# **Supplementary Information**

# Interpenetration Isomers in Isoreticular Amine-tagged Zinc MOFs

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## 1 General experimental

All chemicals used were of analytical grade and purchased from either Sigma Aldrich, VWR Australia or Ajax Finechem Pty Ltd. Dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate was prepared as reported.<sup>1</sup>

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using a Varian Mercury VX-300-MHz NMR spectrometer operating at 300 MHz for <sup>1</sup>H and 75.5 MHz for <sup>13</sup>C or a Varian Inova NMR spectrometer operating at 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C or a Bruker Ascend spectrometer operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. <sup>1</sup>H NMR spectra were referenced to the residual *protio* peaks at  $\delta$  2.50 ppm for *d*<sub>6</sub>-DMSO and 7.26 ppm for CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra were referenced to the solvent peaks at  $\delta$  39.6 ppm for *d*<sub>6</sub>-DMSO and 77.0 ppm for CDCl<sub>3</sub>. For <sup>1</sup>H NMR analysis, MOF samples (~10 mg) were digested by adding 35% DCl in D<sub>2</sub>O (3 µL) and *d*<sub>6</sub>-DMSO (500 µL).

Simultaneous thermogravimetric and differential thermal analysis (TG-DTA) data were obtained using a Shimadzu DTG-60 instrument fitted with a FC-60A flow rate controller and TA-60WS thermal analyser. Measuring parameters of 10 °C min-1 under nitrogen flow or 20 cm<sup>3</sup>min<sup>-1</sup> were used.

Powder X-ray diffraction (PXRD) patterns were recorded on a GBC-MMA X-ray diffractometer with samples mounted on 1" SiO<sub>2</sub> substrates and recorded in the  $2\vartheta$  angle range of 3-30 with a step size of 0.02° at 1° per minute.

Freeze drying was performed using a Christ Alpha 1-2 LDplus Freeze Dryer. Super critical  $CO_2$  (ScCO<sub>2</sub>) processing was performed using a Leica EM CPD030 Critical Point Dryer. Gas adsorption studies were carried out at the Wollongong Isotope and Geochronology Laboratory using a Quantachrome Autosorb MP instrument and high purity nitrogen (99.999 %) and carbon dioxide (99.995 %) gases. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations. Geometric surface areas were calculated following the method of Duren et. al. <sup>2</sup> with a probe diameter set to 3.72 Å to match nitrogen. The diameters of framework atoms were taken from the DREIDING force field and set to their van der Waals diameters by multiplying their Lennard-Jones well-depth diameters,  $\sigma$ , by 21/6.

Elemental microanalysis was performed by the Chemical Analysis Facility at Macquarie University using a PE2400 CHNS/O Elemental Analyzer (PerkinElmer, Shelton, CT, USA) with a PerkinElmer AD-6 Ultra Micro Balance. Each MOF sample was heated at 110 °C for 2 h and analyzed immediately afterward. No heating protocol was employed for the organic samples sent for microanalysis.

### 2 Ligand synthesis

#### 2-Amino-[1, 1'-biphenyl]-4, 4'-dicarboxylic acid, H2bpdc-NH2

**Step 1:** Dimethyl-2-nitro-[1, 1'-biphenyl]-4, 4'-dicarboxylate (2.28 g, 7.23 mmol) dissolved in THF (64 mL) was added to a mixture of 10 % Pd/C catalyst (0.25 g) in chilled MeOH (33 mL). Ammonium formate (2.05 g, 33 mmol) was added portion-wise and the mixture was heated at 60 °C for 2 h. After cooling to RT, the Pd/C was removed by filtration and MeOH and THF were removed by rotary evaporation. The resulting precipitate was taken up in EtOAc (100 mLl), then washed with H<sub>2</sub>O (3 × 100 mL), brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent by rotary evaporation the crude product was purified by passing through a plug of silica gel using chloroform as eluent. Yield 1.93 g (94 %) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  3.86 (2 H, s), 3.92 (3 H, s), 3.95 (3 H, s), 7.19 (1 H, d, *J* = 7.87 Hz), 7.45 (1 H, s), 7.49 (1 H, d, *J* = 7.86 Hz), 7.56 (2 H, d, *J* = 8.18 Hz) 8.14 (2 H, d, *J* = 8.17 Hz).

**Step 2:** 1 M NaOH (2.6 mL, 2.6 mmol) was added to dimethyl-2-amino-[1,1'-biphenyl]-4,4'-dicarboxylate (0.30 g, 1.05 mmol) dissolved in a mixture of THF MeOH (1:1, 6 mL) and was stirred overnight at RT. The organic solvent mixture was removed by rotary evaporation and the residue was diluted with water followed by acidification by 1 M HCl. The resulting precipitate was collected by filtration and air dried. Yield 0.25 g (92 %). <sup>1</sup>H NMR ( $d_6$ -DMSO, 500 MHz):  $\delta$  7.14 (1 H, d, J = 7.89 Hz), 7.25 (1 H, d, J = 7.92 Hz), 7.44 (1 H, s), 7.59 (2 H, d, J = 8.1 Hz), 8.03 (2 H, d, J = 8.13 Hz), 12.74 (2 H, s). m/z (ESI): 256.00 ([M – H]<sup>-</sup>; [C<sub>14</sub>H<sub>11</sub>NO<sub>4</sub> – H]<sup>-</sup> requires 256.21).

#### 2-(Allylamino)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, H<sub>2</sub>bpdc-NH(allyl)



**Step 1:** Allyl bromide (304 μl, 3.53 mmol) was added to dimethyl-2-amino-[1, 1'-biphenyl]-4,4'dicarboxylate (1.00 g, 3.50 mmol) and powdered K<sub>2</sub>CO<sub>3</sub> (0.96 g, 6.95 mmol) in DMF (10 mL). The mixture was heated and stirred at 70 °C overnight before cooling to RT and diluting with water (100 mL). The precipitated solid was collected by filtration and washed with water. The crude product was purified on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> ( $R_f$  0.93). Yield 0.65 g (57 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.79 (2 H, d, *J* = 9.8 Hz), 3.92 (3 H, s), 3.94 (3 H, s), 4.06 (1 H, s(br)), 5.15 (1 H, ddd, *J* = 10.3, 2.8, 1.4 Hz), 5.21 (1 H, ddd, *J* = 17.2, 3.1, 1.6 Hz), 5.89 (1 H, ddt, *J* = 17.1, 10.4, 5.2 Hz), 7.14 (1 H, d, *J* = 7.8 Hz), 7.35 (1H, d, *J* = 1.5 Hz), 7.45 (1 H, dd, *J* = 7.8, 1.6 Hz), 7.52 (2 H, d, *J* = 8.04 Hz), 8.13 (2 H, d, *J* = 8.03 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ 46.23, 52.14, 52.26, 111.63, 116.43, 118.44, 129.13, 129.38, 129.48, 130.00, 130.31, 130.56, 130.74, 130.81, 134.48, 143.37, 144.65, 166.72, 167.35. <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>6</sub>-DMSO, 75 MHz): δ 45.31, 52.22, 52.38, 111.26, 115.43, 117.19, 128.76, 129.42, 129.94, 130.03, 130.19, 130.43, 135.70, 143.49, 145.26, 166.20, 166.67.

**Step 2:** 1 M NaOH (2.7 mL, 2.7 mmol) was added to dimethyl-2-allylamino-[1,1'-biphenyl]-4,4'-dicarboxylate (0.35 g, 1.1 mmol) dissolved in MeOH/THF (1:1, 6 mL) and the mixture was stirred overnight at RT. The organic solvent mixture was removed by rotary evaporation and the residue was diluted with water followed by adding 1 M HCl to precipitate the product. The yellow solid was separated by filtration, washed with water and air dried. Yield 0.310 g (97 %). Found: C, 66.86; H, 4.72; N, 4.14.  $C_{17}H_{15}NO_4 \cdot \frac{1}{2}H_2O$  requires C, 66.66; H, 5.26; N, 4.57. <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO, 500 MHz):  $\delta$  3.74 (2 H, d, *J* = 4.5 Hz), 5.10 (1 H, dd, *J* = 9.9 Hz, 1.5 Hz), 5.18 (1 H, dd, *J* = 17.4 Hz, 1.5 Hz), 5.29 (1 H, t (broad)), 5.85 (1 H, ddt, *J* = 17.4 Hz, 9.9 Hz, 4.5 Hz), 7.11 (1 H, d, *J* = 7.8 Hz), 7.18 (1 H, d, *J* = 1.2 Hz), 7.26 (1 H, dd, *J* = 7.8 Hz, 1.2 Hz), 7.55 (2 H, d, *J* = 8.4 Hz), 7.86 (1 H, d, *J* = 8.1 Hz), 8.04 (2 H, d, *J* = 8.4 Hz) 12.88 (2 H, s). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, *d*<sub>6</sub>-DMSO):  $\delta$  45.45, 111.65, 115.50, 117.59, 129.32, 129.98, 130.15, 130.21, 130.35, 131.38, 135.91, 143.32, 145.21, 167.40, 167.93. m/z (ESI): 296.05 ([M – H]<sup>-</sup>; [C<sub>17</sub>H<sub>15</sub>NO<sub>4</sub> – H]<sup>-</sup> requires 296.28).

#### 2-(Diallylamino)-[1, 1'-biphenyl]-4, 4'-dicarboxylic acid, H<sub>2</sub>bpdc-N(allyl)<sub>2</sub>



**Step 1:** Allyl bromide (265 µL, 3.0 mmol) and ground K<sub>2</sub>CO<sub>3</sub> (0.289 g, 2.1 mmol) were added to dimethyl-2amino-[1,1'-biphenyl]-4,4'-dicarboxylate (0.285 g, 1.0 mmol) dissolved in DMF (4 mL) and the mixture was heated to 80 °C for 48 h. After cooling to RT, the mixture was diluted with water (40 mL) and extracted with EtOAc (2 × 20 mL). The organic extracts were combined and washed with water (6 × 10 mL), brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtering off the drying agent, the solvent was removed by rotary evaporation to yield a yellow oil. This was taken up in hot MeOH (2 mL) and the product crystallised on standing and was collected by filtration and air dried. Yield 0.300 g (85 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  3.80 (4 H, d, *J* = 5.15 Hz), 3.92 (3 H, s), 3.95 (3 H, s), 5.12 (4 H, m), 5.85 (2 H, m), 7.13 (1 H, d, *J* = 7.8 Hz), 7.15 (1 H, d, *J* = 1.56 Hz), 7.35 (1 H, d, *J* = 1.58 Hz), 7.43 (2 H, d, *J* = 8.04 Hz), 8.12 (2 H, d, J = 8.03 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$ 46.23, 52.14, 52.26, 111.46, 116.44, 118.45, 129.13, 129.39, 129.49, 130.31, 130.57, 130.74, 130.84, 134.49, 143.37, 144.65, 166.73, 167.36.

**Step 2:** 1 M NaOH (4 mL, 4 mmol) was added to dimethyl-2-(diallylamino)-[1, 1'-biphenyl]-4,4'dicarboxylate (0.4 g, 1.1 mmol) dissolved in MeOH (10 mL) and the mixture was left to stir at RT for 7 h. The organic solvent was removed by rotary evaporation and the resulting solution was diluted with water and filtered. The clear solution was acidified to pH = 4 using 1 M HCl and the precipitated product was collected by filtration, washed with water and air dried. Yield 0.3 g (81 %). Found: C, 68.05; H, 5.27; N, 3.98.  $C_{20}H_{19}NO_4 \cdot 0.75H_2O$  requires C, 68.45; H, 5.89; N, 3.99. <sup>1</sup>H NMR ( $d_6$ -DMSO, 300 MHz):  $\delta$  3.41 (4 H, d, J = 6.07 Hz), 5.04 (4 H, m); 5.60 (2 H, m), 7.29 (1 H, d, J = 8.29 Hz), 7.61 (2 H, m), 7.67 (2 H, d, J = 8.38 Hz), 8.00 (2 H, d, J = 8.38 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_6$ -DMSO, 75 MHz):  $\delta$  54.62, 118.22, 122.27, 123.64, 128.94, 129.82, 130.89, 131.68, 134.59, 138.68, 144.91, 148.36, 167.48, 167.54. m/z (ESI) 336.10 ([M – H]<sup>-</sup>; [C<sub>20</sub>H<sub>19</sub>NO<sub>4</sub> – H]<sup>-</sup> requires 336.34).

#### 2-(Dimethylamino)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, H<sub>2</sub>bpdc-NMe<sub>2</sub>

**Step 1:** Methyl iodide (175 µl, 2.81 mmol) was added to dimethyl 2-amino-[1, 1'-biphenyl]-4,4'dicarboxylate (0.300 g, 1.05 mmol) and NaHCO<sub>3</sub> (0.176 g, 2.09 mmol) in DMF (7 mL). The reaction mixture was sealed in an Ace Glass pressure tube and heated to 90 °C with stirring for 18 hours. The reaction was cooled down to RT and diluted with water (70 mL) and the product was collected by filtration. The pure yellow product was washed with water and air dried. Yield 0.238 g (73 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.57 (6 H, s), 3.94 (3 H, s), 3.95 (3 H, s), 7.29 (1 H, d, overlap with CDCl<sub>3</sub>), 7.66 (1 H, d, overlap), 7.69 (2 H, d, overlap), 8.07 (2 H, d, *J* = 8.28 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  43.28, 52.11, 52.14, 118.76, 122.55, 128.36, 128.73, 129.76, 130.24, 131.51, 137.05, 145.83, 151.32, 166.95, 167.09.

**Step 2:** 1 M NaOH (1.9 mL, 1.9 mmol) was added to dimethyl 2-(dimethylamino)-[1, 1'-biphenyl]-4,4'dicarboxylate (0.238 g, 0.795 mmol) dissolved in THF/MeOH (1:1, 4 mL) and the mixture was stirred overnight at RT. After removing the organic solvents by rotary evaporation, the solution was diluted with water and acidified with 1 M HCl. The resulting solid was collected by filtration and washed with water. Yield 0.19 g (87%). Found: C, 66.59; H, 5.41; N, 4.87.  $C_{16}H_{15}NO_4$  ¼H<sub>2</sub>O requires C, 66.32; H, 5.39; N, 4.83. <sup>1</sup>H NMR ( $d_6$ -DMSO, 500 MHz):  $\delta$  2.50 (6 H, S, overlapped with DMSO), 7.30 (1 H, d, J = 7.82 Hz), 7.57 (1 H, d, J = 7.84 Hz), 7.61 (1 H, s), 7.67 (2 H, d, J = 8.23 Hz), 7.99 (2 H, d, J = 8.22 Hz), 12.95 (2 H, s). <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_6$ -DMSO, 125 MHz):  $\delta$  43.43, 118.73, 122.84, 128.67, 129.88, 130.7, 131.41, 132.02, 136.69, 145.50, 151.45, 167.58, 167.70. m/z (ESI) 284.00 ([M – H]<sup>-</sup>; [ $C_{16}H_{15}NO_4 – H$ ]<sup>-</sup> requires 284.27).

# 3 <sup>1</sup>H NMR spectra of ligands and digested MOFs







Figure S 2 <sup>1</sup>H NMR spectra of H<sub>2</sub>bpdc, H<sub>2</sub>bpdc-NHallyl, digested WUF-12 and H<sub>2</sub>bpdc-NH<sub>2</sub>. The N-H proton of the NHallyl group at 5.29 ppm is not seen in the acid digestions due to exchange with DCI.



Figure S 3 <sup>1</sup>H NMR spectra of H<sub>2</sub>bpdc, H<sub>2</sub>bpdc-N(allyl)<sub>2</sub>, two examples of digested WUF-13 and a spectrum of H<sub>2</sub>bpdc-NHallyl for comparison.





### 4 Electrospray ionisation mass spectrometry



Figure S 5 Negative mode ESI mass spectrum of (a) H<sub>2</sub>bpdc-NH<sub>2</sub> and (b) digested IRMOF-9-NH<sub>2</sub> (WUF-11).



Figure S 6 Negative mode ESI mass spectrum of (a) H<sub>2</sub>bpdc-NHallyl and (b) digested WUF-12 [Zn<sub>4</sub>O(bpdcNH<sub>2</sub>)<sub>0.58</sub>(bpdcNHallyl)<sub>2.42</sub>].



Figure S 7 Negative mode ESI mass spectrum of (a) H<sub>2</sub>bpdc-N(allyl)<sub>2</sub> and (b) positive mode ESI mass spectrum of digested WUF 13 [Zn<sub>4</sub>O(bpdc-NHallyl)<sub>0.54</sub>(bpdc-N(allyl)<sub>2</sub>)<sub>2.46</sub>].



## 5 Thermogravimetric-differential thermal analysis



Figure S 9 TG—DTA traces for as-synthesised (black) and activated (red) IRMOF-9-NH<sub>2</sub> (WUF-11); solid lines represent the TGA; dotted lines represent the DTA.



Figure S 10 TG—DTA traces for as-synthesised (black) and activated (red) IRMOF-9-NHallyl (WUF-12); solid lines represent the TGA; dotted lines represent the DTA.



Figure S 11 TG—DTA traces for as-synthesised (black) and activated (red) IRMOF-9-N(allyl)<sub>2</sub> (WUF-13); solid lines represent the TGA; dotted lines represent the DTA.



Figure S 12 TG—DTA traces for as-synthesised (black) and activated (red) IRMOF-9-NMe<sub>2</sub> (WUF-14); solid lines represent the TGA; dotted lines represent the DTA.

## 6 Single crystal X-ray diffraction

#### Table S 1 Crystal data and structure refinement for WUF-11-14.

Identification code	WUF-11 (CCDC 1944583)	WUF-12 (CCDC 1944584)	WUF-13 (CCDC 1944585)	WUF14 (CCDC 1944586)
Empirical formula	C <sub>42</sub> H <sub>27</sub> N <sub>3</sub> O <sub>13</sub> Zn <sub>4</sub>	$C_{51}H_{39}N_3O_{13}Zn_4$	C <sub>60</sub> H <sub>47</sub> N <sub>4</sub> O <sub>13</sub> Zn <sub>4</sub>	C46.5H39.5N3O15.5Zn4
Formula weight	1043.14	1163.33	1279.48	1149.77
Temperature/K	292.15	292.0	292.15	292.15
Crystal system	tetragonal	tetragonal	tetragonal	trigonal
Space group	<u>P</u> -421m	P-421m	P-421m	R-3 <i>m</i>
a/Å	17.2045(5)	17.237(2)	17.2000(12)	24.106(3)
b/Å	17.2045(5)	17.237(2)	17.2000(12)	24.106(3)
c/Å	17.1507(12)	17.1207(17)	17.2000(12)	30.383(3)
a/°	90	90	90	90
$\beta^{\circ}$	90	90	90	90
$\gamma/^{\circ}$	90	90	90	120
Volume/Å <sup>3</sup>	5076.5(5)	5086.5(14)	5088.4(8)	15290(3)
Ζ	2	2	2	6
$\rho_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	0.682	0.760	0.835	0.749
$\mu/\text{mm}^{-1}$	1.317	1.346	1.378	1.358
F(000)	1048.0	1180.0	1304.0	3501.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.15	0.25 × 0.15 × 0.08	0.02 × 0.15 × 0.20	0.3 × 0.2 × 0.2
Radiation (/Å)	Cu Kα (λ = 1.54187)	Cu Kα (λ = 1.54178)	Cu Kα (λ = 1.54178)	CuKα (λ = 1.54178)
$2\Theta$ range for data collection/°	14.562 to 143.938	14.534 to 124.762	11.504 to 102.08	14.422 to 100.822
Index ranges	$-15 \le h \le 20, -20 \le k \le 21, -20 \le l$	$-16 \le h \le 19, -19 \le k \le 12, -17 \le l$	$-9 \le h \le 8, -17 \le k \le 11, -16 \le l \le$	-19 ≤ h ≤ 22, -23 ≤ k ≤ 24, -30 ≤ l
	≤ 20	≤ 19	17	≤ 30
Reflections collected	25622	21815	8985	24808
Independent reflections	4898 [R <sub>int</sub> = 0.0409, R <sub>sigma</sub> =	4077 [R <sub>int</sub> = 0.0371, R <sub>sigma</sub> =	2768 [R <sub>int</sub> = 0.0630, R <sub>sigma</sub> =	1942 [R <sub>int</sub> = 0.1332, R <sub>sigma</sub> =
	0.0313]	0.0392]	0.0699]	0.0833]
Data/restraints/parameters	4898/117/146	4077/158/147	2768/291/148	1942/84/126
Goodness-of-fit on $F^2$	1.123	1.447	1.452	1.438
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0937, wR_2 = 0.2793$	$R_1 = 0.1181, wR_2 = 0.3268$	$R_1 = 0.1370, wR_2 = 0.3486$	R <sub>1</sub> = 0.1289, wR <sub>2</sub> = 0.3677
Final R indexes [all data]	$R_1 = 0.1084, wR_2 = 0.2962$	$R_1 = 0.1483, wR_2 = 0.3790$	$R_1 = 0.1737, wR_2 = 0.3916$	R <sub>1</sub> = 0.1721, wR <sub>2</sub> = 0.3934
Largest diff. peak/hole / e Å <sup>-3</sup>	0.68/-0.55	0.76/-0.97	0.78/-0.67	1.11/-1.48
Flack parameter	0.5ª	0.3(2) <sup>b</sup>	0.43(2) <sup>c</sup>	

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<sup>a</sup> Refined as inversion twin.

- <sup>b</sup> Refined as inversion twin with scales 0.7(2), 0.3(2).
- <sup>c</sup> Refined as 3 component twin: Twin law (010/001/100); scales 0.748(11), 0.142(8) and 0.110.
- <sup>d</sup> The quasi-cubic unit cell on rhombohedral axes has a = 17.212 Å and  $\alpha = 88.9^{\circ}$ .

#### Notes on the structures and refinements

The structures presented here contain large voids that are filled by solvent. In each of the refinements, solvent molecules residing in these voids were not located and this is typical of MOF structures containing such voids. The electron density contribution from the solvent is not accounted for in the refinements. This can be addressed by the use of routines such as SQUEEZE<sup>3</sup> or calcsolv in Olex<sup>2[4]</sup> to provide a measure of the unaccounted electron density and give improvements in the refinement statistics. Here we have used TGA to estimate solvent content and present the crystallographic results without modification. All structures have been determined on solvated non-activated material, which has substantial solvent content.

### IRMOF-9-NH2 WUF 11 Zn4O(bpdcNH2)3

The data for **WUF-11** was collected at 293 K using CuK $\alpha$  ( $\lambda = 1.54184$  Å) radiation and the structure was solved and refined in the space group *P*-42<sub>1</sub>*m*. The asymmetric unit of **WUF-11** is shown in Fig. S13 and consists of two Zn atoms each laying across orthogonal mirror planes and which are bridged by a half ligand (O2, O3, C1-C6) at full occupancy. The phenyl ring C2-C7 was fitted as a hexagon and allowed to rotate in the refinement. The quaternary carbons of the second half-linker (C10, C11, C14, C15, C18 and C19) and the  $\mu$ -oxido atom (O1) rest at the confluence of the orthogonal mirror planes in the space group. The remaining linker carbon atoms (C12, C13, C16, C17) lie on orthogonal mirror planes. The nitrogen atoms of the pendant amino tag groups were not located in the Fourier synthesis. The large ellipsoids of the carbons to which the nitrogen atoms are attached indicate significant thermal motion that would result in smearing out the electron density of these atoms. These atoms were fixed in the structure to enable surface area calculations together with their hydrogen atoms subject to chemically sensible bond lengths and positions and occupancy factors but were not included in the refinement. Consequently, the amino groups N16 N6 are disordered. Phenyl rings of the linker were refined subject to similarity restraints and hydrogens attached CH, and NH<sub>2</sub> were placed in calculated positions.



Figure S 13 An ORTEP plot, with ellipsoids shown at the 50% probability level, of the asymmetric unit of IRMOF-9-NH<sub>2</sub> (WUF-11) [Zn<sub>4</sub>O(bpdc-NH<sub>2</sub>)<sub>3</sub>]. Hydrogen atoms are shown but not labelled, for clarity.

#### **IRMOF-9-NHallyl WUF-12**

The data for WUF-12 was collected at 293 K using CuK $\alpha$  ( $\lambda = 1.54184$  Å) radiation and the structure was solved and refined in the space group P-421m with very similar unit cell parameters as for WUF-11. The asymmetric unit of WUF-12 is shown in Fig. S14 and consists of the same arrangement of two half Zn atoms, two half linkers and an oxo-atom at the core of the SBU, so the structural description of these features is the same as for WUF-11. In the same way as before, the tag groups were placed into the structure to enable calculation of surface area and their positions and occupancies and isotropic parameters were fixed and not included in the refinement. This was done for full NHallyl (NHCH<sub>2</sub>CH=CH<sub>2</sub>) arms attached to the independent half linkers. The data quality was not as high as for WUF-11 and several restraints were applied in order to build a decent model for refinement. The phenyl ring C2-C7 was fitted as a hexagon and allowed to rotate in the refinement. A similarity restraint was applied to the phenyl ring C25-C29. Carbons 28 and 29 were not well behaved and a distance restraint was also applied Aromatic CH's were placed in calculated positions with riding coordinates and fixed isotropic parameters at 1.2 times their parent atoms. Overall the structural analysis confirms the framework and the mode of interpenetration. Notwithstanding microanalytical, NMR and mass-spectrometric data indicating about 19% of bpdcNH<sub>2</sub>, the model was not further complicated by incorporating this species.



Figure S 14 An ORTEP plot, with ellipsoids shown at the 50% probability level, of the asymmetric unit of IRMOF-9-NHallyl (WUF-12). Hydrogen atoms are shown but not labelled, for clarity.

#### IRMOF-9-N(allyl)<sub>2</sub> WUF-13

The data for **WUF-13** was collected at 293 K using CuK $\alpha$  ( $\lambda = 1.54184$  Å) radiation and the structure was solved and refined in the space group *P*-42<sub>1</sub>*m*. The unit cell parameters show metric cubic parameters but tetragonal symmetry. The data were refined as a 3-component twin (twin law: (010/001/100) with scales 0.748(11), 0.142(8) and 0.110.

The asymmetric unit of **WUF-13** is shown in Fig. S15 and consists of two half Zn atoms, two half linkers and an oxido-atom at the core of the SBU, as seen for WUF-11 and WUF-12. The diallyl tag groups were placed into the structure on independent half-linkers to enable calculation of surface area. Their positions, occupancies and isotropic parameters were fixed and not included in the refinement. The data quality meant a host of restraints were needed for a stable model for refinement. The aromatic ring based on C4-C9 was fitted as a regular hexagon and refined as free rotating group. The attached tag group was assigned half occupancy. The aromatic rings based on C12-C15 and C16-C19 were refined with 1-2 distance (1.38 Å with sigma of 0.02 Å) and 1-3 distance restraints (2.40 Å with sigma of 0.02 Å) and for coplanarity. Hydrogens attached to aromatic rings were refined with riding coordinates with fixed  $U_{\rm iso}$  1.2 times that of their carrier atoms. The tag group attached to C14 was placed in Part -1 and atoms that have alternative positions assigned appropriate occupancies. The distances from the aromatic ring to the carboxyl carbons were restrained (C12-C11, C20-C19, 1.50 Å with sigma of 0.02 Å). SIMU and DELU and restraints to approximate to isotropic behaviour were applied to all carbon and oxygen atoms. Notwithstanding microanalytical and mass-spectrometric data indicating about 18% of bpdcNHallyl, the model was not further complicated by incorporating this species.



Figure S 15 An ORTEP plot, with ellipsoids shown at the 50% probability level, of the asymmetric unit of IRMOF-9-N(allyl)<sub>2</sub> (WUF-13). Hydrogen atoms are shown but not labelled, for clarity.

### IRMOF-9-NMe<sub>2</sub> WUF-14 Zn<sub>4</sub>O(bpdcNMe<sub>2</sub>)<sub>3</sub>

The data for **WUF-14** was collected at 293 K using CuK $\alpha$  ( $\lambda = 1.54184$  Å) radiation and the structure was solved and refined in the space group *R*-3*m*. The asymmetric unit of **WUF-14** is shown in Fig S16. The defining symmetry element is a mirror plane that bisects O1W Zn1 O4 Zn2 O1 O2 C1 C2 C4 C8 C11 C12 C21 and O3W. This means phenyl ring connected to C2 and C5 (C3 C4 C6 and C7) lies across this plane and is disordered together with its dimethylamino group (each position having half occupancy). This phenyl ring was modelled as a regular hexagon. O1W Zn1and O4 lie on 3-fold rotational and rotoinversion axes and this generates the Zn<sub>4</sub>O SBU in the structure. O3W also lies on another of these axes. The coordination of O1W gives Zn1 a coordination number of 5 and trigonal bipyramidal geometry (Fig S17 a, b). The nitrogen atom of the pendant dimethylamino tag groups was located in the Fourier synthesis, however, the attached methyl groups were not. The dimethylamino group was subject to restraints for chemically sensible bond lengths and positions to enable surface area calculations but were not included in the refinement. The dimethylamino group hydrogens were fixed in the structure.



Figure S 16 An ORTEP plot, with ellipsoids shown at the 50% probability level, of the asymmetric unit of IRMOF-9-NMe<sub>2</sub> (WUF-14). Hydrogen atoms are shown but not labelled, for clarity.



**Figure S 17** Views of the SBU in IRMOF-9-NMe<sub>2</sub> (**WUF-14**) showing the 5-coordinate nature of Zn1. (a) Ball and stick and (b) with Zn SBU atoms as polyhedra. Selected atoms are labelled.

### 7 IRMOF-9 Structures

Table S 2 Crystallographic data with ligand structures and classifications for IRMOF-9 and functionalised analogues.

	MOF code	CCDC	Space group	Cell (/Å, /º)	Temp. (/K)	Starting Ligand Structure	Туре	Reference
1	IRMOF-9	175580	Pnnm	a = 17.1469(8) b = 23.3222(10) c = 25.2552(12) $\alpha = \beta = \gamma = 90$	153(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	II	M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, <i>Science</i> , 2002, <b>295</b> , 469-472.
2		691966	C2/m	a = 22.7990(19) b = 25.218(3) c = 17.1200(17) $\beta = 98.207(4)$	150(2)		111	A. D. Burrows, C. Frost, M. F. Mahon and C. Richardson, <i>Angew.</i> <i>Chem. Int. Ed.</i> , 2008, <b>47</b> , 8482- 8486.
3	MUF-6	826055	P-42₁m	a = b = 17.2215(4) c = 17.1168(12) $\alpha = \beta = \gamma = 90$	292(2)	HO <sub>2</sub> C - CO <sub>2</sub> H	II	R. K. Deshpande, G. I. N. Waterhouse, G. B. Jameson and S. G. Telfer, <i>Chem. Commun.</i> , 2012, <b>48</b> , 1574-1576.
4		725565	C2/m	a = 25.0111(9) b = 22.9843(9) c = 17.1959(3) $\beta = 96.404(4)$	170(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, <i>Chem.</i> <i>Commun.</i> , 2009, 4218-4220.
5		725566	R-3m	a = b = 23.8212(3) c = 30.2938(11) $\alpha = \beta = 90, \gamma = 120$	170(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, <i>Chem.</i> <i>Commun.</i> , 2009, 4218-4220.
6		725567	C2/m	a = 25.1670(4) b = 23.2000(3) c = 17.1020(3) $\beta = 93.561(1)$	150(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, <i>Chem.</i> <i>Commun.</i> , 2009, 4218-4220.

7		R-3c	a = b = 22.6523(6) c = 65.9502(16) $\alpha = \beta = 90, \gamma = 120$	293(2)	HO <sub>2</sub> C-CO <sub>2</sub> H		TH. Park, K. Koh, A. G. Wong-Foy and A. J. Matzger, <i>Cryst. Growth</i> <i>Des.</i> , 2011, <b>11</b> , 2059-2063.
8	898759	R-3c	a = b = 22.7345(13) c = 64.308(7) $\alpha = \beta = 90, \ \gamma = 120$	173(2)		111	I. Boldog, L. Xing, A. Schulz and C. Janiak, <i>Comptes Rendus Chimie</i> , 2012, <b>15</b> , 866-877.
9		C2/m	a = 24.3627(7) b = 23.9175(7) c = 17.0679(5) $\beta = 91.5200(10)$	100(2)	$HO_2C  CO_2H$	111	J. M. Roberts, O. K. Farha, A. A. Sarjeant, J. T. Hupp and K. A. Scheidt, <i>Cryst. Growth Des.</i> , 2011, <b>11</b> , 4747-4750.
10	831357	R-3m	a = b = 23.5302(8) c = 31.5110(14) $\alpha = \beta = 90, \gamma = 120$	150(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	D. Rankine, A. Avellaneda, M. R. Hill, C. J. Doonan and C. J. Sumby, <i>Chem. Commun.</i> , 2012, <b>48</b> , 10328- 10330.
11	910203	C2/m	a = 26.0930(15) b = 21.5800(15) c = 17.2380(19) $\beta = 92.593(4)$	150(2)		111	A. D. Burrows, S. O. Hunter, M. F. Mahon and C. Richardson, <i>Chem.</i> <i>Commun.</i> , 2013, <b>49</b> , 990-992.
12	904635	<i>R</i> -3	a = b = 23.6899(4) c = 30.8058(7) $\alpha = \beta = 90, \gamma = 120$	130(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	W. W. Lestari, P. Lönnecke, M. B. Sárosi, H. C. Streit, M. Adlung, C. Wickleder, M. Handke, WD. Einicke, R. Gläser and E. Hey- Hawkins, <i>CrystEngComm</i> , 2013, <b>15</b> , 3874.
13	971480	<i>R</i> -3	a = b = 24.4801(10) c = 29.1304(19) $\alpha = \beta = 90, \ \gamma = 120$	150(2)		111	R. Babarao, C. J. Coghlan, D. Rankine, W. M. Bloch, G. K. Gransbury, H. Sato, S. Kitagawa, C. J. Sumby, M. R. Hill and C. J.

								Doonan, Chem. Commun., 2014, <b>50</b> , 3238-3241.
14	β-MUF-9	1437610	Pn-3m	a = b = c = 17.0842(9) $\alpha = \beta = \gamma = 90$	153(2)	HO <sub>2</sub> C CO <sub>2</sub> H	I	A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F. X. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. van der Veen and S. G. Telfer, <i>Nat.</i> <i>Chem.</i> , 2016, <b>8</b> , 250-257.
15	(R/S)-β- MUF-10	1437611	P4232	a = b = c = 17.188(4) $\alpha = \beta = \gamma = 90$	293(2)	$HO_2C$ $CO_2H$ R/S $N$ $NPh$ $Ph$	1	A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F. X. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. van der Veen and S. G. Telfer, <i>Nat.</i> <i>Chem.</i> , 2016, <b>8</b> , 250-257.
16	β-MUF-11	1438094	Pn-3m	a = b = c = 17.0462(9) $\alpha = \beta = \gamma = 90$	143(2)	HO <sub>2</sub> C CO <sub>2</sub> H	I	A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F. X. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. van der Veen and S. G. Telfer, <i>Nat.</i> <i>Chem.</i> , 2016, <b>8</b> , 250-257.
17	β-MUF-12	1438095	Pn-3m	a = b = c = 17.1820(6) $\alpha = \beta = \gamma = 90$	293(2)	HO <sub>2</sub> C rac- A-BrPh 4-BrPh	I	A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F. X. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. van der Veen and S. G. Telfer, <i>Nat.</i> <i>Chem.</i> , 2016, <b>8</b> , 250-257.
18	WUF-1	1501497	C2/m	a = 24.670(5) b = 23.940(4) c = 17.201(5) $\beta = 91.221(15)$	292	HO <sub>2</sub> C-CO <sub>2</sub> H	111	T. A. Ablott, M. Turzer, S. G. Telfer and C. Richardson, <i>Cryst. Growth</i> <i>Des.</i> , 2016, <b>16</b> , 7067-7073.
19	WUF-10	1503491	C2/m	a = 24.6493(15) b = 24.0029(12) c = 17.2267(12) $\beta = 91.311(6)$	292		111	M. R. Bryant, A. D. Burrows, C. J. Kepert, P. D. Southon, O. T. Qazvini, S. G. Telfer and C. Richardson, <i>Cryst. Growth Des.</i> , 2017, <b>17</b> , 2016- 2023.

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20		1563596	R-3c	a = b = 24.4635(15) c = 112.996(8) $\alpha = \beta = 90, \ \gamma = 120$		HO <sub>2</sub> C-CO <sub>2</sub> H	111	S. Glomb, D. Woschko, G. Makhloufi and C. Janiak, <i>ACS App.</i> <i>Mater. Interfaces,</i> 2017, <b>9</b> , 37419- 37434.
21	WUF-19	1872644	C2/m	a = 24.468 b = 24.0292 c = 17.1491 $\beta = 90.869$	292(1)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	M. R. Bryant, T. A. Ablott, S. G. Telfer, L. Liu and C. Richardson <i>CrystEngComm</i> , 2019, <b>21</b> , 60–64.
22	WUF-22(14)	1912370	C2/m	a = 24.3610(12) b = 24.2585(10) c = 17.2141(12) $\beta = 91.458(6)$	292(1)	HO <sub>2</sub> C-CO <sub>2</sub> H	111	L. Conte, TY. Zhou, O. T. Qazvini, L. Liu, D. R. Turner, S. G. Telfer and C. Richardson, <i>Aust. J. Chem.</i> , 2019, <b>72</b> , 811-816.
23	WUF-11		P-421m	a = b = 17.2045(5) c = 17.1507(12) $\alpha = \beta = \gamma = 90$	293(2)	HO <sub>2</sub> C-CO <sub>2</sub> H NH <sub>2</sub>	11	This work
24	WUF-12		P-421m	a = b = 17.237(2) c = 17.1207(17) $\alpha = \beta = \gamma = 90$	293(2)	HO <sub>2</sub> C-CO <sub>2</sub> H	11	This work
25	WUF-13		P-421m	a = b = 17.2000(12) c = 17.2000(12) $\alpha = \beta = \gamma = 90$	293(2)		11	This work
26	WUF-14		R-3m	a = b = 24.106(3) c = 30.383(3) $\alpha = \beta = 90, \gamma = 120$	293(2)		111	This work

## 8 Powder X-ray diffraction





Figure S 18 PXRD patterns for IRMOF-9-NH<sub>2</sub> (WUF-11). Calculated (black; bottom); assynthesised (blue; centre); activated (red; top).

Figure S 19 PXRD patterns for IRMOF-9-NHallyl (WUF-12). Calculated (black; bottom); assynthesised (blue; centre); activated (red; top).





Figure S 20 PXRD patterns for IRMOF-9-N(allyl)<sub>2</sub> (WUF-13). Calculated (black; bottom); assynthesised (blue; centre); activated (red; top).

Figure S 21 PXRD patterns for IRMOF-9-NMe<sub>2</sub> (WUF-14). Calculated (black; bottom); assynthesised (blue; centre); activated (red; top).

## 9 Crystal annealing and desolvation studies

The annealing experiments were performed by heating as synthesised crystals in fresh dry DMF for 48 h at 80 °C. Two crystals were selected for measurement of their size.



Figure S 22 Images of crystal 1 (bottom row) and crystal 2 (top row) of IRMOF-9-N(allyl)<sub>2</sub> (WUF-13) before (left hand side) and after solvothermal annealing (right hand side).

Entry	Before (mm)	After (mm)	Change (%)
Crystal 1	0.751 × 0.701	0.729 × 0.692	2.9 × 1.3
Crystal 2	0.823 × 0.771	0.806 × 0.744	2.1 × 3.5

Table S 3 The sizes of two crystals before and after solvothermal annealing of IRMOF-N(allyl)<sub>2</sub>.

Desolvation experiments were carried out at ambient temperature as follows: crystals from a DMF solution were selected and placed on a glass slide under a calibrated optical microscope. Any excess DMF on the glass slide was quickly wicked away with a Kim wipe and the crystal size along two dimensions was immediately measured (the third vertical dimension was not measured). The size measurement was repeated after 1, 2, 3, 24 and 48 hours. In the analysis for IRMOF-9-NH<sub>2</sub> (**WUF-11**), crystal 6 was seen to be damaged when viewed under the microscope, so no analysis was performed. Similarly, for IRMOF-9-N(allyl)<sub>2</sub> (**WUF-13**), crystal 3 and crystal 6 were seen to be damaged after magnifying to measure their sizes, so no analysis was performed on them. The measurements of the IRMOF-9-NH<sub>2</sub> crystals are listed in Table S4 and the measurements of the IRMOF-9-N(allyl)<sub>2</sub> crystals are listed in Table S5. Normalised plots of crystal size versus time for IRMOF-9-NH<sub>2</sub> (**WUF-11**) are presented in Figures S23 and S24. Images of IRMOF-9-N(allyl)<sub>2</sub> (**WUF-13**) crystals are presented in Figure S25 with a magnified view of crystal 9 provided at 0, 1, 24 and 48 hours, as a representative example. Normalised plots of crystal size versus time for IRMOF-9-N(allyl)<sub>2</sub> (**WUF-13**) are presented in Figures S26 and S27.

Prior to the desolvation experiment, crystals from the samples were analysed by <sup>1</sup>H NMR spectroscopy by digestion in  $d_6$ -DMSO and DCl after filtration and briefly air-drying (< 5 minutes). This analysis was performed again on bulk samples of IRMOF-9-NH<sub>2</sub> (**WUF-11**) and IRMOF-9-N(allyl)<sub>2</sub> (**WUF-13**) that had been left to air dry for 48 hours.

Time	0		0.5		1		2		3		3		3 24		48	
	dimensio	dimensio	dimension													
	n 1 (mm) (%)	n 2 (mm) (%)	1 (mm) (%)	2 (mm) (%)												
Crystal 1	0.750	0.718	0.749	0.712	0.747	0.702	0.743	0.682	0.718	0.618	0.706	0.591	0.703	0.571		
	(100)	(100)	(99.87)	(99.16)	(99.60)	(97.77)	(99.07)	(94.99)	(95.73)	(86.07)	(94.13)	(82.31)	(93.73)	(79.53)		
Crystal 2	0.577	0.571	0.534	0.516	0.498	0.505	0.487	0.498	0.482	0.489	0.454	0.478	0.447	0.442		
	(100)	(100)	(92.55)	(90.37)	(86.31)	(88.44)	(84.40)	(87.22)	(83.54)	(85.64)	(78.68)	(83.71)	(77.47)	(77.41)		
Crystal 3	0.822	0.817	0.763	0.747	0.753	0.720	0.749	0.702	0.737	0.692	0.679	0.670	0.679	0.630		
	(100)	(100)	(92.82)	(91.43)	(91.61)	(88.13)	(91.12)	(85.92)	(89.66)	(84.70)	(82.60)	(82.01)	(82.60)	(77.11)		
Crystal 4	0.630	0.673	0.575	0.607	0.539	0.598	0.537	0.596	0.523	0.560	0.489	0.534	0.484	0.523		
	(100)	(100)	(91.27)	(90.19)	(85.56)	(88.86)	(85.24)	(88.56)	(83.02)	(83.21)	(77.62)	(79.35)	(79.35)	(77.71)		
Crystal 5	0.731	0.757	0.702	0.735	0.689	0.712	0.671	0.707	0.628	0.672	0.600	0.652	0.599	0.634		
	(100)	(100)	(96.03)	(97.09)	(94.25)	(94.06)	(91.79)	(93.39)	(85.91)	(88.77)	(82.08)	(86.13)	(81.94)	(83.75)		
Crystal 6																
Crystal 7	0.561	0.571	0.487	0.545	0.476	0.515	0.476	0.512	0.470	0.493	0.442	0.475	0.435	0.465		
	(100)	(100)	(86.81)	(95.45)	(84.85)	(90.19)	(84.85)	(89.67)	(83.78)	(86.34)	(78.79)	(83.19)	(77.54)	(81.44)		
Crystal 8	0.630	0.575	0.552	0.564	0.505	0.552	0.503	0.532	0.487	0.525	0.475	0.503	0.459	0.471		
	(100)	(100)	(87.62)	(98.09)	(80.16)	(96.00)	(79.84)	(92.52)	(77.30)	(91.30)	(75.40)	(87.48)	(72.86)	(81.91)		
Crystal 9	0.681	0.647	0.620	0.584	0.590	0.563	0.589	0.562	0.554	0.537	0.553	0.534	0.538	0.528		
	(100)	(100)	(91.04)	(90.26)	(86.64)	(87.02)	(86.49)	(86.86)	(81.35)	(83.00)	(81.20)	(82.53)	(79.00)	(81.61)		
Crystal	0.533	0.636	0.508	0.619	0.481	0.589	0.481	0.588	0.452	0.565	0.424	0.533	0.413	0.527		
10	(100)	(100)	(95.31)	(97.33)	(90.24)	(92.61)	(90.24)	(92.45)	(84.80)	(88.84)	(79.55)	(83.81)	(77.49)	(82.86)		

Table S 4 Measurements of IRMOF-9-NH $_2$  (WUF-11) crystals during the desolvation experiment.



**Figure S 23** A graph displaying the reduction in size of IRMOF-9-NH<sub>2</sub> (**WUF-11**) crystals 1-5 during the desolvation experiment. D1 and D2 stand for dimension 1 and dimension 2, respectively.



**Figure S 24** A graph displaying the reduction in size of IRMOF-9-NH<sub>2</sub> (**WUF-11**) crystals 7-10 during the desolvation experiment. D1 and D2 stand for dimension 1 and dimension 2, respectively.

Time	0		1		2	2			24		48	
	dime nsion 1 (mm) (%)	dimensi on 2 (mm) (%)	dimensi on 1 (mm) (%)	dimensi on 2 (mm) (%)								
Crystal 1	0.501	0.507	0.450	0.463	0.445	0.451	0.445	0.449	0.422	0.421	0.411	0.416
	(100)	(100)	(89.8)	(91.3)	(88.8)	(89.0)	(88.8)	(88.6)	(84.2)	(83.0)	(82.0)	(82.1)
Crystal 2	0.495	0.555	0.470	0.527	0.466	0.52	0.45	0.509	0.421	0.497	0.411	0.494
	(100)	(100)	(94.9)	(95.0)	(94.1)	(93.7)	(90.9)	(91.7)	(85.1)	(89.6)	(83.0)	(89.0%)
Crystal 3												
Crystal 4	0.508	0.413	0.464	0.372	0.456	0.369	0.446	0.36	0.434	0.336	0.418	0.323
	(100)	(100)	(91.3)	(90.1)	(89.8)	(89.3)	(87.8)	(87.2)	(85.4)	(81.4)	(82.3)	(78.2)
Crystal 5	0.448	0.629	0.398	0.586	0.394	0.579	0.393	0.565	0.389	0.559	0.365	0.548
	(100)	(100)	(88.8)	(93.1)	(87.9)	(92.1)	(87.7)	(89.8)	(86.8)	(88.9)	(81.5)	(87.1)
Crystal 6												
Crystal 7	0.572	0.668	0.534	0.641	0.523	0.617	0.512	0.608	0.501	0.588	0.473	0.570
	(100)	(100)	(93.4)	(96.0)	(91.4)	(92.4)	(89.5)	(91.0)	(87.6)	(88.0)	(82.7)	(85.3)
Crystal 8	0.626	0.65	0.567	0.622	0.557	0.603	0.542	0.59	0.536	0.582	0.524	0.560
	(100)	(100)	(90.6)	(95.7)	(89.0)	(92.8)	(86.6)	(90.8)	(85.6)	(89.5)	(83.7)	(86.2)
Crystal 9	0.575 (100)	0.558 (100)	0.543 (94.4)	0.532 (95.3)	0.520 (90.4)	0.508 (91.0)	0.496 (86.3)	0.493 (88.4)	0.490 (85.2)	0.480 (86.0)	0.471 (82.1)	0.463 (83.2)

Table S 5 Measurements of IRMOF-9-N(allyl)<sub>2</sub> (WUF-13) crystals during the desolvation experiment.



Figure S 25 Images of IRMOF-9-N(allyl)<sub>2</sub> (WUF-13) crystals (a) at the start, (b) after 1 hour (c) after 48 hours, and close-up views of crystal 9 with measurement dimensions (d) at the start, (e) after 1 hour, (f) after 24 hours and (g) after 48 hours of the desolvation experiment.



**Figure S 26** A graph displaying the reduction in size of  $IRMOF-9-N(allyl)_2$  (**WUF-13**) crystals 1-5 during the desolvation experiment. D1 and D2 stand for dimension 1 and dimension 2, respectively.



**Figure S 27** A graph displaying the reduction in size of IRMOF-9-N(allyl)<sub>2</sub> (**WUF-13**) crystals 7-9 during the desolvation experiment. D1 and D2 stand for dimension 1 and dimension 2, respectively.

## **10** Gas adsorption







Figure S 28 N<sub>2</sub> Isotherm for IRMOF-9-NH<sub>2</sub> WUF-11 at 77 K.

BET summary	WUF-11	
Slope	1.538	
Intercept	1.455e-03	
Correlation coefficient, r	0.999989	
C constant	1058.383	
Surface Area	2261.550 m²/g	
Relative Pressure, P/Po	Volume @ STP (cc/g)	1 / [ W((Po/P) - 1) ]
9.01494e-03	472.6580	1.5399e-02
9.96480e-03	478.3856	1.6834e-02
1.20730e-02	488.9013	2.0000e-02
1.50541e-02	498.5017	2.4532e-02
2.59363e-02	516.2603	4.1267e-02
3.58752e-02	524.8744	5.6723e-02

Figure S 29 N<sub>2</sub> Isotherm for IRMOF-9-NHallyl WUF-12 at 77 K.

BET summary	WUF-12	
Slope	1.660	
Intercept	1.618e-03	
Correlation coefficient, r	0.999990	
C constant	1027.225	
Surface Area	2095.448 m²/g	
Balativa Drassura D/Da	Valuma @ STD (as/a)	$1 / [M//(D_0/D) - 1)]$
Relative Pressure, P/P0	volume @ STP (cc/g)	1/[VV((PO/P)-1)]
8.03810e-03	431.4082	1.5029e-02
8.03810e-03 9.05664e-03	431.4082 438.6656	1.5029e-02 1.6670e-02
8.03810e-03 9.05664e-03 1.00242e-02	431.4082 438.6656 444.0931	1.5029e-02 1.6670e-02 1.8243e-02
8.03810e-03 9.05664e-03 1.00242e-02 1.20769e-02	431.4082 438.6656 444.0931 452.0962	1,5029e-02 1.6670e-02 1.8243e-02 2.1635e-02
Relative Pressure, P/P0   8.03810e-03   9.05664e-03   1.00242e-02   1.20769e-02   1.51214e-02	431.4082   438.6656   444.0931   452.0962   460.7404	1,5029e-02 1.6670e-02 1.8243e-02 2.1635e-02 2.6663e-02



Figure S 30 N<sub>2</sub> Isotherm for IRMOF-9-N(allyl)<sub>2</sub> WUF-13 at 77 K.

BET summary	WUF-13	
Slope	2.174	
Intercept	1.421e-03	
Correlation coefficient, r	0.999999	
C constant	1531.283	
Surface Area	1600.584 m²/g	
Relative Pressure, P/Po	Volume @ STP (cc/g)	1 / [ W((Po/P) - 1) ]
8.05200e-03	342.7974	1.8946e-02
9.08491e-03	346.3174	2.1182e-02
9.97264e-03	348.7917	2.3107e-02
1.21251e-02	353.6022	2.7773e-02
1.52077e-02	358.5514	3.4460e-02
2.58484e-02	368.3404	5.7638e-02



Figure S 31 N<sub>2</sub> Isotherm for IRMOF-9-NMe<sub>2</sub> WUF-14 at 77 K.

BET summary	WUF 14	
Slope	2.067	
Intercept	1.585e-03	
Correlation coefficient, r	0.999995	
C constant	1304.668	
Surface Area	1683.584 m²/g	
Relative Pressure, P/Po	Volume @ STP (cc/g)	1 / [ W((Po/P) - 1) ]
8.01509e-03	354.5704	1.8233e-02
9.05150e-03	359.5128	2.0329e-02
9.99420e-03	363.0449	2.2248e-02
1.21975e-02	369.3874	2.6747e-02
1.50938e-02	374.9500	3.2703e-02
2.67627e-02	387.0916	5.6839e-02
3.41121e-02	391.5604	7.2166e-02



Figure S 32 Pore size distributions calculated from the QSDFT kernel for N<sub>2</sub> at 77 K on carbon with slit/cylindrical pores for IRMOF-9-NH<sub>2</sub> (WUF-11), IRMOF-9-NHallyl (WUF-12), IRMOF-9-N(allyl)<sub>2</sub> (WUF-13) and IRMOF-9-NMe<sub>2</sub> (WUF-14).

### 10.2 CO<sub>2</sub> Isotherms





Figure S 33 CO<sub>2</sub> adsorption isotherms for WUF-11-14 at 196 K.

Figure S 34 CO<sub>2</sub> adsorption isotherms for WUF-11-14 at 196 K in log scale.



Figure S 35 CO<sub>2</sub> adsorption/desorption isotherms for IRMOF-9-NH<sub>2</sub> (WUF-11) at 196 K.



Figure S 37 CO<sub>2</sub> adsorption/desorption isotherms for IRMOF-9-N(allyl)<sub>2</sub> (WUF-13) at 196 K.



Figure S 36 CO<sub>2</sub> adsorption/desorption isotherms for IRMOF-9-NHallyl (WUF-12) at 196 K.



Figure S 38 CO<sub>2</sub> adsorption/desorption isotherms for IRMOF-9-NMe<sub>2</sub> (WUF-14) at 196 K.



Figure S 39 CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms at 298 K for WUF-11-14.



Figure S 40  $CO_2$  adsorption/desorption isotherms at 298 K for WUF-11-12.



Figure S 41 CO<sub>2</sub> adsorption/desorption isotherms at 298 K for WUF-13-14.





Figure S 42 CO<sub>2</sub> adsorption isotherms at 293 K for WUF-11-14.



Figure S 43 CO<sub>2</sub> adsorption/desorption isotherms at 288 K for WUF-11 and WUF-14.

Figure S 44 CO<sub>2</sub> adsorption isotherms at 283 K for WUF-11-14.





Figure S 45 CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms at 273 K for WUF-11-14.



Figure S 46 CO<sub>2</sub> adsorption/desorption isotherms at 273 K for WUF-11-12.

Figure S 47 CO<sub>2</sub> adsorption/desorption isotherms at 273 K for WUF-13-14.

Table S 6 CO<sub>2</sub> uptake at 1 bar in cm<sup>3</sup>g<sup>-1</sup> by WUF-11-14

Structure	273	283 K	288 K	293 K	298 K
	к				
IRMOF-9-NH <sub>2</sub>	40.87	33.14	28.39	24.89	22.83
WUF-11					
IRMOF-9-NHallyl	50.48	37.83		30.86	27.49
WUF-12					
IRMOF-9-N(allyl) <sub>2</sub>	47.45	31.84		26.87	24.65
WUF-13					
IRMOF-9-NMe <sub>2</sub>	55.37	43.43	39.57	35.02	31.34
WUF-14					



Figure S 48







Figure S 50



Figure S 51

#### 10.4 Qst Calculations

Isosteric heat of adsorption ( $Q_{st}$ ) values were calculated from isotherms measured at 273 K and 298 K for  $CO_2$ . The isotherms were first fit to a virial equation:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

Where *N* is the amount of gas adsorbed at the pressure *P*, *a* and *b* are virial coefficients, *m* and *n* are the number of coefficients require to adequately describe the isotherm. To calculate  $Q_{st}$ , the fitting parameters from the above equation were used for the following equation:

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



Figure S 52 Virial equation fits for CO<sub>2</sub> adsorption isotherms of IRMOF-9-NH<sub>2</sub> (WUF-11).



Figure S 53 Virial equation fits for CO<sub>2</sub> adsorption isotherms of WUF-12.



Figure S 54 Virial equation fits for CO<sub>2</sub> adsorption isotherms of WUF-13.



Figure S 55 Virial equation fits for CO<sub>2</sub> adsorption isotherms of IRMOF-9-NMe<sub>2</sub> (WUF-14).

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