Ligand Cross-Links as a Design Element in Oligo- and PolyMOFs

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SUPPORTING INFORMATION

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A. Materials

The following reagents were procured and used without further purification: 2-hydroxyterephthalic acid (Ambeed Co., 99%); 1,5-dibromopentane (TCI America, 98%); 1,6-dibromohexane (Sigma Aldrich, 96%); 1,7-dibromoheptane (TCI America, 98%); 1,2-bis(bromomethyl)benzene (Sigma Aldrich, 97%), 1,3-bis(bromomethyl)benzene (Combi Blocks Ltd., 98%); 1,4-bis(bromomethyl)benzene (Sigma Aldrich, 97%); diethyl-2,5-hydroxyterephthalate (Combi Blocks Ltd., 97%); 18-crown-6 (Alfa Aesar, 99%); zinc nitrate hexahydrate (Sigma Aldrich, 99%); 1,4-diazabicyclo[2.2.2]octane (DABCO, Thermo Fisher Scientific, 98%); 1,4-benzenedicarboxylic acid (Acros Organics, 99%). Other reagents and solvents were procured from standard chemical vendors and used without further purification.

B. Characterization

Column Chromatography. Silica column chromatography was performed using a TeledyneISCO CombiFlash Rf+ automated system.

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 appropriate solvent peak. MOF samples were acid digested using a mixture of 10 µL of 35% DCl solution in D_2O and 700 µL of DMSO-d_6, followed by sonication for 30 s.

ESI-MS Analysis. Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer, and the data were analyzed using the Xcalibur software suite.

SEM Imaging. Prior to SEM experiments, the DMF all samples were stored under was replaced with $CHCl_3$ and the $CHCl_3$ 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 an Ir sputter coating for 60 seconds. Imaging was carried out using a FEI Apreo SEM instrument using a 10 kV energy source under vacuum.

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 Kα (λ = 1.5418 Å) X-ray source was operated at 40 kV and 40 mA in Bragg-Brentano geometry. Each pattern was collected in a 2θ range of 4° to 40°, with a step size of 0.02° and a scan speed of 0.4 seconds per step. Pawley refinements were carried out using the DIFFRAC.TOPAS software package (Bruker AXS GmbH). Parameters were refined simultaneously.

N_2 Sorption. Prior to gas sorption experiments, the DMF all samples were stored under was replaced with $CHCl_3$ and the $CHCl_3$ was replaced three times and decanted after centrifugation. MOF samples were surface dried using filter paper and then activated under high vacuum at 120 °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. The temperature

was maintained over the duration of each experiment using liquid nitrogen in a 3 L Dewar flask. Surface areas were determined using the BETSI program (Osterrieth, J. W.; Rampersad, J.; Madden, D.; et al. *Adv. Mater.* **2022,** *34* (27), 2201502). Experiments were run in triplicate and error margins are reported as the standard error of the mean. Pore size distributions were calculated using the Horvath-Kawazoe module as implemented in the Microactive software suite (Micromeritics Inc., GA). Pore volumes were calculated at a P/P_0 value of 0.95 or the highest pressure preceding the onset of interparticle condensation.

TGA Analysis. TGA experiments were conducted using surface-dried MOF samples after DMF exchange, placed in a 90 µL ceramic crucible. Samples were analyzed on a TA Instruments SDT 650 Simultaneous Thermal Analyzer DSC/TGA using a temperature range of 30-500 °C, scanning at 10 °C/min under nitrogen flow (75 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}.

C. Ligand Synthesis

The synthesis of dimethyl-2-hydroxyterephthalate was carried out as per Tanabe *et al.* (Tanabe, K. K.; Allen, C. A.; Cohen, S. M., *Angew. Chem. Int. Ed.* **2010,** *49* (50), 9730-9733). The synthesis of 2,2'-(Butane-1,4-diylbis(oxy))diterephthalic acid was adapted from the general procedure of Dodson *et al.* The syntheses of 2,2'-(Pentane-1,5-diylbis(oxy))diterephthalic acid (pentyl(bdc)$_2$), 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'-((((2,5-dicarboxy-1,4-phenylene)bis(oxy))bis(pentane-5,1-diyl))bis(oxy))diterephthalic acid (pentyl$_2$(bdc)$_3$) were carried out as per Dodson *et al.* wth minor modifications (Dodson, R. A.; Park, J.; Kim, J.; Cliffe, M. J.; Cohen, S. M., *Inorg. Chem.* **2022,** *61* (31), 12284-12292). The syntheses of 2,2'-((1,2-phenylenebis(methylene))bis(oxy))diterephthalic acid (o-xylyl(bdc)$_2$), 2,2'-((1,3-phenylenebis(methylene))bis(oxy))diterephthalic acid (m-xylyl(bdc)$_2$), and 2,2'-((1,4-phenylenebis(methylene))bis(oxy))diterephthalic acid (p-xylyl(bdc)$_2$) were carried out as per Allen *et al.* with minor modifications (Allen, C.; Cohen, S., *Inorg. Chem.* **2014,** *53* (13), 7014-7019.). The syntheses of the pentyl-linked bdc polyether (pbdc-5a) and heptyl-linked bdc polyether (pbdc-7a) were carried out as per Zhang *et al* (Zhang, Z.; Nguyen, H. T. H.; Miller, S. A.; Cohen, S. M., *Angew. Chem. Int. Ed.* **2015,** *54* (21), 6152-6157.).

Dimethyl-2-hydroxyterephthalate

2-hydroxyterephthalic acid (10.0 g, 0.055 mol) was dissolved in 500 mL of MeOH. Conc. H_2SO_4 (2 mL) was added and the solution was refluxed overnight (appx. 18 h). After cooling the reaction to room temperature, MeOH was removed under vacuum. The remaining solution was neutralized with an excess of saturated $NaHCO_3$ (aq.) and the product was extracted with CH_2Cl_2. The organic layer was isolated, washed with brine, and dried over sodium sulfate. CH_2Cl_2 was removed under vacuum

to obtain a yellow solid. Yield: 7.5 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 10.76 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.52 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H).

2,2'-(Butane-1,4-diylbis(oxy))diterephthalic acid (butyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 20 mL of DMF in a 50 mL round-bottomed flask while stirring. To this mixture, 1,4-Dibromobutane (0.41 mL, 0.73 g, 3.4 mmol) was added dropwise while stirring. The temperature was increased to 100 °C and the reaction was allowed to proceed for 20 hours. Excess potassium carbonate was filtered off and solvent was removed to yield an oil. This product was dissolved in ethyl acetate, washed with water, brine, and dried over sodium sulfate. The solid thus obtained was purified by recrystallization (DCM:MeOH) to yield a pale yellow solid.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 0.71 g (56% over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.67 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 1.4 Hz, 2H), 7.54 (dd, *J* = 7.8, 1.4 Hz, 2H), 4.16 (s, 4H), 1.93 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ [ppm] = 167.20, 166.72, 156.95, 134.45, 130.33, 126.06, 120.99, 113.54, 67.96, 25.23; HRMS (ESI) calculated for $[C_{20}H_{17}O_{10}]^-$: *m/z* = 417.0827, found *m/z* = 417.0828.

2,2'-(Pentane-1,5-diylbis(oxy))diterephthalic acid (pentyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and anhydrous potassium carbonate(1.88 g, 13.6 mmol, 4 eq.) were combined in 20 mL of DMF in a 50 mL round-bottomed flask while stirring. To this mixture, 1,5-Dibromopentane (0.46 mL, 0.78 g, 3.4 mmol) was added dropwise while stirring. The temperature was increased to 100 °C and the reaction was allowed to proceed for 20 hours. Excess potassium carbonate was filtered off and solvent was removed to yield an oil. This product was dissolved in ethyl acetate, washed with water, brine, and dried over sodium sulfate. The solid thus obtained was purified by column chromatography (Hexane:EtOAc) to yield the methyl ester in the form of a white solid.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 1.04 g (79% over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.66 (d, 1H), 7.57 (s, 1H), 7.54 (d, 7.9 Hz, 1H), 4.10 (t, 6.2 Hz, 4H), 1.81 (m, 2H).

2,2'-(Hexane-1,6-diylbis(oxy))diterephthalic acid (hexyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and anhydrous potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 20 mL of DMF in a 50 mL round-bottomed flask while stirring. To this mixture, 1,6-Dibromohexane (0.59 mL, 0.93 g, 3.8 mmol) was added dropwise while stirring. The temperature was increased to 100 °C and the reaction was allowed to proceed for 20 hours. Excess potassium carbonate was filtered off and solvent was removed to yield an oil. This product was dissolved in ethyl acetate, washed with water, brine, and dried over sodium sulfate. The solid thus obtained was purified by column chromatography (Hexane:EtOAc) to yield the methyl ester in the form of a white solid.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 0.90 g (66% over two steps). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ(ppm) = 7.65 (d, 1H), 7.55 (s, 1H), 7.53 (d, 7.8 Hz, 1H), 4.08 (t, 6.1 Hz, 4H), 1.74 (m, 4H), 1.50 (m, 4H).

2,2'-(Heptane-1,7-diylbis(oxy))diterephthalic acid (heptyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and anhydrous potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 20 mL of DMF in a 50 mL round-bottomed flask while stirring. To this mixture, 1,7-Dibromoheptane (0.58 mL, 0.88 g, 3.4 mmol) was added dropwise while stirring. The temperature was increased to 100 °C and the reaction was allowed to proceed for 20 hours. Excess potassium carbonate was filtered off and solvent was removed to yield an oil. This product was dissolved in ethyl acetate, washed with water, brine, and dried over sodium sulfate. The solid thus obtained was purified by column chromatography (Hexane:EtOAc) to yield the methyl ester in the form of a white solid.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 1.09 g (79 % over two steps). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ(ppm) = 7.66 (d, 8.1 Hz, 2H), 7.55 (s, 2H), 7.53 (d, 8.0 Hz, 2H), 4.08 (t, 6.0 Hz, 4H), 1.74 (m, 4H), 1.47 (m, 4H), 1.40 (m, 2H).

2,2'-((1,2-Phenylenebis(methylene))bis(oxy))diterephthalic acid (o-xylyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 75 mL of DMF in a 100 mL round-bottomed flask while stirring. To

this mixture, 1,2-bis(bromomethyl)benzene (0.897 g, 3.4 mmol) was added in small portions while stirring. The temperature was increased to 100 °C and the reaction was allowed to proceed overnight before cooling. Excess potassium carbonate was filtered off and the ester product was precipitated using excess water, filtered, washed with water, and dried under vacuum.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 1.07 g (75% over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.74 – 7.70 (m, 4H), 7.67 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.39 (m, 2H), 5.46 (s, 4H).

2,2'-((1,3-Phenylenebis(methylene))bis(oxy))diterephthalic acid (m-xylyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 75 mL of DMF in a 100 mL round-bottomed flask while stirring. To this mixture, 1,3-bis(bromomethyl)benzene (0.897 g, 3.4 mmol) was added in small portions while stirring. The temperature was increased to 100 ℃ and the reaction was allowed to proceed overnight before cooling. Excess potassium carbonate was filtered off and the ester product was precipitated using excess water, filtered, washed with water, and dried under vacuum.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 1.10 g (77% over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.76 – 7.67 (m, 4H), 7.63 (s, 1H), 7.61 – 7.56 (d, 2H), 7.49 (d, 2H), 7.47 – 7.41 (m, 1H), 5.27 (s, 4H).

2,2'-((1,4-Phenylenebis(methylene))bis(oxy))diterephthalic acid (p-xylyl(bdc)$_2$)

Dimethyl 2-hydroxyterephthalate (1.50 g, 7.1 mmol, 2.1 eq.), and potassium carbonate (1.88 g, 13.6 mmol, 4 eq.) were combined in 75 mL of DMF in a 100 mL round-bottomed flask while stirring. To this mixture, 1,4-bis(bromomethyl)benzene (0.897 g, 3.4 mmol) was added in small portions while stirring. The temperature was increased to 100 ℃ and the reaction was allowed to proceed overnight before cooling. Excess potassium carbonate was filtered off and the ester product was precipitated using excess water, filtered, washed with water, and dried under vacuum.

Ester hydrolysis was carried out by stirring the methyl ester in 70 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 100 mL of 1 M HCl. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 1.21 g (85% over two steps). ^{1}H

NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.74 – 7.66 (m, 4H), 7.58 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.53 (s, 4H), 5.27 (s, 4H).

2,2'-((((2,5-dicarboxy-1,4-phenylene)bis(oxy))bis(pentane-5,1-diyl))bis(oxy))diterephthalic acid (pentyl$_2$(bdc)$_3$)

Dimethyl 2-hydroxyterephthalate (2.1 g, 1 eq., 10 mmol) and potassium carbonate (2.1 g, 1.5 eq., 15 mmol) were added to 2-butanone (30 mL) in a 250 mL two-necked flask and stirred. To this mixture, 1,5-dibromopentane (10 g, 6.1 mL, 4.5 eq., 45 mmol) was added in small aliquots. 18-crown-6 (30 mg, 0.011 eq., 0.11 mmol) was added and the suspension was heated to 90 °C for 16 hours. The solvent was then removed via vacuum and the resulting oil was dissolved in CH_2Cl_2, washed with water, brine, dried with sodium sulfate, filtered, and purified via column chromatography (Hexane:EtOAc) to yield the dimethyl 2-((bromopentyl)oxy)terephthalate intermediate as a yellow oil which was allowed to solidify overnight. Yield: 1.8 g (50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.77 (d, 8.0 Hz, 1H), 7.60 (d, 8.0 Hz, 1H), 7.58 (s, 1H), 4.09 (t, 6.3 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.43 (t, 6.8 Hz, 2H), 1.93 (m, 2H), 1.86 (m, 2H), 1.65 (m, 2H).

To 1.3 g of the obtained dimethyl 2-((bromopentyl)oxy)terephthalate intermediate (3.6 mmol, 2.3 eq.), diethyl 2,5-dihydroxyterephthalate (0.41 g, 1.6 mmol, 1.0 eq.), potassium carbonate (0.66 g, 4.8 mmol, 3.0 eq.), 18-crown-6 (8 mg, 0.03 mmol), and 2-butanone (10 mL) were added in a 50 mL round-bottomed flask while stirring. The mixture was heated to 90 °C for 16 hours. The reaction mixture was then cooled to room temperature and extracted from 50 mL H_2O with 3×30 mL $CHCl_3$. The combined organic phases were washed with brine, dried with sodium sulfate, filtered, and purified via column chromatography (Hexane:EtOAc) to yield the esterified trimer.

Ester hydrolysis was carried out by stirring the methyl ester in 60 mL of a 1 M solution of NaOH in a 3:3:1 mixture of water, THF, and methanol at room temperature overnight. The volatile component was removed by rotary evaporation and the solution was acidified using 1 M HCl until precipitation was no longer apparent. The white solid obtained was washed with 0.1 M HCl and dried under vacuum. Yield 0.76 g (68 % over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.66 (d, 7.9 Hz, 2H), 7.57 (s, 2H), 7.54 (d, 7.9 Hz, 2H), 7.28 (s, 2H), 4.09 (t, 6.1 Hz, 4H), 4.00 (t, 6.3 Hz, 4H), 1.77 (m, 8H), 1.61 (m, 4H).

pbdc-5a

1.20 g of diethyl-2,5-hydroxyterephthalate (4.7 mmol) was added to a suspension of 2.60 g of potassium carbonate in 10 ml of acetone and 23 ml of DMSO in a 100 ml flask and stirred at RT for 5 minutes. 0.64 ml of 1,5-dibromopentane (1.10 g, 4.75 mmol) was added dropwise under continuous stirring, and the temperature was raised to 100 °C. The reaction was continued for 24 hours and cooled

to room temperature. 50 ml of water was added and the polymeric solid was collected by centrifugation, and washed with acetone and methanol.

Ester hydrolysis was carried out by adding 0.70 g of the polymeric ester to a solution of 2.80 g of KOH in 21 ml of 1:1 DMSO:H_2O while stirring continuously, and heating to 80 °C for 8 hours. After cooling to RT, the solution was acidified using 1 M HCl, and the obtained precipitate was collected by centrifugation, washed with 0.1 M HCl, and dried under vacuum. Yield 0.80 g (65 % over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.27 (s, 2H), 3.99 (t, *J* = 6.3 Hz, 4H), 1.74 (t, *J* = 7.1 Hz, 4H), 1.58 (m, 2H). MALDI-TOF-MS approx. M_N = 10314 Da, degree of polymerization: 39 repeat units.

pbdc-7a

1.20 g of diethyl-2,5-hydroxyterephthalate (4.7 mmol) was added to a suspension of 2.60 g of potassium carbonate in 10 ml of acetone and 23 ml of DMSO in a 100 ml flask and stirred at RT for 5 minutes. 0.81 ml of 1,7-dibromoheptane (1.22 g, 4.75 mmol) was added dropwise under continuous stirring, and the temperature was raised to 100 °C. The reaction was continued for 24 hours and cooled to room temperature. 50 ml of water was added and the polymeric solid was collected by centrifugation and washed with acetone and methanol.

Ester hydrolysis was carried out by adding 0.70 g of the polymeric ester to a solution of 2.8 g of KOH in 21 ml of 1:1 DMSO:H_2O while stirring continuously, and heating to 80 °C for 8 hours. After cooling to RT, the solution was acidified using 1 M HCl, and the obtained precipitate was collected, washed with 0.1 M HCl, and dried under vacuum. Yield 0.50 g (36 % over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 7.25 (s, 2H), 3.97 (m, 4H); 1.68 (m, 4H); 1.62-1.25 (m, 6H). MALDI-TOF-MS approx. M_N = 5807 Da, degree of polymerization: 20 repeat units.

D. MOF Synthesis

Solvothermal MOF synthesis procedures are adapted from Wang *et al.* (Wang, Z.; Tanabe, K. K.; Cohen, S. M., *Chem. Eur. J.* **2010,** *16* (1), 212-217). Rapid room temperature syntheses are adapted from Hungerford *et al*. (Hungerford, J.; Walton, K. S., *Inorg. Chem.* **2019,** *58* (12), 7690-7697).

pcu-DMOF-1 solvothermal synthesis

$Zn(NO_3)_2{\cdot}6H_2O$ (156 mg, 0.52 mmol) and 1,4-benzenedicarboxylic acid (BDC, 102 mg, 0.61 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature

was held at 120 °C for 24 h. The filtered precipitate was air dried. The crystalline powder obtained from the filtrate were collected, washed three times with DMF, and stored in DMF. Yield: 25 mg, 17 %.

kag-DMOF-1 rapid synthesis

A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 140 mg, 1.25 mmol) and triethylamine (0.35 ml) in 15 ml of DMF was mixed with a solution of 436 mg of $Zn(NO_3)_2 \cdot 6H_2O$ (1.47 mmol) and 243 mg (1.47 mmol) of terephthalic acid in 15 ml of DMF, stirring at 200 rpm for 4 hours. The solid was washed three times with DMF and stored under DMF. Yield: 122 mg, 29 %.

butyl(bdc)$_2$-DMOF-1 ([Zn$_2$(butyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and butyl(bdc)$_2$, (125 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 24 mg, 14 %.

pentyl(bdc)$_2$-DMOF-1 ([Zn$_2$(pentyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and pentyl(bdc)$_2$, (131.5 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 21 mg, 10 %.

hexyl(bdc)$_2$-DMOF-1 ([Zn$_2$(hexyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and hexyl(bdc)$_2$, (136 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two

7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield was too low to be determined.

heptyl(bdc)$_2$-DMOF-1 ([Zn$_2$(heptyl(bdc)$_2$)(DABCO)] solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and heptyl(bdc)$_2$, (138 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 8 mg, 4%. Multiple batches were combined for gas sorption and ^{1}H NMR studies.

o-xylyl(bdc)$_2$-DMOF-1 ([Zn$_2$(o-xylyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and *o*-xylyl(bdc)$_2$, (142 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 18 mg, 10 %.

m-xylyl(bdc)$_2$-DMOF-1 ([Zn$_2$(m-xylyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and *m*-xylyl(bdc)$_2$, (142 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 23 mg, 13 %.

p-xylyl(bdc)$_2$-DMOF-1 ([Zn$_2$(p-xylyl(bdc)$_2$)(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and *p*-xylyl(bdc)$_2$, (142 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg, 0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The crystalline powder obtained was collected, washed three times with DMF, and stored in DMF. Yield: 34 mg, 19 %.

pentyl$_2$(bdc)$_3$-DMOF-1 ([Zn$_3$(pentyl$_2$(bdc)$_3$)(DABCO)$_{1.5}$]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (78 mg, 0.26 mmol) and pentyl$_2$(bdc)$_3$ (70 mg, 0.10 mmol) were dissolved in 3.75 mL of dimethylformamide (DMF) in a vial. A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 54 mg, 0.48 mmol) in 3.75 mL of DMF was then added to this solution, which immediately generated a white precipitate. The mixture was filtered and the filtrate was collected in a scintillation vial (20 mL capacity). The vial was placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 24 h. The solid was washed three times with DMF and stored under DMF. Yield: 20 mg, 11 %.

pbdc-5a-DMOF-1 ([Zn$_2$(pbdc-5a)$_2$(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (78 mg, 0.26 mmol) and pbdc-5a (78 mg, 0.3 mmol) were dissolved in 3.75 mL of dimethylformamide (DMF) in a vial. A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 54 mg, 0.48 mmol) in 3.75 mL of DMF was then added to this solution, which immediately generated a beige precipitate. The vial was placed in a sand bath, and the bath was transferred to an oven preheated to 120 °C for 24 h. The solid was washed three times with DMF and stored under DMF. Yield: 24 mg, 24 %.

pbdc-7a-DMOF-1 ([Zn$_2$(pbdc-7a)$_2$(DABCO)]) solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (78 mg, 0.26 mmol) and pbdc-7a (85 mg, 0.3 mmol) were dissolved in 3.75 mL of dimethylformamide (DMF) in a vial. A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 54 mg, 0.48 mmol) in 3.75 mL of DMF was then added to this solution, which immediately generated a beige precipitate. The vial was placed in a sand bath, and the bath was transferred to an oven preheated to 120 °C for 24 h. The solid was washed three times with DMF and stored under DMF. Yield: 30 mg, 28 %.

pentyl(bdc)$_2$-DMOF-1 ([Zn$_2$(pentyl(bdc)$_2$)(DABCO)]) "prolonged" solvothermal synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (156 mg, 0.52 mmol) and pentyl(bdc)$_2$, (131.5 mg, 0.30 mmol) were dissolved in 7.5 mL of dimethylformamide (DMF). A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 108 mg,

0.96 mmol) in 7.5 mL of DMF was then added to this solution, which immediately generated a large amount of white precipitate. The mixture was filtered and the filtrate was collected and divided into two 7.5 mL portions in two scintillation vials (20 mL capacity each). The vials were placed in a sand bath in an oven preheated to 120 °C. The temperature was held at 120 °C for 7 or 14 days. The solid was washed three times with DMF and stored under DMF.

pentyl(bdc)$_2$-DMOF-1 ([Zn$_2$(pentyl(bdc)$_2$)(DABCO)]) rapid synthesis

A solution of DABCO (14 mg, 0.125 mmol) and triethylamine (0.035 ml) in 1.5 ml of DMF was mixed with a solution of 43.6 mg of $Zn(NO_3)_2 \cdot 6H_2O$ (0.147 mmol) and 31.7 mg of pentyl(bdc)$_2$ (0.074 mmol) in 1.5 ml of DMF, stirring at 200 rpm for 4 hours. The solid was washed three times with DMF and stored under DMF.

heptyl(bdc)$_2$-DMOF-1 ([Zn$_2$(heptyl(bdc)$_2$)(DABCO)]) rapid synthesis

A solution of DABCO (14 mg, 0.125 mmol) and triethylamine (0.035 ml) in 1.5 ml of DMF was mixed with a solution of 43.6 mg of $Zn(NO_3)_2 \cdot 6H_2O$ (0.147 mmol) and 33.7 mg of heptyl(bdc)$_2$ (0.074 mmol) in 1.5 ml of DMF, stirring at 200 rpm for 4 hours. The solid was washed three times with DMF and stored under DMF.

E. CCDC Search

The Cambridge Structural Database (version 5.45, November 2023) was searched using the ConQuest (2023.3.0) interface (Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2016,** *72* (2), 171-179). Search queries and number of hits are listed in Table S4. C-O bonds were defined as acyclic to exclude cyclic ethers from search results.

F. Supplementary Tables

Table S1. Summary of Pawley refinement parameters.

Compound	Reference structure	Space Group	*a* (Å)	*c* (Å)	R_{wp}
pcu-DMOF-1	WAFKAQ (pcu *np*)	I4/mcm	15.1165	19.2693	15.291
kag-DMOF-1	ZnBD*h*	P$\bar{3}$m1	21.6644	9.7222	6.894
butyl(bdc)$_2$-DMOF-1	ZnBD*h*	P$\bar{3}$m1	21.6592	9.6936	12.554
pentyl(bdc)$_2$-DMOF-1	ZnBD*h*	P$\bar{3}$m1	21.5740	9.6343	12.411
heptyl(bdc)$_2$-DMOF-1	WAFKEU (pcu *lp*)	P4/mmm	10.9107	9.6247	9.144
ox(bdc)$_2$-DMOF-1	WAFKEU (pcu *lp*)	P4/mmm	10.9199	9.6417	11.778
mx(bdc)$_2$-DMOF-1	WAFKEU (pcu *lp*)	P4/mmm	10.9014	9.6523	13.859
px(bdc)$_2$-DMOF-1	WAFKEU (pcu *lp*)	P4/mmm	10.9160	9.6630	9.469
pentyl$_2$(bdc)$_3$-DMOF-1	WAFKEU (pcu *lp*)	P4/mmm	10.9573	9.6975	9.764

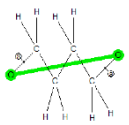
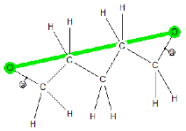
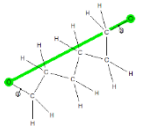
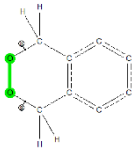
Table S2. Summary of BET surface areas and peak pore widths calculated from 77 K N_2 isotherms.

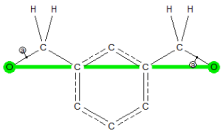
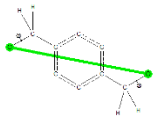
Compound	BET Surface Area (m^2/g)	Peak HK Pore Width (Å)	Pore Volume (cm^3/g)
pcu-DMOF-1	1779±58	6.14	0.732
kag-DMOF-1	1813±22	6.28, 11.26	0.863
butyl(bdc)$_2$-DMOF-1	841±60	6.61, 10.46	0.429
pentyl(bdc)$_2$-DMOF-1	1150±4	6.73, 10.21	0.578
heptyl(bdc)$_2$-DMOF-1	962±1	6.05	0.443
ox(bdc)$_2$-DMOF-1	1093±84	6.36	0.503
mx(bdc)$_2$-DMOF-1	892±1	< 5.52	0.439
px(bdc)$_2$-DMOF-1	631±38	6.38	0.418
pentyl$_2$(bdc)$_3$-DMOF-1	448±88	6.48	0.160
pbdc-5a-DMOF-1	100±6	7.52	0.248
pbdc-7a-DMOF-1	251±5	7.25	0.332

Table S3. Summary of digestion ^{1}H NMR ligand ratios.

Compound	DABCO protons per bdc ligand
pcu-DMOF-1	5.97
kag-DMOF-1	5.67
butyl(bdc)$_2$-DMOF-1	12.42
pentyl(bdc)$_2$-DMOF-1	12.60
hexyl(bdc)$_2$-DMOF-1	13.18 (without activation)
heptyl(bdc)$_2$-DMOF-1	12.60
ox(bdc)$_2$-DMOF-1	14.20
mx(bdc)$_2$-DMOF-1	12.15
px(bdc)$_2$-DMOF-1	12.71
pentyl$_2$(bdc)$_3$-DMOF-1	19.55
pbdc-5a-DMOF-1	4.08, 6.21 (without activation)
pbdc-7a-DMOF-1	6.40

Table S4. CSD Seach queries and parameters for O···O spacer distance distributions.

Spacer	Search Query	Structure Hits	Distinct Distances
n-butyl		186	230
n-pentyl		68	83
n-hexyl		113	132
n-heptyl		7	8
o-xylyl		172	309

m-xylyl		495	1490
p-xylyl		261	345

G. Supplementary Figures

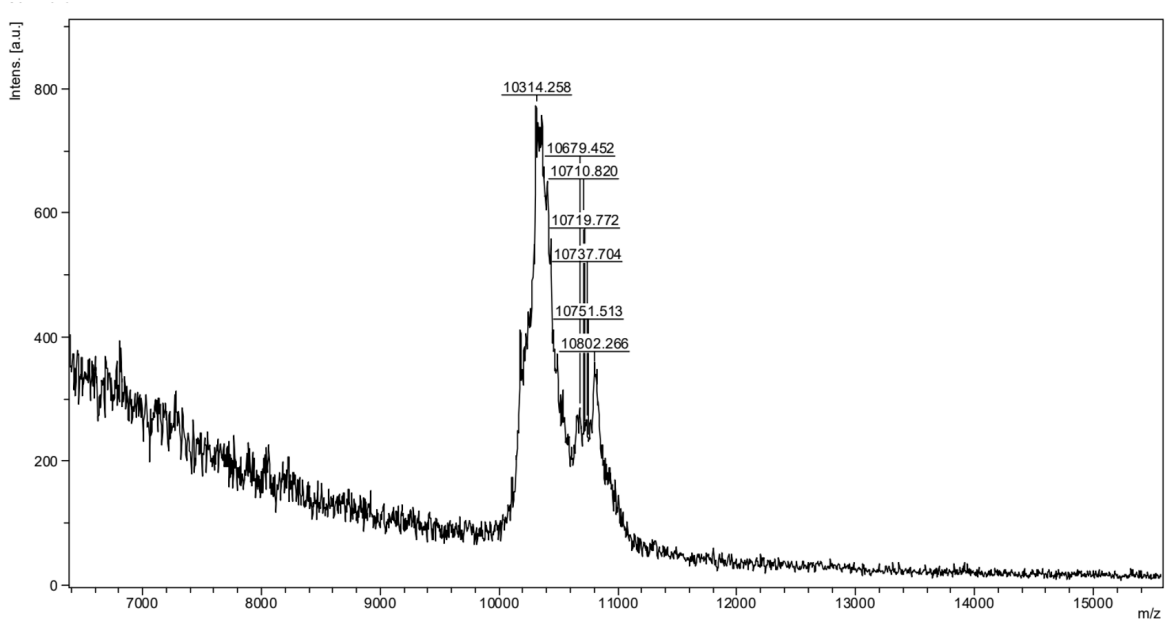


Figure S1. MALDI-TOF mass spectrum of pbdc-5a.

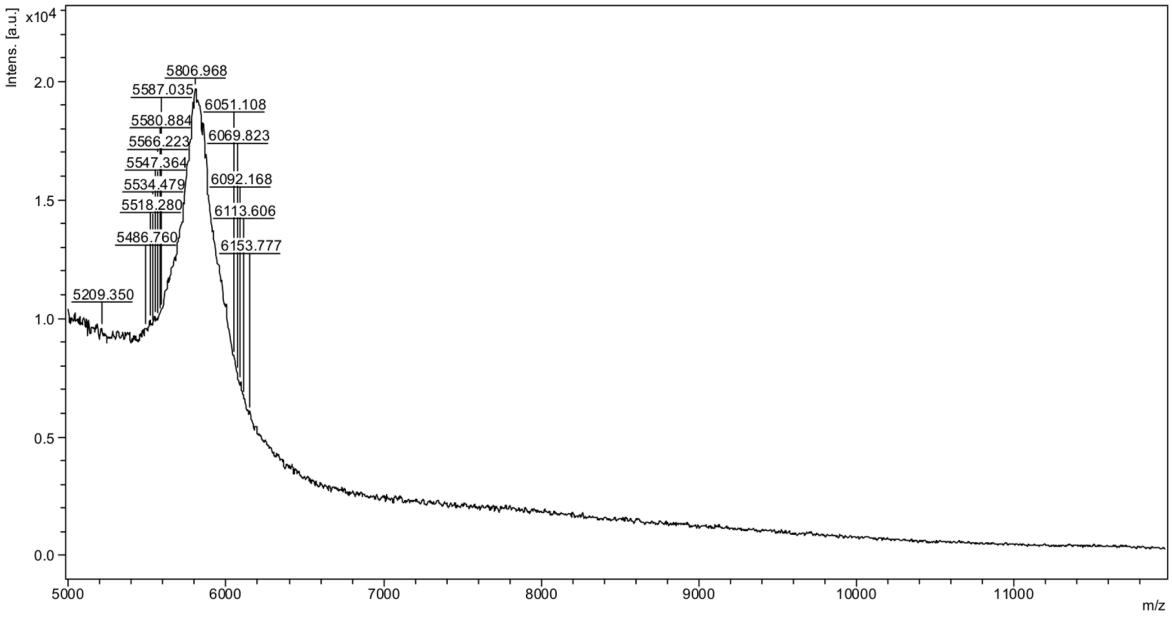


Figure S2. MALDI-TOF mass spectrum of pbdc-7a.

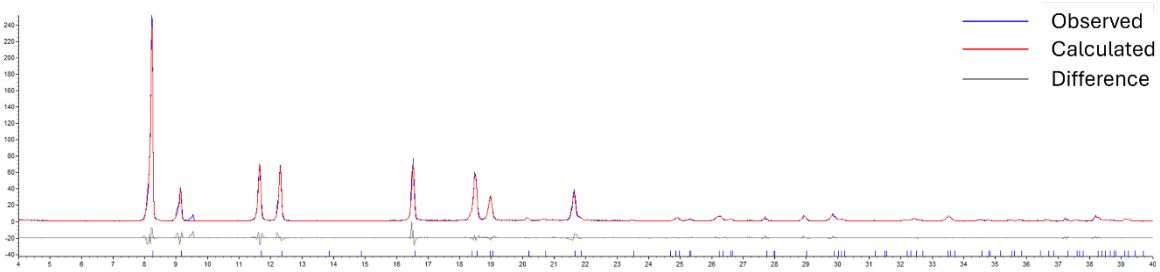


Figure S3 Pawley fit of PXRD data for pcu-DMOF-1.

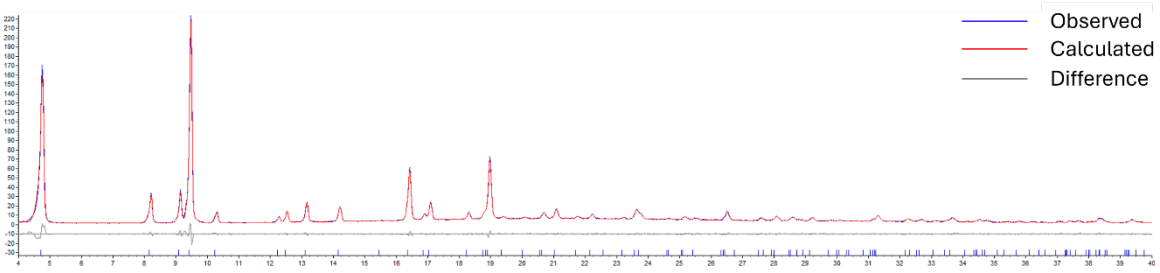


Figure S4. Pawley fit of PXRD data for kag-DMOF-1.

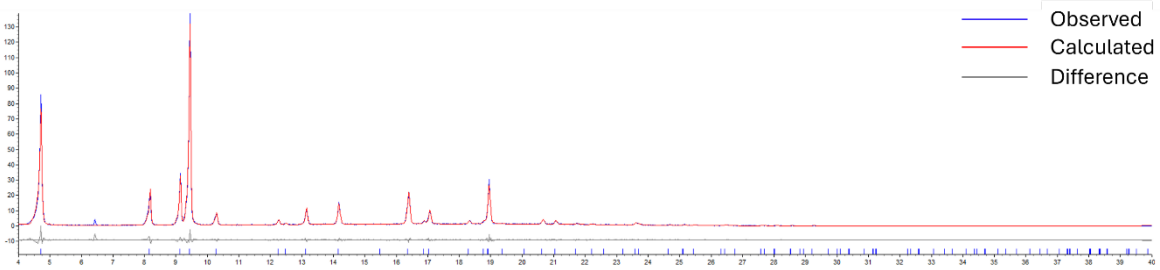


Figure S5. Pawley fit of PXRD data for butyl(bdc)$_2$-DMOF-1.

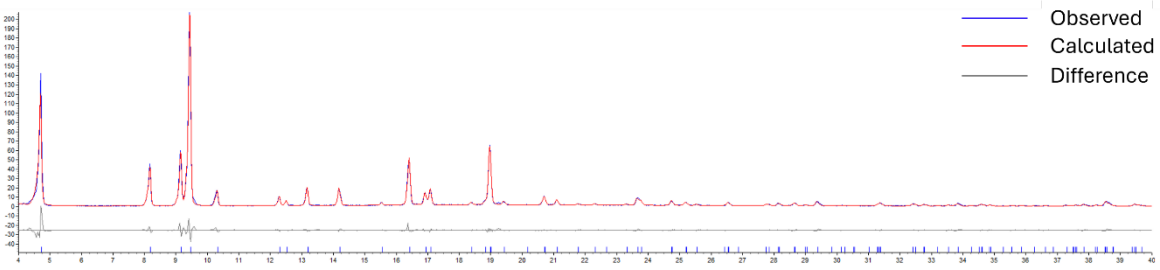


Figure S6. Pawley fit of PXRD data for pentyl(bdc)$_2$-DMOF-1.

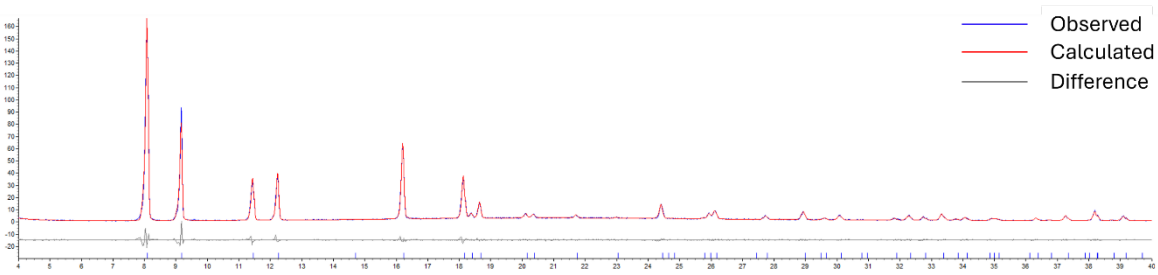


Figure S7. Pawley fit of PXRD data for heptyl(bdc)$_2$-DMOF-1.

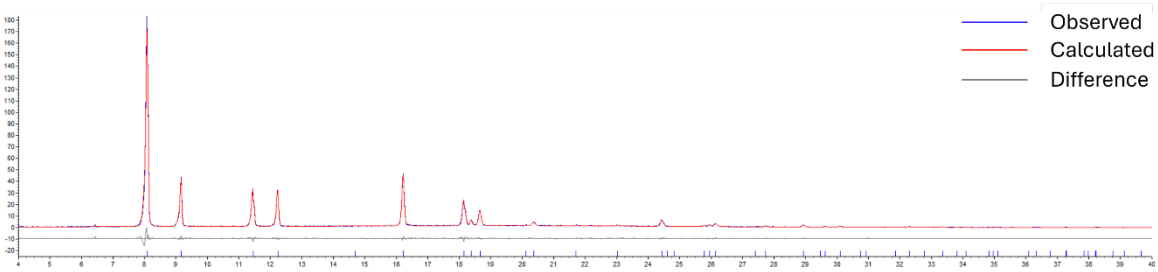


Figure S8. Pawley fit of PXRD data for o-xylyl(bdc)$_2$-DMOF-1.

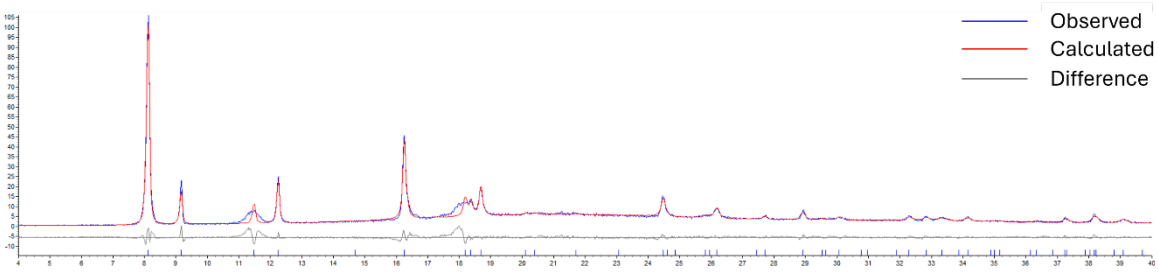


Figure S9. Pawley fit of PXRD data for m-xylyl(bdc)$_2$-DMOF-1.

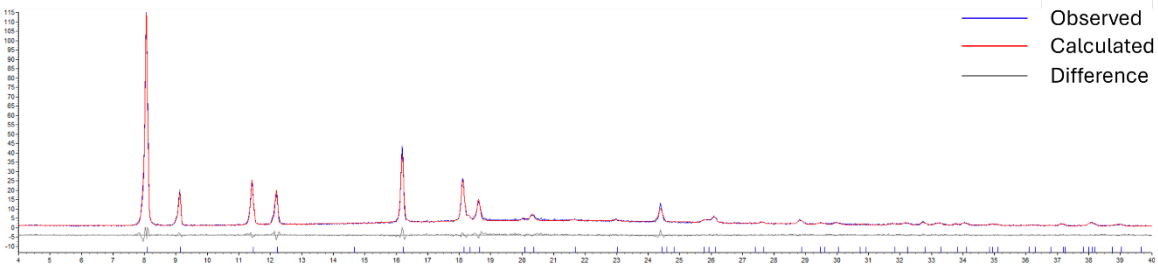


Figure S10. Pawley fit of PXRD data for p-xylyl(bdc)$_2$-DMOF-1.

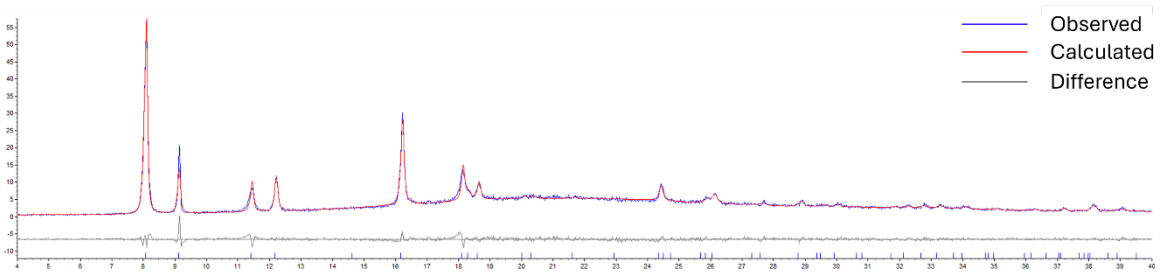


Figure S11. Pawley fit of PXRD data for pentyl$_2$(bdc)$_3$-DMOF-1.

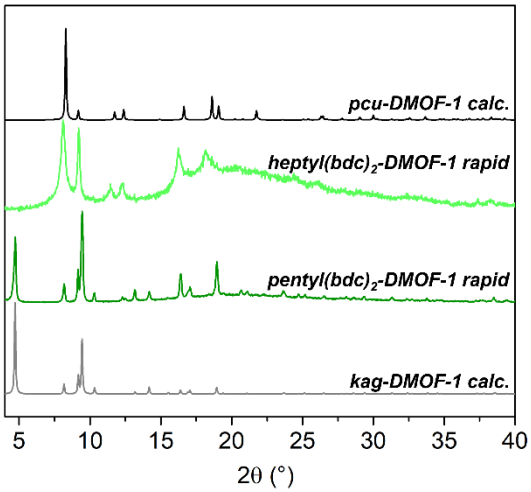


Figure S12. PXRD patterns of DMOFs synthesised using pentyl(bdc)$_2$ and heptyl(bdc)$_2$ under rapid, kinetically controlled conditions.

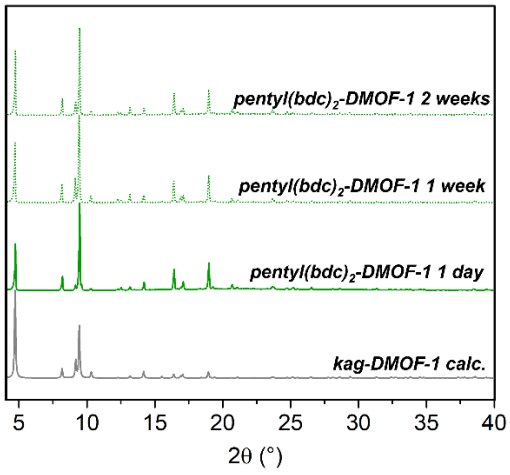


Figure S13. PXRD patterns of pentyl(bdc)$_2$-DMOF-1 prepared using varied synthesis times, in comparison with kag-DMOF-1.

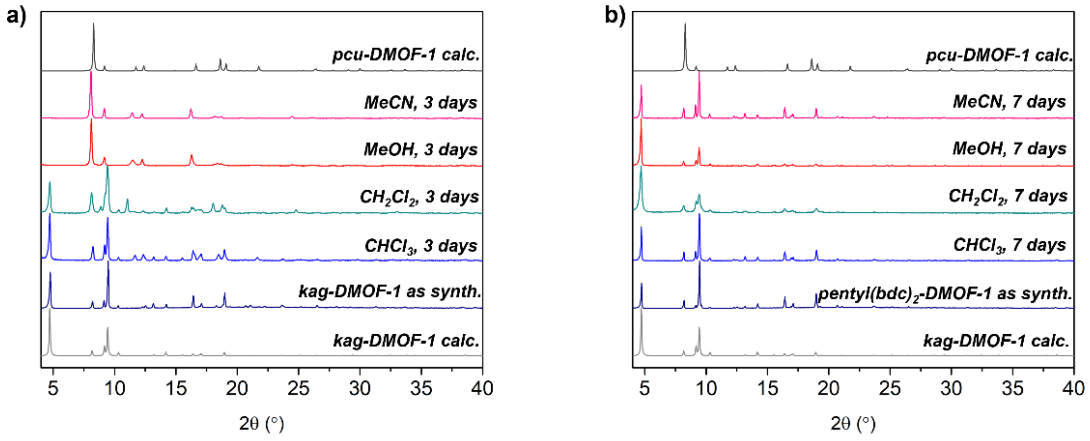


Figure S14. PXRD patterns of (a) kag-DMOF-1 and (b) pentyl(bdc)$_2$-DMOF-1 after soaking in various solvents for 3 days and 1 week respectively.

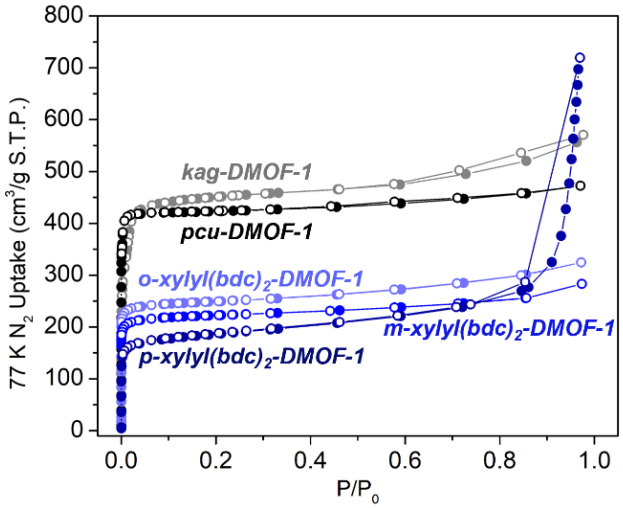


Figure S15. N_2 sorption isotherms (77 K) of xylyl-tethered DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1. Closed symbols represent adsorption and open symbols represent desorption.

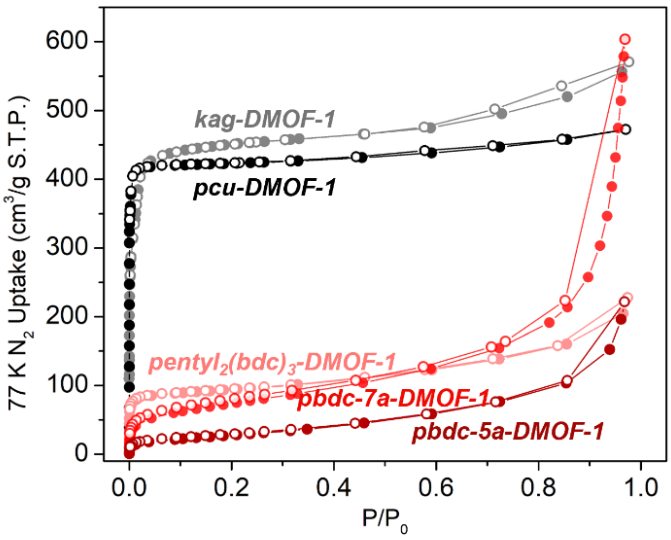


Figure S16. N_2 sorption isotherms (77 K) of trimer and polymer-based DMOFs in comparison with pcu-DMOF-1 and kag-DMOF-1. Closed symbols represent adsorption and open symbols represent desorption.

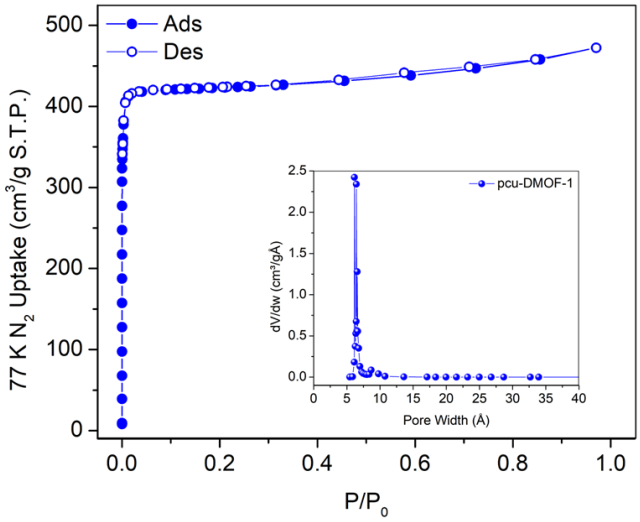


Figure S17. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for pcu-DMOF-1.

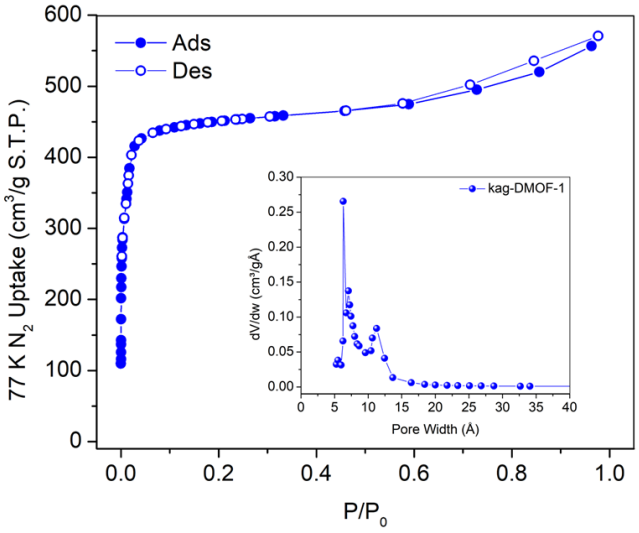


Figure S18. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for kag-DMOF-1.

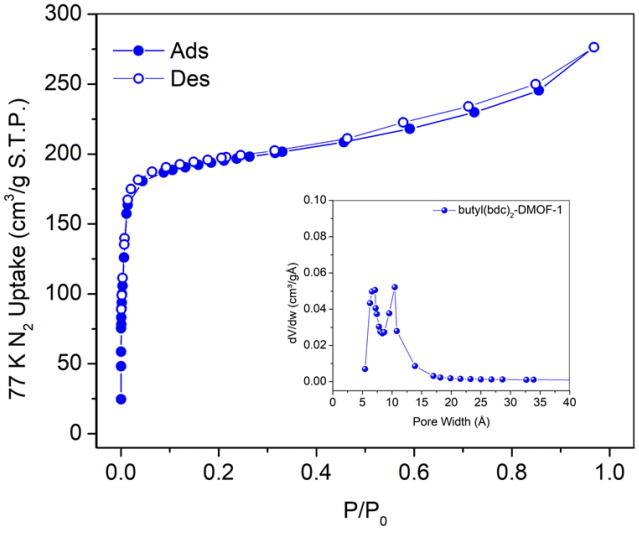


Figure S19. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for butyl(bdc)$_2$-DMOF-1.

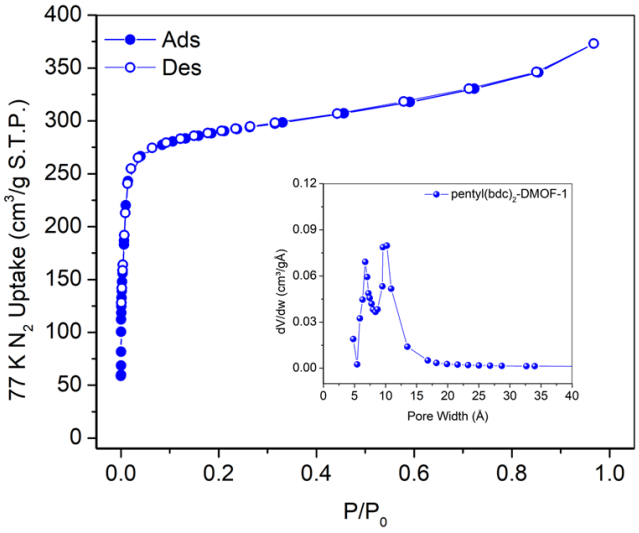


Figure S20. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for pentyl(bdc)$_2$-DMOF-1.

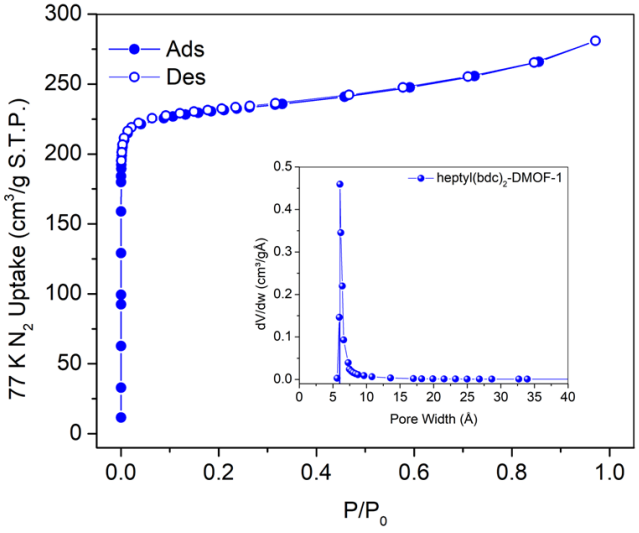


Figure S21. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for heptyl(bdc)$_2$-DMOF-1.

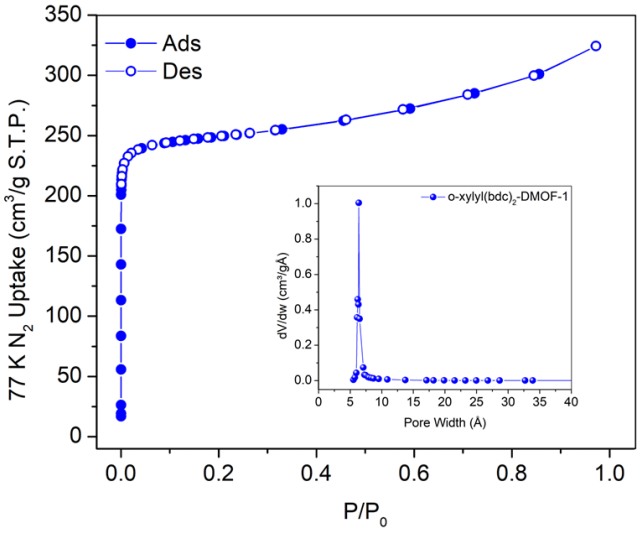


Figure S22. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for o-xylyl(bdc)$_2$-DMOF-1.

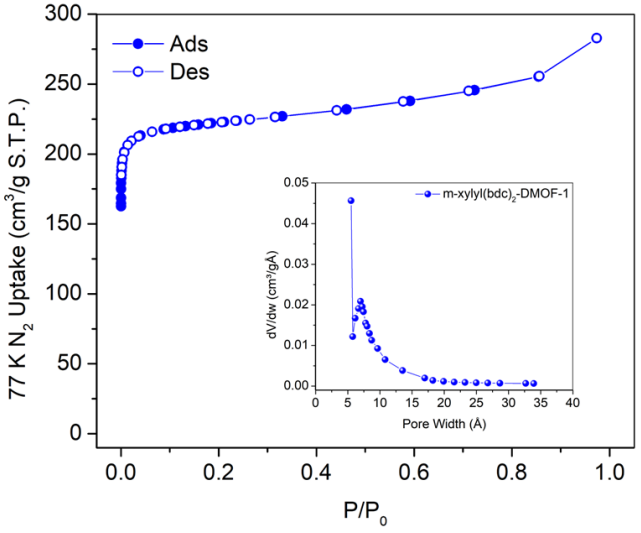


Figure S23. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for m-xylyl(bdc)$_2$-DMOF-1.

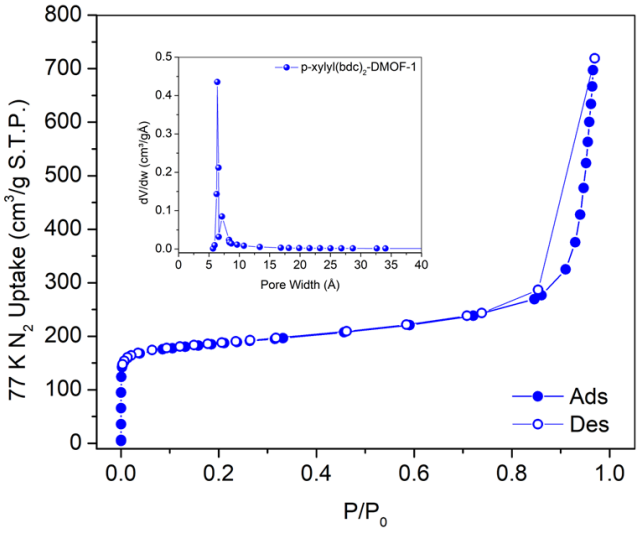


Figure S24. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for p-xylyl$(bdc)_2$-DMOF-1.

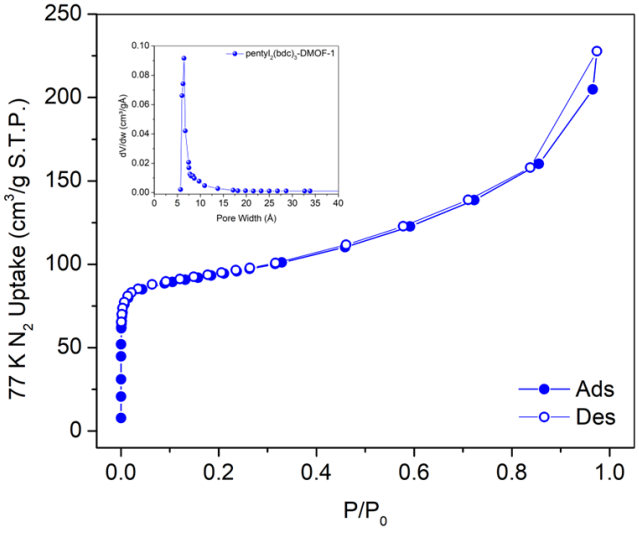


Figure S25. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for pentyl$_2$$(bdc)_3$-DMOF-1.

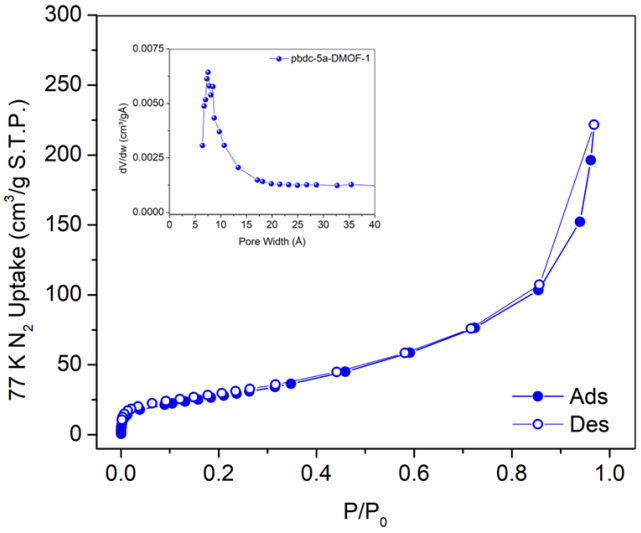


Figure S26. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for pbdc-5a-DMOF-1.

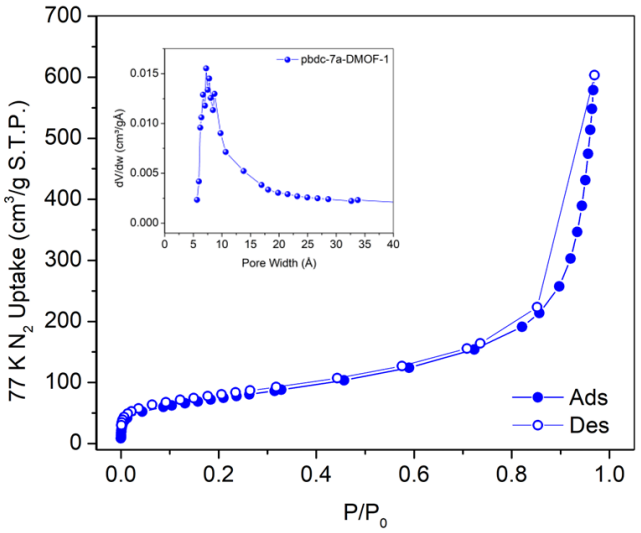


Figure S27. 77 K N_2 sorption isotherm and HK pore size distribution (inset) for pbdc-7a-DMOF-1.

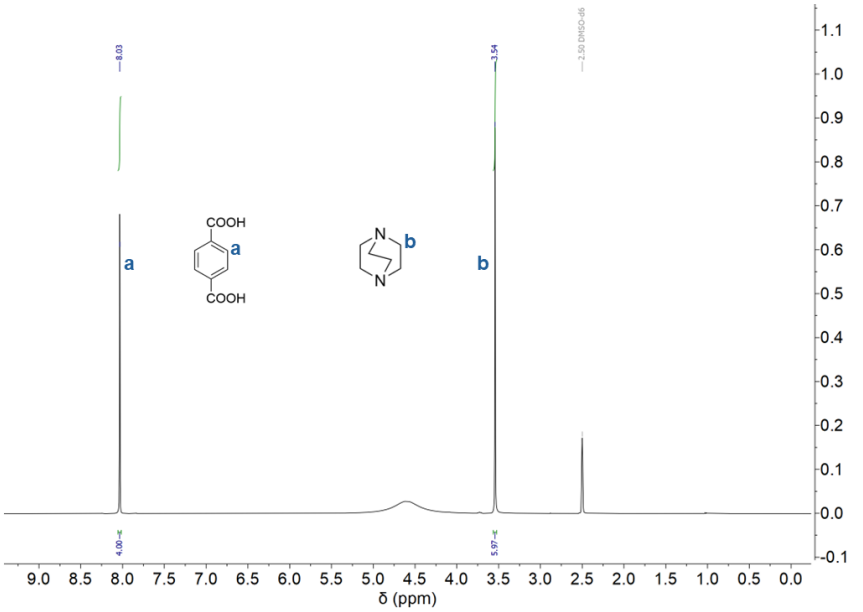


Figure S28. ^{1}H NMR spectrum of digested pcu-DMOF-1.

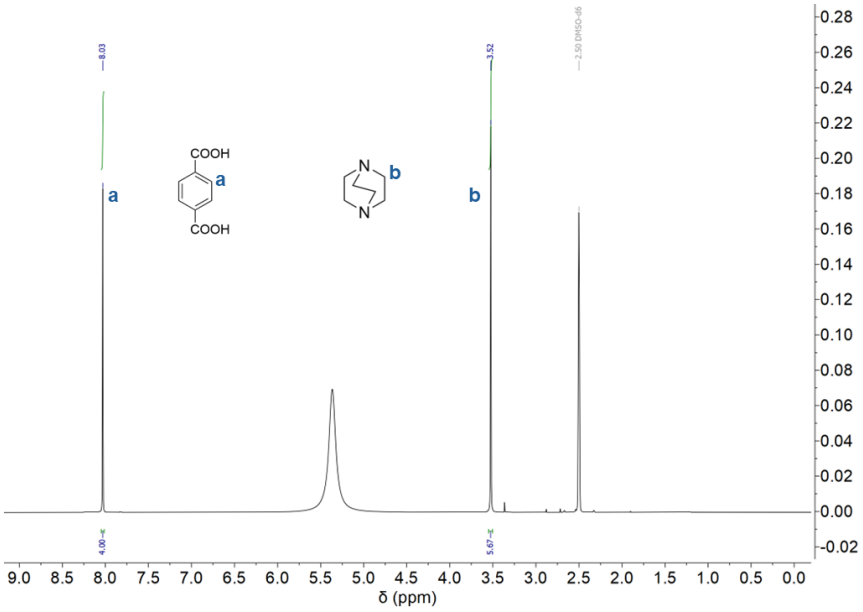


Figure S29. ^{1}H NMR spectrum of digested kag-DMOF-1.

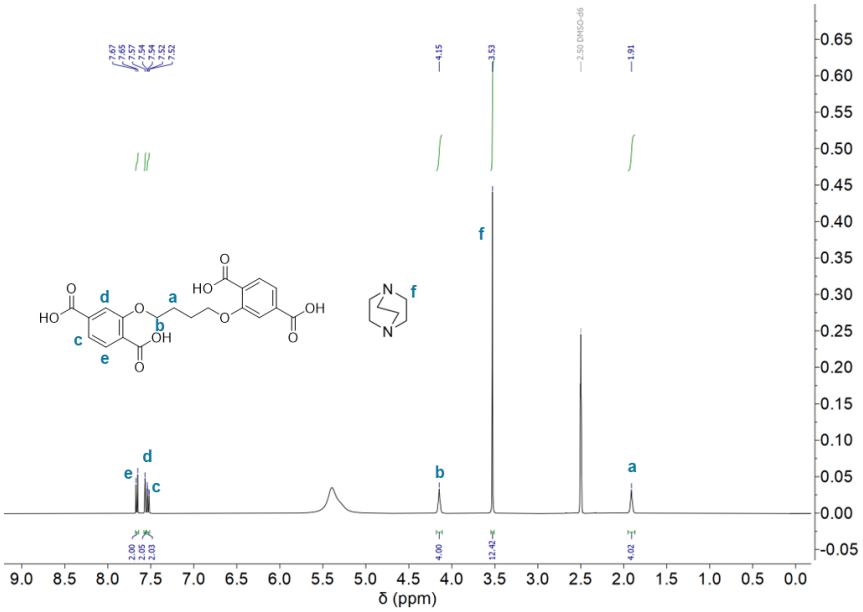


Figure S30. ^{1}H NMR spectrum of digested butyl(bdc)$_2$-DMOF-1.

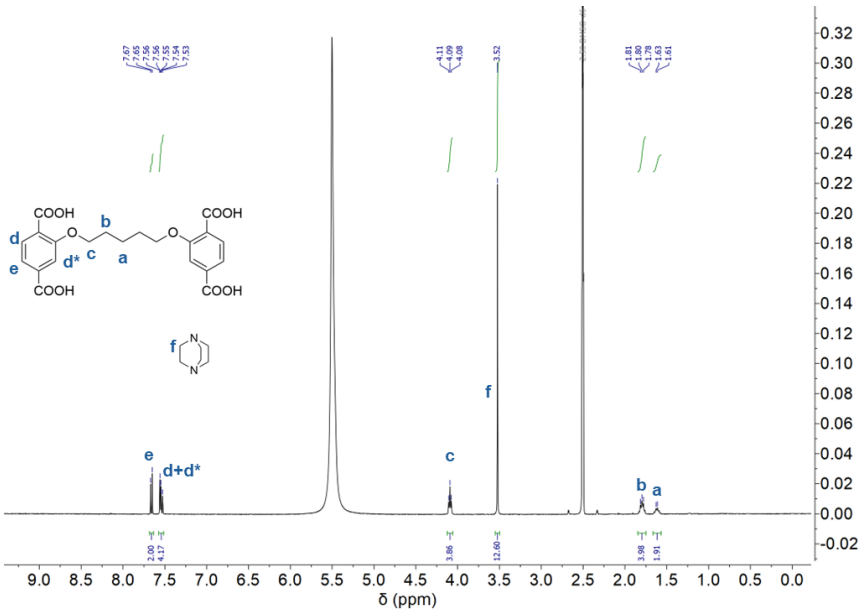


Figure S31. ^{1}H NMR spectrum of digested pentyl(bdc)$_2$-DMOF-1.

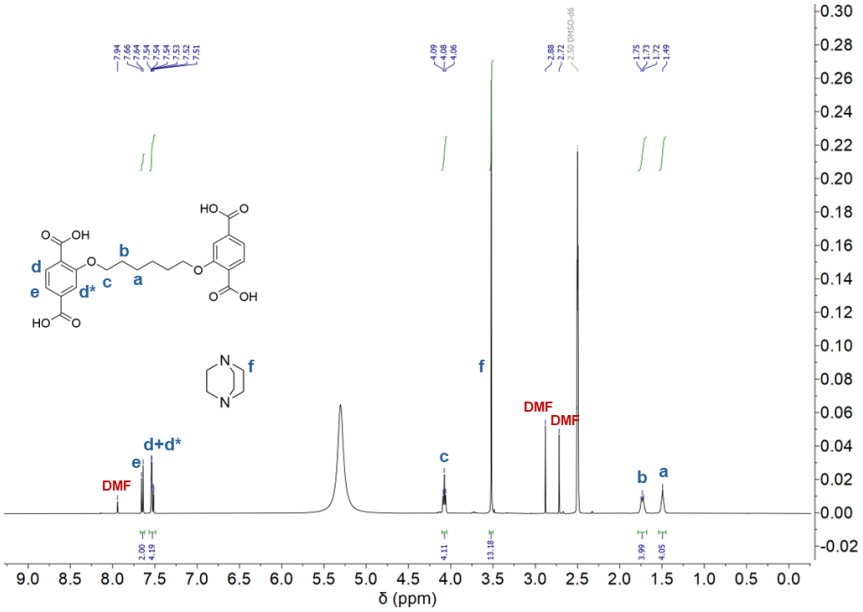


Figure S32. ^{1}H NMR spectrum of digested hexyl(bdc)$_2$-DMOF-1.

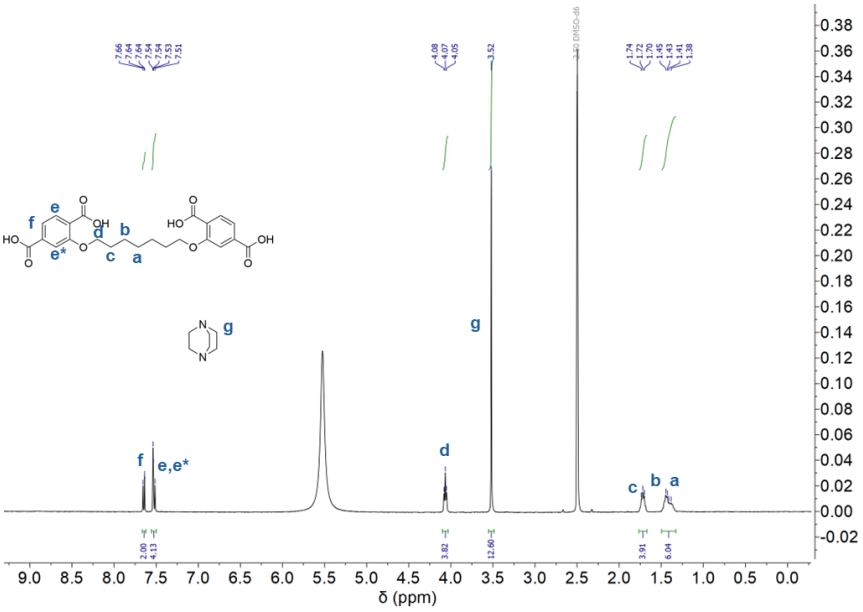


Figure S33. ^{1}H NMR spectrum of digested heptyl(bdc)$_2$-DMOF-1.

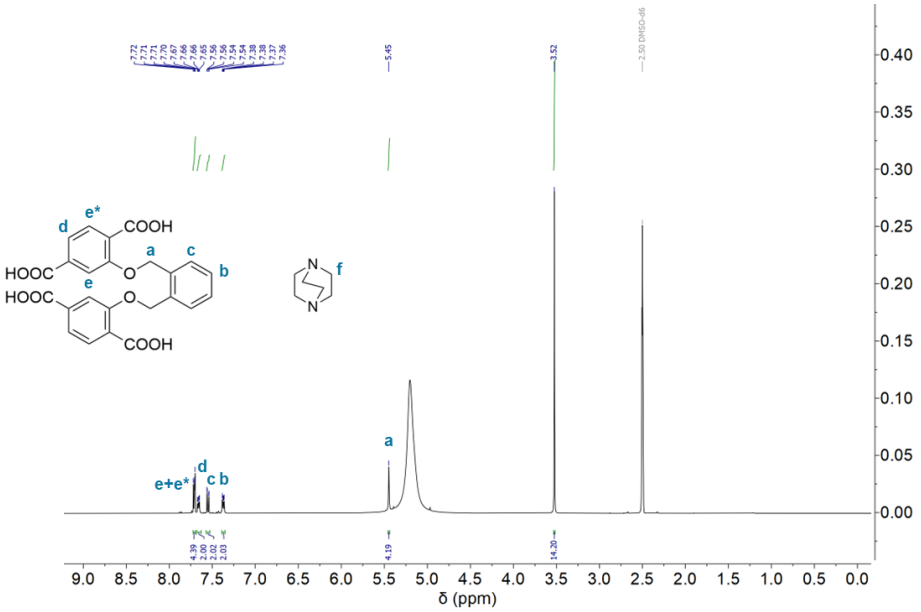


Figure S34. ^{1}H NMR spectrum of digested o-xylyl(bdc)$_2$-DMOF-1.

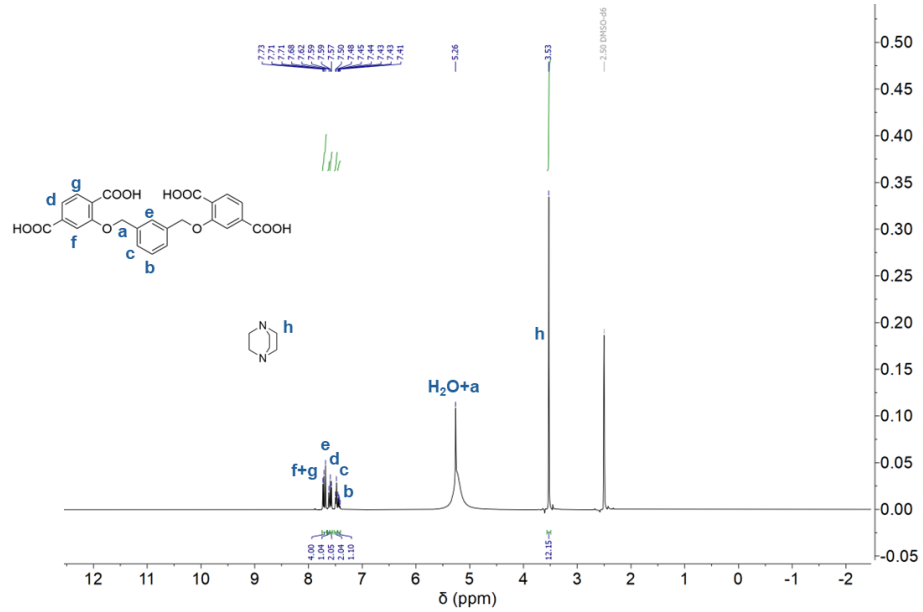


Figure S35. ^{1}H NMR spectrum of digested m-xylyl(bdc)$_2$-DMOF-1.

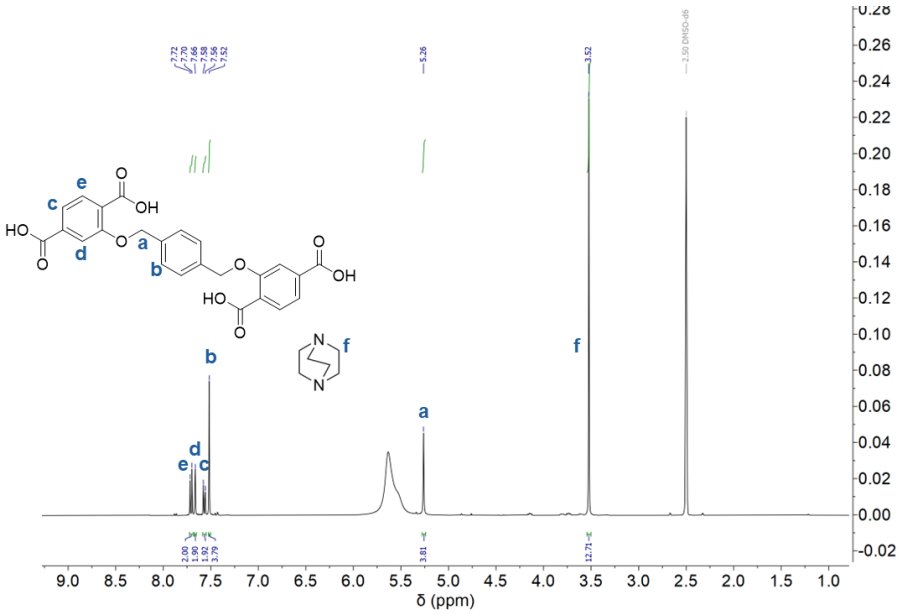


Figure S36. ^{1}H NMR spectrum of digested p-xylyl(bdc)$_2$-DMOF-1.

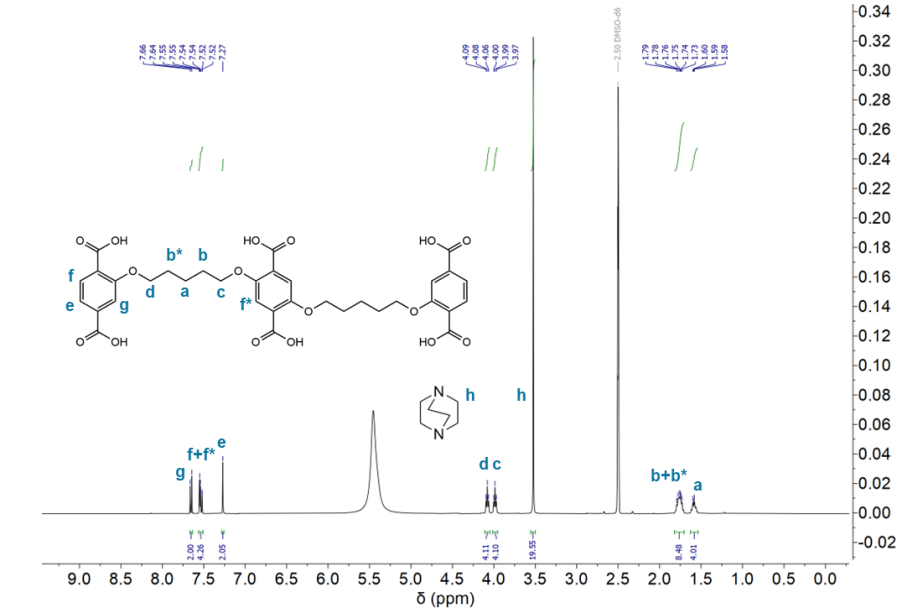


Figure S37. ^{1}H NMR spectrum of digested pentyl$_2$(bdc)$_3$-DMOF-1.

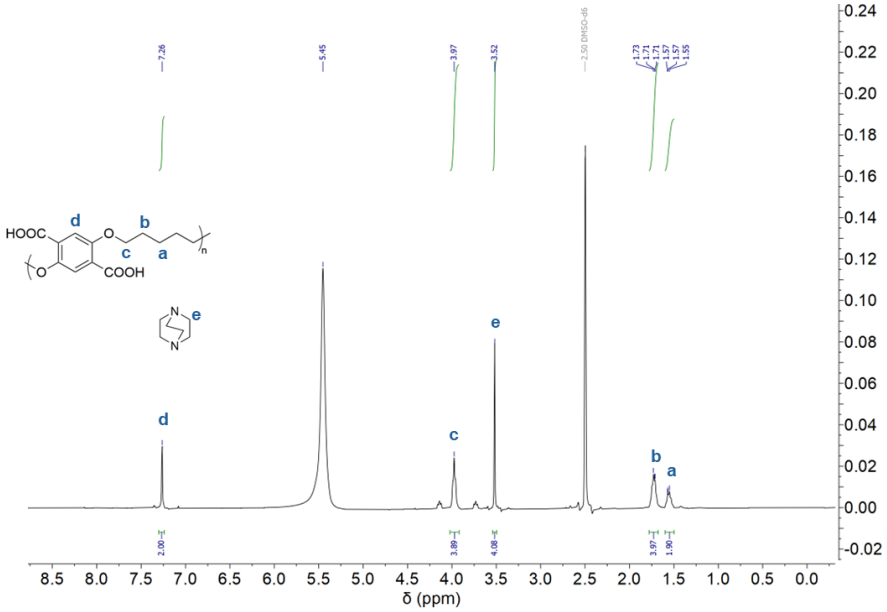


Figure S38. ^{1}H NMR spectrum of digested pbdc-5a-DMOF-1.

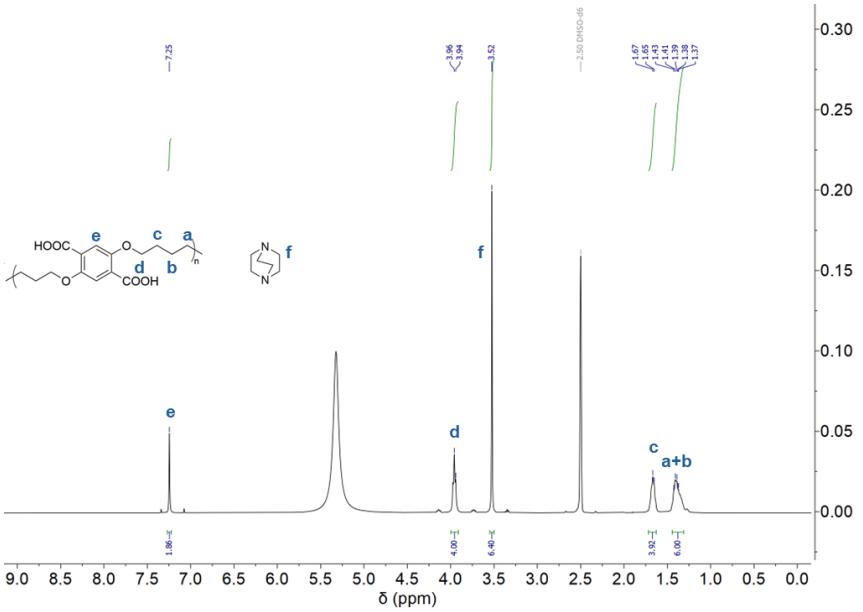


Figure S39. ^{1}H NMR spectrum of digested pbdc-7a-DMOF-1.

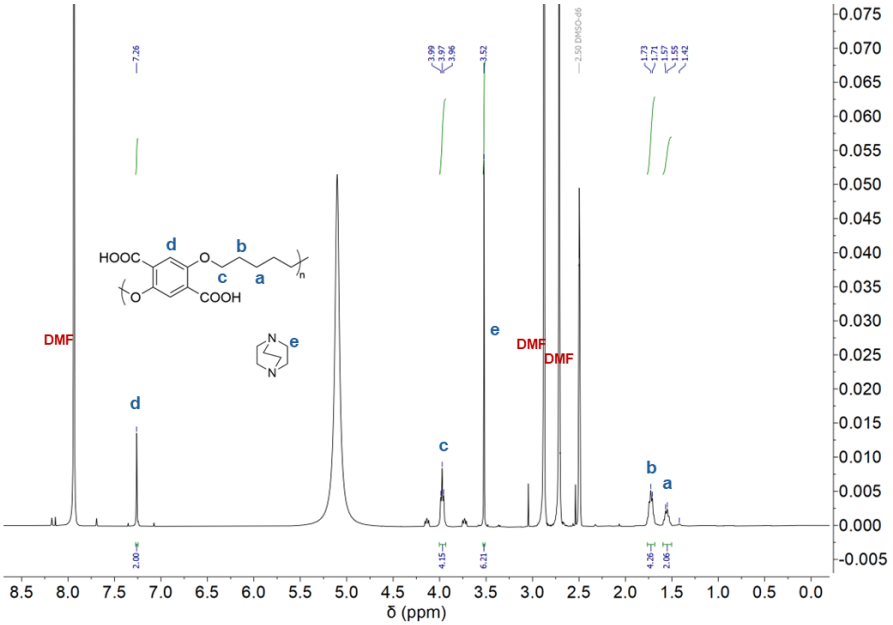


Figure S40. ^{1}H NMR spectrum of digested pbdc-5a-DMOF-1 without activation.

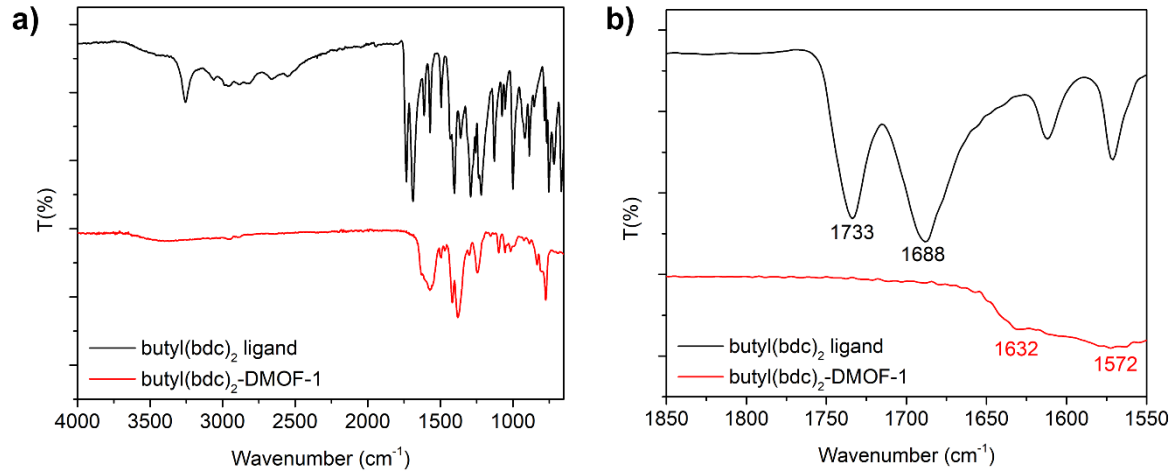


Figure S41. FTIR spectrum of activated butyl(bdc)$_2$-DMOF-1 compared to the butyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

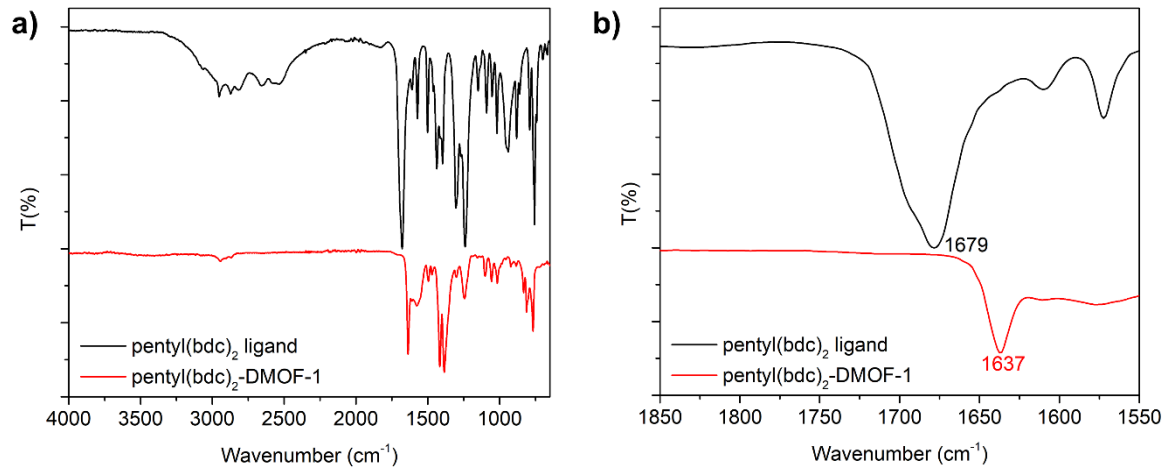


Figure S42. FTIR spectrum of activated pentyl(bdc)$_2$-DMOF-1 compared to the pentyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

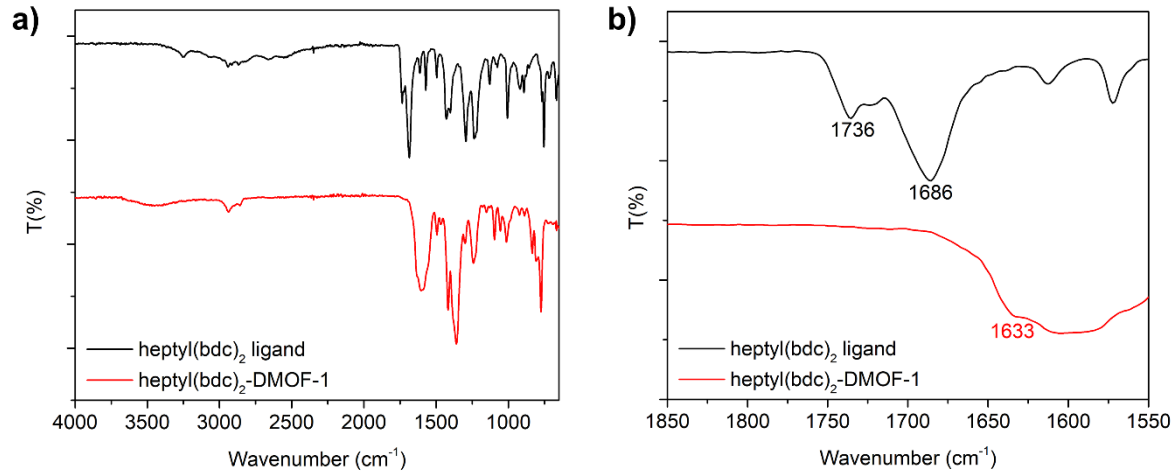


Figure S43. FTIR spectrum of activated heptyl(bdc)$_2$-DMOF-1 compared to the heptyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

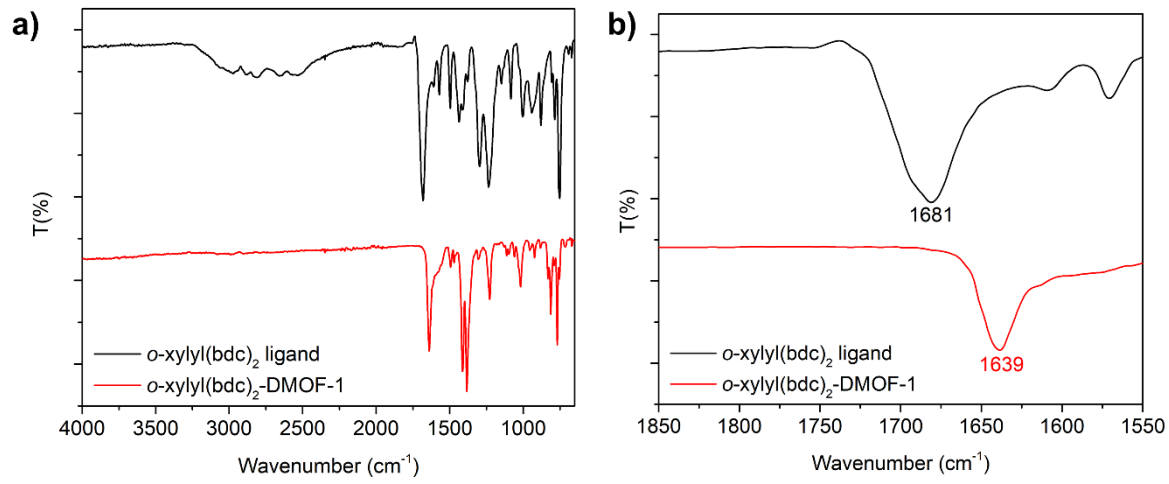


Figure S44. FTIR spectrum of activated o-xylyl(bdc)$_2$-DMOF-1 compared to the o-xylyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

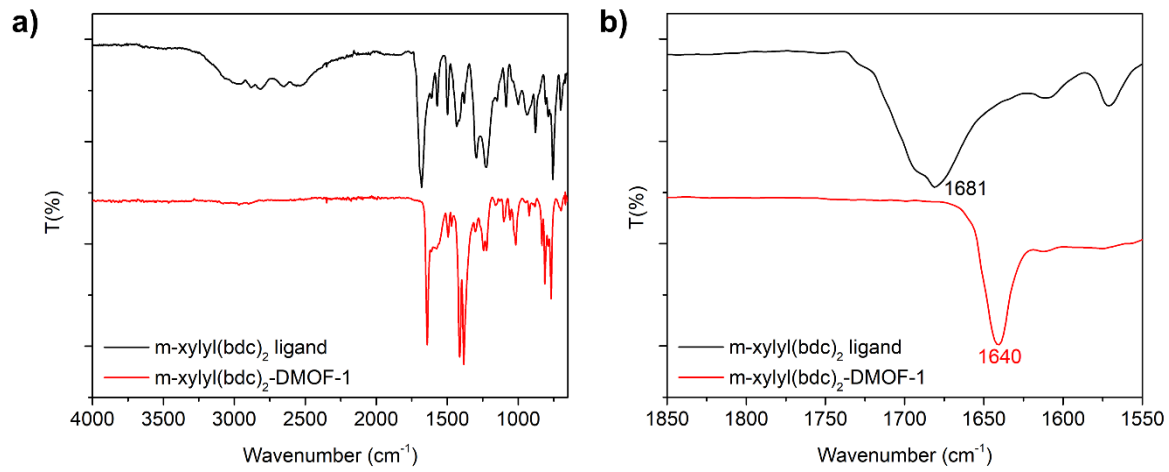


Figure S45. FTIR spectrum of activated m-xylyl(bdc)$_2$-DMOF-1 compared to the m-xylyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

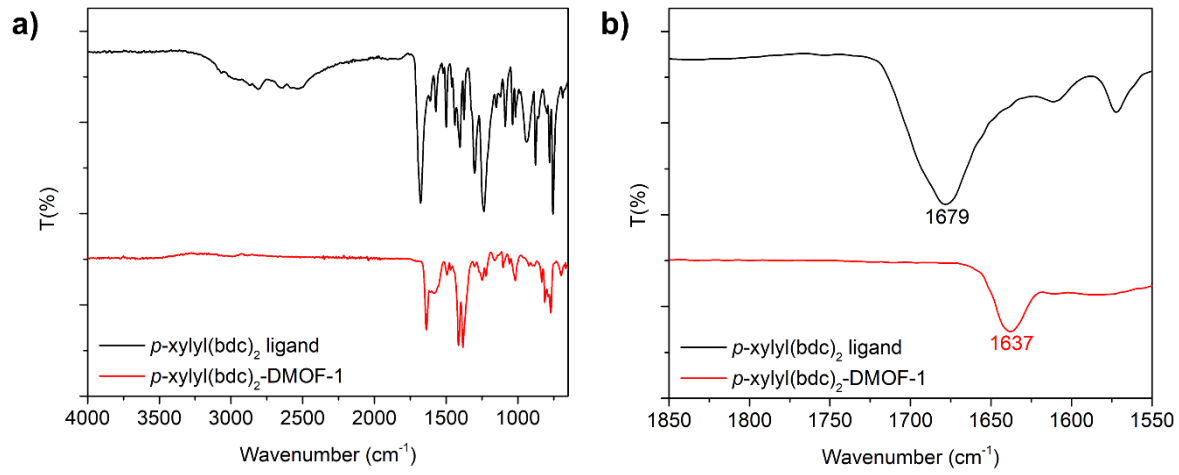


Figure S46. FTIR spectrum of activated p-xylyl(bdc)$_2$-DMOF-1 compared to the p-xylyl(bdc)$_2$ ligand; (a) full spectrum, (b) zoomed in.

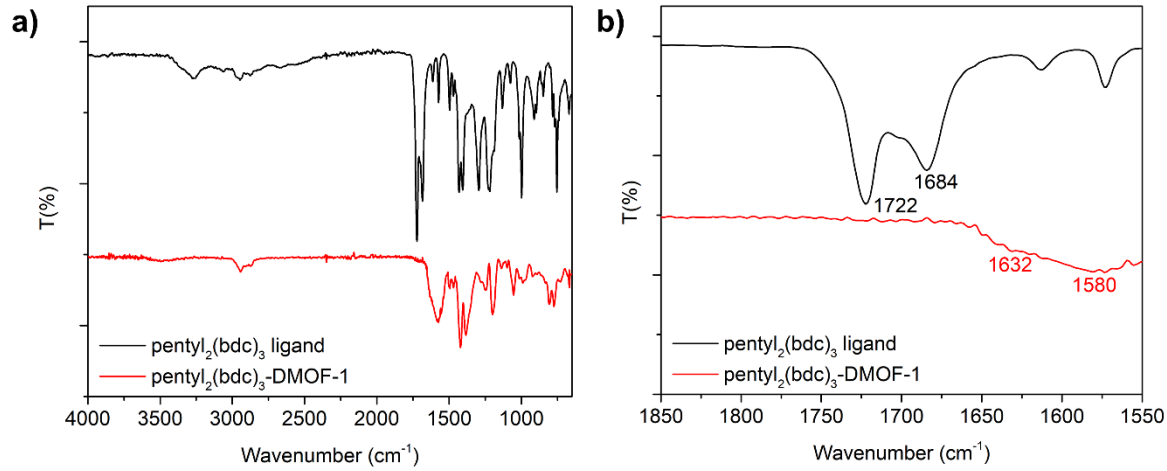


Figure S47. FTIR spectrum of activated pentyl$_2$(bdc)$_3$-DMOF-1 compared to the pentyl$_2$(bdc)$_3$ ligand; (a) full spectrum, (b) zoomed in.

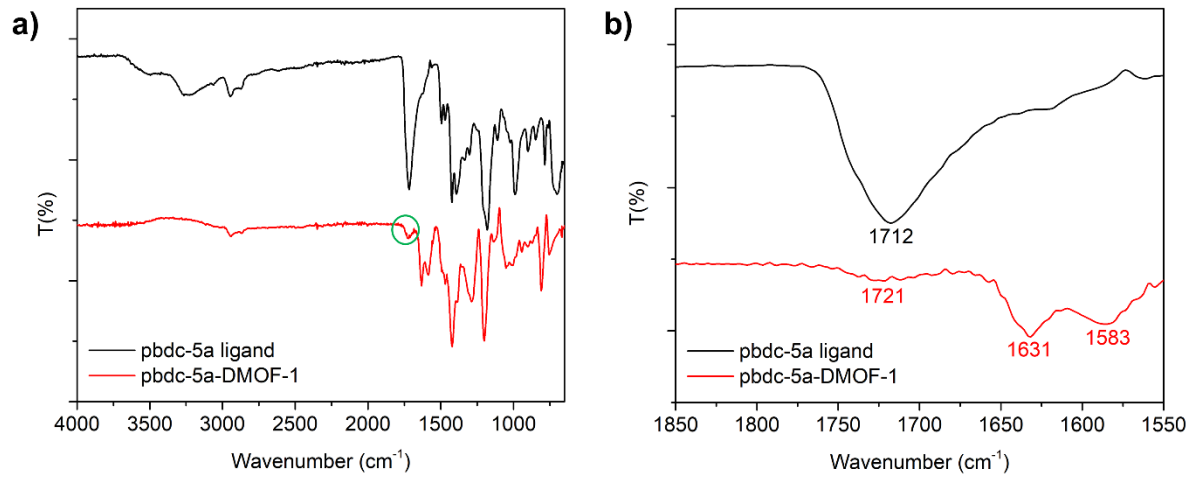


Figure S48. FTIR spectrum of activated pbdc-5a-DMOF-1 compared to the pbdc-5a ligand; (a) full spectrum, ν_sC=O shoulder highlighted in green circle, (b) zoomed in.

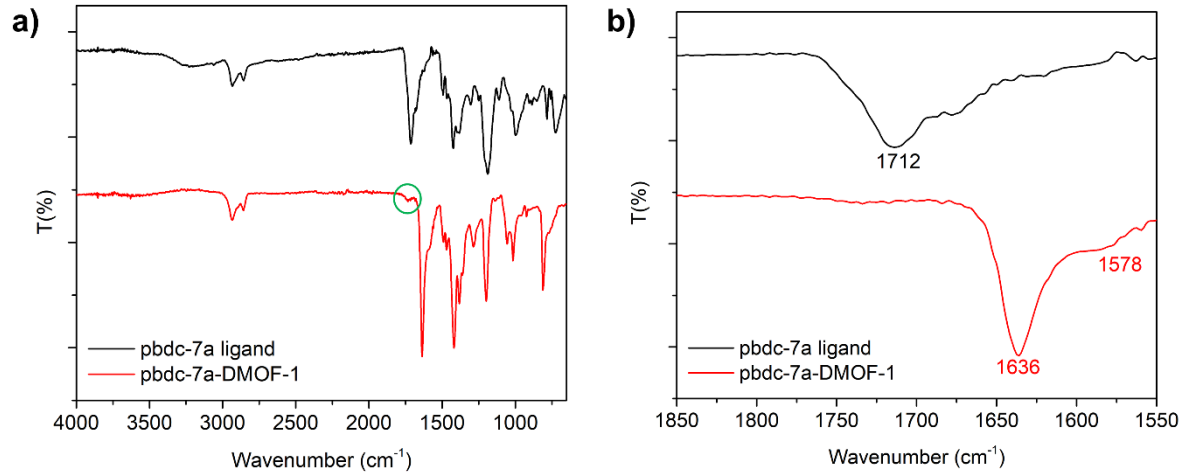


Figure S49. FTIR spectrum of activated pbdc-7a-DMOF-1 compared to the pbdc-7a ligand; (a) full spectrum, ν_sC=O shoulder highlighted in green circle, (b) zoomed in.

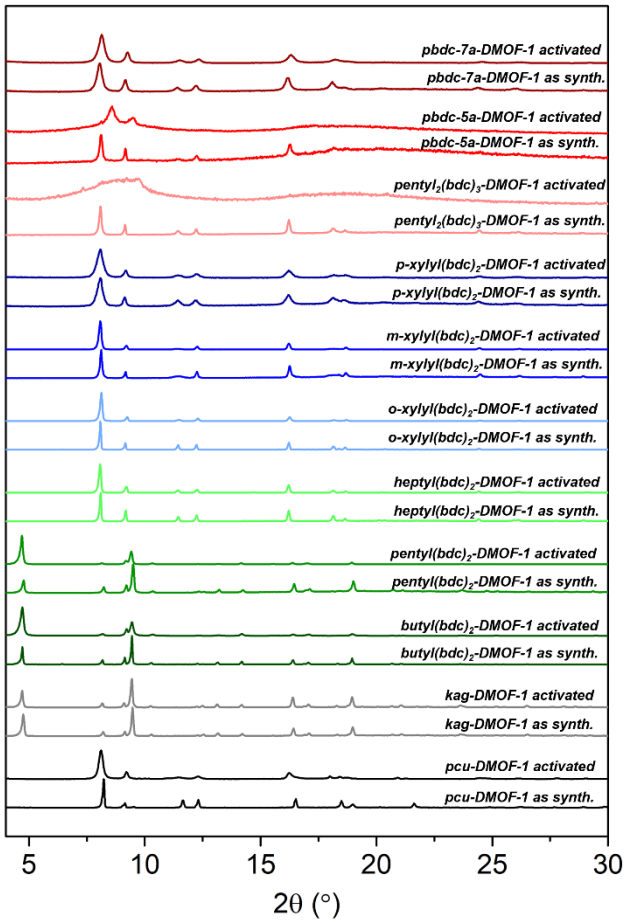


Figure S50. PXRD patterns of oligo- and poly-DMOFs as synthesised and after solvent removal by activation.

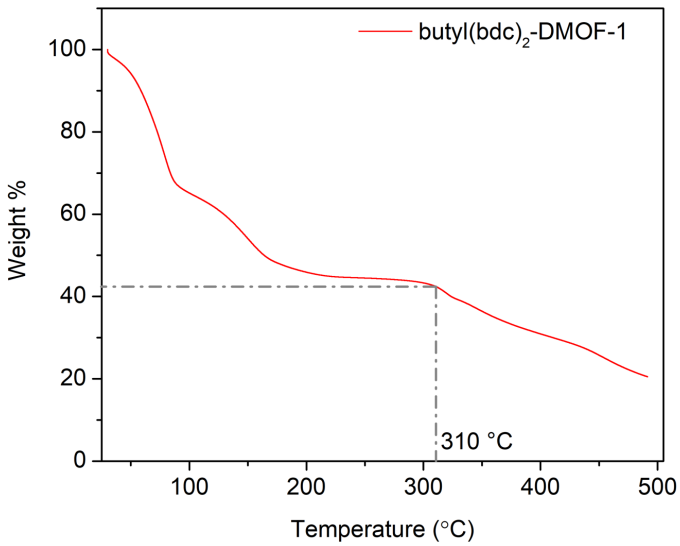


Figure S51. TGA curve of butyl(bdc)$_2$-DMOF-1.

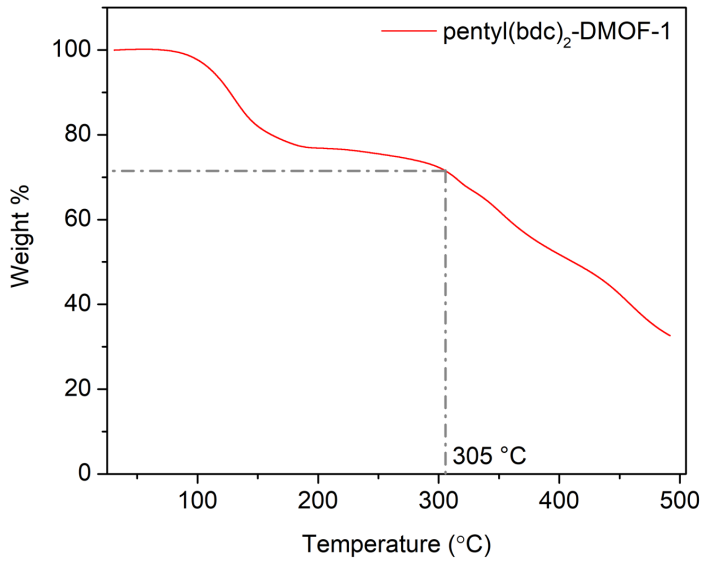


Figure S52. TGA curve of pentyl(bdc)$_2$-DMOF-1.

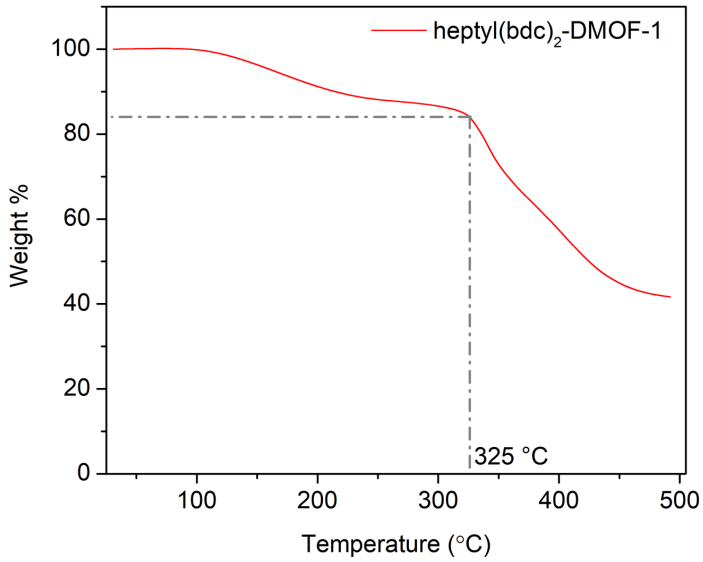


Figure S53. TGA curve of heptyl(bdc)$_2$-DMOF-1.

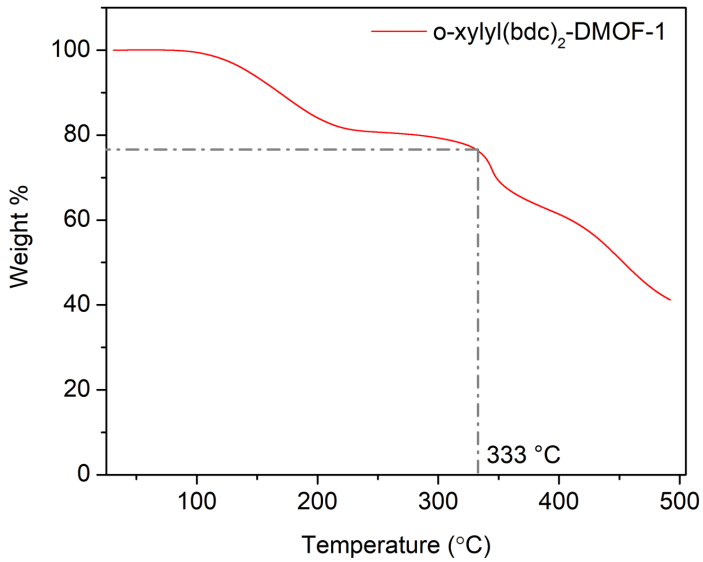


Figure S54. TGA curve of o-xylyl(bdc)$_2$-DMOF-1.

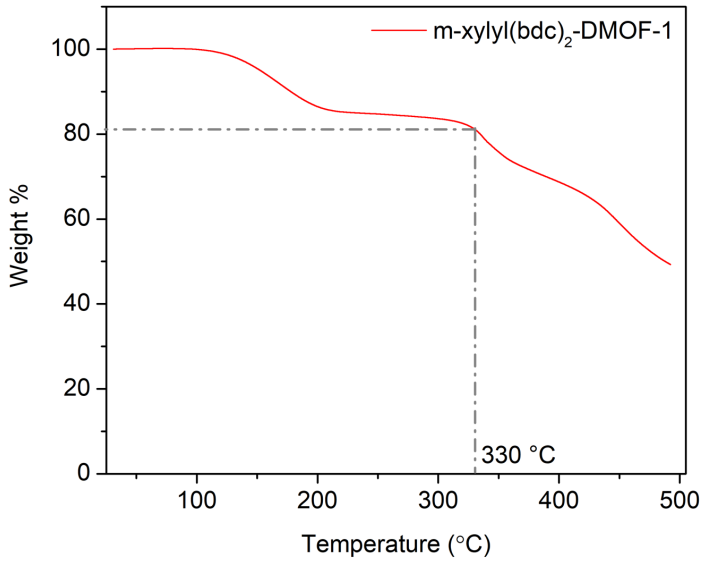


Figure S55. TGA curve of m-xylyl(bdc)$_2$-DMOF-1.

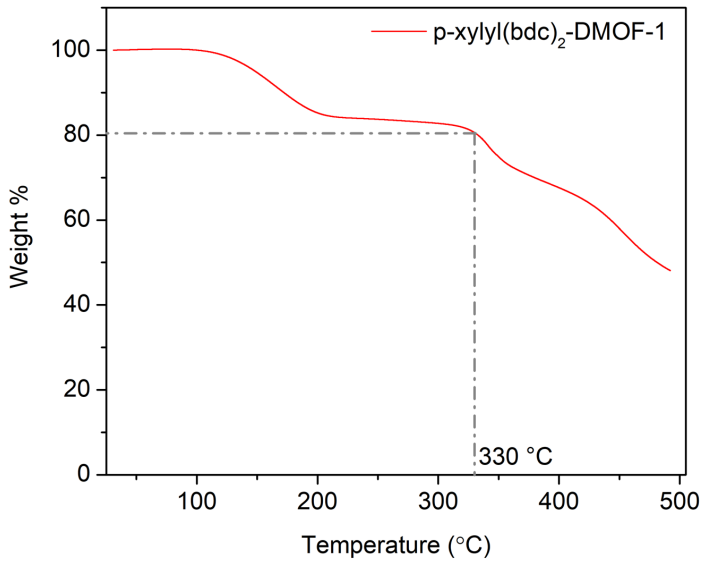


Figure S56. TGA curve of p-xylyl(bdc)$_2$-DMOF-1.

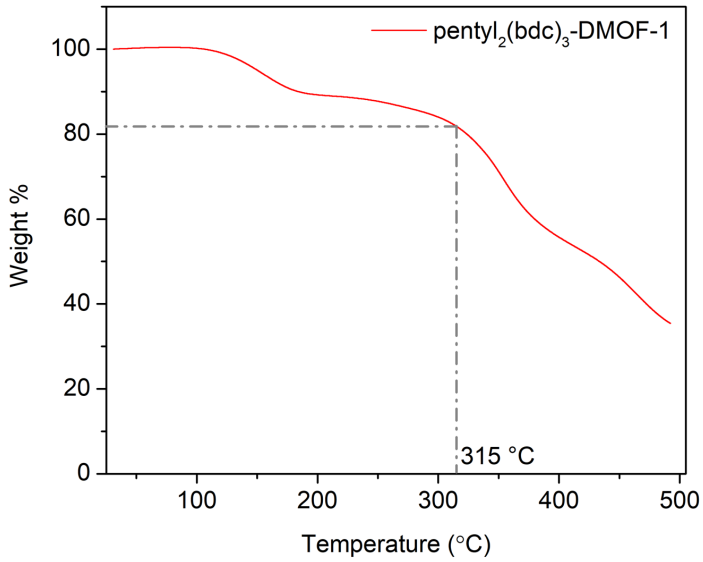


Figure S57. TGA curve of pentyl$_2$(bdc)$_3$-DMOF-1.

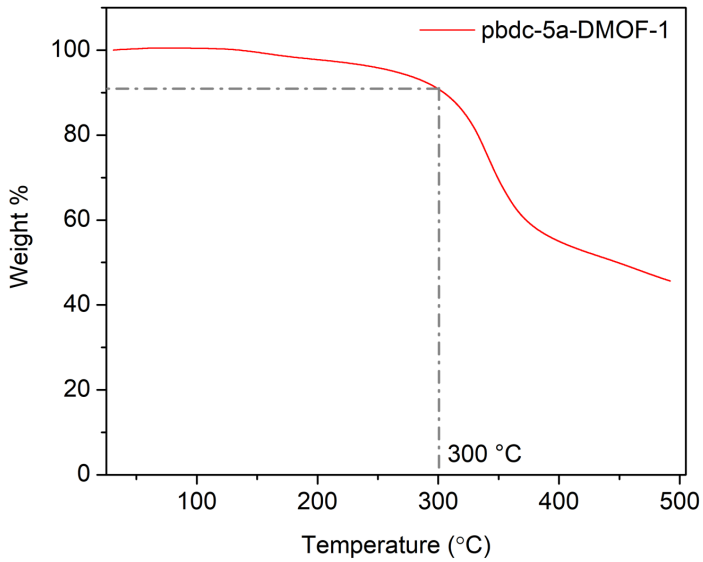


Figure S58. TGA curve of pbdc-5a-DMOF-1.

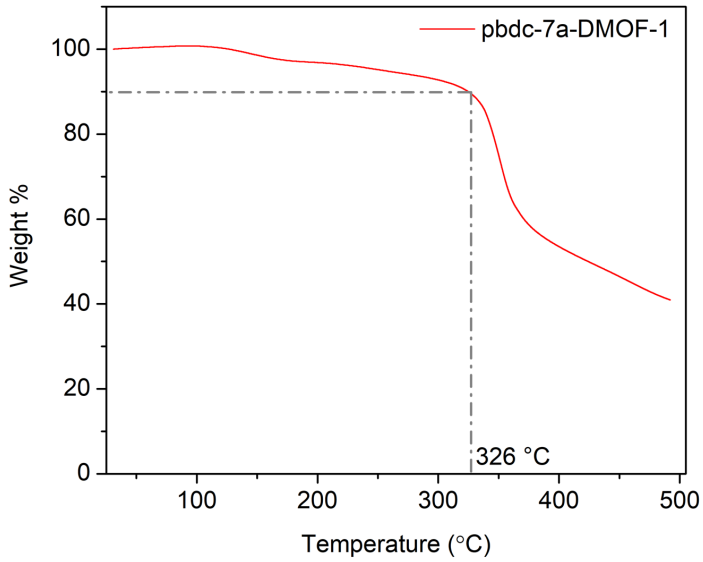


Figure S59. TGA curve of pbdc-7a-DMOF-1.

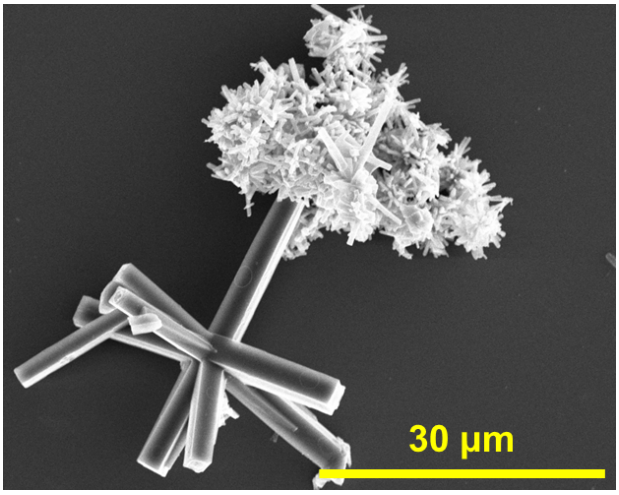


Figure S60. SEM image of pentyl$_2$(bdc)$_3$-DMOF-1.

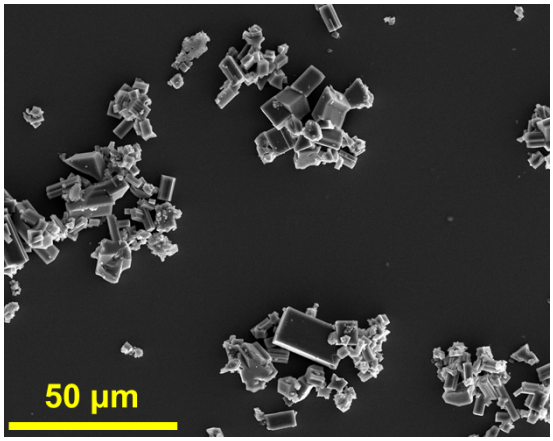


Figure S61. SEM image of m-xylyl(bdc)$_2$-DMOF-1.

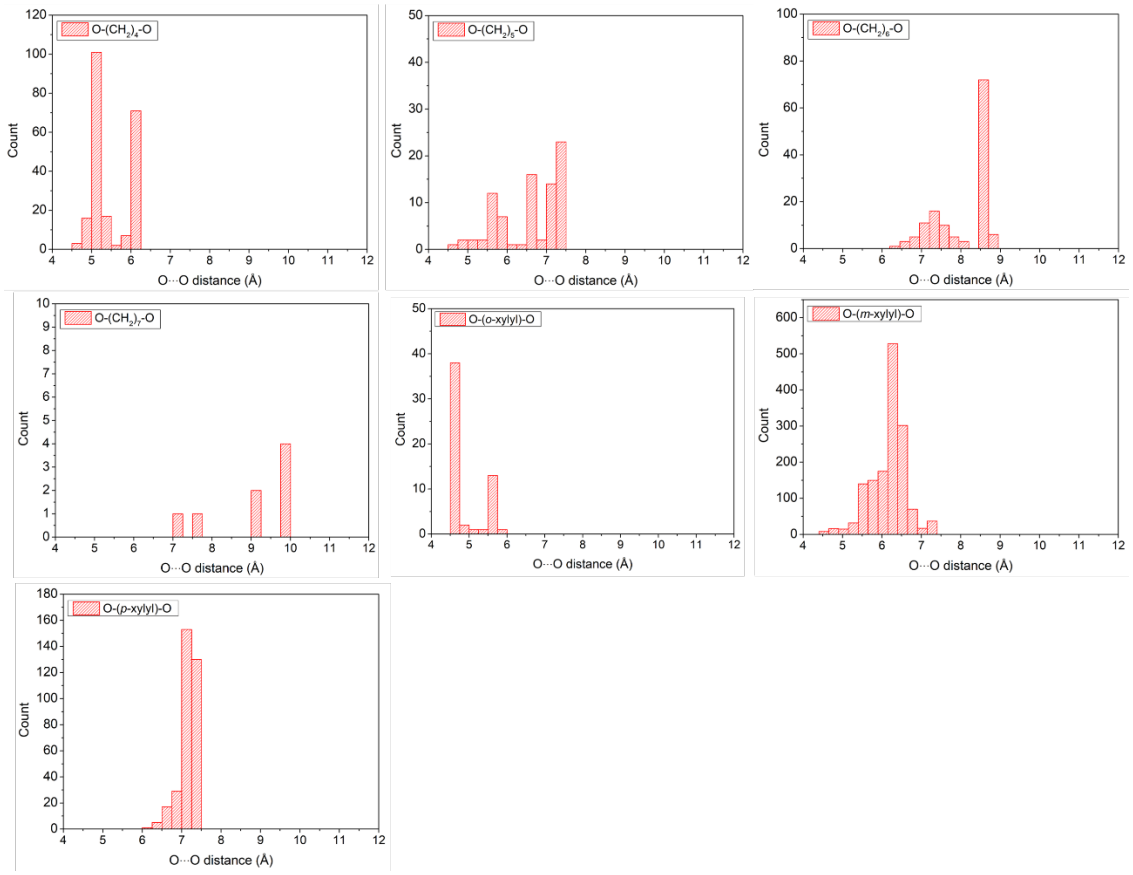


Figure S62. Histograms of O···O distances corresponding to different *n*-alkyl and xylyl spacer units in the CCDC database.