20.** TEM-EDX elemental mapping of MTV-polyMOF-5\_2\_1.



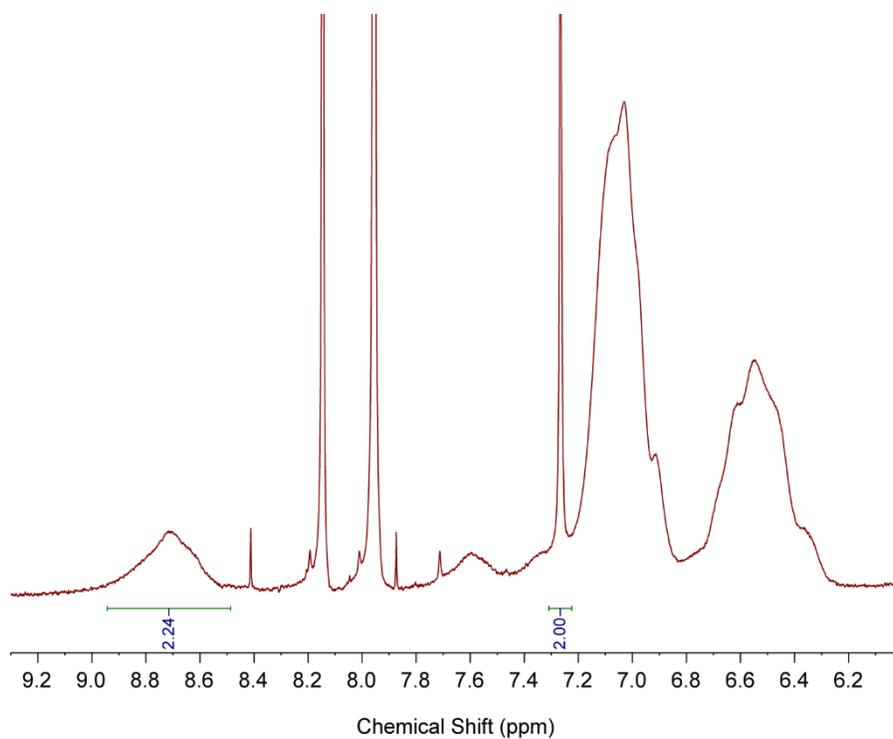
**Figure S21.** EDX sum spectrum of MTV-polyMOF-5\_2\_1.



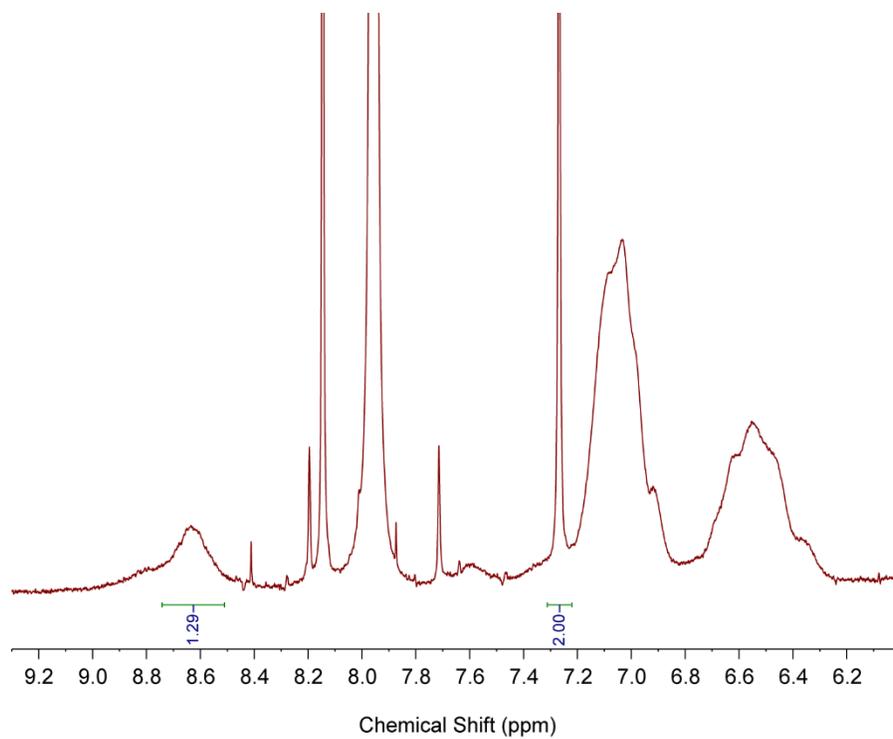
**Scheme S2.** Synthesis of polymer ligand **MTV-polyMOF-5-PS<sub>x</sub><sub>y</sub>**.



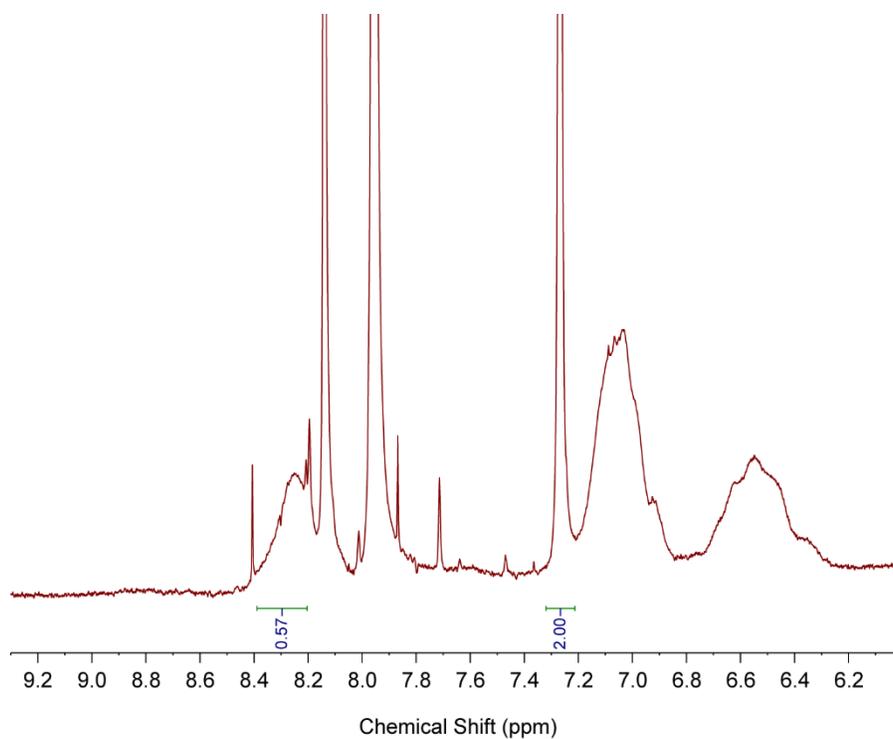
**Figure S22.** Powder X-ray diffractogram of **MTV-polyMOF-5-PS<sub>x</sub><sub>y</sub>**, synthesized from  $x$  equivalents of **pbdc-7a** and  $y$  equivalents of **PS-*b*-pabdc-0a**.



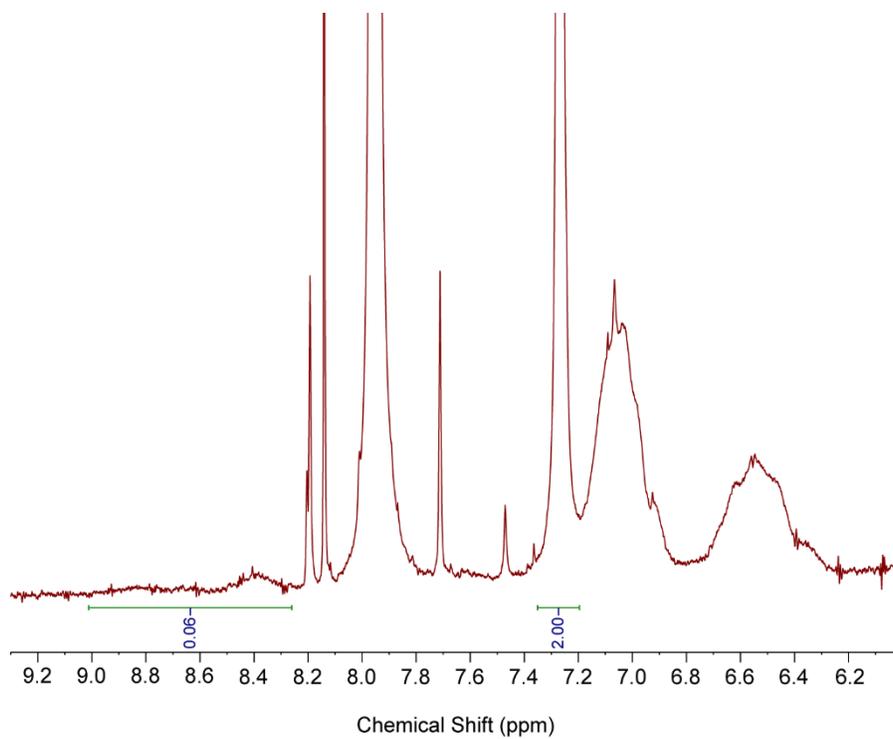
**Figure S23.**  $^1\text{H}$  NMR spectrum of **MTV-polyMOF-5-PS\_1\_2** digested in DCI/DMSO- $d_6$ .



**Figure S24.**  $^1\text{H}$  NMR spectrum of **MTV-polyMOF-5-PS\_1\_1** digested in DCI/DMSO- $d_6$ .



**Figure S25.** <sup>1</sup>H NMR spectrum of **MTV-polyMOF-5-PS\_2\_1** digested in DCI/DMSO-*d*<sub>6</sub>.



**Figure S26.** <sup>1</sup>H NMR spectrum of **MTV-polyMOF-5-PS\_10\_1** digested in DCI/DMSO-*d*<sub>6</sub>.

## 2. General Information

### Materials and Experimental Methods

Starting materials and solvents were purchased from commercial suppliers (Sigma-Aldrich, TCI, AK Scientific Inc, Cambridge Isotope Laboratories, Inc.). Styrene was passed through a short basic alumina plug immediately prior to use. All other chemicals were used without purification.

Column chromatography was performed on a Biotage® Isolera One with Accelerated Chromatographic Isolation flash chromatography system, using Biotage® KP-Sil SNAP cartridges at the recommended flow rates. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz Bruker AVANCE NMR spectrometer. Chemical shifts are reported in parts per million (ppm), and are referenced to residual solvent peaks.

Gel permeation chromatography (GPC) analyses were carried out on an Agilent 1260 Infinity system at a flow rate of 1 mL/min using 0.025 M LiBr in *N,N*-dimethylformamide (DMF) as eluent. Samples were filtered through 0.2 μm, 13 mm PTFE syringe filters before injection. A T-rEX refractive index detector (Wyatt) and a DAWN EOS 18 angle light scattering (MALS) detector (Wyatt) were used for polymer analysis. Respective *dn/dc* values were obtained by injection of known concentrations of polymer samples. Where indicated, some GPC analyses were performed on an Agilent 1260 Infinity system using a chloroform mobile phase at a flow rate of 1 mL/min. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector and light scattering (LS) for molecular weight analysis was monitored using a Wyatt Dawn Heleos II detector.

Preparatory GPC (PrepGPC) was performed on a JAI Preparative Recycling GPC equipped with a 2.5HR and a 2H (20 mm ID x 600 mm length) JAIGEL column in series. Chloroform was used as the eluent and samples were filtered through 0.2 μm, 13 mm PTFE syringe filters before injection. The samples were monitored by both refractive index and UV (200–800 nm) detection.

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance II diffractometer equipped with a  $\theta/2\theta$  Bragg-Brentano geometry and Ni-filtered CuK $\alpha$  radiation (K $\alpha_1$  = 1.5406 Å, K $\alpha_2$  = 1.5444 Å, K $\alpha_2$ / K $\alpha_1$  = 0.5). The tube voltage and current were 40 kV and

40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of the appropriate material on a zero-background silicon crystal plate.

Scanning electron microscopy (SEM) was performed in a Zeiss Merlin high-resolution SEM. Samples were transferred to conductive carbon tape on a sample holder disk.

Nitrogen and CO<sub>2</sub> adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer. A typical sample of 40-100 mg of polyMOF, pre-activated at 105 °C to remove all residual solvent, was transferred to a pre-weighed analysis tube. The tube with sample inside was weighed again to determine the mass of the sample. The tube was capped with a Micromeritics TranSeal and transferred to the analysis port of the gas sorption analyzer. Nitrogen and CO<sub>2</sub> isotherms were measured using UHP grade (99.999%) N<sub>2</sub> and CO<sub>2</sub>. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K and CO<sub>2</sub> analyses were performed in a 298 K water bath. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

### 3. Synthetic Methods

#### Synthesis of pbdc-7a

Diethyl 2,5-dihydroxyterephthalate (2.0 g, 7.9 mmol), 1,7-dibromoheptane (1.34 mL, 7.9 mmol), and potassium carbonate (4.35 g, 31.5 mmol) were dissolved in 34 mL of DMF. The suspension was heated to 100 °C and stirred overnight. The reaction was cooled to room temperature and 85 mL of water was added to precipitate a solid. The solid was isolated by centrifugation and washed with acetone (3x35) and methanol (3x35 mL) by repeated suspension and centrifugation and then dried overnight under vacuum at 60 °C. The polymers were analyzed by CHCl<sub>3</sub> GPC in ester-form before they were hydrolyzed. The polymer (1.0 g) was hydrolyzed by a 1M aqueous solution of KOH (800 mg, 100 eq) in THF (15 mL) at 80 °C overnight. The polymer was precipitated from solution by the addition of 1M HCl and then washed with acetone (3x35 mL) and methanol (3x35 mL) as before. The polymer was then dried under vacuum overnight at 60 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 1.42 (6H, m), 1.68 (4H, t), 3.98 (2H, t), 7.27 (2H, s), 12.91 (2H, br s)

<sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 25.83, 28.90, 29.15, 69.65, 115.97, 125.93, 150.92, 167.32

#### Dimethyl 2-acrylamidoterephthalate (abdc-0e)

In a round bottom flask, dimethyl aminoterephthalate (3.00 g, 14.3 mmol) and triethylamine (10.00 mL, 71.7 mmol) were dissolved in 60 mL of anhydrous dichloromethane. This solution was stirred in a 0° C ice bath as a solution of acryloyl chloride (4.64 mL, 57.4 mmol) in 20 mL of dry dichloromethane was added dropwise over the course of 30 minutes. The reaction was then warmed slowly to room temperature and stirred overnight at room temperature, generating a large amount of a brown precipitate. The solvent was evaporated and the remaining solids were suspended in 1 M HCl and then extracted in dichloromethane. The organic extracts were washed with a saturated solution of sodium bicarbonate and then brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude solid was purified on a silica gel column using 0% to 25% ethyl acetate in hexanes (eluting at 22%) to give 1.63 g of the product in 43.3% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.97 (3H, s), 3.99 (3H, s), 5.86 (1H, dd), 6.36 (1H, dd), 6.47 (1H, dd), 7.79 (1H, d), 8.13 (1H, d), 9.46 (1H, s), 11.29 (1H, s)

### Synthesis of **pabdc-0a**

Acrylamide monomer **abdc-0e** (200 mg, 0.76 mmol, 1 eq), DDMAT (8.3 mg, 0.022 mmol, 0.03 eq), and AIBN (1.3 mg, 0.0076 mmol, 0.01 eq) were combined in a 3 mL dram vial. The vial was brought into a nitrogen-filled glovebox, where the solids were dissolved in anhydrous DMF (2 mL). The solution was stirred and heated at 70 °C for 3 h. The reaction was quenched by submerging the vial into an ice bath and opening to air. The solvent was evaporated and the remaining viscous yellow material was purified by Preparatory GPC (Prep GPC) to give the isolated polymer as a powder. The trithiocarbonate end group was removed by stirring a solution of the polymer with lauroyl peroxide (4 eq) and AIBN (40 eq) in toluene at 70 °C overnight under nitrogen. The polymer was then isolated by Prep GPC. Hydrolysis was performed by addition of a 1 M aqueous solution of KOH (100 eq) to a methanol solution of the polymer and stirring at 35 °C overnight. The product was precipitated with 1 M HCl.

### Synthesis of **PSt-*b*-pabdc-0a**

Styrene, DDMAT, and AIBN were added into a 10 mL Schlenk flask in a ratio of (750:5:1). The neat solution was subjected to 3 freeze-pump-thaw cycles, then stirred and heated at 80 °C for 24 hours, before it was opened to air and cooled to room temperature. The polymer was precipitated 3 times in methanol, and redissolved in THF before each precipitation. The yellow-tinted powder was then dried under vacuum. The monomer **abdc-0e** was dissolved in DMF at a concentration of 0.38 M, along with the polystyrene macromonomer and AIBN in a ratio of 100:3:1, as described above. The sealed vial was stirred and heated to 70 °C for 4 hours, before being exposed to air and cooled to room temperature. The solvent was evaporated and the polymer was isolated by Prep GPC. The trithiocarbonate end group was removed by stirring a solution of the polymer with lauroyl peroxide (4 eq) and AIBN (40 eq) in toluene at 70 °C overnight under nitrogen. The polymer was then isolated by Prep GPC. Hydrolysis was performed by addition of

a 1 M aqueous solution of KOH (100 eq) to a DMF solution of the polymer and stirring at 35 °C overnight. The product was precipitated with 1 M HCl.

### Synthesis of Zn-pbdc-7a-xeq

For each reaction, **pabdc-0a**, the desired amount of 1,4-benzenedicarboxylic acid (H<sub>2</sub>bdc), and 3 eq. of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (based on total H<sub>2</sub>bdc) were dissolved in DMF (0.1224M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for all reactions) in a nitrogen-filled glovebox. The vials were placed in a preheated isothermal oven at 100 °C for 24 h. The DMF was decanted and the solids were washed with anhydrous DMF (3x20 mL) by soaking overnight before exchanging for fresh DMF. The same process was repeated with anhydrous DCM (3x20 mL) and the solids were then dried under vacuum at 85 °C overnight.

### Synthesis of MTV-polyMOF-5\_x\_y and MTV-polyMOF-5-PS\_x\_y

In a 20 mL scintillation vial, appropriate amounts of **pbdc-7a** and either **pabdc-0a** or **PS-b-pabdc-0a** (calculated based on the degree of polymerization of the polymer ligands and the target linker ratio), were added along with 3 eq. of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (based on total H<sub>2</sub>bdc). The reagents were dissolved in DMF (0.1224M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for all reactions) and the vial was placed in a preheated isothermal oven at 100 °C for 24 h. A solid was collected by centrifugation at 4000 rpm for 10 min. The solids were then washed with anhydrous DMF (3x5 mL) before analysis.

#### 4. Gas Sorption Isotherm Data<sup>1,2</sup>

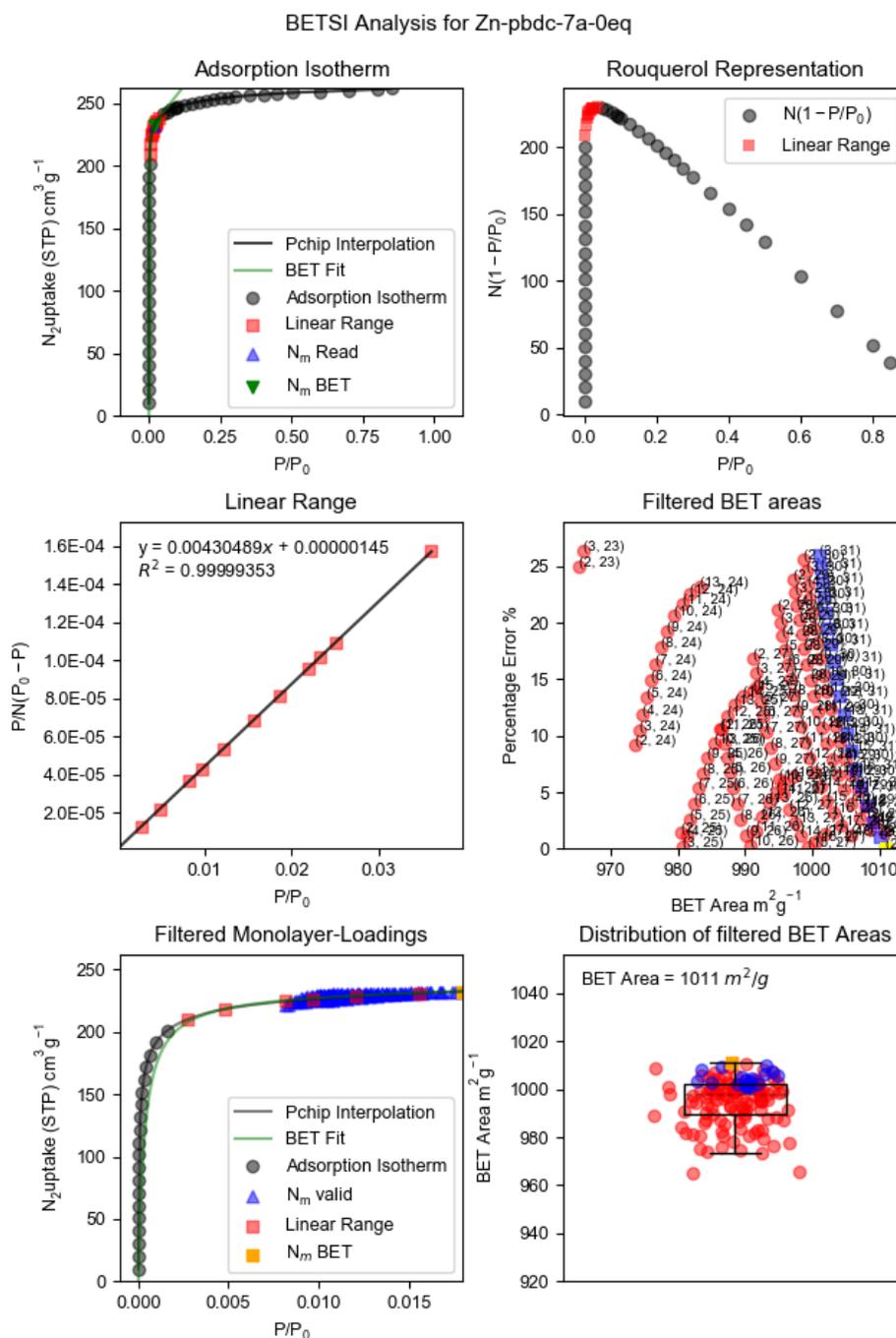


Figure S27. BETSI analysis of Zn-pbdc-7a-0eq.

BETSI Analysis for Zn-pbdc-7a-1eq

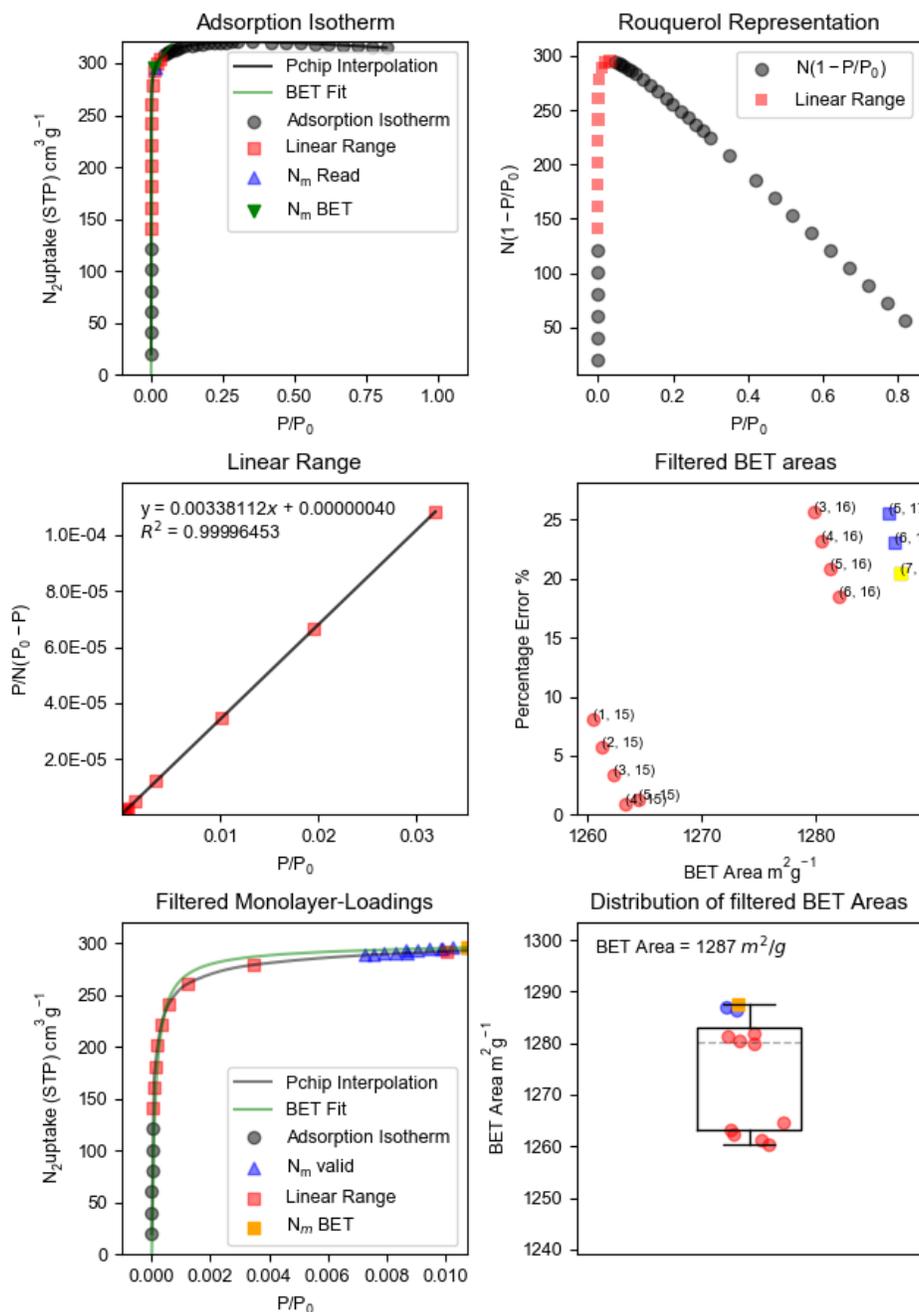


Figure S28. BETSI analysis of Zn-pbdc-7a-1eq.

BETSI Analysis for Zn-pbdc-7a-3eq

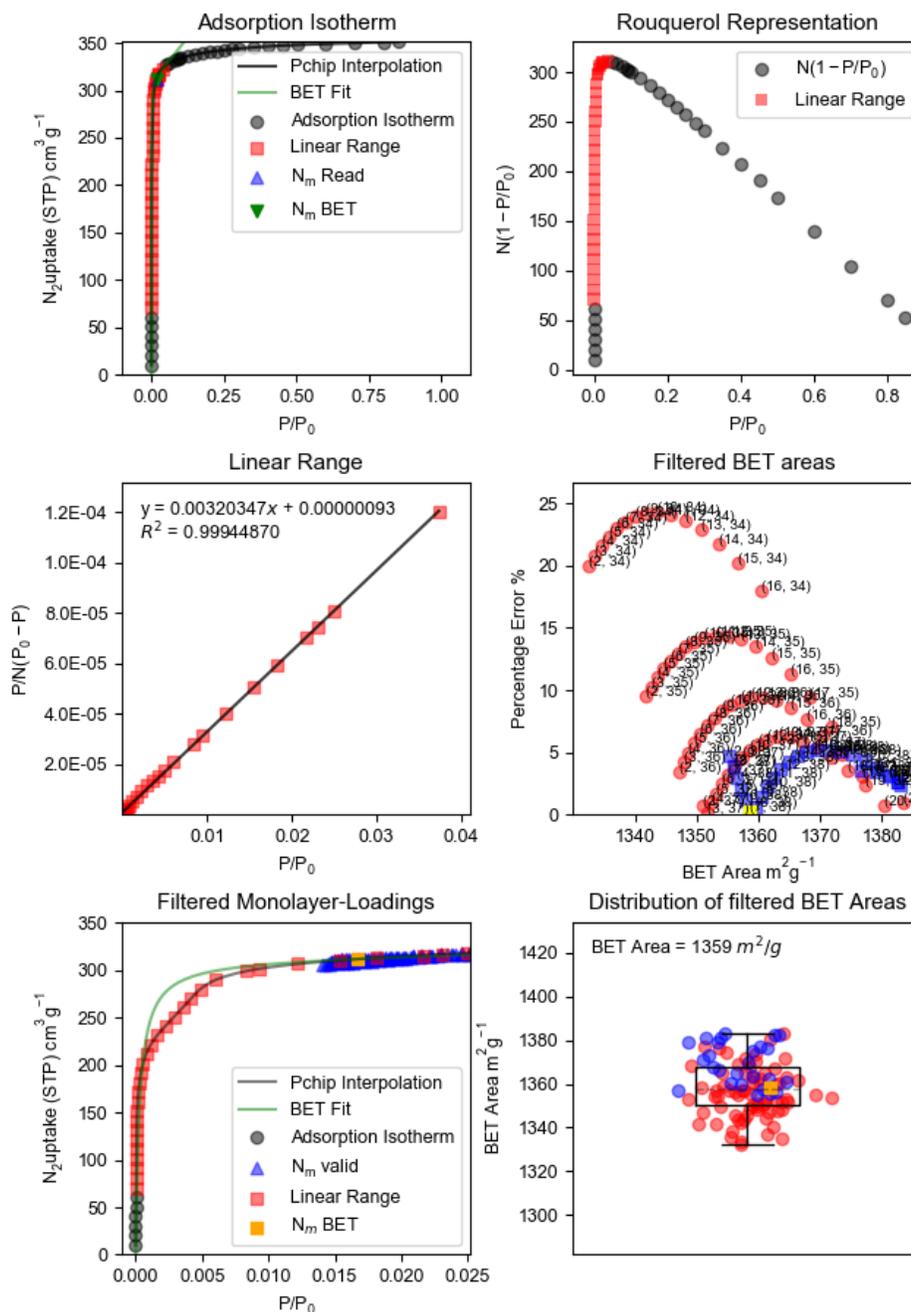


Figure S29. BETSI analysis of Zn-pbdc-7a-3eq.

BETSI Analysis for Zn-pbdc-7a-15eq

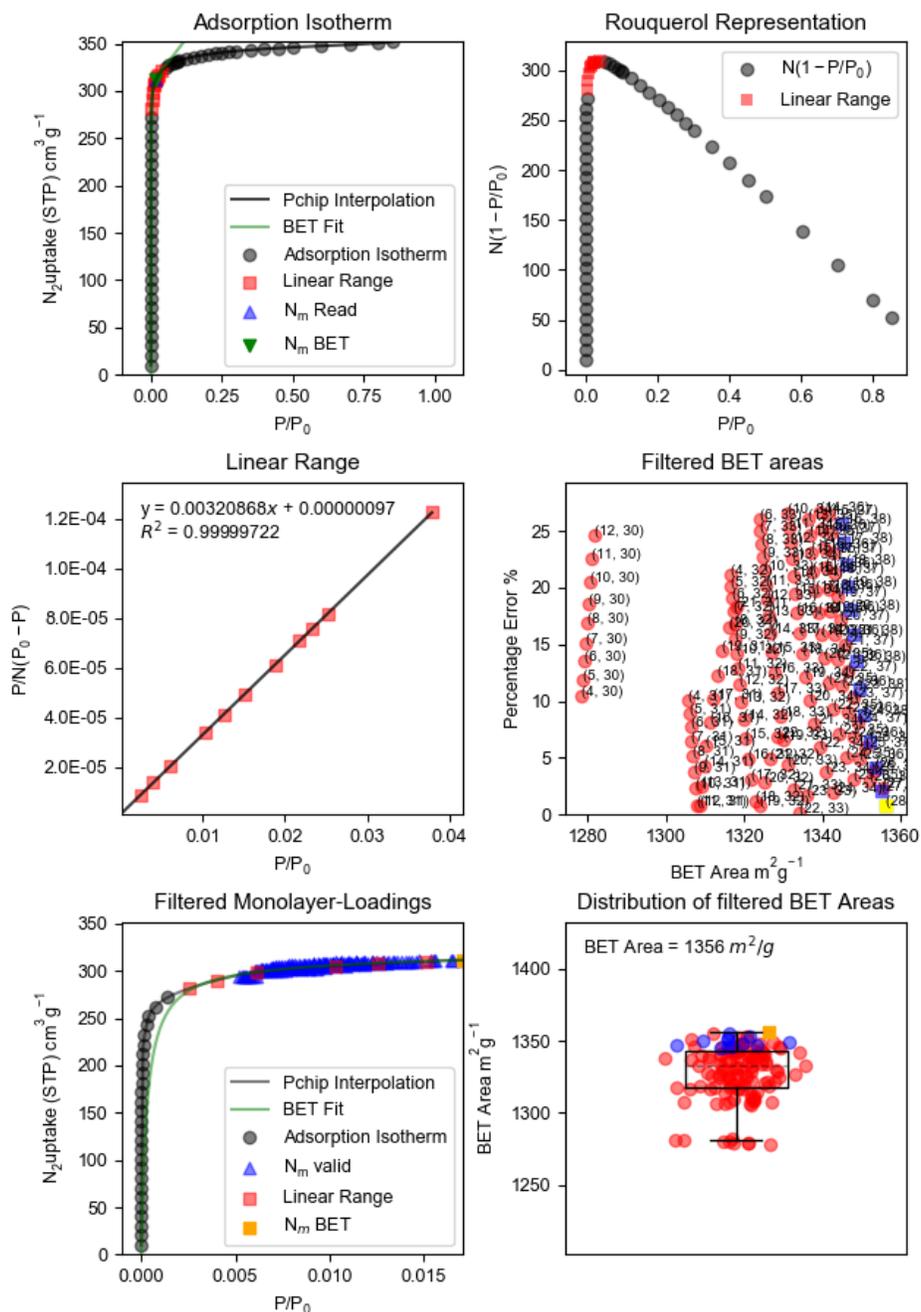


Figure S30. BETSI analysis of Zn-pbdc-7a-15eq.

BETSI Analysis for Zn-pbdc-7a-30eq

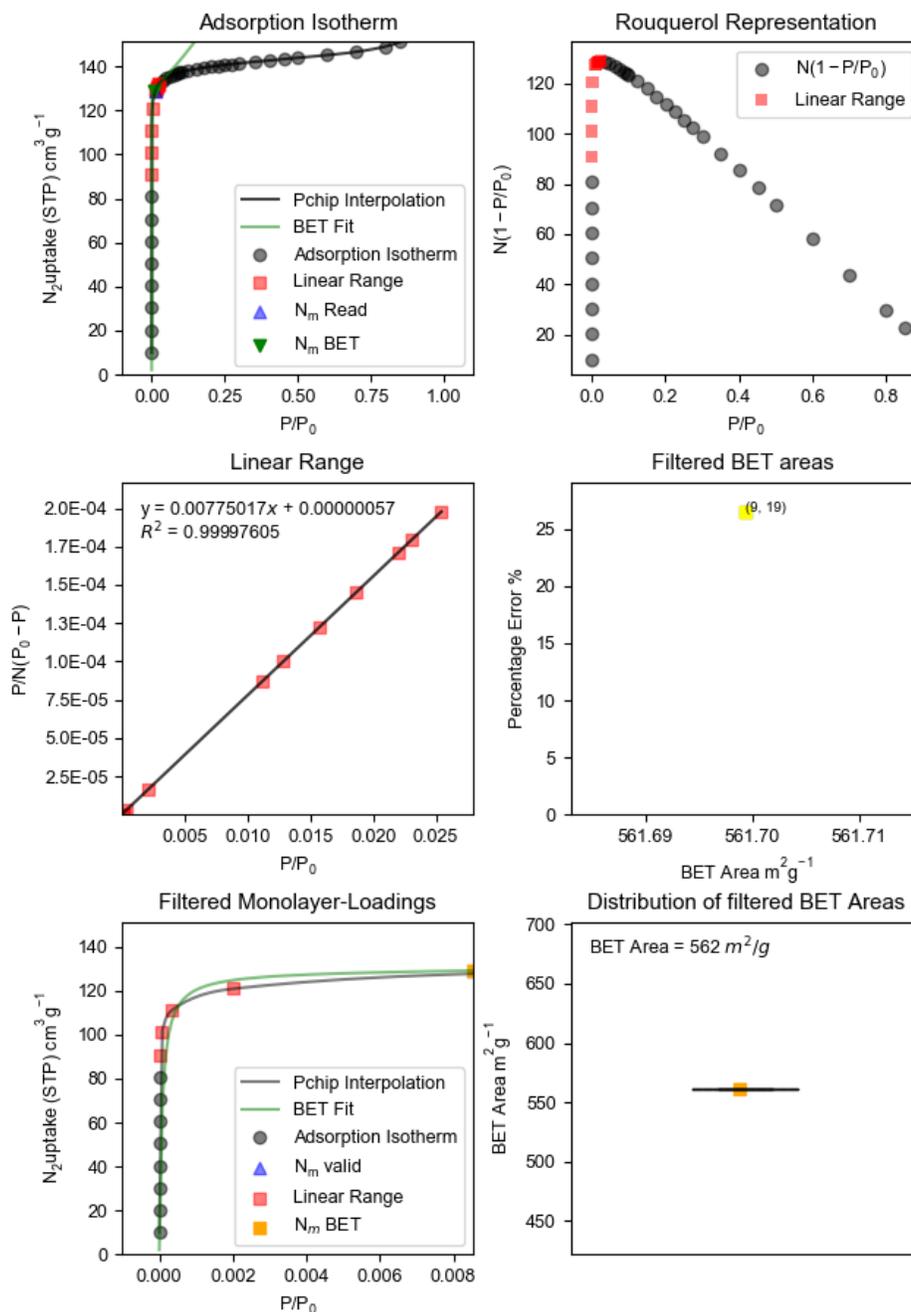
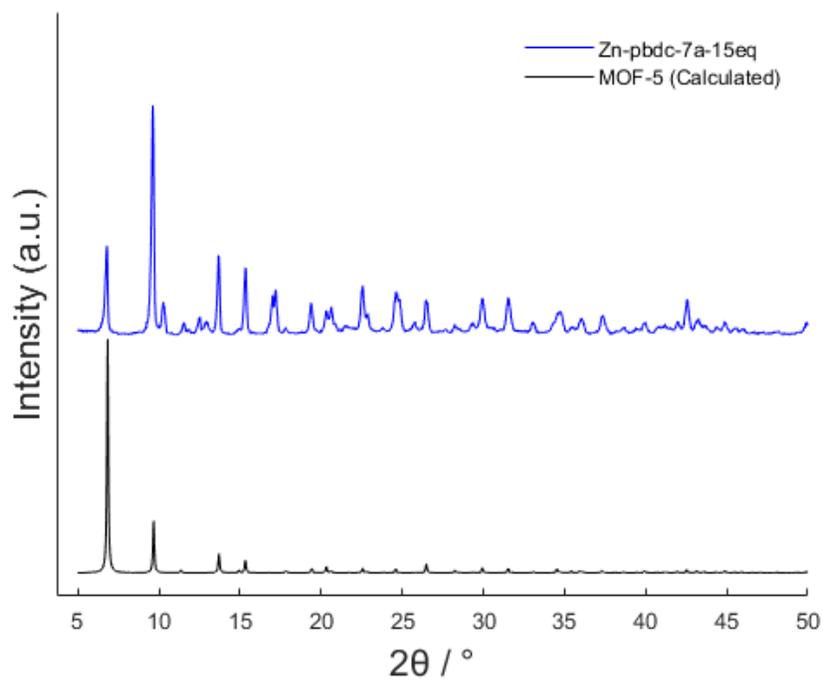
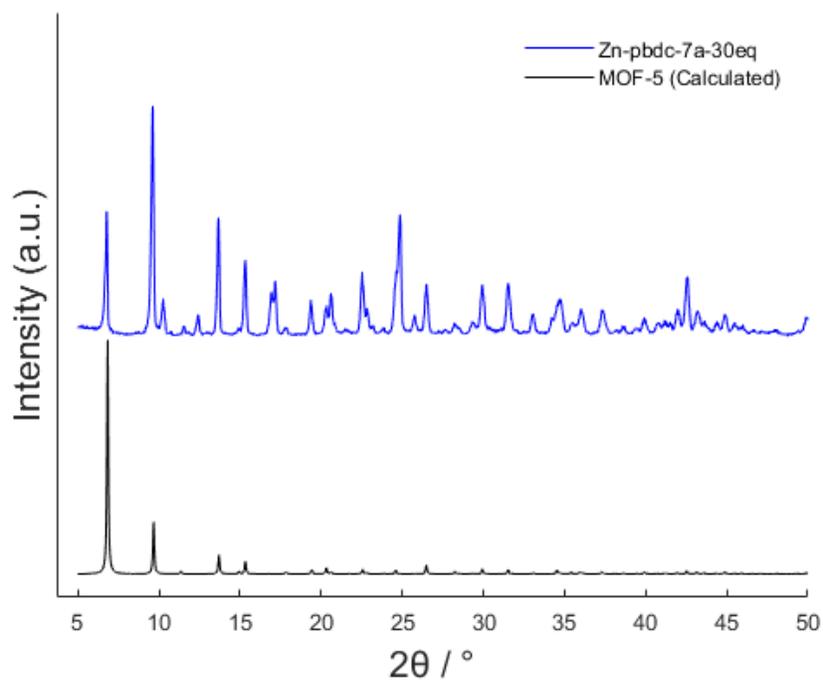


Figure S31. BET plot of Zn-pbdc-7a-30eq with best fit line.

## 5. Powder X-ray Diffraction Data

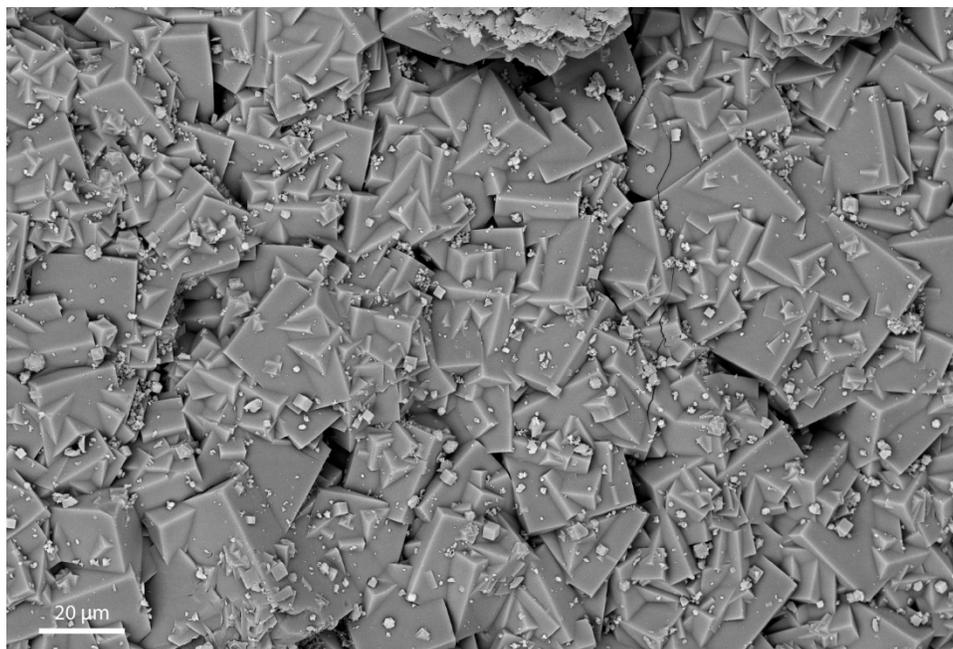


**Figure S32.** Powder X-ray diffractogram of **Zn-pbdc-7a-15eq**.

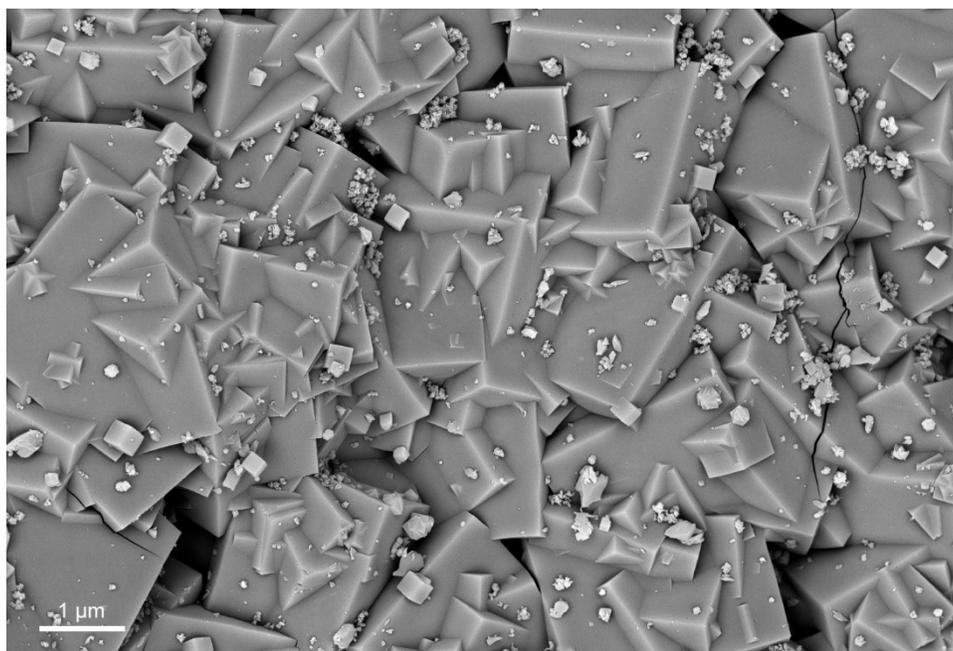


**Figure S33.** Powder X-ray diffractogram of **Zn-pbdc-7a-30eq**.

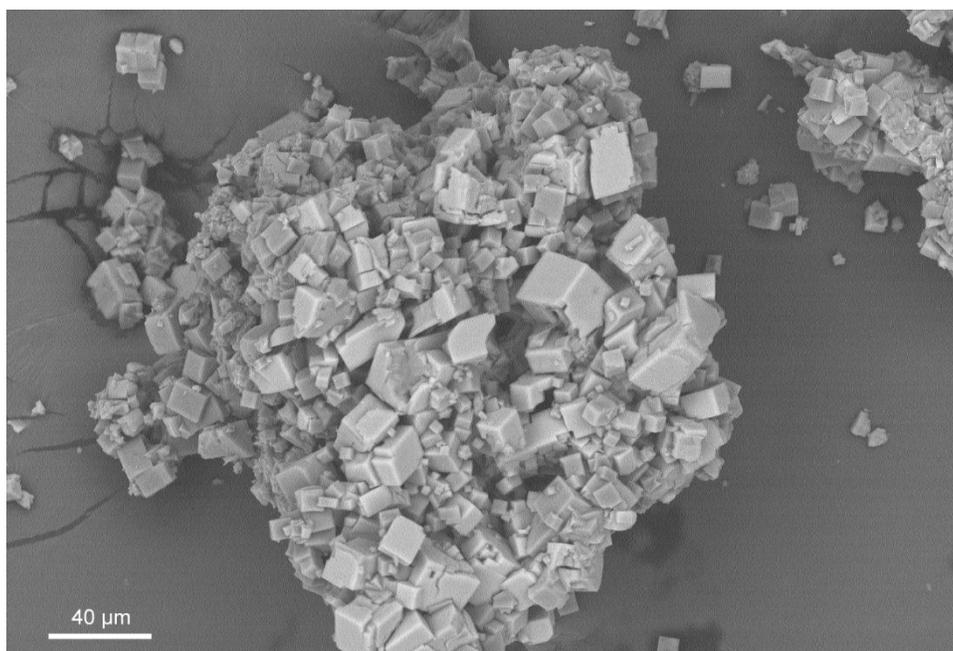
## 6. Scanning Electron Microscopy Data



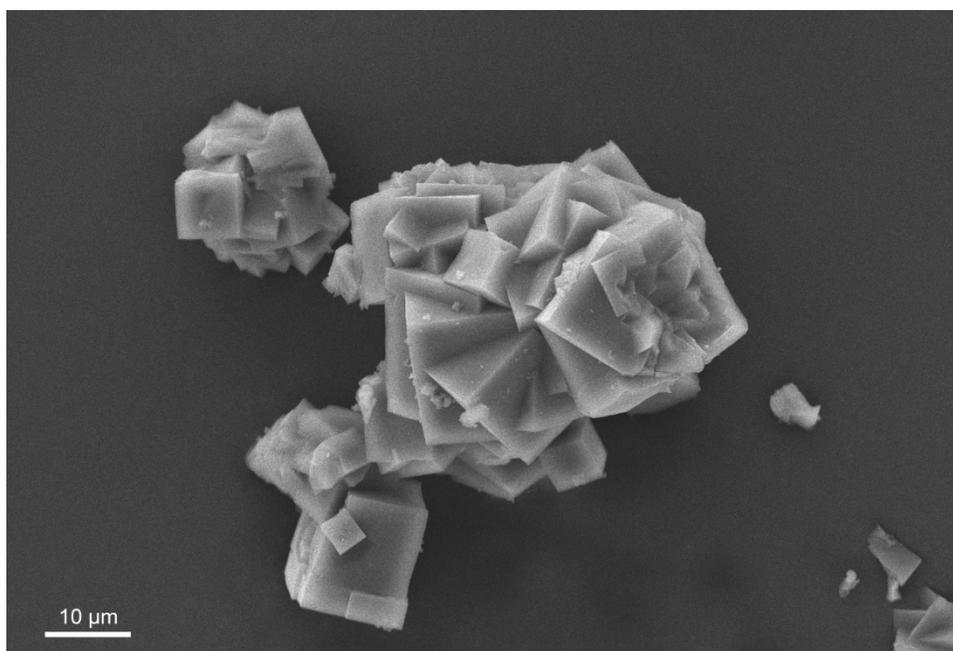
**Figure S34.** SEM image of Zn-pbdc-7a-0eq.



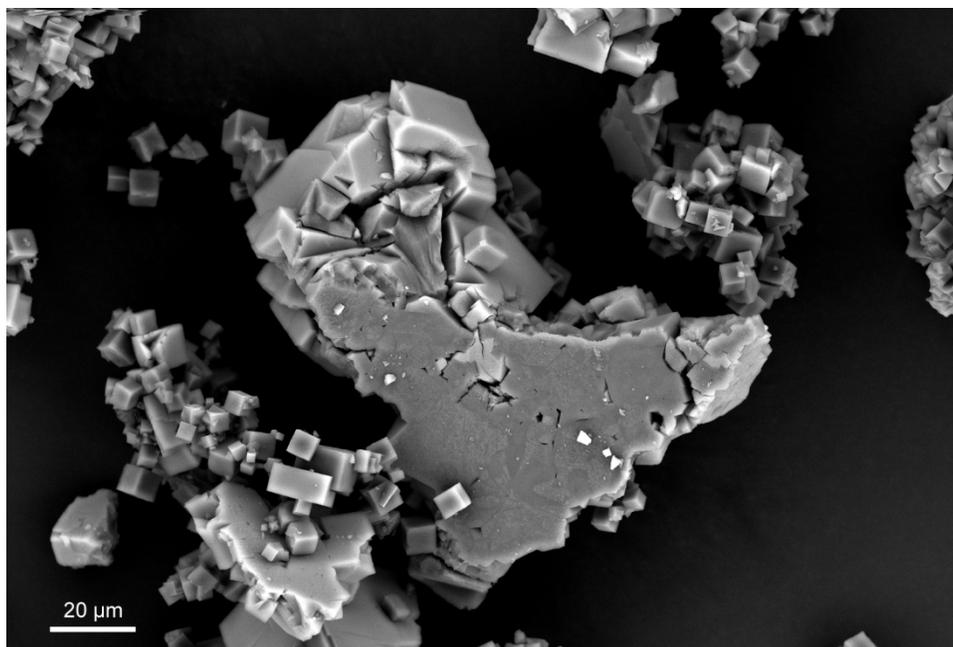
**Figure S35.** SEM image of Zn-pbdc-7a-0eq.



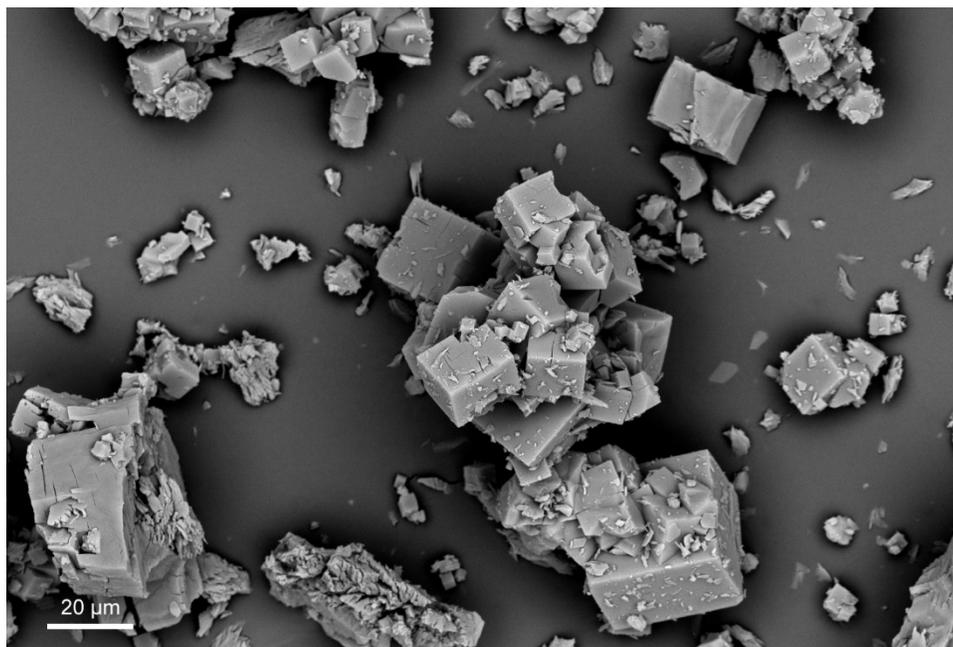
**Figure S36.** SEM image of Zn-pbdc-7a-1eq.



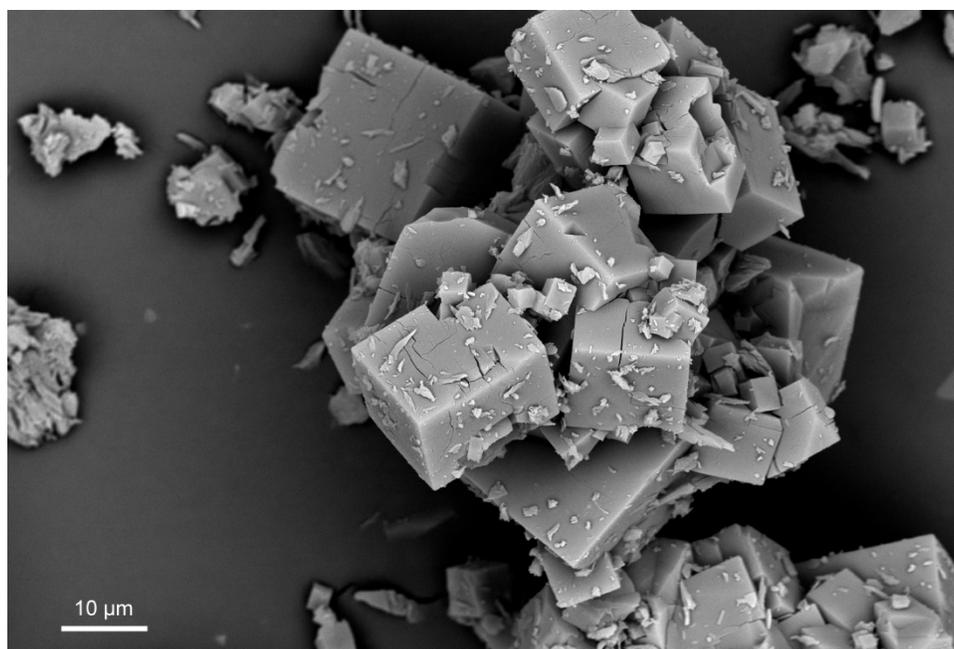
**Figure S37.** SEM image of Zn-pbdc-7a-1eq.



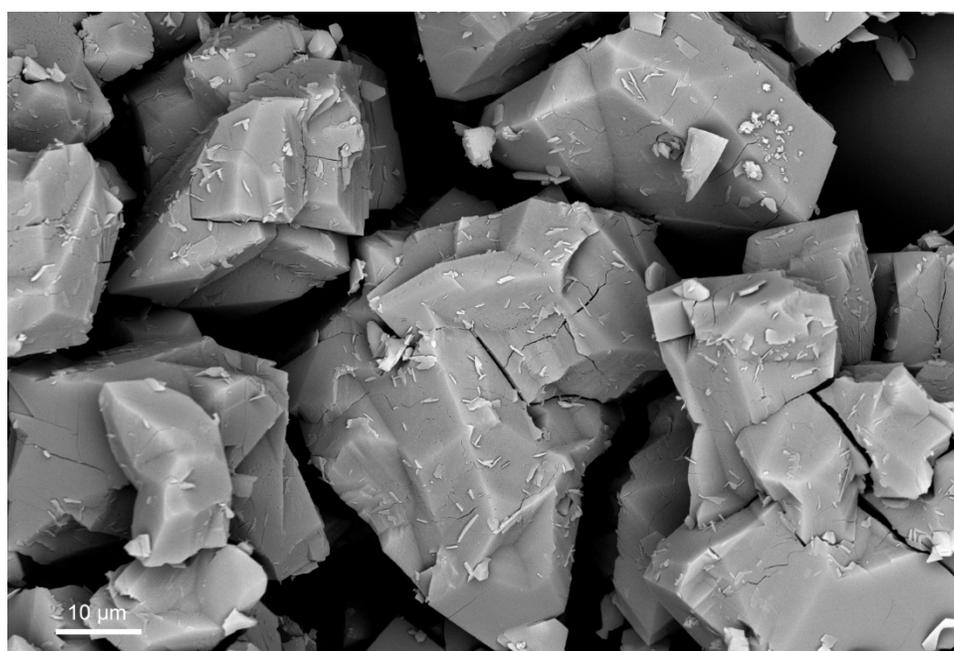
**Figure S38.** SEM image of Zn-pbdc-7a-3eq.



**Figure S39.** SEM image of Zn-pbdc-7a-15eq.



**Figure S40.** SEM image of Zn-pbdc-7a-15eq.



**Figure S41.** SEM image of Zn-pbdc-7a-30eq.

## 7. References

1. GitHub - fairen-group/betsi-gui: BET Surface Identification - a program that fully implements the rouquerol criteria, <https://github.com/fairen-group/betsi-gui>, (accessed 13 October 2022).
2. J. W. M. Osterrieth, J. Rampersad, D. Madden, N. Rampal, L. Skoric, B. Connolly, M. D. Allendorf, V. Stavila, J. L. Snider, R. Ameloot, J. Marreiros, C. Ania, D. Azevedo, E. Vilarrasa-Garcia, B. F. Santos, X. H. Bu, Z. Chang, H. Bunzen, N. R. Champness, S. L. Griffin, B. Chen, R. B. Lin, B. Coasne, S. Cohen, J. C. Moreton, Y. J. Colón, L. Chen, R. Clowes, F. X. Coudert, Y. Cui, B. Hou, D. M. D'Alessandro, P. W. Doheny, M. Dincă, C. Sun, C. Doonan, M. T. Huxley, J. D. Evans, P. Falcaro, R. Ricco, O. Farha, K. B. Idrees, T. Islamoglu, P. Feng, H. Yang, R. S. Forgan, D. Bara, S. Furukawa, E. Sanchez, J. Gascon, S. Telalović, S. K. Ghosh, S. Mukherjee, M. R. Hill, M. M. Sadiq, P. Horcajada, P. Salcedo-Abraira, K. Kaneko, R. Kukobat, J. Kenvin, S. Keskin, S. Kitagawa, K. ichi Otake, R. P. Lively, S. J. A. DeWitt, P. Llewellyn, B. v. Lotsch, S. T. Emmerling, A. M. Pütz, C. Martí-Gastaldo, N. M. Padial, J. García-Martínez, N. Linares, D. MasPOCH, J. A. Suárez del Pino, P. Moghadam, R. Oktavian, R. E. Morris, P. S. Wheatley, J. Navarro, C. Petit, D. Danaci, M. J. Rosseinsky, A. P. Katsoulidis, M. Schröder, X. Han, S. Yang, C. Serre, G. Mouchaham, D. S. Sholl, R. Thyagarajan, D. Siderius, R. Q. Snurr, R. B. Goncalves, S. Telfer, S. J. Lee, V. P. Ting, J. L. Rowlandson, T. Uemura, T. Iiyuka, M. A. van der Veen, D. Rega, V. van Speybroeck, S. M. J. Rogge, A. Lammaire, K. S. Walton, L. W. Bingel, S. Wuttke, J. Andreato, O. Yaghi, B. Zhang, C. T. Yavuz, T. S. Nguyen, F. Zamora, C. Montoro, H. Zhou, A. Kirchon and D. Fairen-Jimenez, *Advanced Materials*, 2022, **34**, 2201502.