

# Variable Water Adsorption in Amino Acid Derivative based Homochiral Metal Organic Frameworks

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## Supporting Information

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## Section S1: Detailed synthetic procedures of ligands and MOFs

### with PXRD patterns:

**Materials:** Cd(COOCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, L-leucine, L-serine, L-threonine, sodium borohydride, and 4-pyridinecarboxaldehyde were purchased from Aldrich Chemicals. All starting materials were used without further purification. All experimental operations were performed in air.

### Synthesis of Ligands:

**2-((pyridin-4-yl)methylamino)-4-methylpentanoic acid.HCl [L1<sub>Cl</sub>].** The ligand (**L1<sub>Cl</sub>**) was prepared using a modified literature procedure. To an aqueous solution (10 mL) of L-leucine (2 g, 15 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.78 g, 7.5 mmol), 4-pyridinecarboxaldehyde (1.60 g, 15 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and cooled in an ice bath. NaBH<sub>4</sub> (0.76 g, 20.4 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3 N HCl was used to adjust the pH to 5–6. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL×3), and the filtrate was evaporated to get a white powder. Yield: 2.7 g, 70%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3406; ν<sub>as</sub>(CO<sub>2</sub>), 1626; ν<sub>s</sub>(CO<sub>2</sub>), 1412. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>3</sub> (0.90, d, 6H), -CH (1.66, m, 1H), -CH<sub>2</sub> (2.19, dd, 2H), -HN-CH (3.55, d, 1H), -HN (3.69, m, 1H), -CH<sub>2</sub> (4.19, s, 2H), py-H (7.49, d, 2H), py-H (8.56, d, 2H).

**2-((pyridin-4-yl)methylamino)-4-methylpentanoic acid. HBr [L1<sub>Br</sub>].** The ligand (**L1<sub>Br</sub>**) was prepared exactly as L1<sub>Cl</sub>, except HBr was used instead of HCl for pH adjustment. Yield: 3.0 g, 66%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3414; ν<sub>as</sub>(CO<sub>2</sub>), 1612; ν<sub>s</sub>(CO<sub>2</sub>), 1409. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>3</sub> (0.92, d, 6H), -CH (1.65, m, 1H), -CH<sub>2</sub> (2.19, dd, 2H), -HN-CH (3.57, d, 1H), -HN (3.71, m, 1H), -CH<sub>2</sub> (4.17, s, 2H), py-H (7.48, d, 2H), py-H (8.46, d, 2H).

**2-((pyridin-4-yl)methylamino)-3-hydroxypropanoic acid.HCl [L2<sub>Cl</sub>].** To an aqueous solution (10 mL) of L-serine (2 g, 19 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.99 g, 9.5 mmol), 4-pyridinecarboxaldehyde (2.03 g, 19 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and

cooled in an ice bath. NaBH<sub>4</sub> (0.76 g, 20.4 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3 N HCl was used to adjust the pH to 5–6. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL×3), and the filtrate was evaporated to get a white powder. Yield: 2.6 g, 60%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3420; ν<sub>as</sub>(CO<sub>2</sub>), 1602; ν<sub>s</sub>(CO<sub>2</sub>), 1410. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>2</sub> (3.65, dd, 2H), -HN-CH (3.58, m, 1H), -CH<sub>2</sub> (4.19, s, 2H), py-H (7.45, d, 2H), py-H (8.52, d, 2H).

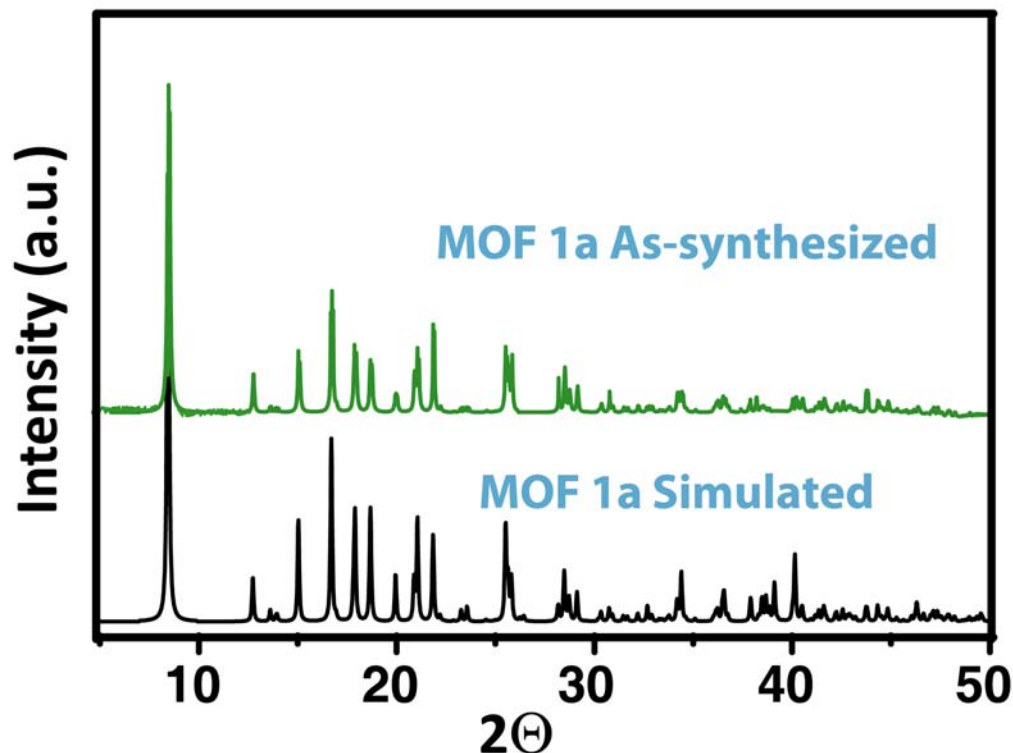
**2-((pyridin-4-yl)methylamino)-3-hydroxypropanoic acid.HBr [L2<sub>Br</sub>].** The ligand (**L2<sub>Br</sub>**) was prepared exactly as L2<sub>Cl</sub> except HBr was used instead of HCl for pH adjustment. Yield: 3.3 g, 63%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3382; ν<sub>as</sub>(CO<sub>2</sub>), 1619; ν<sub>s</sub>(CO<sub>2</sub>), 1412. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>2</sub> (3.61, dd, 2H), -HN-CH (3.53, m, 1H), -CH<sub>2</sub> (4.22, s, 2H), py-H (7.47, d, 2H), py-H (8.52, d, 2H).

**2-((pyridin-4-yl)methylamino)-3-hydroxybutanoic acid.HCl [L3<sub>Cl</sub>].** To an aqueous solution (10 mL) of L-threonine (2 g, 16 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.84 g, 8.0 mmol), 4-pyridinecarboxaldehyde (1.71 g, 16 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and cooled in an ice bath. NaBH<sub>4</sub> (0.75 g, 20.0 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3 N HCl was used to adjust the pH to 5–6. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL×3), and the filtrate was evaporated to get a white powder. Yield: 2.7 g, 70% yield. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3353; ν<sub>as</sub>(CO<sub>2</sub>), 1597; ν<sub>s</sub>(CO<sub>2</sub>), 1412. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>3</sub> (1.18, dd, 2H), -CH (3.72, dd, 1H), -HN-CH (3.55, m, 1H), -CH<sub>2</sub> (4.20, s, 2H), py-H (7.46, d, 2H), py-H (8.50, d, 2H).

**2-((pyridin-4-yl)methylamino)-3-hydroxybutanoic acid.HBr [L3<sub>Br</sub>].** The ligand (**L3<sub>Br</sub>**) was prepared exactly as L3<sub>Cl</sub>, except HBr was used instead of HCl for pH adjustment. Yield: 3.4 g, 75% yield. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3382; ν<sub>as</sub>(CO<sub>2</sub>), 1607; ν<sub>s</sub>(CO<sub>2</sub>), 1409. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): -CH<sub>3</sub> (1.21, dd, 2H), -CH (3.74, dd, 1H), -HN-CH (3.53, m, 1H), -CH<sub>2</sub> (4.21, s, 2H), py-H (7.44, d, 2H), py-H (8.49, d, 2H).

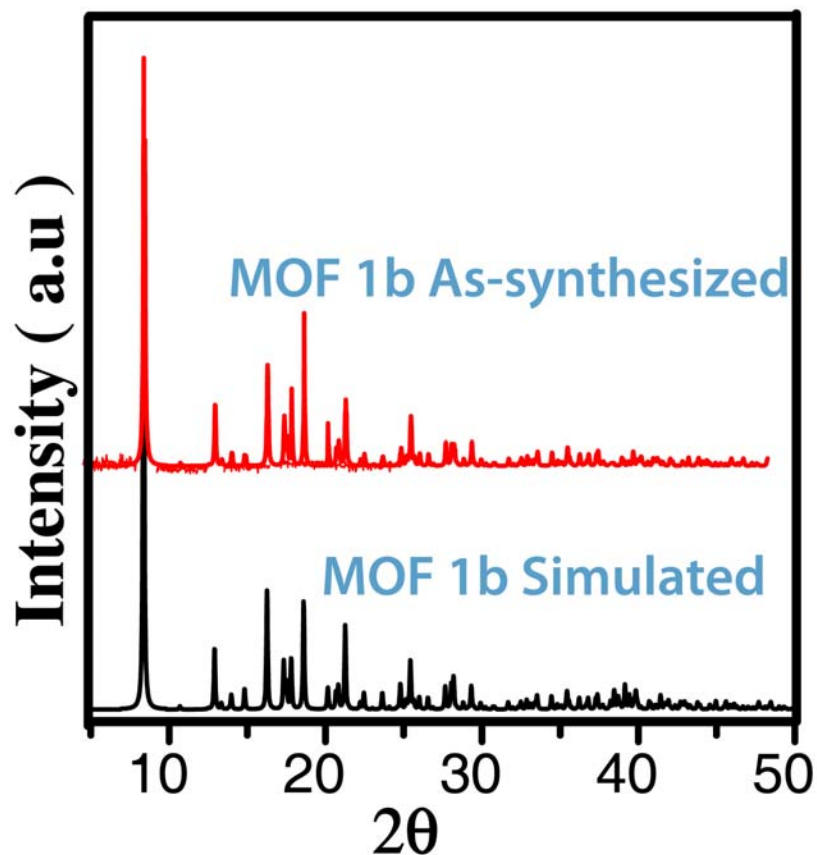
**Synthesis of MOFs:** Ligands ( $I-L_X$  where  $X = Cl^-$ ,  $Br^-$ ) were synthesized by using above procedures. Taking same equivalent ligand and metal salt in a capped vial, the mixture was heated at 90 °C for 24 h in water medium. Although rod shaped crystals appear within 5-6 h of heating the mixture, but overall yield increases only after heating the sample for 24 h. There is no further increase in yield by keeping the heating more than 24 h. For good quality crystals, the ideal concentration is the 0.1 mmol of ligand and metal salt in 2 ml water. Crystals were stable inside the solvent water and open air for a long time (more than six months) without losing its crystallinity. MOFs were almost insoluble in most of the common solvents once crystallized from mother solution. Phase pure crystals (confirmed by powder XRD) can be synthesized in a gram scale with ~ 70-75 % of yield.

**[{Cd(L1Cl)(Cl)}(H<sub>2</sub>O)]<sub>∞</sub> (1a).** To an aqueous solution (2 mL) of L1Cl (0.05 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.025 g, 65%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3421; ν<sub>N-H</sub>, 2927; ν<sub>as</sub>(CO<sub>2</sub>), 1598; ν<sub>s</sub>(CO<sub>2</sub>), 1400. Elemental analysis: calcd C (37.22%), H (4.94%), N (7.23%); found C (38.20%), H (4.88%), N (7.25%).



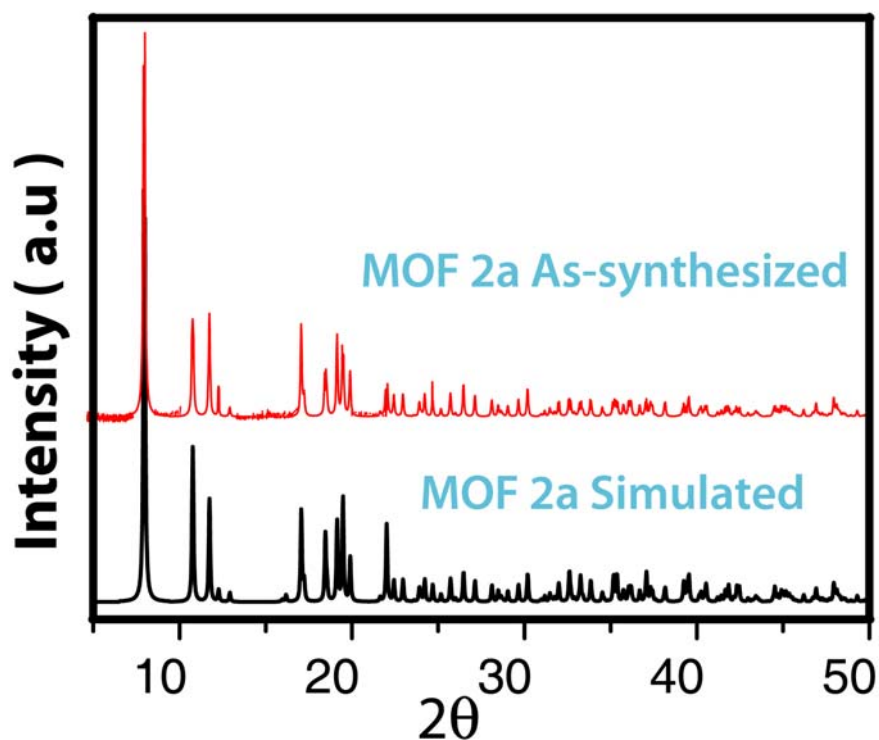
**Figure S1.** Comparison of the experimental PXRD pattern of as-synthesized MOF **1a** (top) with the simulated from its single crystal structure (bottom).

**[Cd(L1<sub>Br</sub>)(Br)]<sub>∞</sub> (1b).** To an aqueous solution (2 mL) of L1<sub>Br</sub> (0.06 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.024 g, 60%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3430; ν<sub>N-H</sub>, 2956; ν<sub>as</sub>(CO<sub>2</sub>), 1582; ν<sub>s</sub>(CO<sub>2</sub>), 1424. Elemental analysis: calcd C (34.84%), H (4.14%), N (6.77%); found C (34.81%), H (4.11%), N (6.75%).



**Figure S2.** Comparison of the experimental PXRD pattern of as-synthesized MOF **1b** (top) with the simulated from its single crystal structure (bottom).

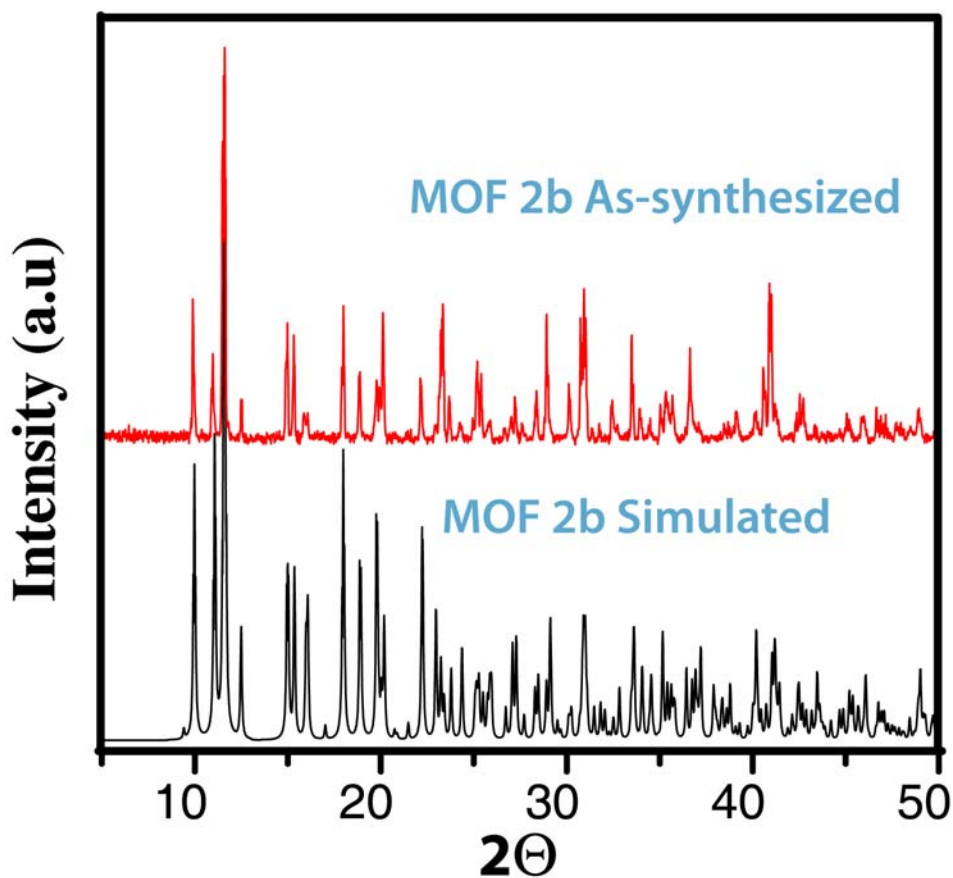
**[{Cd(L2<sub>Cl</sub>)(Cl)}(H<sub>2</sub>O)]<sub>∞</sub> (2a).** To an aqueous solution (2 mL) of L2<sub>Cl</sub> (0.046 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.023 g, 62%. IR (KBr, cm<sup>-1</sup>): ν<sub>as</sub>(CO<sub>2</sub>), 1625; ν<sub>s</sub>(CO<sub>2</sub>), 1512. Elemental analysis: calcd C (32.19%), H (3.51%), N (7.50%); found C (32.2%), H (3.48%), N (7.47%).



**Figure S3.** Comparison of the experimental PXRD pattern of as-synthesized MOF **2a** (top) with the simulated from its single crystal structure (bottom).

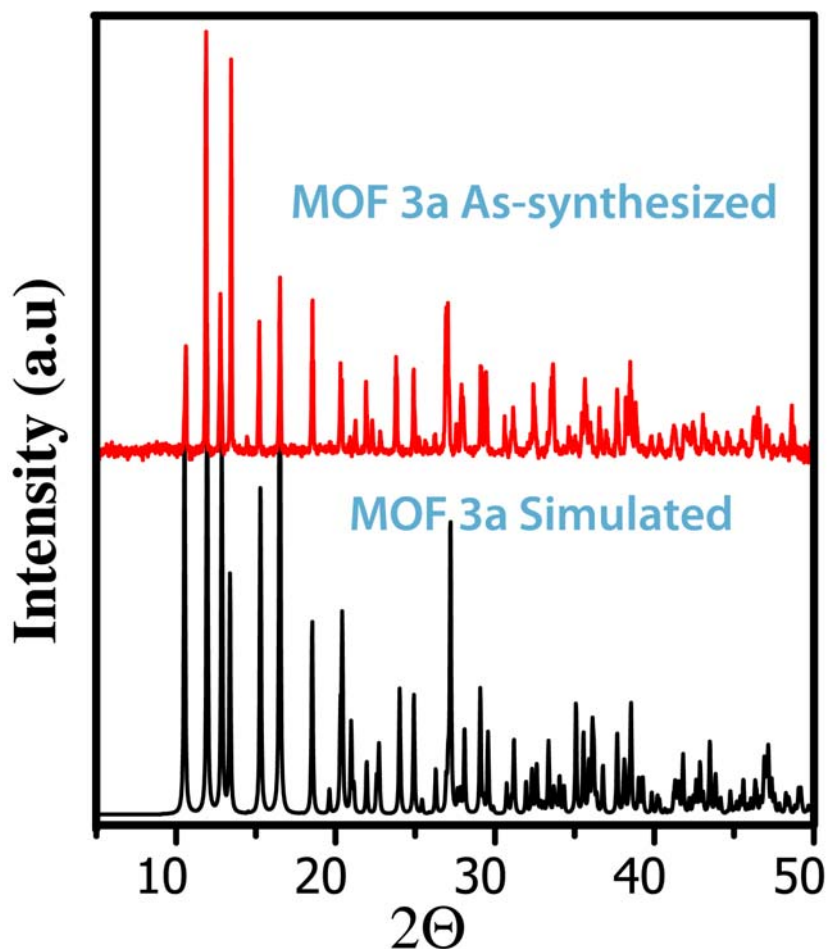


**[{Cd<sub>2</sub>(L2<sub>Br</sub>)<sub>2</sub>(Br)<sub>2</sub>}(H<sub>2</sub>O)<sub>3</sub>]<sub>∞</sub> (2b).** To an aqueous solution (2 mL) of L2<sub>Br</sub> (0.055 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.024 g, 58%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3445; ν<sub>as</sub>(CO<sub>2</sub>), 1550; ν<sub>s</sub>(CO<sub>2</sub>), 1427. Elemental analysis: calcd C (26.07%), H (3.40%), N (6.75%); found C (26.0%), H (3.41%), N (6.69%).



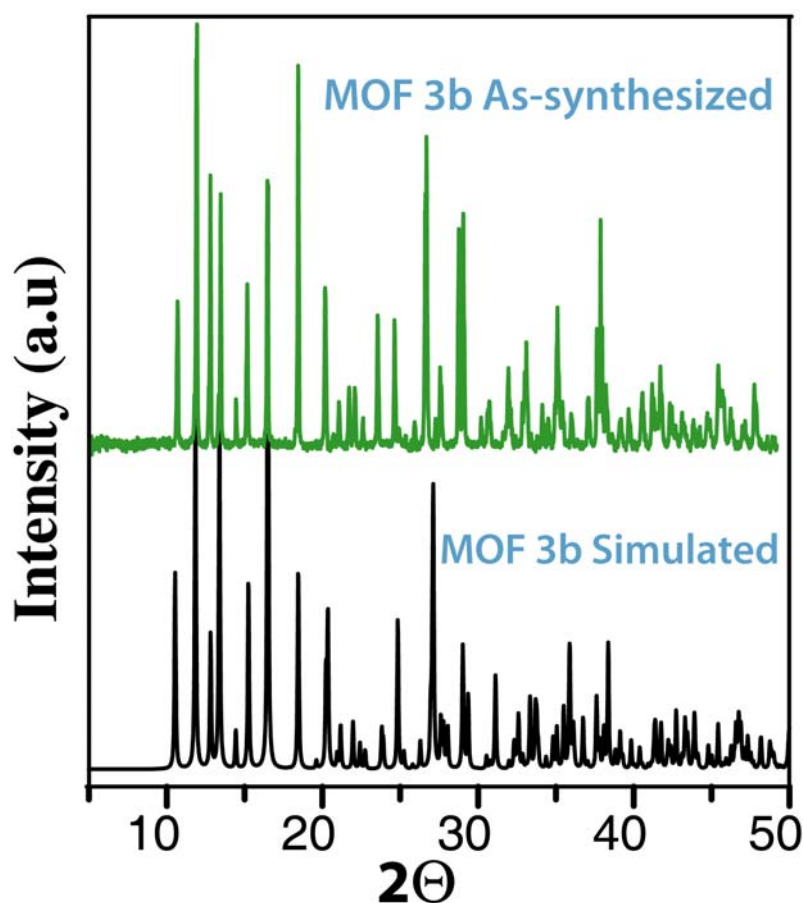
**Figure S4.** Comparison of the experimental PXRD pattern of as-synthesized MOF **2b** (top) with the simulated from its single crystal structure (bottom).

**[{Cd(L3<sub>Cl</sub>)(Cl)}(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub> (3a).** To an aqueous solution (2 mL) of L3<sub>Cl</sub> (0.05 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.027 g, 70%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3642; ν<sub>as</sub>(CO<sub>2</sub>), 1593; ν<sub>s</sub>(CO<sub>2</sub>), 1433. Elemental analysis: calcd C (30.55%), H (4.35%), N (7.12%); found C (30.52%), H (4.36%), N (7.14%).



**Figure S5.** Comparison of the experimental PXRD pattern of as-synthesized MOF **3a** (top) with the simulated from its single crystal structure (bottom).

**[{Cd(L3<sub>Br</sub>)(Br)}(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub> (3b).** To an aqueous solution (2 mL) of L3<sub>Br</sub> (0.058 g, 0.2 mmol), Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5 mL vial for 24 h at 90 °C to produce rod-shaped transparent crystals. Yield: 0.028 g, 65%. IR (KBr, cm<sup>-1</sup>): ν<sub>OH</sub>, 3686; ν<sub>N-H</sub>, 2924; ν<sub>as</sub>(CO<sub>2</sub>), 1580; ν<sub>s</sub>(CO<sub>2</sub>), 1395. Elemental analysis: calcd C (27.44%), H (3.91%), N (6.40%); found C (27.41%), H (3.92%), N (6.41%).



**Figure S6.** Comparison of the experimental PXRD pattern of as-synthesized MOF **3b** (top) with the simulated from its single crystal structure (bottom).

## Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures:

**X-Ray crystallography:** All single-crystal data were collected on a Bruker SMART APEX three-circle diffractometer equipped with a CCD area detector (Bruker Systems Inc.)<sup>14a</sup> and operated at 1500 W power (50 kV, 30 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of the Cd-MOFs reported in this paper were mounted on nylon CryoLoops (Hampton Research) with Paratone-N (Hampton Research). Data were integrated using Bruker SAINT software.<sup>14b</sup> Data were subsequently corrected for absorption by the program SADABS.<sup>14c</sup> Space group determinations and tests for merohedral twinning were carried out using XPREP. In all cases, the highest possible space group was chosen. All structures were solved by direct methods and refined using the SHELXTL 97<sup>14d</sup> software suite. Atoms were located from iterative examination of difference F-maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 $\times$ U<sub>eq</sub> of the attached C atoms. Hydrogen atoms attached to the lattice water molecules in **1a–3a/b** and to the side arm oxygen atoms of **2b** and **3b** could not be located or fixed. All structures were examined using the Addsym subroutine of PLATON<sup>14e</sup> to ensure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. The Supporting Information contains a detailed data collection strategy and crystallographic data (Table S1– S6 in SI) for the MOFs reported in this paper. Crystallographic data (excluding

structure factors) for the structures reported in this paper have also been deposited with the CCDC as deposition Nos. CCDC 851353-851358 [available free of charge, on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K.; fax +44 (1223) 336 033; E-mail [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

### **General Data Collection and Refinement Procedures:**

The single crystal data was collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K $\alpha$  radiation ( $\lambda=0.71073$  Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystal of the Cd-MOFs reported in the paper was mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Crystals were flash frozen to 293(2) K in a liquid nitrogen cooled stream of nitrogen. Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In this case frame widths of  $0.5^\circ$  was judged to be appropriate and full hemispheres of data were collected using the *BrukerSMART*<sup>1</sup> software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to re-determine unit cell parameters for data integration and to check for rotational twinning using CELL-NOW<sup>2</sup>. In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data was integrated using Bruker SAINT<sup>3</sup> software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data was subsequently corrected for absorption by the program SADABS<sup>3</sup>. The space group determinations and test for merohedral twinning was carried out using *XPREP*<sup>4</sup>. In this case, the highest possible space group was chosen. The structure was solved by direct method and refined using the *SHELXTL* 97<sup>5-6</sup> software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) except

hydrogen atoms attached to the lattice water molecules in **1a/b–3a/b** and side arm oxygen atoms of **2b** and **3b** could not be located or fixed. The optimal crystals suitable for analysis were generally small and weakly diffracting. The structure was examined using the *Addsym* subroutine of PLATON<sup>7</sup> to assure that no additional symmetry could be applied to the models. For these structures we noted that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by some research groups.<sup>8-17</sup> The ellipsoid in ORTEP<sup>19</sup> diagrams are displayed at the 50% probability level unless noted otherwise.

1. Bruker (2005). *APEX2*. Version 5.053. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2004). *CELL\_NOW*. University of Göttingen, Germany. Steiner, Th. *Acta Cryst.* 1998, B54, 456.
3. Bruker (2004). *SAINT-Plus* (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA.
4. Sheldrick, G. M. (2002). *SADABS* (Version 2.03) and *TWINABS* (Version 1.02). University of Göttingen, Germany.
5. Sheldrick, G. M. (1997). *SHELXS '97* and *SHELXL '97*. University of Göttingen, Germany.
6. WINGX
7. A.L. Spek (2005) PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.
8. Dakin, L. A., Ong P. C., Panek, J. S., Staples, R. J. & Stavropoulos, P. *Organometallics* **2000**, 19, 2896.
9. Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, 124, 2568.
10. Eddaoudi, M., Kim, J., Vodak, D., Sudik, A., Wachter, J., O'Keeffe, M. & Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, 99, 4900.

11. Heintz, R. A.; Zhao, H.; Ouyang, X.; Grandinetti, G.; Cowen, J.; Dunbar, K. R. *Inorg. Chem.* **1999**, 38,144.
12. Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2000**, 39, 3843.
13. Grosshans, P., Jouaiti, A., Hosseini, M. W. & Kyritsakas, N. *New J. Chem.* **2003**, 27,793.
14. Takeda, N., Umemoto, K., Yamaguchi, K. & Fujita, M. *Nature (London)* **1999**, 398,794.
15. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, 295,469.
16. Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, 44, 72.
17. Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, 40, 478.
18. Koh, L. L.; Ranford, J. O.; Robinson, W. T.; Svensson, J. O.; Tan, A. L. C.; Wu, D.; *Inorg. Chem.* **1996**, 35, 6466.
19. C. K. Johnson, *ORTEP, Report ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.



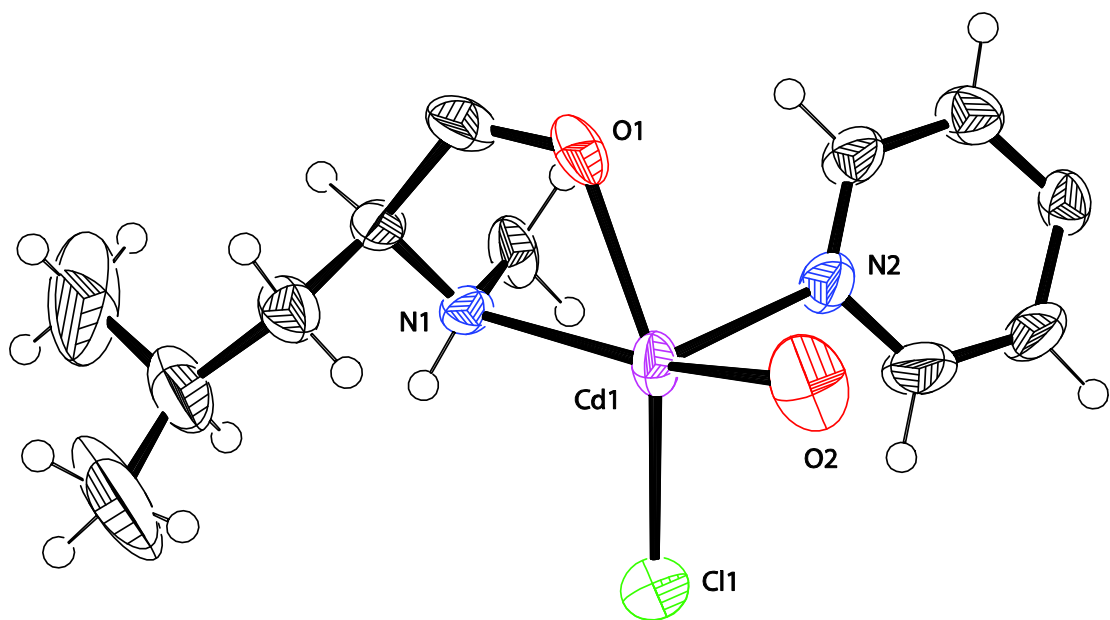
### Experimental and Refinement Details for MOF **1a**

A colourless rod shaped crystal of **1a** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the lattice water molecules in **1a** could not be located or fixed. MOF **1a** contains one ligand and one chloride atom and metal atom with one lattice water in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0475$  ( $F > 2\sigma F$ ) and  $wR2 = 0.1079$  (all data) with GOF = 1.033.



**Table S1. Crystal data and structure refinement for MOF 1a.**

Empirical formula	C <sub>12</sub> H <sub>17</sub> Cl N <sub>2</sub> O <sub>3</sub> Cd
Formula weight	385.14
CCDC No.	851353
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	<i>a</i> = 7.123(3) Å $\alpha$ = 90.00°
	<i>b</i> = 13.896(5) Å $\beta$ = 90.00°
	<i>c</i> = 15.893(6) Å $\gamma$ = 90.00°
Volume	1573(11) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.626
Absorption coefficient	1.563
<i>F</i> (000)	768
Reflections collected	3677
Independent reflections	3445
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.033
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0434, <i>wR</i> 2 = 0.1059
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0475, <i>wR</i> 2 = 0.1079



**Figure S7.**ORTEP drawing of the asymmetric unit of MOF **1a**. Thermal ellipsoids set to 50% probability level.

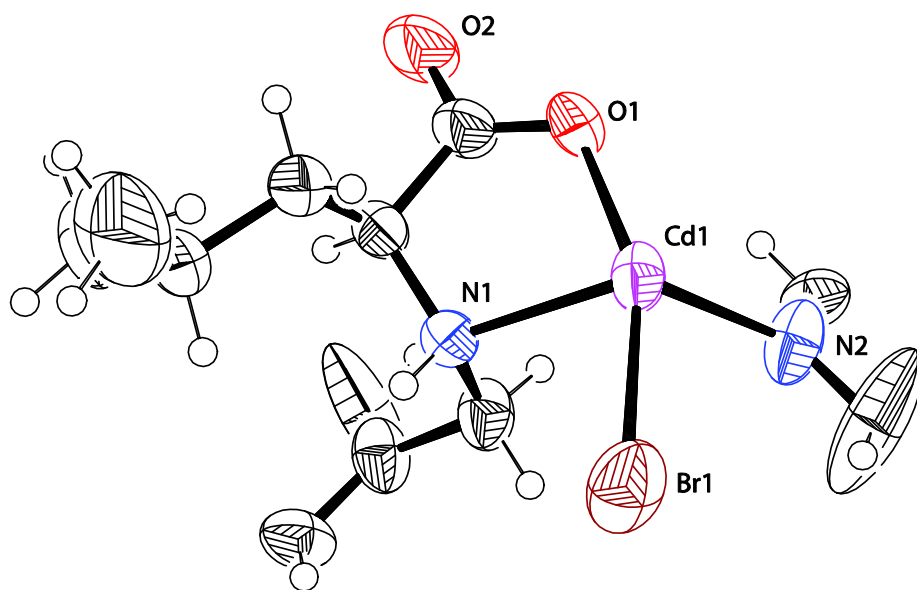


### Experimental and Refinement Details for MOF **1b**

A colourless rod shaped crystal of **1b** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. MOF **1b** contains one ligand and one bromine atom and metal atom in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0461$  ( $F > 2\sigma F$ ) and  $wR2 = 0.1342$  (all data) with GOF = 1.066.

**Table S2. Crystal data and structure refinement for MOF 1b.**

Empirical formula	C <sub>12</sub> H <sub>17</sub> Br N <sub>2</sub> O <sub>3</sub> Cd		
Formula weight	413.59		
CCDC No.	851354		
Temperature	296(2)K		
Wavelength	0.71073Å		
Crystal system	Orthorhombic		
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>		
Unit cell dimensions	a=7.2389(6) Å	$\alpha$ = 90.00°	
	b = 13.7041(11) Å	$\beta$ = 90.00°	
	c = 16.5286(13) Å	$\gamma$ = 90.00°	
Volume	1639.9(2) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.675		
Absorption coefficient	3.779		
F(000)	808		
Reflections collected	3871		
Independent reflections	3568		
Goodness-of-fit on F2	1.066		
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1300		
R indices (all data)	R1 = 0.0461, wR2 = 0.1342		



**Figure S8.**ORTEP drawing of the asymmetric unit of MOF **1b**. Thermal ellipsoids set to 50% probability level.

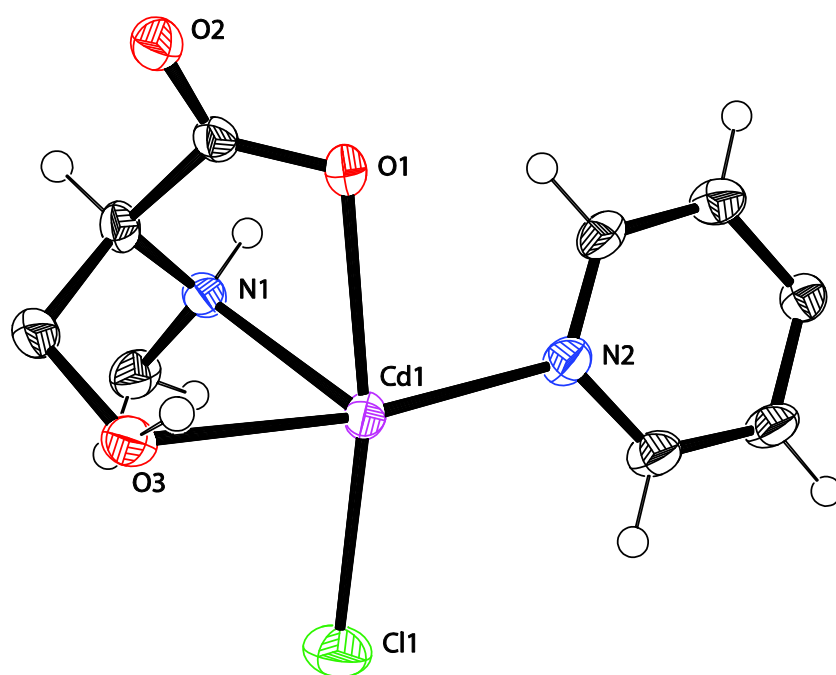


### Experimental and Refinement Details for MOF **2a**

A colorless rod shaped crystal of **2a** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the lattice water molecules of **2a** could not be located or fixed. MOF **2a** contains one ligand and one chloride atom and metal atom in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0341$  ( $F > 2\sigma F$ ) and  $wR2 = 0.0956$  (all data) with GOF = 1.097.

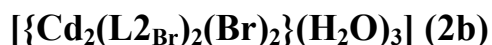
**Table S3. Crystal data and structure refinement for MOF 2a.**

Empirical formula	C <sub>9</sub> H <sub>11</sub> Cl N <sub>2</sub> O <sub>4</sub> Cd	
Formula weight	359.06	
CCDC No.	851355	
Temperature	296(2)K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	<i>a</i> = 5.8751(17) Å	$\alpha = 90.00^\circ$
	<i>b</i> = 15.067(4) Å	$\beta = 90.00^\circ$
	<i>c</i> = 16.416(5) Å	$\gamma = 90.00^\circ$
Volume	1453.1(7) Å <sup>3</sup>	
<i>Z</i>	4	
Density (calculated)	1.641	
Absorption coefficient	1.689	
F(000)	704	
Reflections collected	3420	
Independent reflections	3389	
Goodness-of-fit on F <sup>2</sup>	1.097	
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> = 0.0336, wR <sub>2</sub> = 0.0952	
R indices (all data)	R <sub>1</sub> = 0.0341, wR <sub>2</sub> = 0.0956	



**Figure S9.**ORTEP drawing of the asymmetric unit of MOF **2a**.Thermal ellipsoids set to 50% probability level.



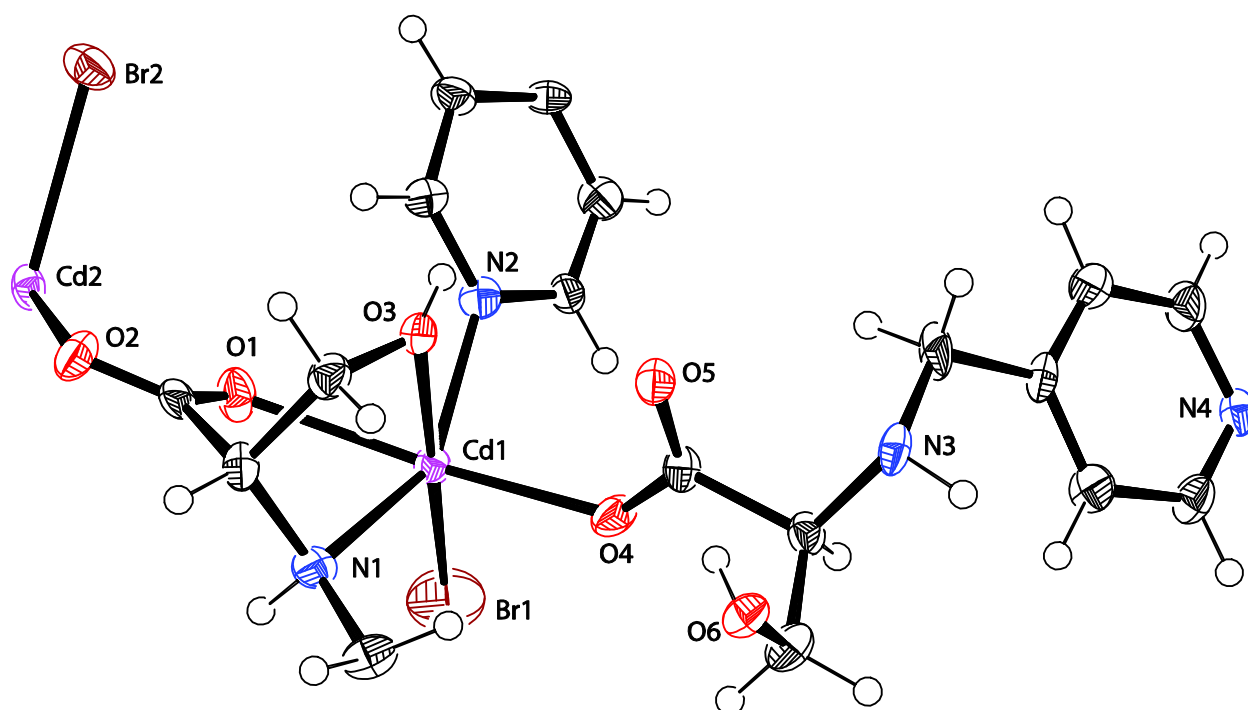


### Experimental and Refinement Details for MOF 2b

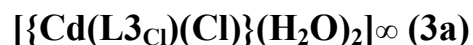
A colorless rod shaped crystal of **2b** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the lattice water molecules in and one side arm oxygen atoms of **2b** could not be located or fixed. MOF **2b** contains one ligand and one bromine atom and metal atom in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0506$  ( $F > 2\sigma F$ ) and  $wR2 = 0.1344$  (all data) with GOF = 1.067.

**Table S4. Crystal data and structure refinement for MOF 2b.**

Empirical formula	$C_{18} H_{21} Br_2 N_4 O_9 Cd_2$	
Formula weight	822.01	
CCDC No.	851356	
Temperature	296(2)K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 9.4628(12) \text{ Å}$	$\alpha = 90.00^\circ$
	$b = 15.1900(19) \text{ Å}$	$\beta = 110.630(2)^\circ$
	$c = 10.0319(12) \text{ Å}$	$\gamma = 90.00^\circ$
Volume	$1349.5(3) \text{ Å}^3$	
Z	2	
Density (calculated)	2.020	
Absorption coefficient	4.587	
F(000)	790	
Reflections collected	6139	
Independent reflections	5890	
Goodness-of-fit on F <sup>2</sup>	1.067	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0485, wR2 = 0.1325$	
R indices (all data)	$R1 = 0.0506, wR2 = 0.1344$	



**Figure S10.**ORTEP drawing of the asymmetric unit of MOF **2b**.Thermal ellipsoids set to 50% probability level.

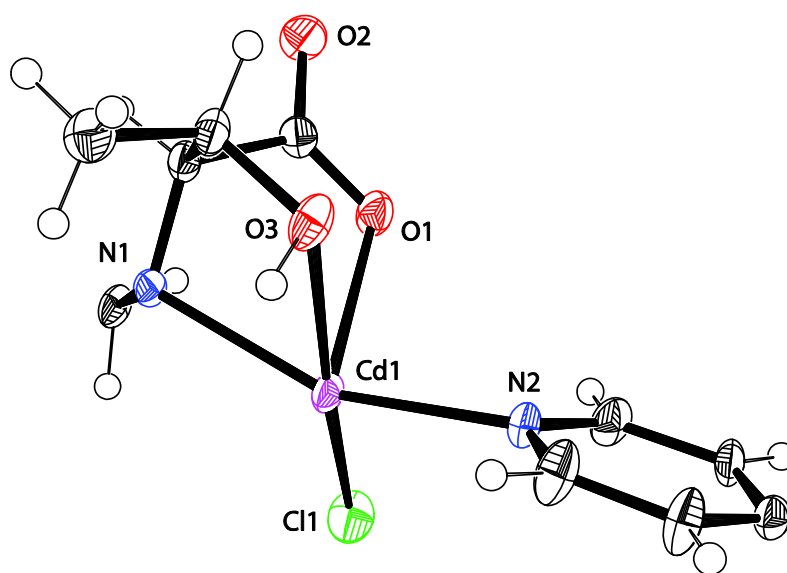


### Experimental and Refinement Details for MOF **3a**

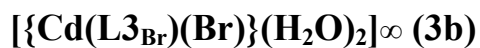
A colorless rod shaped crystal of **3a** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the lattice water molecules of **3a** could not be located or fixed. MOF **3a** contains one ligand and one chloride atom and metal atom in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0189$  ( $F > 2\sigma F$ ) and  $wR2 = 0.0501$  (all data) with GOF = 1.021.

**Table S5. Crystal data and structure refinement for MOF 3a.**

Empirical formula	$C_{10} H_{13} Cl N_2 O_5 Cd$	
Formula weight	389.08	
CCDC No.	851357	
Temperature	296(2)K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 17.661(15) \text{ Å}$	$\alpha = 90.00^\circ$
	$b = 17.661(15) \text{ Å}$	$\beta = 110.5280(10)^\circ$
	$c = 10.5104(16) \text{ Å}$	$\gamma = 90.00^\circ$
Volume	$712.45(11) \text{ Å}^3$	
Z	2	
Density (calculated)	1.814	
Absorption coefficient	1.736	
F(000)	384	
Reflections collected	2583	
Independent reflections	2571	
Goodness-of-fit on F <sup>2</sup>	1.021	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0189, wR2 = 0.0501$	
R indices (all data)	$R1 = 0.0190, wR2 = 0.0501$	



**Figure S11.**ORTEP drawing of the asymmetric unit of MOF **3a**.Thermal ellipsoids set to 50% probability level.



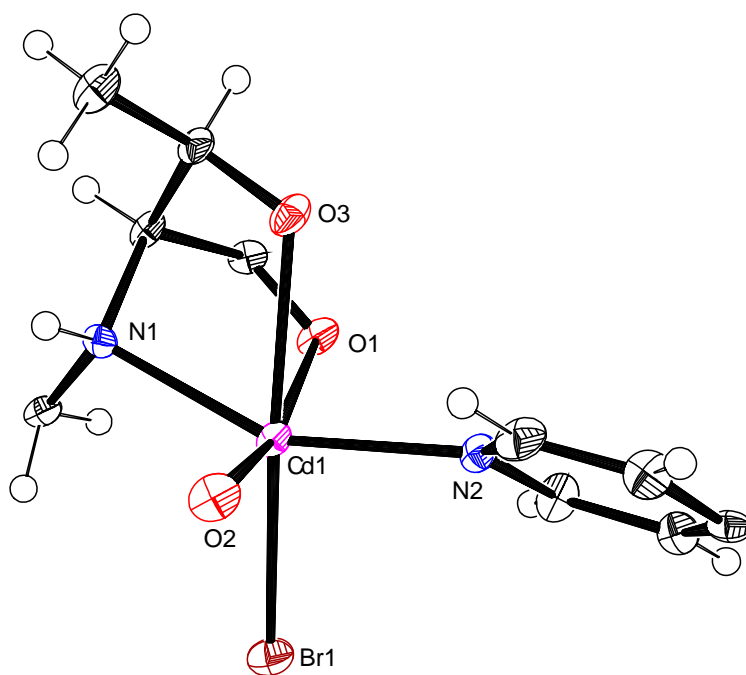
### Experimental and Refinement Details for MOF **3b**

A colorless rod shaped crystal of **3b** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the lattice water molecules and side arm oxygen atoms of **3b** could not be located or fixed. MOF **3b** contains one ligand and one bromine atom and metal atom in the asymmetric unit. It should be noted that other supporting characterization data are consistent with the crystal structure. Final full matrix least-squares refinement on  $F^2$  converged to  $R1 = 0.0630$  ( $F > 2\sigma F$ ) and  $wR2 = 0.1450$  (all data) with GOF = 1.081.

**Table S6. Crystal data and structure refinement for MOF 3b.**

Empirical formula	C <sub>10</sub> H <sub>13</sub> Br N <sub>2</sub> O <sub>5</sub> Cd	
Formula weight	432.53	
CCDC No.	851358	
Temperature	296(2)K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 <sub>1</sub>	
Unit cell dimensions	<i>a</i> = 7.9689(12) Å	$\alpha = 90.00^\circ$
	<i>b</i> = 10.7406(15) Å	$\beta = 110.444(13)^\circ$
	<i>c</i> = 8.9501(13) Å	$\gamma = 90.00^\circ$
Volume	717.80(18) Å <sup>3</sup>	
<i>Z</i>	2	
Density (calculated)	2.001	
Absorption coefficient	4.320	
F(000)	418	
Reflections collected	2245	
Independent reflections	2197	
Goodness-of-fit on F <sup>2</sup>	1.081	
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> = 0.0625, wR <sub>2</sub> = 0.1446	
R indices (all data)	R <sub>1</sub> = 0.0630, wR <sub>2</sub> = 0.1450	





**Figure S12.**ORTEP drawing of the asymmetric unit of MOF **3b**. Thermal ellipsoids set to 50% probability level.

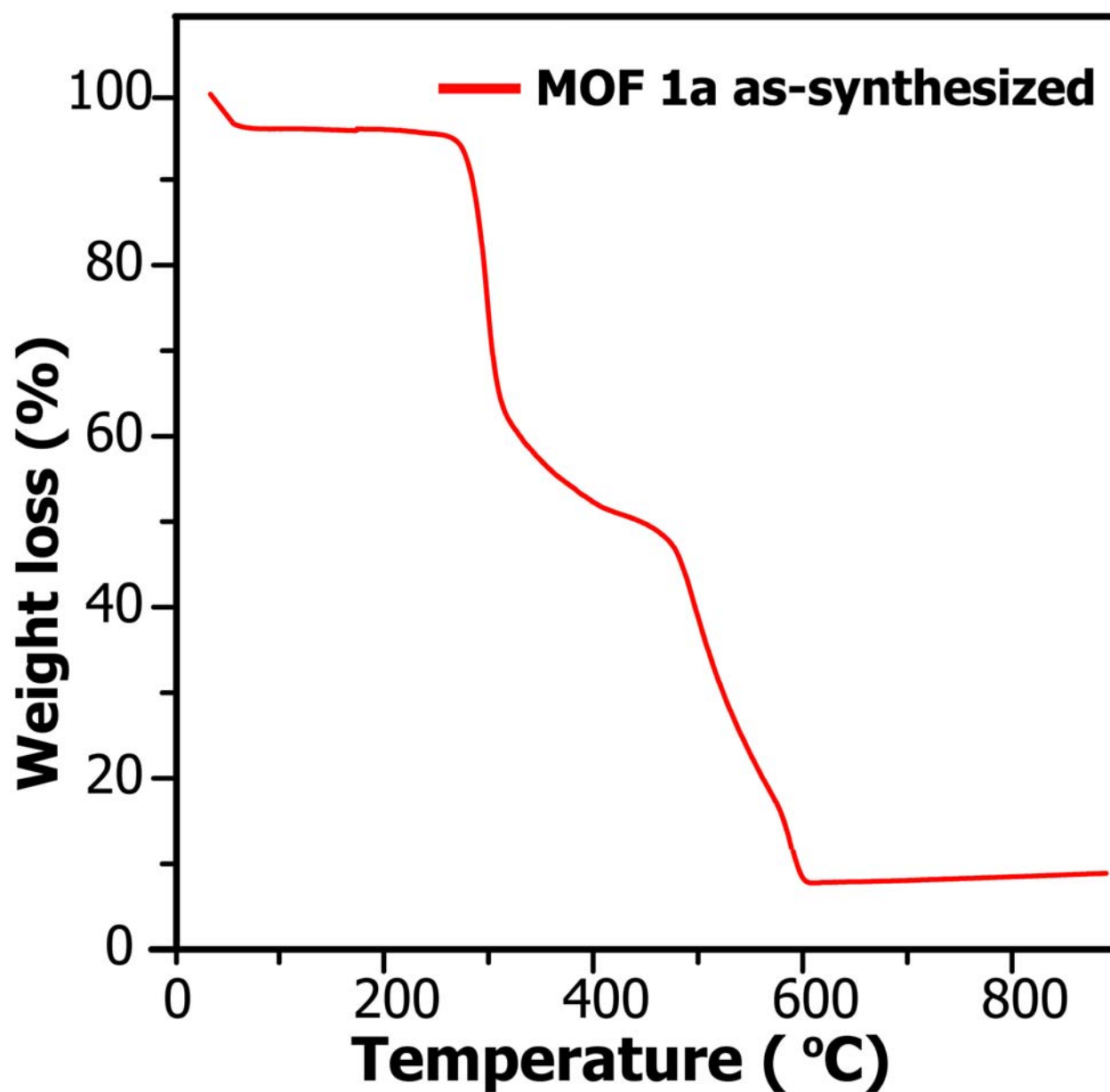
**Table S7. Crystal Data and Structure Refinement for the MOFs (1a-3b) in this study.**

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>
Formula	C <sub>12</sub> H <sub>17</sub> Cl N <sub>2</sub> O <sub>3</sub> Cd	C <sub>12</sub> H <sub>17</sub> Br N <sub>2</sub> O <sub>2</sub> Cd	C <sub>9</sub> H <sub>11</sub> Cl N <sub>2</sub> O <sub>4</sub> Cd	C <sub>18</sub> H <sub>21</sub> Br <sub>2</sub> N <sub>4</sub> O <sub>9</sub> Cd <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> Cl N <sub>2</sub> O <sub>5</sub> Cd	C <sub>10</sub> H <sub>13</sub> Br N <sub>2</sub> O <sub>5</sub> Cd
<i>Mr</i>	385.14	413.59	359.06	822.01	389.08	432.53
CCDC No.	851353	851354	851355	851356	851357	851358
Temperature	296(2)K	296(2)K	296(2)K	296(2)K	296(2)K	296(2)K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å )	7.123(3)	7.2398(6)	5.8751(17)	9.4628(12)	7.9060(7)	7.9689(12)
<i>b</i> (Å )	13.896(5)	13.7041(11)	15.067(4)	15.1900(19)	10.7338(10)	10.7406(15)
<i>c</i> (Å )	15.893(6)	16.5286(13)	16.416(5)	10.0319(12)	8.9647(8)	8.9501(13)
$\beta$ (°)				110.630(2)	110.5280(10)	110.444(13)
V[Å <sup>3</sup> ]	1573.1(11) Å <sup>3</sup>	1639.9(2)Å <sup>3</sup>	1453.1(7) Å <sup>3</sup>	1349.5(3) Å <sup>3</sup>	712.45(11) Å <sup>3</sup>	717.80(18) Å <sup>3</sup>
<i>Z</i>	4	4	4	2	2	2
$\rho$ /g cm <sup>-1</sup>	1.626	1.675	1.641	2.020	1.814	2.001
$\mu$ /mm <sup>-1</sup>	1.563	3.779	1.689	4.587	1.736	4.320
<i>F</i> (000)	768	808	704	790	384	418
Flack parameter	0.01(5)	0.0009(2)	0.0009(1)	0.055(14)	-0.02(2)	0.11(3)
Reflections collected	3677	3871	3420	6139	2583	2245
Independent reflections	3445	3568	3389	5890	2571	2197
GOF	1.033	1.066	1.097	1.067	1.021	1.081
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0434, <i>wR</i> <sub>2</sub> = 0.1059	<i>R</i> <sub>1</sub> = 0.0421, <i>wR</i> <sub>2</sub> = 0.1300	<i>R</i> <sub>1</sub> = 0.0336, <i>wR</i> <sub>2</sub> = 0.0952	<i>R</i> <sub>1</sub> = 0.0485, <i>wR</i> <sub>2</sub> = 0.1325	<i>R</i> <sub>1</sub> = 0.0189, <i>wR</i> <sub>2</sub> = 0.0501	<i>R</i> <sub>1</sub> = 0.0625, <i>wR</i> <sub>2</sub> = 0.1446
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0475, <i>wR</i> <sub>2</sub> = 0.1079	<i>R</i> <sub>1</sub> = 0.0461, <i>wR</i> <sub>2</sub> = 0.1342	<i>R</i> <sub>1</sub> = 0.0341, <i>wR</i> <sub>2</sub> = 0.0956	<i>R</i> <sub>1</sub> = 0.0506, <i>wR</i> <sub>2</sub> = 0.1344	<i>R</i> <sub>1</sub> = 0.0190, <i>wR</i> <sub>2</sub> = 0.0501	<i>R</i> <sub>1</sub> = 0.0630, <i>wR</i> <sub>2</sub> = 0.1450

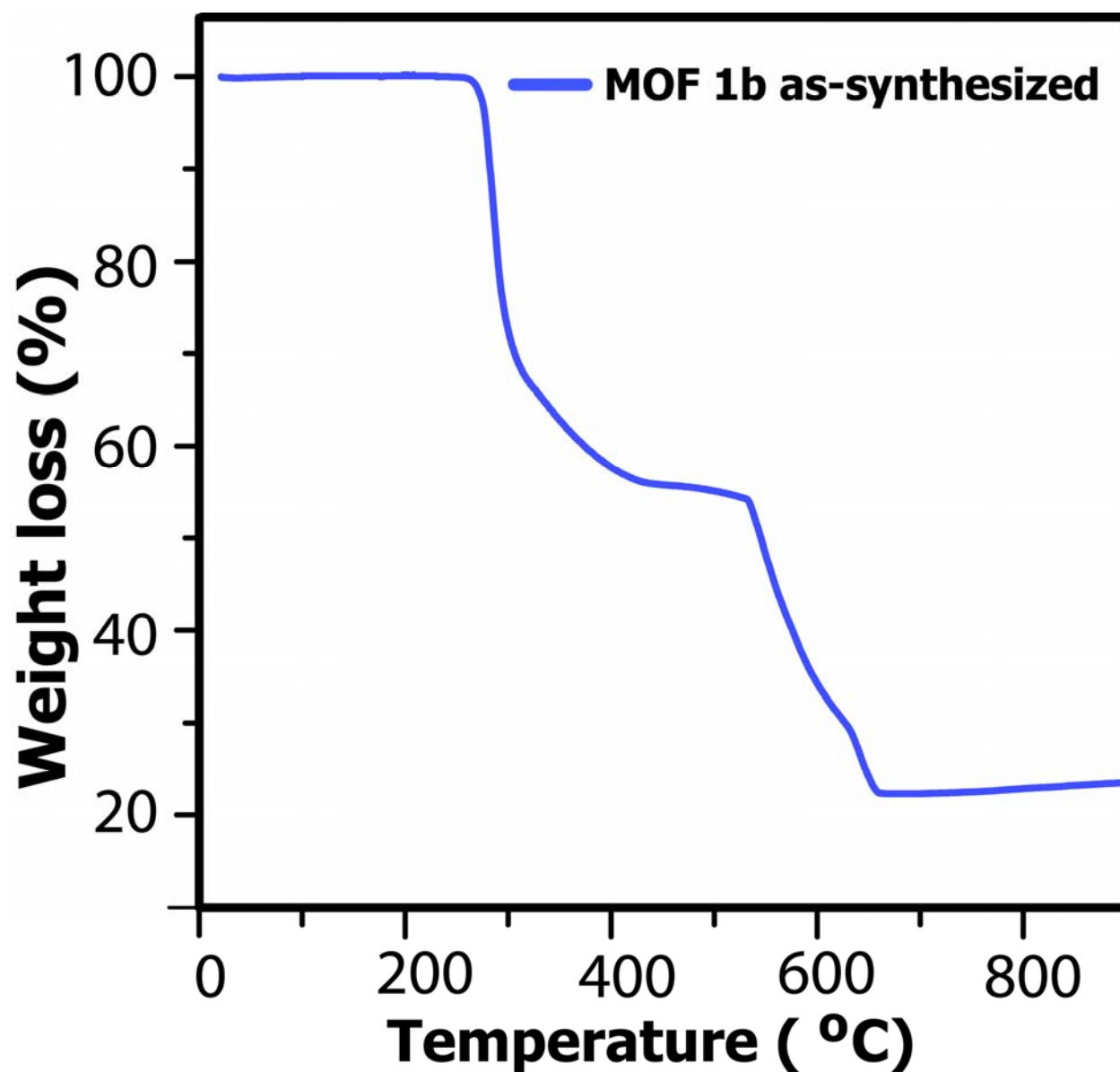
**Table S8. Selected bond lengths (Å) and Bond angles (°) for the MOFs (1a-3b).**

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>
Atoms	Bond Lengths(Å)	Bond Lengths(Å)	Bond Lengths(Å)	Bond Lengths(Å)	Bond Lengths(Å)	Bond Lengths(Å)
Cd1 N1	2.352(4)	2.372(4)	2.357(3)	2.364(7)	2.334(2)	2.332(7)
Cd1 N2	2.302(5)	2.312(5)	2.284(4)	2.277(7)	2.287(3)	2.302(7)
Cd1 O1	2.323(4)	2.303(5)	2.449(3)	2.357(6)	2.383(2)	2.386(8)
Cd 1 O2/O4	2.425(5)	2.215(5)	2.289(3)	2.287(5)	2.250(2)	2.243(8)
Cd 1 Cl/Br	2.4780(17)	2.6013(9)	2.4699(12)	2.6510(15)	2.5241(7)	2.6559(11)
Cd 1 O3			2.511(3)	2.486(6)	2.4898(17)	2.479(6)
	Bond Angles(°)	Bond Angles(°)	Bond Angles(°)	Bond Angles(°)	Bond Angles(°)	Bond Angles(°)
N2 Cd1 N1	104.16(16)	106.84(17)	107.82(13)	149.0(2)	155.42(7)	155.6(3)
N2 Cd1 O2/O4	86.66(18)	87.5(2)	87.63(12)	100.0(2)	88.18(9)	87.3(3)
N1 Cd1 O2/O4	161.91(18)	159.41(19)	139.43(11)	95.8(2)	99.72(12)	99.9(4)
N2 Cd1 O1	94.09(15)	93.66(18)	87.28(11)	86.6(2)	94.36(8)	94.9(3)
N1 Cd1 O1	71.31(13)	71.71(14)	66.46(11)	69.3(2)	72.49(11)	72.4(3)
O2/O4 Cd1 O1	93.78(18)	93.1(2)	77.47(10)	156.6(2)	165.52(8)	165.0(3)
N2 Cd1 Cl1	96.68(13)	96.20(15)	102.56(10)	97.32(16)	95.10(6)	94.2(2)
N1 Cd1 Cl/Br	90.15(11)	87.40(11)	105.96(9)	107.30(16)	107.12(6)	107.98(17)
O2 Cd1 Cl/Br	103.14(15)	106.05(18)	106.80(8)	96.34(15)	95.56(6)	96.4(2)
O1 Cd1 Cl/Br	160.40(10)	158.74(9)	169.30(7)	105.15(17)	98.40(6)	98.28(18)
N2 Cd1 O3			169.55(11)	83.9(2)	85.78(7)	98.28(18)
O2 Cd1 O3			86.64(10)	83.09(18)	93.58(10)	93.4(3)
N1 Cd1 O3			71.56(11)	71.7(2)	70.61(6)	70.8(2)
O1 Cd1 O3			82.95(9)	75.2(2)	72.44(9)	72.0(3)
Cl/Br Cd1 O3			87.48(8)	178.75(15)	170.84(8)	170.2(3)

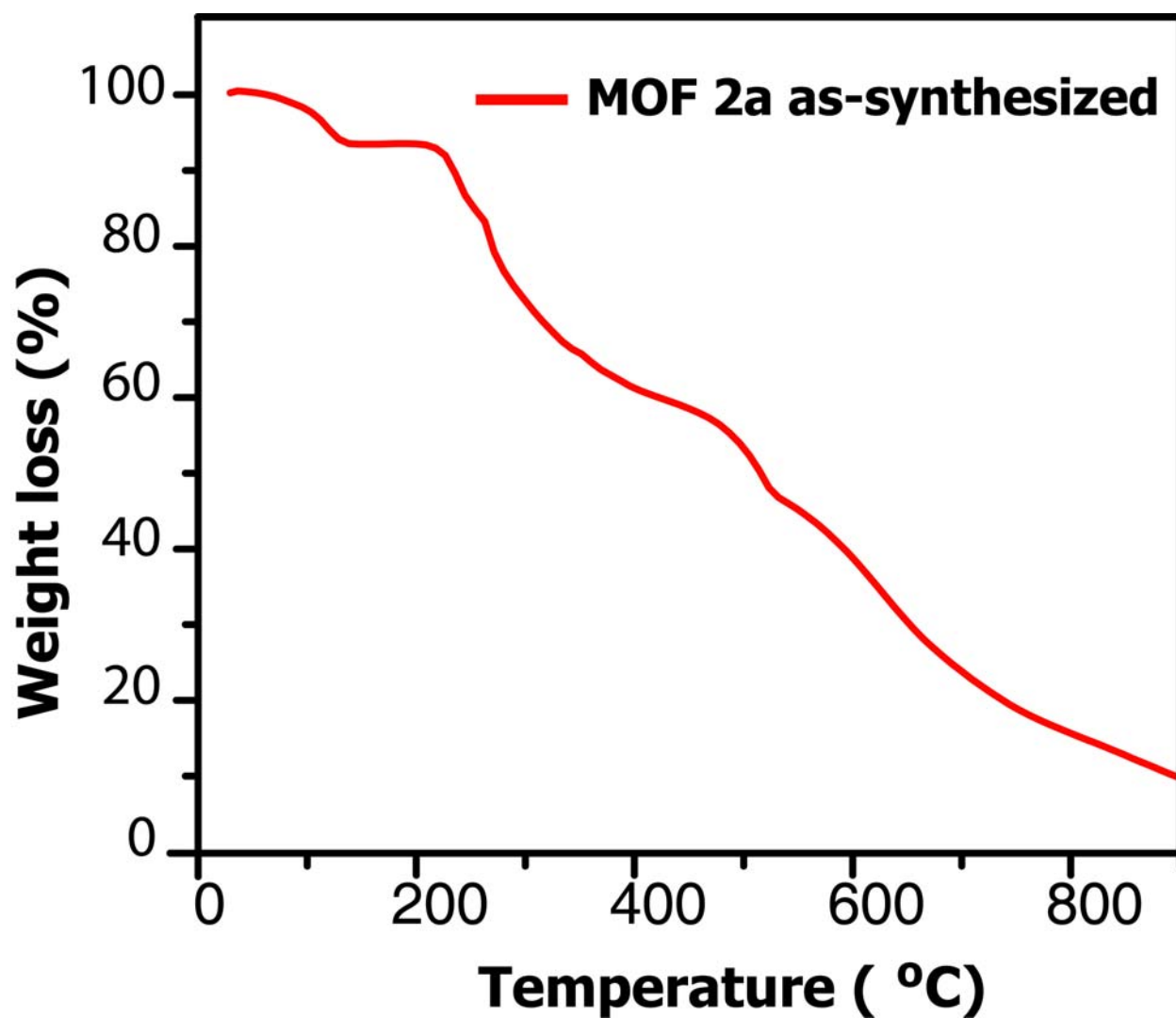
### Section S3. Thermal stability and TGA data of MOFs:



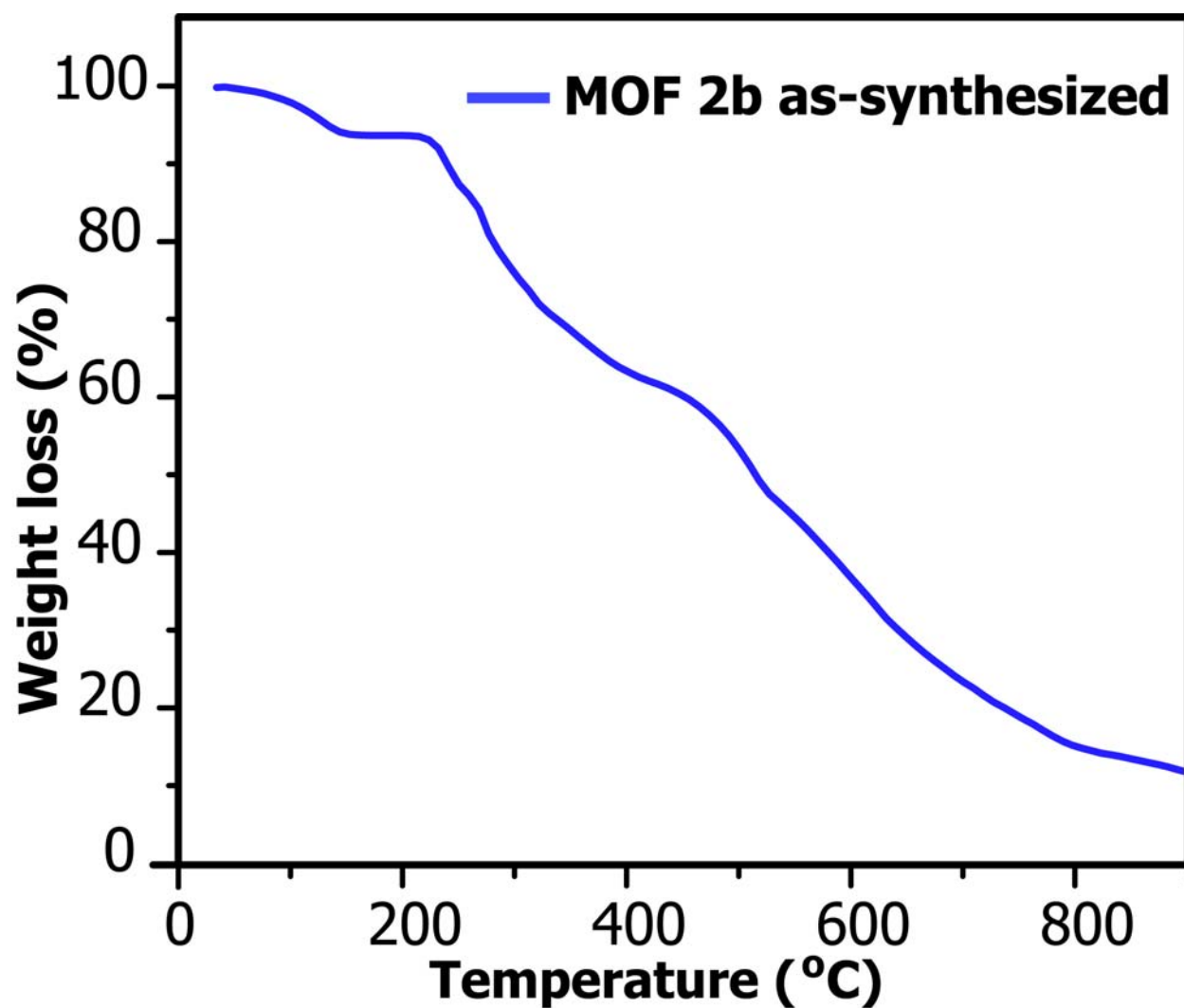
**Figure S13.** Thermal Gravimetric analysis (TGA) of MOF 1a showing a gradual loss in lattice water molecule between the temperature range of 40-80 °C with a stability of framework integrity upto 270 °C.



**Figure S14.** Thermal Gravimetric analysis (TGA) of MOF **1b** showing no weight loss at initial stage (40-80 °C) due to absence of lattice water molecule with a stability of the framework architecture upto 270 °C.

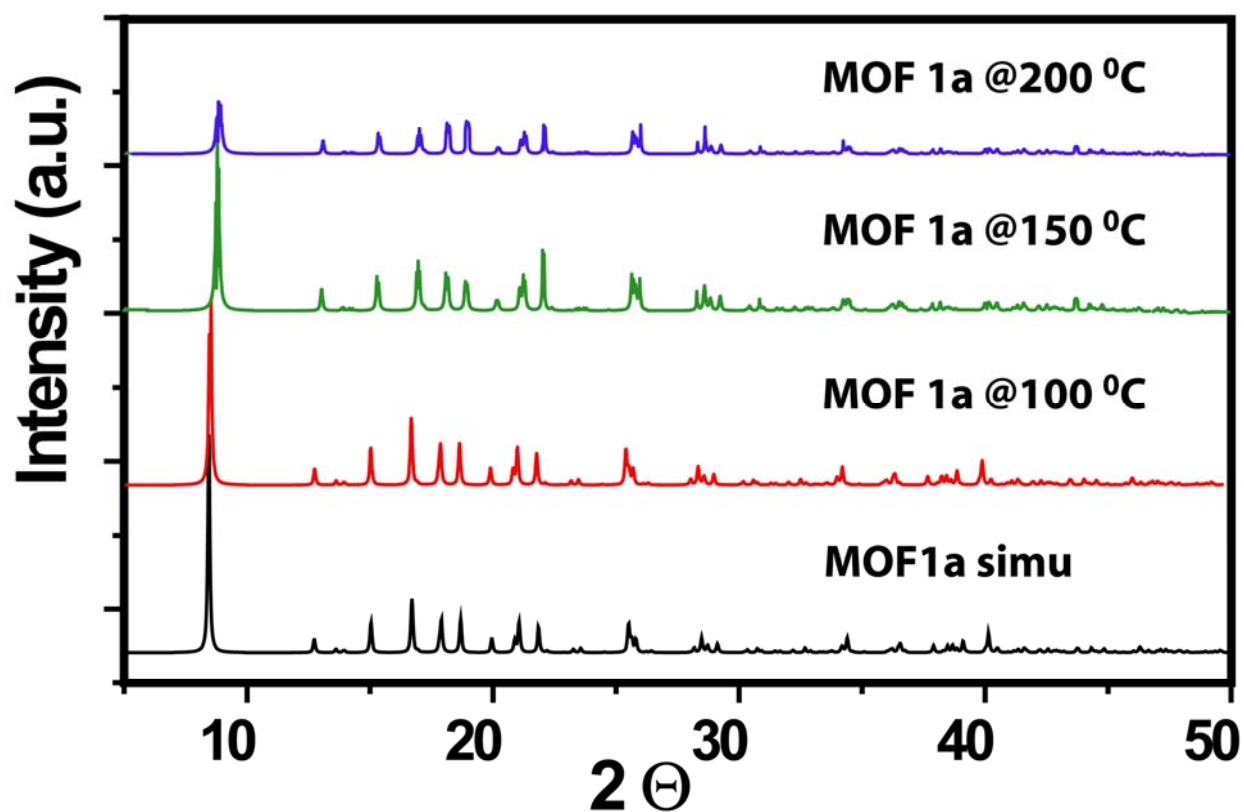


**Figure S15.** Thermal Gravimetric analysis (TGA) of MOF **2a** showing a gradual loss of lattice water molecule between the temperature range of 40-100 °C with a stability of the framework upto 270 °C.



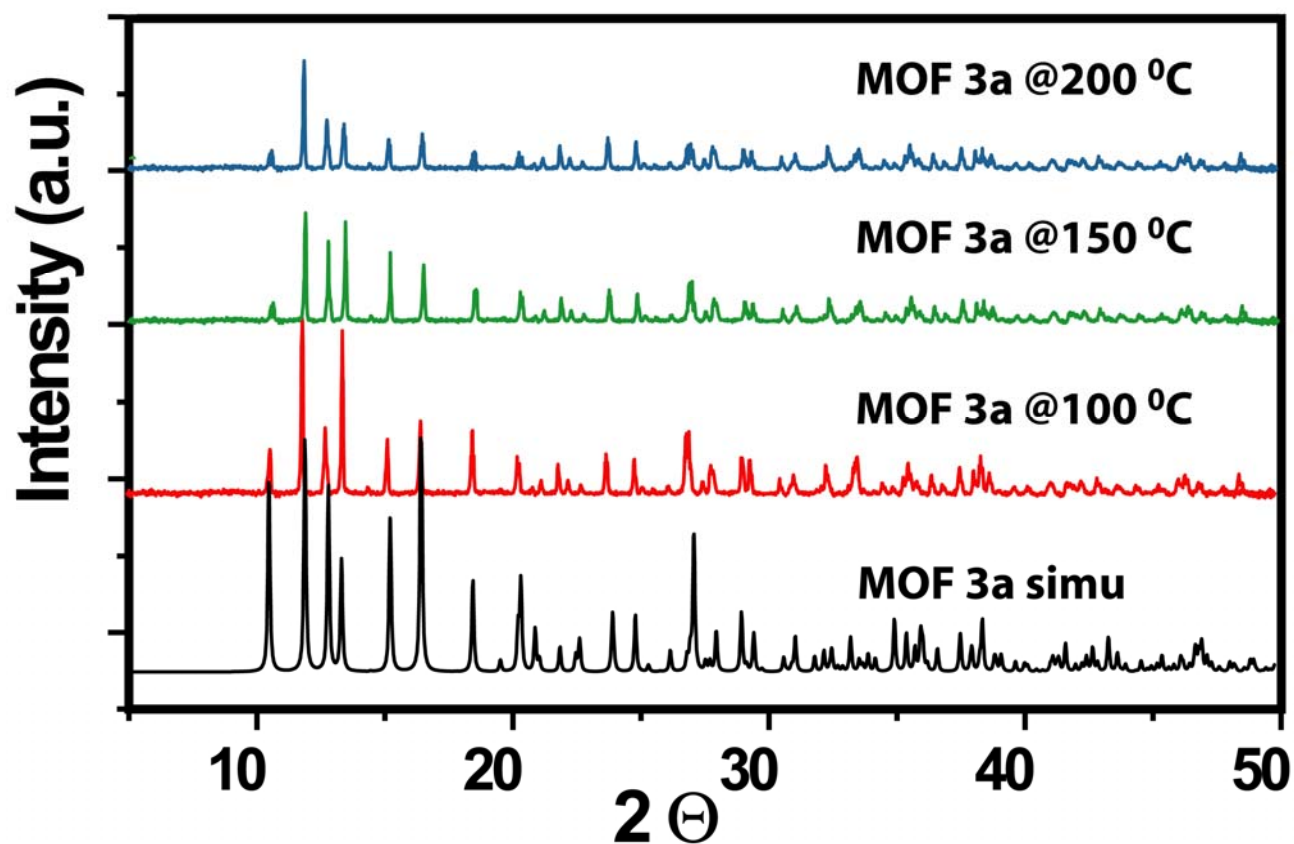
**Figure S16.** Thermal Gravimetric analysis (TGA) of MOF **2b** showing a gradual weight loss due to escape of lattice water molecule between the temperature range of 40-100 °C, with a stability of the molecular framework upto 270 °C.

### Variable Temperature Powder XRD of the MOFs:

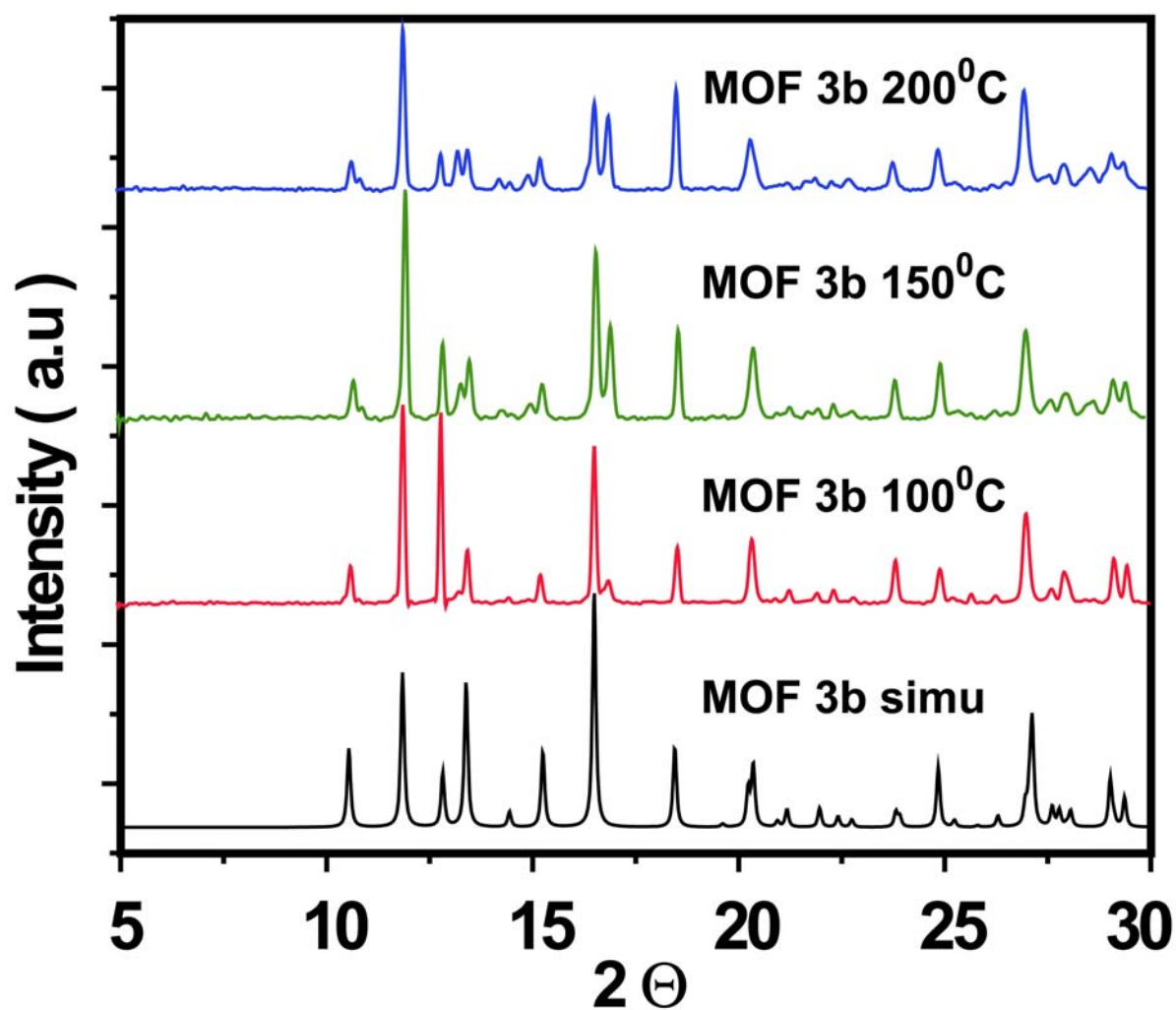


**Figure S17:** Variable temperature Powder XRD of MOF **1a** upto 200 °C showing significant agreement between simulated and experimental pattern, which alludes to structural rigidity as well as retention of crystallinity at elevated temperature ranges.



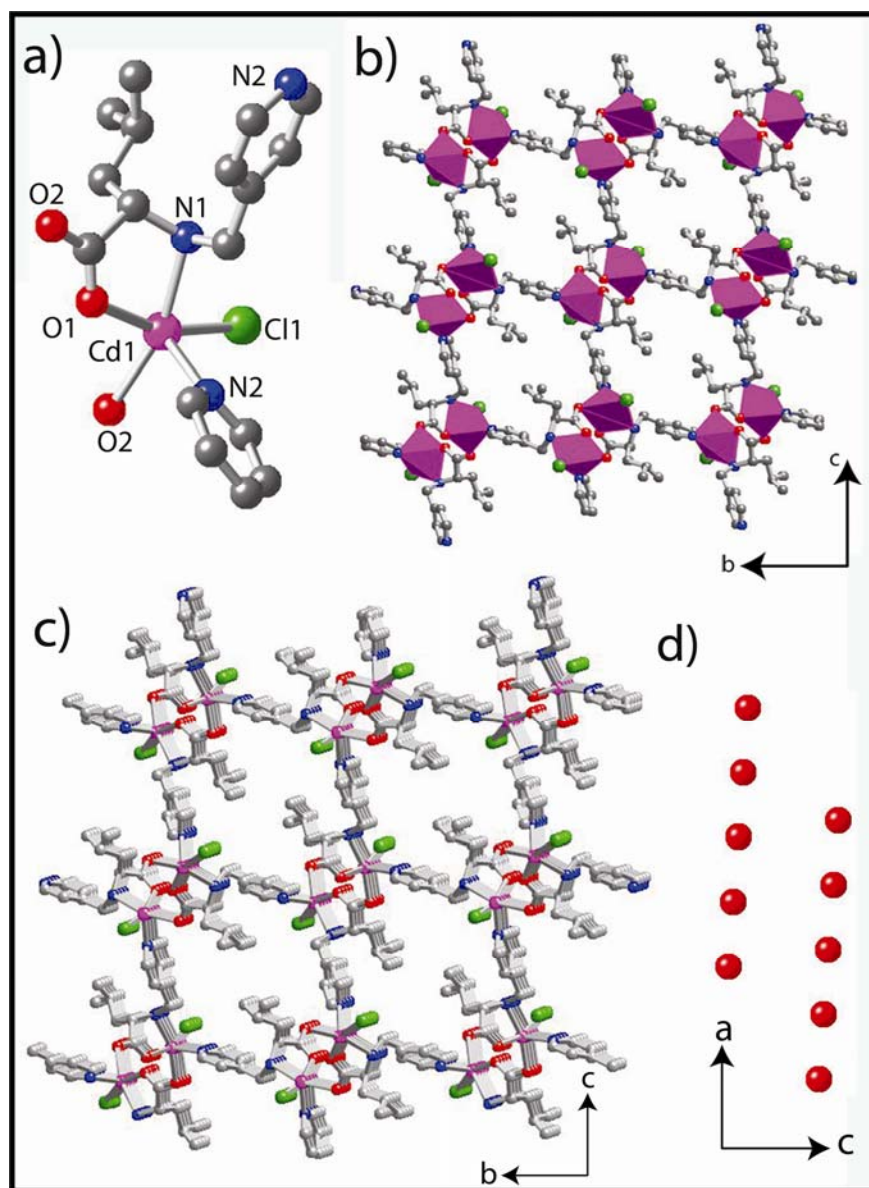


**Figure S18:** Variable temperature Powder XRD of MOF **3a** upto 200 °C showing significant agreement between simulated and experimental pattern, which alludes to structural rigidity as well as retention of crystallinity at elevated temperature ranges. However peak splitting at  $\theta = 27.5^\circ$  refers flexibility of the two dimensional layers.

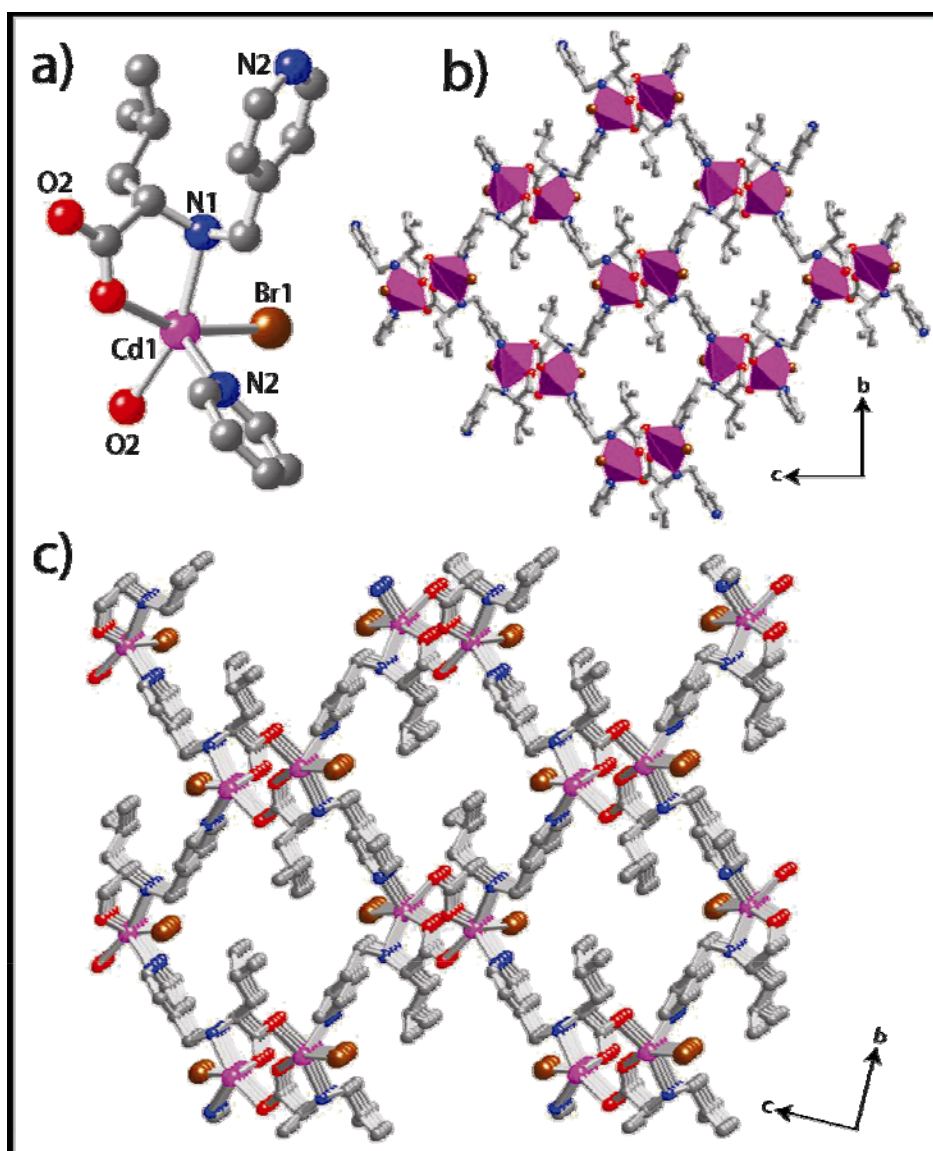


**Figure S19:** Variable temperature Powder XRD of MOF **3b** upto 200 °C showing significant agreement between simulated and experimental pattern, which alludes to structural rigidity as well as retention of crystallinity at elevated temperature ranges. However peak splitting at  $\theta = 16.5^\circ$  refers flexibility of the two dimensional layers.

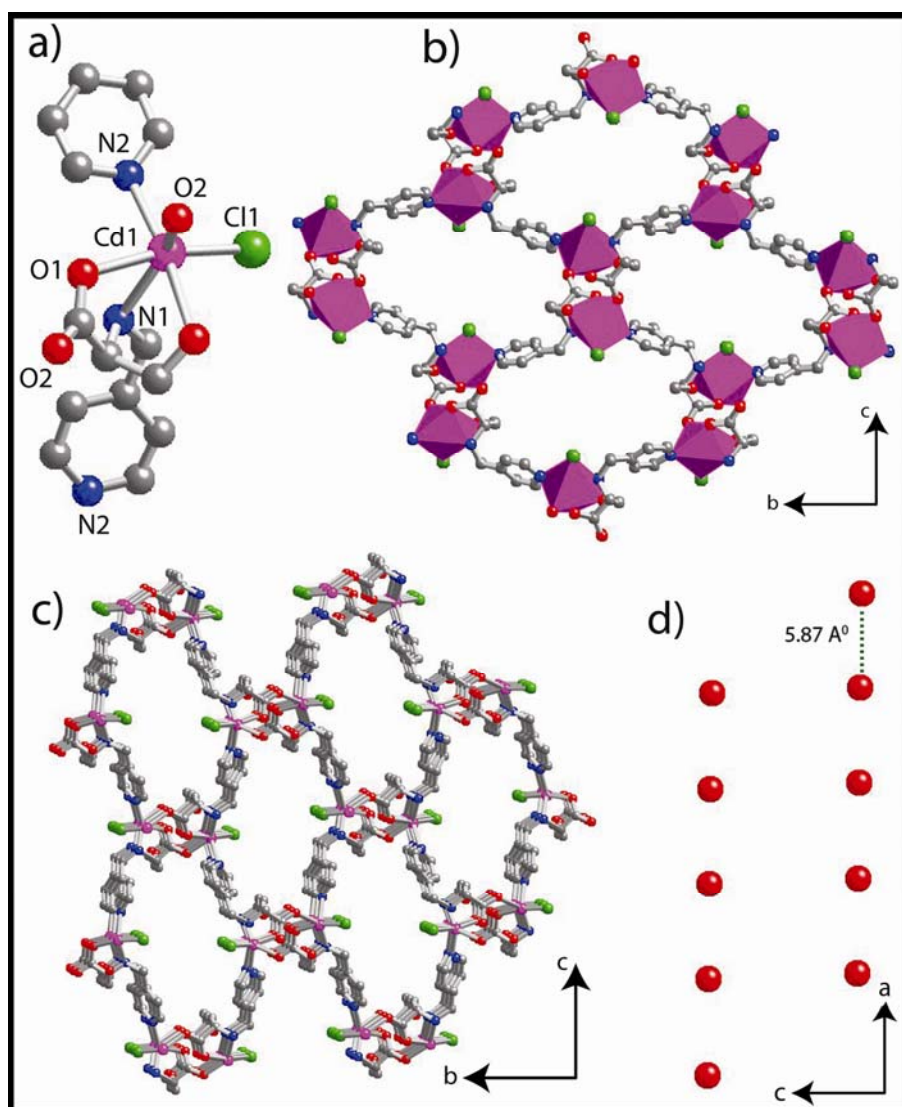
## Section S4. Lattice figures of the MOFs (1a-3b)



**Figure S20.** (a) SBU representation of the MOF **1a**. (b) Polyhedra representation of lattice **1a** viewed down the a-axis. Pink polyhedra represent Cadmium centers, and chlorine atoms are shown as green balls. (c) 3D Lattice arrangement of **1a**, showing a 1D pore along the a-axis. (d) lattice water arrangements showing along b-axis.

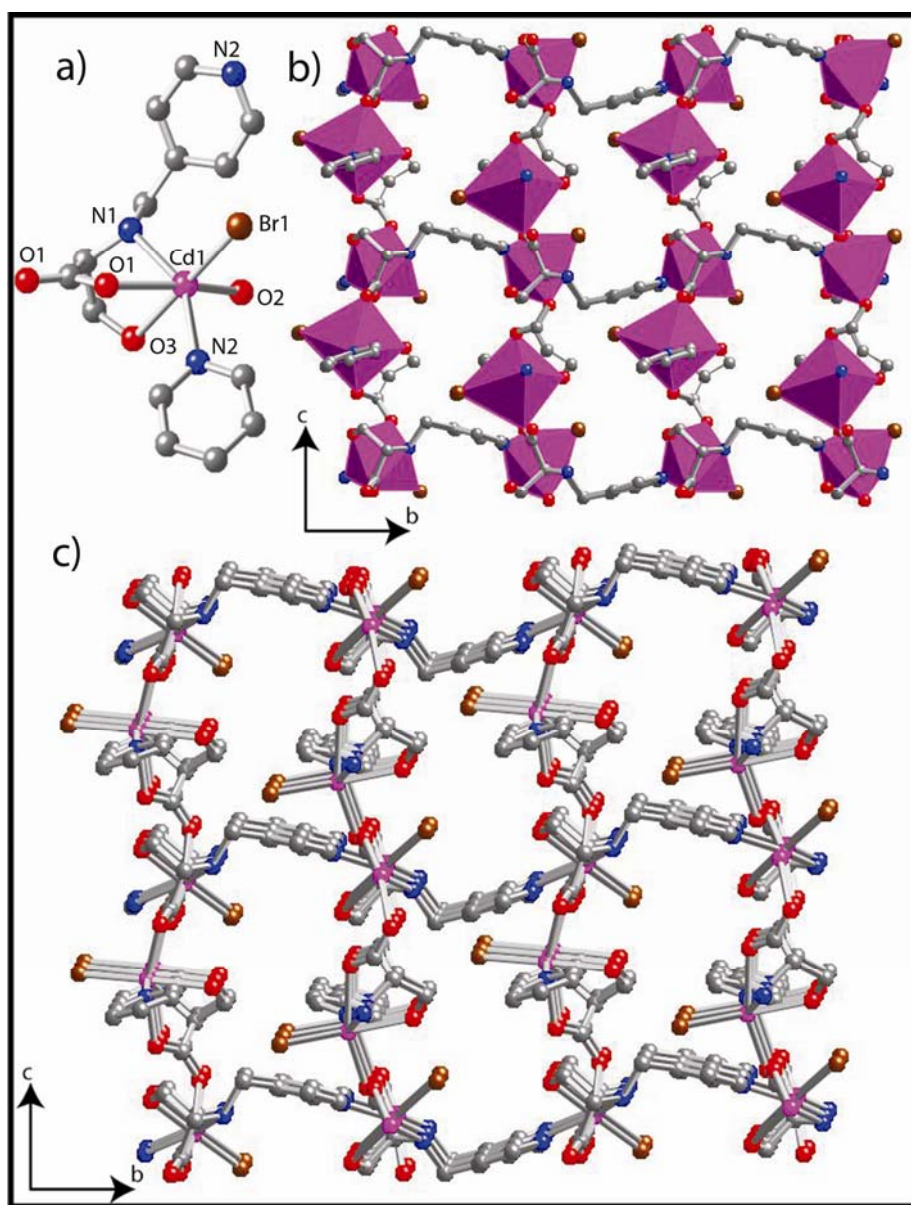


**Figure S21.** (a) SBU representation of the MOF **1b**. (b) Polydehra representation of lattice **1b** viewed down the a-axis. Pink polyhedra represent Cadmium centers, and bromine atoms are shown as gray balls. (c) 3D Lattice arrangement of **1b**, showing a 1D pore along the a-axis and isopropyl group of the side arm has pointed towards pore.

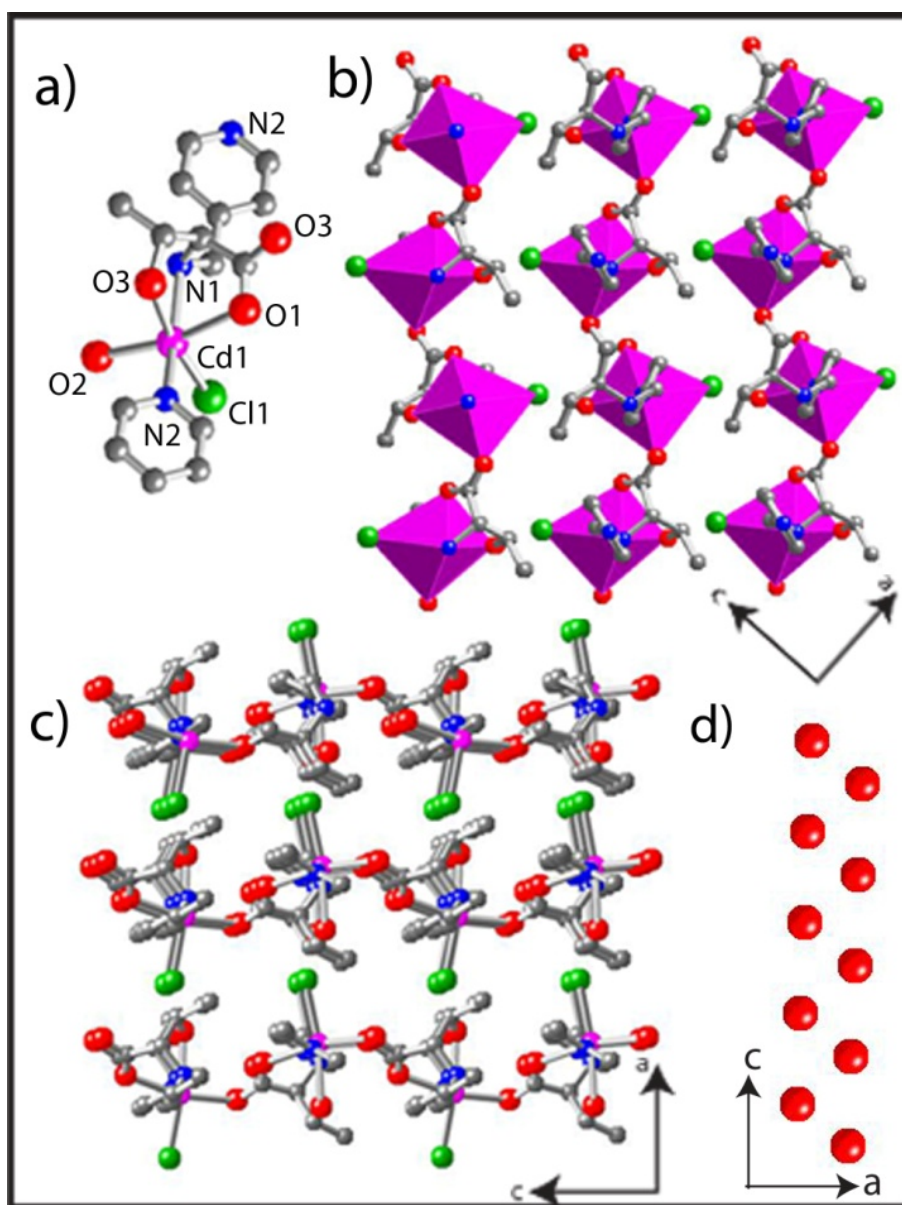


**Figure S22.** (a) SBU representation of the MOF **2a**. (b) Polydehbra representation of lattice **2a** viewed down the a-axis. Pink polyhedra represent Cadmium centers, and chlorine atoms are shown as green balls. (c) 3D Lattice arrangement of **2a**, showing a 1D pore along the a-axis. (d) lattice water arrangements showing along b-axis.

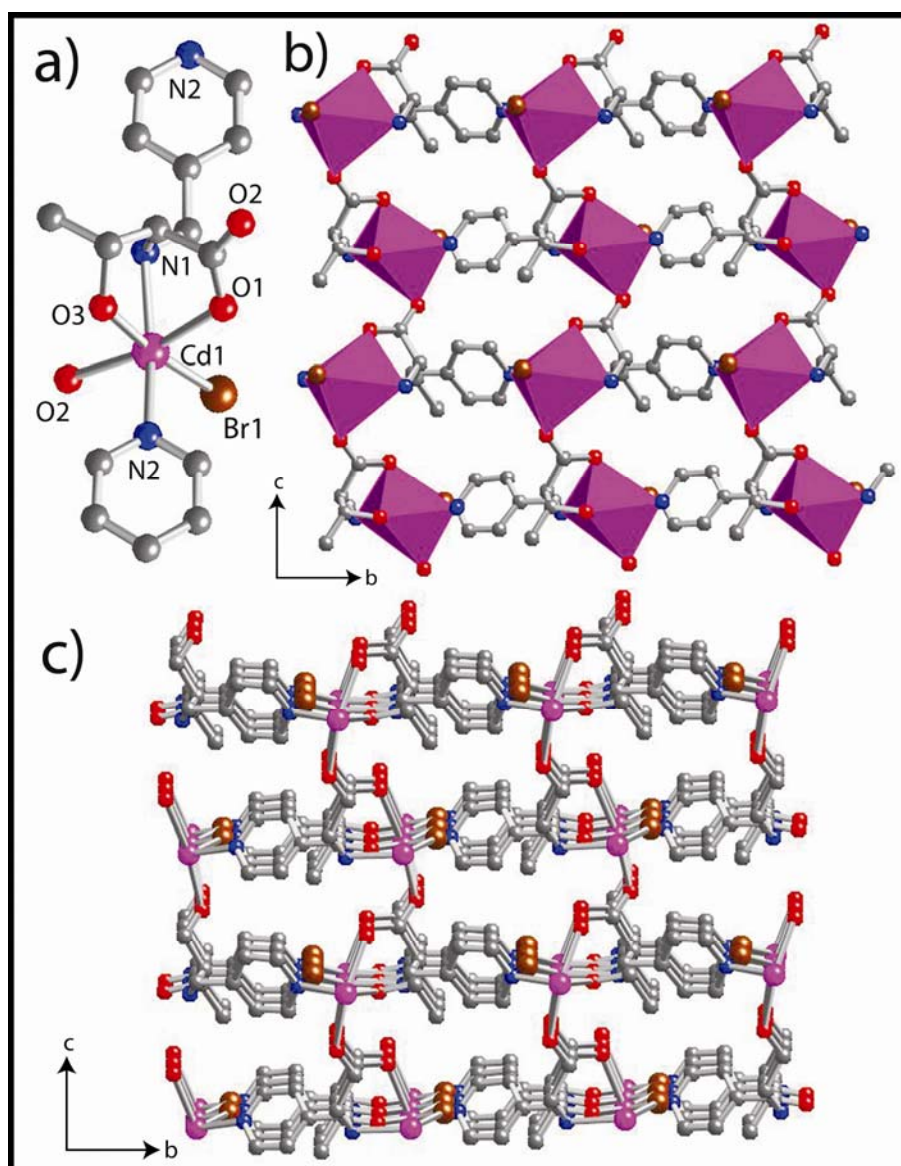




**Figure S23.** (a) SBU representation of the MOF **2b**. (b) Polydehbra representation of lattice **2b** viewed down the a-axis. Pink polyhedra represent Cadmium centers, and bromine atoms are shown as gray balls. (c) 3D Lattice arrangement of **2b**, showing a 1D pore along the a-axis.

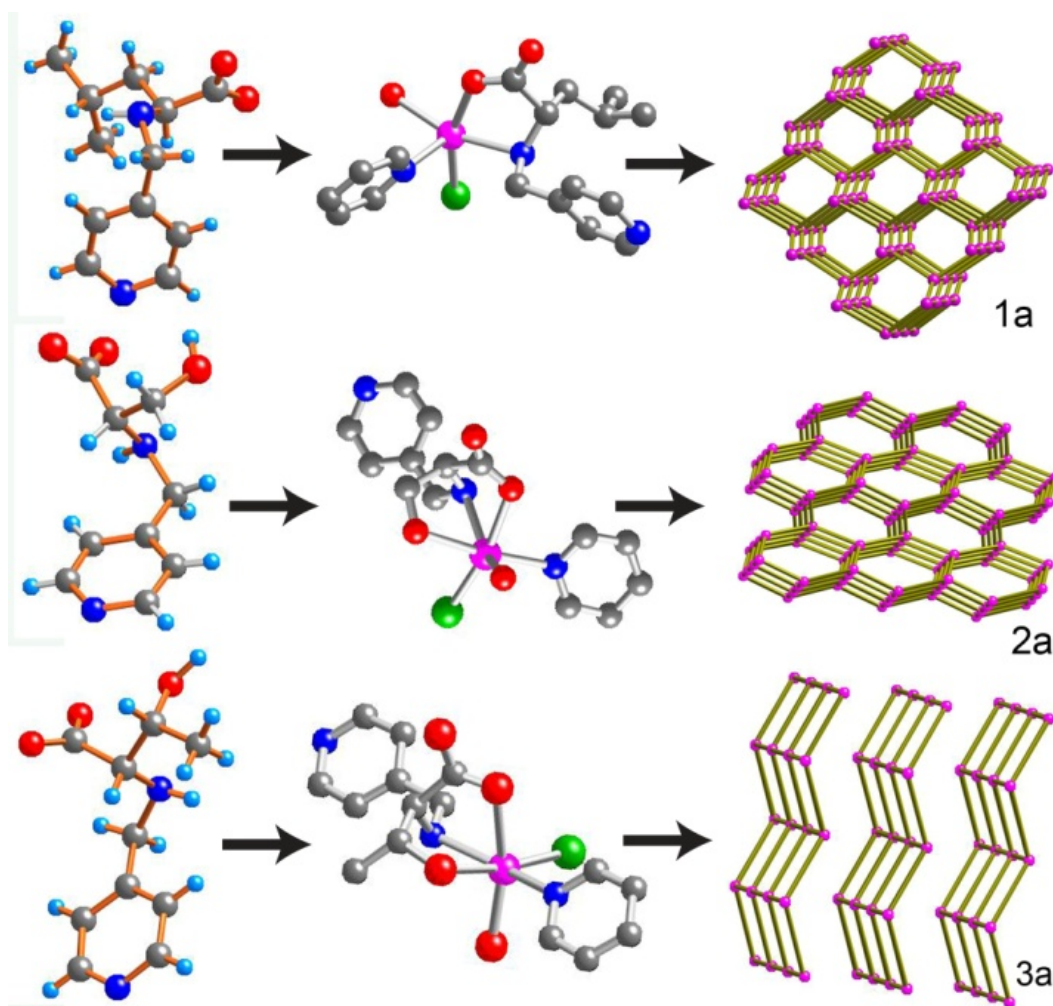


**Figure S24.** (a) SBU representation of the MOF **3a**. (b) Polyhedra representation of lattice **3a** viewed down the b-axis. Pink polyhedra represent Cadmium centers, and chlorine atoms are shown as green balls. (c) 3D Lattice arrangement of **3a**, showing a 1D pore along the b-axis. (d) lattice water arrangements showing along b-axis.

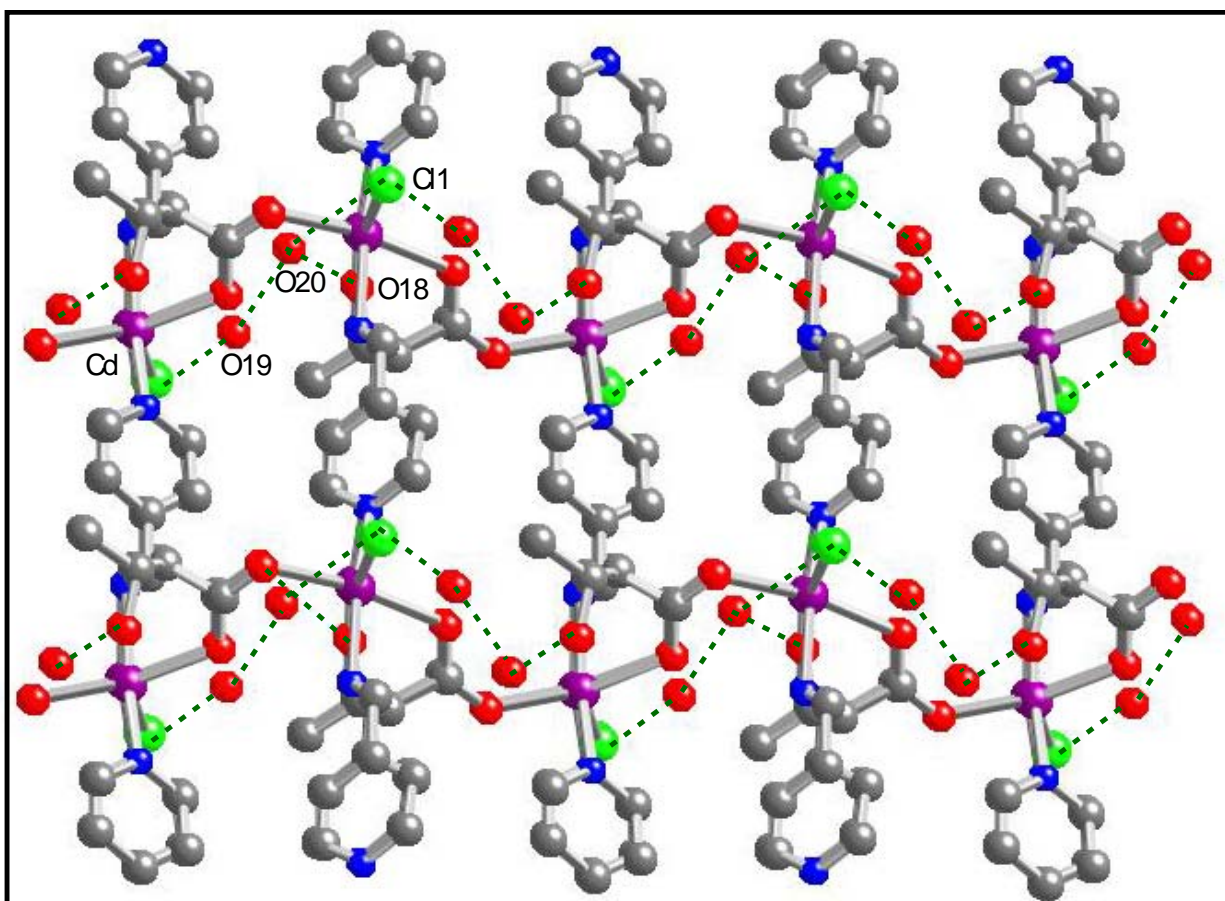


**Figure S25.** (a) SBU representation of the MOF **3b**. (b) Polydehra representation of lattice **3b** viewed down the a-axis. Pink polyhedra represent Cadmium centers, and chlorine atoms are shown as green balls. (c) 3D Lattice arrangement of **3b**, showing a 1D pore along the a-axis.





**Figure S26.** (a) Comparison of MOFs **1a**, **2a**, and **3a** with their links, SBUs, topological simplification model showing different lattice arrangements.



**Figure S27.** Hydrogen bonding representation of MOF **3a**. All solvent water molecules are forming a chain by different H-bonding with halogen atoms and there is a hydrophilic and hydrophobic separation.

Section S5. Water sorption data for the MOFs:

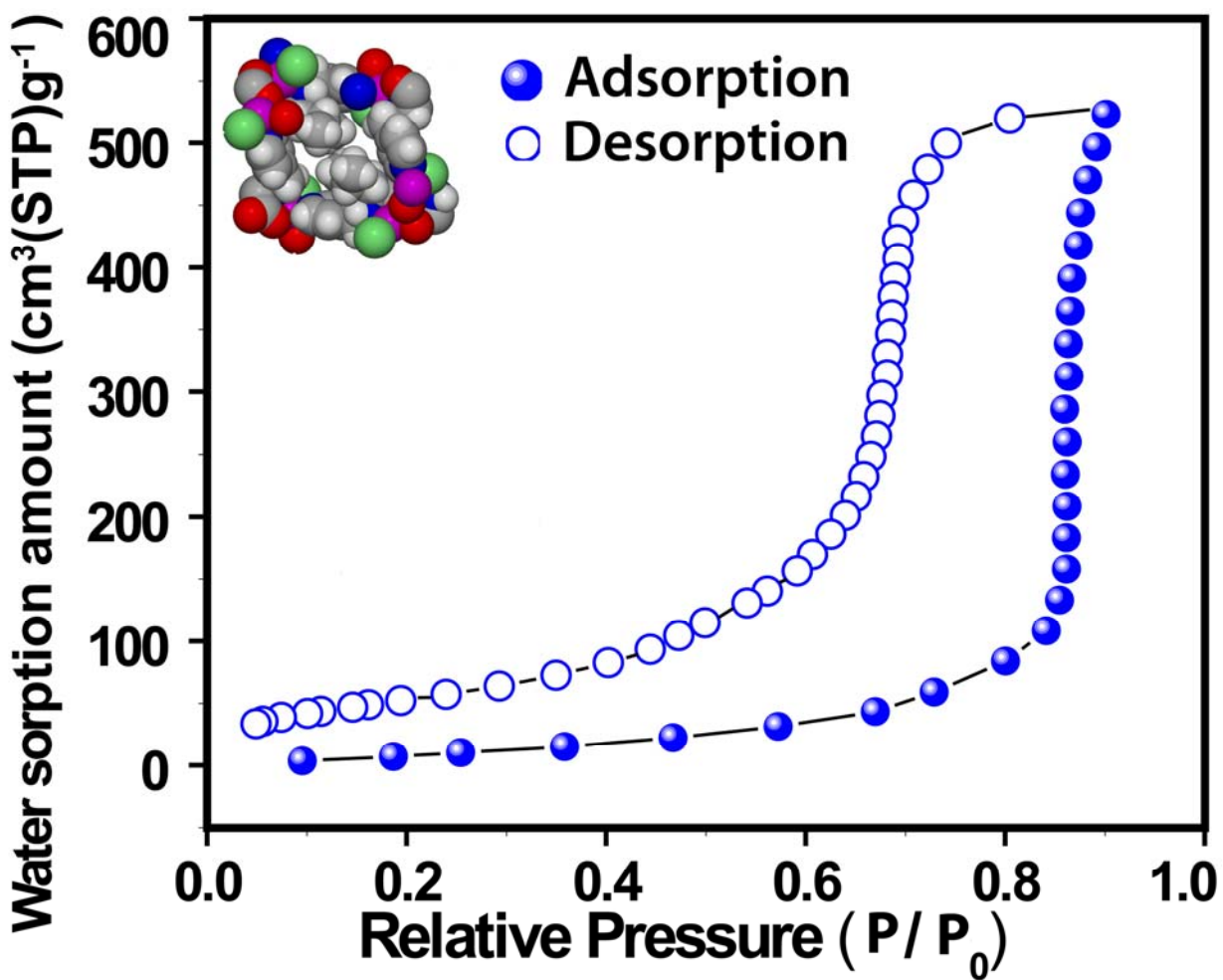


Figure S28: Water sorption isotherm for MOF 1a.

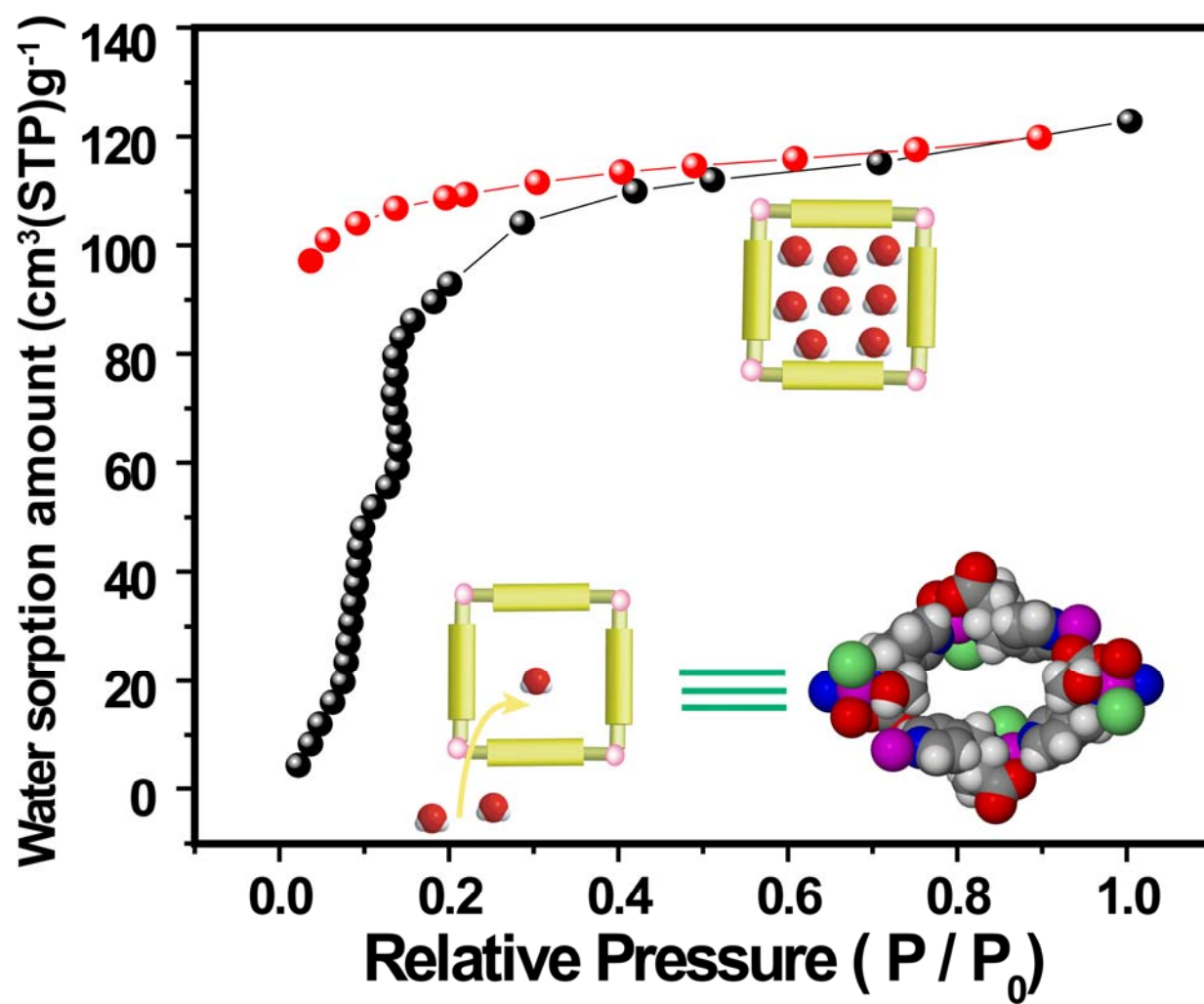


Figure S29: Water sorption isotherm for MOF 2a.

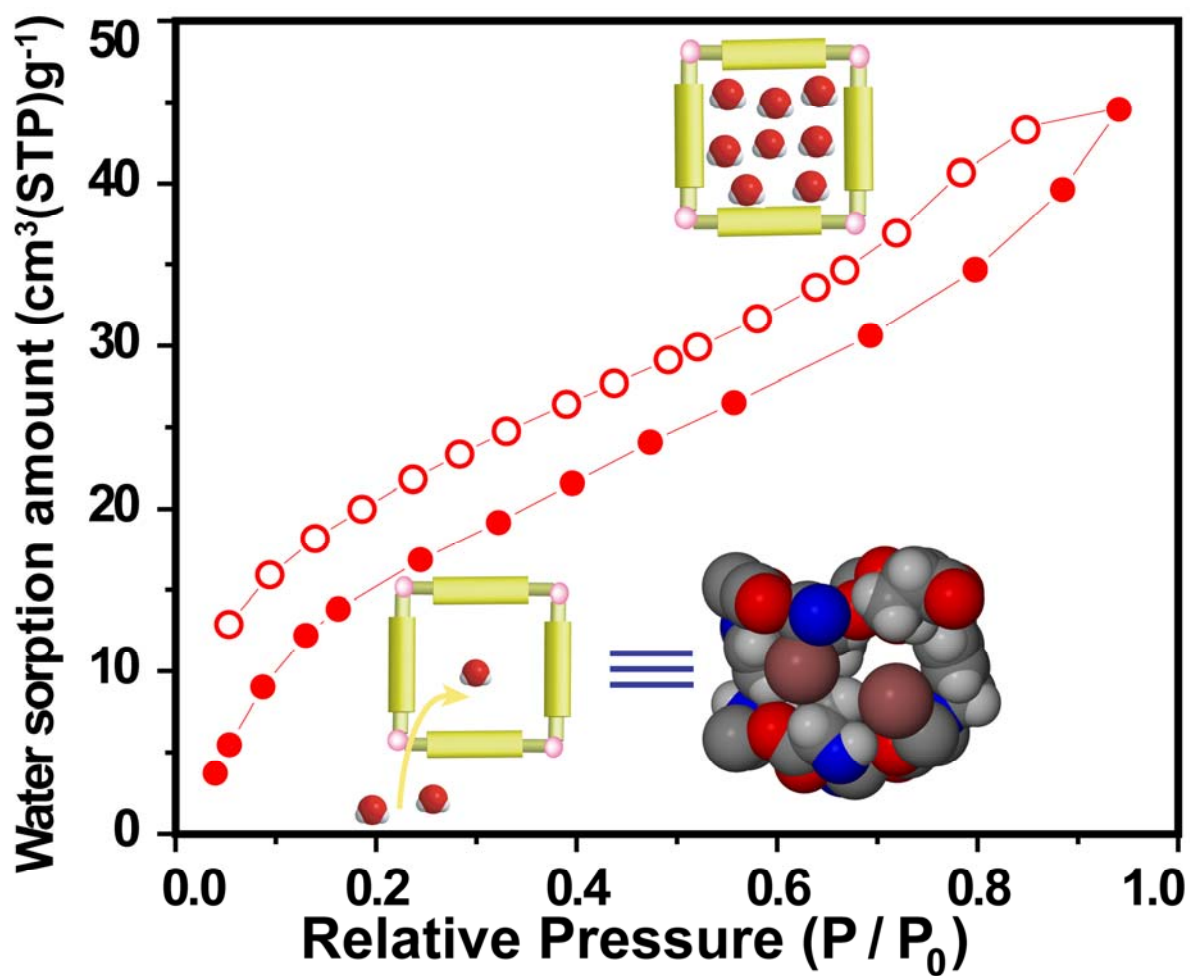


Figure S30: Water sorption isotherm for MOF 2b.

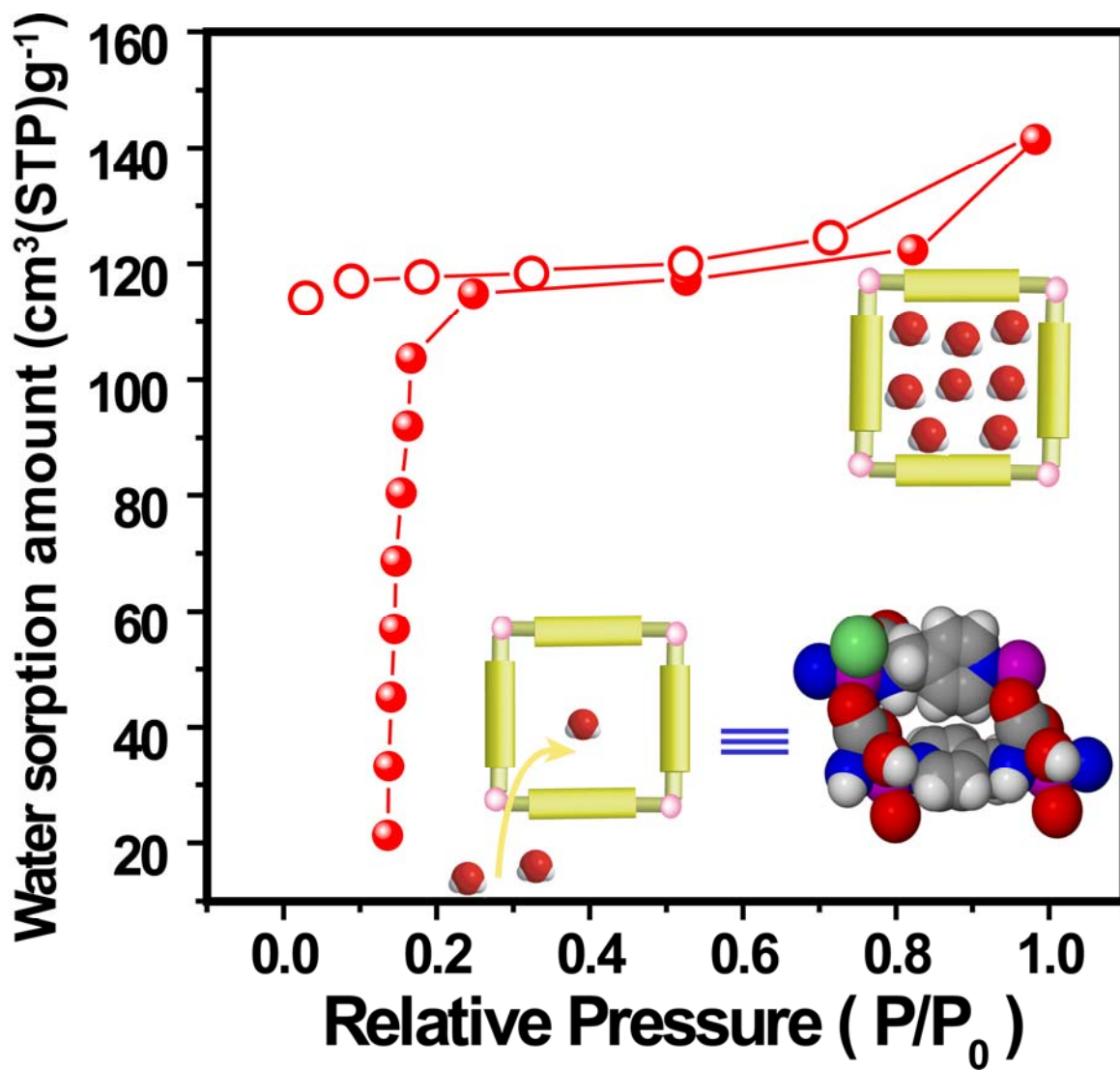


Figure S31: Water sorption isotherm for MOF 3a.