Supplementary Material (ESI) for Chemical Communications
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Supplementary Materials

I. Experimental Details

I.1. General Considerations.

All chemicals were used as obtained without further purification: cadmium (II) nitrate tetrahydrate, benzoic acid, methanol, *N*,*N*-dimethylformamide, 4-cyanopyridine, sodium azide, and triethylamine hydrochloride were purchased from Aldrich; The ligand 4-(2H-tetrazol-5-yl)pyridine was prepared according to literature methods [1].

1. Tao, Jun; Ma, Zhi-Jie; Huang, Rong-Bin; and Zheng, Lan-Sun *Inorg. Chem.* **2004**, 43, 6133-6135.

I.2. Syntheses

I.2.1. 4-(2H-tetrazol-5-yl)pyridine (4-Hpt)

A mixture of 4-cyanopyridine (4.16 g, 40.0 mmol), NaN_3 (11.7 g, 180 mmol), and triethylamine hydrochloride (24.7 g, 180 mmol) in 150 mL of toluene and 30 mL of methanol was heated at reflux in a 500-mL round-bottom flask for 3 days. Upon cooling to room temperature, 100 mL of an aqueous solution of NaOH (1 M) was added, and the mixture was stirred for 30 min. The aqueous layer was treated with ca. 100 mL of diluted HCl (1 M) until no further white precipitate formed. The precipitate was then collected by filtration, dried in the air, and dissolved in aqueous NaOH (1 M). The resulting clear, colorless solution was titrated with ca. 75 mL of diluted HCl (1 M) until the pH of the solution was 5.0. The ensuing white precipitate was washed with successive aliquots of chilled distilled water (3 x 50 mL), methanol (2 x 50 mL), and acetone (50 mL) to afford 4.9 g (83%) of product. Anal. Calcd for $C_6H_5N_5$ (dried): C, 48.9; H, 3.43; N, 47.6. Found: C, 48.3; H, 3.52; N, 47.3. IR (KBr pellet, cm^{-1}): 3066 (m), 2329 (m, br), 1889 (m, br), 1636 (m, br), 1430 (s), 1409 (s), 1377 (s), 1321 (w), 1204 (m), 1176 (m), 1116 (m), 1053 (s), 896 (s), 746 (s) cm^{-1}.

I.2.2. $[Cd_4(4\text{-pt})_6(OH)_2(DMF)_4]$ •12DMF (1•12DMF).

A solution of $Cd(NO_3)_2$•$4H_2O$ (200 mg, 0.65 mmol) in 1 ml of DMF was mixed with a solution of 4-Hpt (67 mg, 0.46 mmol) in 5 mL of DMF. The mixture was heated to 80^{o}C for 3 days upon which colorless cube shaped crystals of **1•12DMF** were isolated in 90%

yield which were suitable for X-ray diffraction. Compound **1•12DMF** was desolvated under dynamic vacuum at room temperature for 48 h to provide **1**. Anal. Calcd (desolvated sample **1**): C, 34.9; H, 3.29; N, 28.8. Found: C, 35.0; H, 3.48; N, 28.5. IR (KBr pellet, cm^{-1}): 3392(b), 3089(w), 3033(w), 2932(w), 2870(w), 1670(s), 1620(s), 1492(w), 1430(m), 1375(s), 1303(w), 1252(w), 1215(w), 1098(m), 1057(w), 1011(m), 836(m), 708(m), 657(w), 529(w), 458(w).

I.2.3. $[Cd_4(4\text{-}pt)_6(OH)_2(H_2O)_4] \bullet xH_2O$ (1a) and $[Cd_4(4\text{-}pt)_6(OH)_2(H_2O)_4]$ (1'). Crystals of $[Cd_4(4\text{-}pt)_6(OH)_2(DMF)_4] \bullet 12DMF$ **(1•12DMF)** were immersed in H_2O at 80°C for 24 h, and the extract was decanted. Fresh H_2O was subsequently added, and the crystals were allowed to soak for and additional 24 h 80°C to give $[Cd_4(4\text{-}pt)_6(OH)_2(H_2O)_4] \bullet xH_2O$ **(1a).** Compound **1a** was subsequently desolvated under vacuum to give $[Cd_4(4\text{-}pt)_6(OH)_2(H_2O)_4]$ (**1'**). Anal. Calcd (desolvated sample **1'**): C, 30.2; H, 2.39; N, 29.3. Found: C, 30.6; H, 2.26; N, 29.4. IR (KBr pellet, cm^{-1}): 3392(b), 3089(w), 3033(w), 1620(s), 1559(w), 1446(m), 1430(m), 1369(w), 1226(m), 1129(w), 1057(w), 1011(m), 836(m), 754(m), 708(s), 535(m), 458(w).

I.2.4. $[Cd_4Cl_3(4\text{-}pt)_4(OH)(DMF)_3] \bullet 8DMF \bullet 14MeOH$ (2•8DMF•14MeOH). A solution of $Cd(NO_3)_2 \bullet 4H_2O$ (200 mg, 0.65 mmol) in 5 mL of methanol was added to a solution of 4-Hpt (67 mg, 0.46 mmol) in 5 mL of DMF creating a white precipitate. An aqueous solution of HCl (0.3 mL, 6 M) was added dropwise to the mixture while stirring, until a clear solution was obtained. The mixture was heated to 80°C for 3 days upon which colorless plates of **2•8DMF•14MeOH** which were suitable for X-ray diffraction were isolated in 80% yield. Samples of **2•8DMF•14MeOH** were desolvated under dynamic vacuum to provide $[Cd_4Cl_3(4\text{-}pt)_4(OH)(DMF)_3]$ **(2).** Anal. Calcd for $C_6H_5N_5$ (desolvated sample **2**): C, 28.8; H, 2.78; N, 23.4. Found: C, 29.1; H, 2.95; N, 23.2. IR (KBr pellet, cm^{-1}): 3437(b), 3089(w), 3033(w), 2926(w), 2872(w), 1672(s), 1620(s), 1559(w), 1498(w), 1451(m), 1430(m), 1384(m), 1303(w), 1257(w), 1221(w), 1175(w), 1092(m), 1062(w), 1006(m), 847(m), 760(w), 708(m), 660(w), 535(w), 462(w).

I.2.5. $[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]\bullet xH_2O$ (2a) and $[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]$ (2').

Crystals of $[Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3]\bullet 8DMF\bullet 14MeOH$ **(2•8DMF•14MeOH)** were immersed in H_2O at 80°C for 24 h, and the extract was decanted. Fresh H_2O was subsequently added, and the crystals were allowed to soak for and additional 24 h 80°C to provide $[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]\bullet xH_2O$ **(2a)**. Compound **2a** was placed in dynamic vacuum for 48 h to effect desolvation to give $[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]$ **(2').** Anal. Calcd (desolvated sample **2'**): C, 23.79; H, 1.91; N, 23.12. Found: C, 23.61; H, 2.16; N, 23.34. IR (KBr pellet, cm^{-1}): 3392(b), 3089(w), 3033(w), 1620(s), 1559(w), 1451(m), 1430(m), 1369(w), 1221(m), 1129(w), 1062(w), 1011(m), 842(m), 754(w), 708(m), 535(w), 460(w).

I.2.6. $[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H_2O)_2]\bullet 10DMF$ (3•10DMF)

A solution of $CdCl_2\bullet 2.5H_2O$ (200 mg, 0.88 mmol) in 1 mL of DMF was added to a solution of 4-Hpt (67 mg, 0.46 mmol) in 5 mL of DMF yielding a white precipitate. An aqueous solution of HCl (0.3 mL, 6 M) was added dropwise to the mixture while stirring, until a clear solution appeared. The mixture was heated to 80°C for 3 days upon which colorless plates of **3•10DMF** suitable for X-ray diffraction were isolated in 75% yield. The desolvated material $[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H2O)_2]$ (**3**) was prepared bb evacuating a sample of **3•10DMF** under dynamic vacuum for 24 h. Anal. Calcd (desolvated sample **3**): C, 23.4; H, 2.22; N, 20.0. Found: C, 23.1; H, 2.02; N, 19.9. IR (KBr pellet, cm^{-1}): 3441(b), 3086(w), 3033(w), 2926(w), 2865(w), 1672(s), 1620(m), 1559(w), 1498(w), 1430(m), 1379(m), 1322(w), 1252(w), 1226(w), 1175(w), 1092(m), 1057(w), 1011(m), 842(m), 752(w), 713(m), 678(w), 657(w), 535(m), 462(w).

I.2.7. $[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]\bullet xH_2O$ (3a) and $[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]$ (3').

Crystals of $[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H_2O)_2]\bullet 10DMF$ **(3)** were immersed in H_2O at 80°C for 24 h, and the extract was decanted. Fresh H_2O was subsequently added, and the crystals were allowed to soak for and additional 24 h 80°C to provide $[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]\bullet xH_2O$ (**3a**). Compound **3a** was then subjected to dynamic vacuum for 48 h to give the desolvated $[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]$ (**3'**). Anal. Calcd (desolvated sample **3'**): C, 20.1; H,

1.69; N, 19.6. Found: C, 20.3; H, 1.76; N, 19.4. IR (KBr pellet, cm^{-1}): 3392(b), 3089(w), 3033(w), 1620(w), 1559(w), 1451(w), 1430(m), 1375(w), 1221(m), 1011(m), 836(m), 760(w), 713(m), 535(w), 462(w).

I.3. X-ray Crystallography.

Structural measurements were performed on a Bruker-AXS SMART-CCD diffactometer at low temperature (90 K) using graphite-monochromated Mo Kα radiation ($\lambda_{Mo\ K\alpha}$= 0.71073Å). The data were corrected for Lorentz and polarization effects and absorption using SADABS. The structures were solved by direct methods. All non-hydrogen atoms were refined anistropically. After all of the non-hydrogen atoms were located, the model was refined against F^2, initially using isotropic and later anistropic thermal displacement parameters. Hydrogen atoms were introduced in calculated positions and refined isotropically. Neutral atom scattering coefficients and anomalous dispersion corrections were taken from the *International Tables*, Vol. C. All calculations were performed using SHELXTL crystallographic software packages. The contribution of the solvent to the diffraction patterns were subtracted from the observed data by the SQUEEZE method implemented in PLATON. The final formula was calculated from elemental analyses combined with TGA analysis.

1. A.L.Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
2. A.L.Spek, J.Appl.Cryst. 2003, 36, 7-13.

Crystal data. **1**•12DMF: $C_{84}H_{138}Cd_4N_{46}O_{18}$, FW = 2530.0, cubic space group $Pa\bar{3}$, a = 41.5947(4)Å, V = 71963.8(12)$Å^3$, Z = 24, D_c = 1.401 g cm^{-3}, μ(Mo-K_α) = 7.76 cm^{-1}, 21,144 independent reflections (1,158,528 collected), R_1 = 0.1152, wR_2 = 0.2548 (all data). **2**•8DMF•14MeOH: $C_{69}H_{142}Cd_4Cl_3N_3O_{24}$, FW = 2346.09, orthorhombic space group *Pbcn*, a = 35.5933(10)Å, b = 20.8616(6)Å, c = 22.0238(6)Å, V = 16487.1(8)$Å^3$, Z = 8, D_c = 1.890 g cm^{-3}, μ(Mo-K_α) = 12.14 cm^{-1}, 14416 independent reflections (160,645 collected), R_1 = 0.0900, wR_2 = 0.2343. **3**•10DMF: $C_{30}H_{52}Cd_{2.5}Cl_3N_{16}O_7$, FW = 1136.23, monoclinic space group *C2/c*, a = 29.728(5)Å, b = 12.530(2)Å, c = 20.920(4)Å, β =

114.847(4)°, V = 7071(2)Å^3, Z = 4, D_c = 2.135 g cm^{-3}, μ(Mo-K$_\alpha$) = 17.99 cm^{-1}, 5064 independent reflections (33,877 collected), R_1 = 0.0860, wR_2 = 0.2154. In all cases, the structures include large regions of disordered molecules of crystallization, which could not be modeled as discrete atomic sites. PLATON/SQUEEZE was used to calculate the diffraction contribution of the solvent molecules to produce a set of solvent free diffraction intensities. In addition, the carbon and nitrogen atoms of the coordinated DMF molecules are grossly disordered and could not be modeled as discrete atomic sites. The final formulae were calculated from elemental analyses combined with TGA analyses.

I.4. Low-pressure gas adsorption measurements.

All gas adsorption measurements were obtained using a Micromeritics ASAP 2020 volumetric gas adsorption instrument. Samples of $[Cd_4(4\text{-pt})_6(OH)_2(DMF)_4]$ •12DMF (**1•12DMF**), $[Cd_4(4\text{-pt})_6(OH)_2(H_2O)_4]$ •xH$_2$O (**1a**), $[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]$ •xH$_2$O (**2a**), and $[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]$ •xH$_2$O (**3a**) were immersed in methanol for 24 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were allowed to soak for and additional 24 h to remove any residual H_2O and DMF. The methanol extract was then decanted and the crystals were treated with dichoromethane similarly to remove the methanol solvates. The treated crystalline samples were then collected by vacuum filtration and transferred to preweighed analysis tubes which were then capped with a Transeal to prevent intrusion of atmospheric moisture during transfers and weighing. The sample was then evacuated under dynamic vacuum at 35°C until the outgas rate was less than 2 mTorr/min. The evacuated analysis tubes containing degassed samples of **1**, **1'**, **2'** and **3'** were then weighed to determine the mass of sample (typically 100-175 mg). For all isotherms, warm and cold free space correction measurements were taken using ultrahigh purity helium gas. The H_2 and N_2 isotherms at 77K were measured in liquid nitrogen baths using UHP grade gas sources.

II. Crystallographic Tables

Table 1. Crystal data and structure refinement for $[Cd_4(OH)_2(4\text{-pt})_6(DMF)_4]$•12DMF (**1**•12DMF).

Identification code	pa-3	
Empirical formula	C84 H138 Cd4 N46 O18	
Formula weight	2530.00	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Pa-3	
Unit cell dimensions	a = 41.5947(4) Å	α= 90°.
	b = 41.5947(4) Å	β= 90°.
	c = 41.5947(4) Å	γ = 90°.
Volume	71963.8(12) $Å^3$	
Z	24	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.735 mm^{-1}	
F(000)	31200	
Crystal size	0.30 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.62 to 25.01°.	
Index ranges	-49<=h<=49, -49<=k<=49, -49<=l<=49	
Reflections collected	1,158,528	
Independent reflections	21144 [R(int) = 0.0897]	
Completeness to theta = 25.01°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8006 and 0.8006	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21144 / 0 / 685	
Goodness-of-fit on F^2	1.215	
Final R indices [I>2sigma(I)]	R1 = 0.1152, wR2 = 0.2379	
R indices (all data)	R1 = 0.1232, wR2 = 0.2548	
Largest diff. peak and hole	1.468 and -0.571 $e.Å^{-3}$	

Table 2. Selected bond lengths [Å] and angles [°] for **1**•12DMF .

Cd(1)-N(13)	2.249(9)
Cd(1)-N(20)#1	2.272(10)
Cd(1)-O(1)	2.355(12)
Cd(1)-O(2)	2.356(13)
Cd(1)-N(6)	2.358(10)
Cd(1)-N(1)	2.404(9)
Cd(2)-N(8)	2.302(9)
Cd(2)-N(30)#2	2.311(9)
Cd(2)-N(10)#3	2.323(9)
Cd(2)-N(3)	2.336(9)
Cd(2)-O(3)	2.368(12)
Cd(2)-N(11)	2.398(9)
Cd(3)-O(4)	2.298(10)
Cd(3)-N(21)	2.303(9)
Cd(3)-N(25)#4	2.309(10)
Cd(3)-N(26)	2.311(8)
Cd(3)-N(16)	2.326(10)
Cd(3)-N(15)	2.335(10)
Cd(4)-N(17)	2.322(9)
Cd(4)-N(5)#5	2.331(9)
Cd(4)-O(6)	2.365(12)
Cd(4)-O(5)	2.378(11)
Cd(4)-N(27)	2.379(8)
Cd(4)-N(22)	2.382(9)

N(13)-Cd(1)-N(20)#1	176.3(4)
N(13)-Cd(1)-O(1)	89.3(4)
N(20)#1-Cd(1)-O(1)	88.9(4)
N(13)-Cd(1)-O(2)	88.2(4)
N(20)#1-Cd(1)-O(2)	88.7(4)
O(1)-Cd(1)-O(2)	94.7(6)
N(13)-Cd(1)-N(6)	91.7(3)
N(20)#1-Cd(1)-N(6)	91.6(4)
O(1)-Cd(1)-N(6)	88.8(4)
O(2)-Cd(1)-N(6)	176.6(5)
N(13)-Cd(1)-N(1)	89.3(3)
N(20)#1-Cd(1)-N(1)	92.8(3)
O(1)-Cd(1)-N(1)	175.1(4)
O(2)-Cd(1)-N(1)	89.9(5)
N(6)-Cd(1)-N(1)	86.6(3)
N(8)-Cd(2)-N(30)#2	173.1(3)
N(8)-Cd(2)-N(10)#3	94.6(3)
N(30)#2-Cd(2)-N(10)#3	91.5(3)
N(8)-Cd(2)-N(3)	86.6(3)
N(30)#2-Cd(2)-N(3)	90.0(3)
N(10)#3-Cd(2)-N(3)	90.9(3)
N(8)-Cd(2)-O(3)	91.4(4)
N(30)#2-Cd(2)-O(3)	91.9(4)
N(10)#3-Cd(2)-O(3)	90.0(4)
N(3)-Cd(2)-O(3)	178.0(4)
N(8)-Cd(2)-N(11)	90.4(3)
N(30)#2-Cd(2)-N(11)	83.4(3)
N(10)#3-Cd(2)-N(11)	174.2(3)
N(3)-Cd(2)-N(11)	86.5(3)

O(3)-Cd(2)-N(11)	92.8(4)
O(4)-Cd(3)-N(21)	91.9(3)
O(4)-Cd(3)-N(25)#4	86.7(4)
N(21)-Cd(3)-N(25)#4	93.4(3)
O(4)-Cd(3)-N(26)	96.4(3)
N(21)-Cd(3)-N(26)	88.6(3)
N(25)#4-Cd(3)-N(26)	176.3(3)
O(4)-Cd(3)-N(16)	179.0(4)
N(21)-Cd(3)-N(16)	87.1(3)
N(25)#4-Cd(3)-N(16)	93.6(4)
N(26)-Cd(3)-N(16)	83.4(3)
O(4)-Cd(3)-N(15)	89.2(4)
N(21)-Cd(3)-N(15)	178.9(4)
N(25)#4-Cd(3)-N(15)	86.6(3)
N(26)-Cd(3)-N(15)	91.4(3)
N(16)-Cd(3)-N(15)	91.8(4)
N(17)-Cd(4)-N(5)#5	93.1(3)
N(17)-Cd(4)-O(6)	179.6(4)
N(5)#5-Cd(4)-O(6)	86.9(3)
N(17)-Cd(4)-O(5)	88.2(4)
N(5)#5-Cd(4)-O(5)	92.1(4)
O(6)-Cd(4)-O(5)	91.4(4)
N(17)-Cd(4)-N(27)	87.5(3)
N(5)#5-Cd(4)-N(27)	177.5(3)
O(6)-Cd(4)-N(27)	92.6(3)
O(5)-Cd(4)-N(27)	90.4(4)
N(17)-Cd(4)-N(22)	87.6(3)
N(5)#5-Cd(4)-N(22)	89.2(3)
O(6)-Cd(4)-N(22)	92.7(4)
O(5)-Cd(4)-N(22)	175.7(3)
N(27)-Cd(4)-N(22)	88.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 z-1/2,x,-y+3/2 #2 -z+3/2,x+1/2,y #3 y,z,x
#4 -y+3/2,-z+2,x+1/2 #5 x,-y+3/2,z+1/2 #6 x,-y+3/2,z-1/2
#7 z,x,y #8 y,-z+3/2,x+1/2 #9 z-1/2,-x+3/2,-y+2
#10 y-1/2,z,-x+3/2

Table 3. Crystal data and structure refinement for $[Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3]$•8DMF•14MeOH (**2**•8DMF•14MeOH)

Identification code	pbcn	
Empirical formula	C69 H142 Cd4 Cl3 N31 O24	
Formula weight	2346.09	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 35.5933(10) Å	α= 90°.
	b = 20.8616(6) Å	β= 90°.
	c = 22.2038(6) Å	γ = 90°.
Volume	16487.1(8) $Å^3$	
Z	8	
Density (calculated)	1.890 Mg/m^3	
Absorption coefficient	1.214 mm^{-1}	
F(000)	9664	
Crystal size	0.18 x 0.18 x 0.06 mm^3	
Theta range for data collection	2.51 to 25.00°.	
Index ranges	0<=h<=42, 0<=k<=24, 0<=l<=26	
Reflections collected	160,645	
Independent reflections	14416 [R(int) = 0.0000]	
Completeness to theta = 25.00°	99.2 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9307 and 0.8111	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14416 / 0 / 496	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0900, wR2 = 0.2352	
R indices (all data)	R1 = 0.1104, wR2 = 0.2463	
Largest diff. peak and hole	4.040 and -1.239 $e.Å^{-3}$	

Table 4. Selected bond lengths [Å] and angles [°] for **2**•8DMF•14MeOH.

Cd(1)-N(1)	2.224(9)
Cd(1)-N(15)#1	2.280(7)
Cd(1)-O(91)	2.314(11)
Cd(1)-O(90)	2.372(14)
Cd(1)-Cl(1)	2.608(3)
Cd(2)-N(6)	2.282(8)
Cd(2)-N(2)	2.312(9)
Cd(2)-N(20)#2	2.333(8)
Cd(2)-N(11)	2.445(8)
Cd(2)-Cl(1)	2.600(3)
Cd(2)-Cl(2)	2.639(2)
Cd(3)-N(5)#3	2.260(10)
Cd(3)-N(16)	2.299(8)
Cd(3)-N(7)	2.326(9)
Cd(3)-N(12)	2.401(8)
Cd(3)-Cl(2)	2.590(3)
Cd(3)-Cl(3)	2.600(2)
Cd(4)-O(92)	2.302(7)
Cd(4)-N(10)#4	2.368(9)
Cd(4)-N(17)	2.368(8)
Cd(4)-O(93)	2.385(9)
Cd(4)-N(13)	2.472(7)
Cd(4)-Cl(3)	2.614(2)
N(1)-Cd(1)-N(15)#1	158.9(4)
N(1)-Cd(1)-O(91)	87.2(4)
N(15)#1-Cd(1)-O(91)	88.2(3)
N(1)-Cd(1)-O(90)	99.9(4)
N(15)#1-Cd(1)-O(90)	100.4(4)
O(91)-Cd(1)-O(90)	86.8(5)
N(1)-Cd(1)-Cl(1)	90.3(3)
N(15)#1-Cd(1)-Cl(1)	93.7(2)
O(91)-Cd(1)-Cl(1)	177.3(3)
O(90)-Cd(1)-Cl(1)	94.8(3)
N(6)-Cd(2)-N(2)	173.4(3)
N(6)-Cd(2)-N(20)#2	96.6(3)
N(2)-Cd(2)-N(20)#2	89.6(3)
N(6)-Cd(2)-N(11)	89.6(3)
N(2)-Cd(2)-N(11)	83.9(3)
N(20)#2-Cd(2)-N(11)	169.4(3)
N(6)-Cd(2)-Cl(1)	94.3(2)
N(2)-Cd(2)-Cl(1)	86.8(2)
N(20)#2-Cd(2)-Cl(1)	101.5(2)
N(11)-Cd(2)-Cl(1)	86.59(19)
N(6)-Cd(2)-Cl(2)	88.0(2)
N(2)-Cd(2)-Cl(2)	89.8(2)
N(20)#2-Cd(2)-Cl(2)	88.5(2)
N(11)-Cd(2)-Cl(2)	83.12(19)
Cl(1)-Cd(2)-Cl(2)	169.46(8)
N(5)#3-Cd(3)-N(16)	94.7(3)
N(5)#3-Cd(3)-N(7)	91.9(3)
N(16)-Cd(3)-N(7)	173.4(3)
N(5)#3-Cd(3)-N(12)	177.7(3)
N(16)-Cd(3)-N(12)	85.7(3)

N(7)-Cd(3)-N(12)	87.7(3)
N(5)#3-Cd(3)-Cl(2)	90.6(2)
N(16)-Cd(3)-Cl(2)	92.5(2)
N(7)-Cd(3)-Cl(2)	87.3(2)
N(12)-Cd(3)-Cl(2)	87.11(18)
N(5)#3-Cd(3)-Cl(3)	97.0(2)
N(16)-Cd(3)-Cl(3)	88.6(2)
N(7)-Cd(3)-Cl(3)	90.7(2)
N(12)-Cd(3)-Cl(3)	85.32(18)
Cl(2)-Cd(3)-Cl(3)	172.25(8)
O(92)-Cd(4)-N(10)#4	92.9(3)
O(92)-Cd(4)-N(17)	175.4(3)
N(10)#4-Cd(4)-N(17)	91.5(3)
O(92)-Cd(4)-O(93)	90.2(3)
N(10)#4-Cd(4)-O(93)	91.3(3)
N(17)-Cd(4)-O(93)	91.1(3)
O(92)-Cd(4)-N(13)	88.4(2)
N(10)#4-Cd(4)-N(13)	176.9(3)
N(17)-Cd(4)-N(13)	87.2(3)
O(93)-Cd(4)-N(13)	91.6(3)
O(92)-Cd(4)-Cl(3)	89.85(19)
N(10)#4-Cd(4)-Cl(3)	87.7(2)
N(17)-Cd(4)-Cl(3)	89.0(2)
O(93)-Cd(4)-Cl(3)	179.0(2)
N(13)-Cd(4)-Cl(3)	89.44(18)
Cd(2)-Cl(1)-Cd(1)	96.68(8)
Cd(3)-Cl(2)-Cd(2)	93.92(7)
Cd(3)-Cl(3)-Cd(4)	93.32(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2 #2 -x+1/2,-y+3/2,z+1/2 #3 -x+1/2,y+1/2,z
#4 x,-y+2,z-1/2 #5 -x+1/2,y-1/2,z #6 x,-y+2,z+1/2
#7 -x+1/2,-y+3/2,z-1/2

Table 5. Crystal data and structure refinement for $[Cd_5Cl_6(4\text{-pt})(DMF)_2(H_2O)_2]\bullet 10DMF$ (**3**•10DMF)

Identification code	c2c	
Empirical formula	C30 H52 Cd2.50 Cl3 N16 O7	
Formula weight	1136.23	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.728(5) Å	α= 90°.
	b = 12.530(2) Å	β= 114.847(4)°.
	c = 20.920(4) Å	γ = 90°.
Volume	7071(2) $Å^3$	
Z	4	
Density (calculated)	2.135 Mg/m^3	
Absorption coefficient	1.799 mm^{-1}	
F(000)	4568	
Crystal size	0.22 x 0.20 x 0.04 mm^3	
Theta range for data collection	2.62 to 23.26°.	
Index ranges	-32<=h<=29, 0<=k<=13, 0<=l<=23	
Reflections collected	33,877	
Independent reflections	5064 [R(int) = 0.0000]	
Completeness to theta = 23.26°	99.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9315 and 0.6930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5064 / 315 / 306	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0860, wR2 = 0.2225	
R indices (all data)	R1 = 0.1080, wR2 = 0.2340	
Largest diff. peak and hole	3.494 and -1.444 $e.Å^{-3}$	

Table 6. Selected bond lengths [Å] and angles [°] for **3**•10DMF.

Cd(1)-N(8)#1	2.336(10)
Cd(1)-N(3)#1	2.348(10)
Cd(1)-N(1)	2.424(10)
Cd(1)-Cl(3)	2.575(3)
Cd(1)-Cl(1)	2.649(3)
Cd(1)-Cl(2)	2.658(4)
Cd(2)-N(5)#2	2.315(10)
Cd(2)-N(7)	2.341(11)
Cd(2)-N(2)	2.428(11)
Cd(2)-Cl(2)	2.609(4)
Cd(2)-Cl(1)#3	2.636(3)
Cd(2)-Cl(3)	2.665(4)
Cd(3)-O(1)	2.271(13)
Cd(3)-O(1)#4	2.271(13)
Cd(3)-N(10)	2.286(12)
Cd(3)-N(10)#4	2.286(12)
Cd(3)-O(2)	2.363(15)
Cd(3)-O(2)#4	2.363(15)
Cl(1)-Cd(2)#1	2.636(3)
N(8)#1-Cd(1)-N(3)#1	94.0(4)
N(8)#1-Cd(1)-N(1)	88.2(3)
N(3)#1-Cd(1)-N(1)	174.9(3)
N(8)#1-Cd(1)-Cl(3)	174.7(3)
N(3)#1-Cd(1)-Cl(3)	91.1(3)
N(1)-Cd(1)-Cl(3)	86.6(2)
N(8)#1-Cd(1)-Cl(1)	85.4(3)
N(3)#1-Cd(1)-Cl(1)	85.3(3)
N(1)-Cd(1)-Cl(1)	99.4(2)
Cl(3)-Cd(1)-Cl(1)	96.55(11)
N(8)#1-Cd(1)-Cl(2)	88.6(3)
N(3)#1-Cd(1)-Cl(2)	90.1(3)
N(1)-Cd(1)-Cl(2)	85.4(2)
Cl(3)-Cd(1)-Cl(2)	89.95(11)
Cl(1)-Cd(1)-Cl(2)	172.09(11)
N(5)#2-Cd(2)-N(7)	94.2(4)
N(5)#2-Cd(2)-N(2)	166.4(4)
N(7)-Cd(2)-N(2)	91.5(4)
N(5)#2-Cd(2)-Cl(2)	90.6(3)
N(7)-Cd(2)-Cl(2)	174.6(2)
N(2)-Cd(2)-Cl(2)	84.3(3)
N(5)#2-Cd(2)-Cl(1)#3	109.1(3)
N(7)-Cd(2)-Cl(1)#3	83.5(3)
N(2)-Cd(2)-Cl(1)#3	83.8(3)
Cl(2)-Cd(2)-Cl(1)#3	92.60(11)
N(5)#2-Cd(2)-Cl(3)	88.1(3)
N(7)-Cd(2)-Cl(3)	93.5(3)
N(2)-Cd(2)-Cl(3)	79.2(3)
Cl(2)-Cd(2)-Cl(3)	89.06(11)
Cl(1)#3-Cd(2)-Cl(3)	162.63(11)
O(1)-Cd(3)-O(1)#4	179.997(2)
O(1)-Cd(3)-N(10)	89.4(5)
O(1)#4-Cd(3)-N(10)	90.6(5)
O(1)-Cd(3)-N(10)#4	90.6(5)

O(1)#4-Cd(3)-N(10)#4	89.4(5)
N(10)-Cd(3)-N(10)#4	179.999(2)
O(1)-Cd(3)-O(2)	93.0(6)
O(1)#4-Cd(3)-O(2)	87.0(6)
N(10)-Cd(3)-O(2)	87.9(5)
N(10)#4-Cd(3)-O(2)	92.1(5)
O(1)-Cd(3)-O(2)#4	87.0(6)
O(1)#4-Cd(3)-O(2)#4	93.0(6)
N(10)-Cd(3)-O(2)#4	92.1(5)
N(10)#4-Cd(3)-O(2)#4	87.9(5)
O(2)-Cd(3)-O(2)#4	179.997(3)
Cd(2)#1-Cl(1)-Cd(1)	93.97(11)
Cd(2)-Cl(2)-Cd(1)	84.35(12)
Cd(1)-Cl(3)-Cd(2)	84.88(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 x,-y+2,z+1/2 #3 -x+1/2,y-1/2,-z+1/2
#4 -x,-y+1,-z+1 #5 x,-y+2,z-1/2

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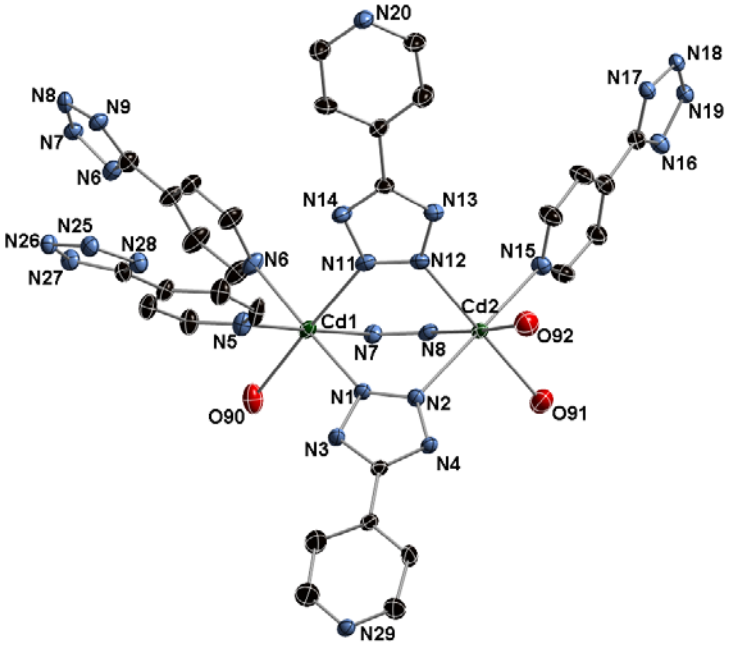
III. Supplementary Figures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N17
N19
N8
N9
N7
N16
N6
N14
N13
N25
N26
N28
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N11
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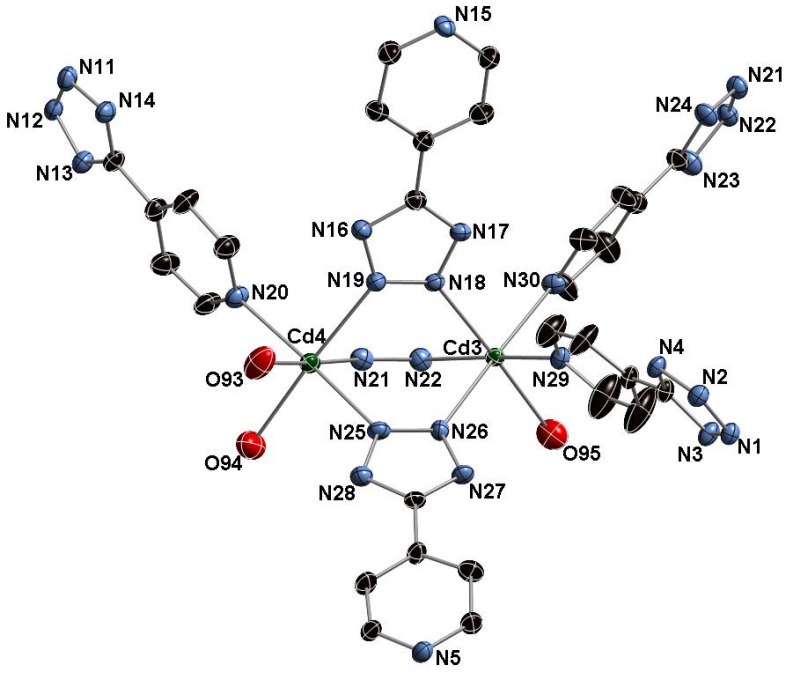
O92
N1
N2
O90
O91
N3
N4
N29


N15
N11
N21
N14
N24
N12
N22
N13
N23
N16
N17
N19
N18
N30
N20
Cd4
Cd3
N4
O93
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N22
N29
N2
N25
N26
O95
N3
N1
O94
N28
N27
N5

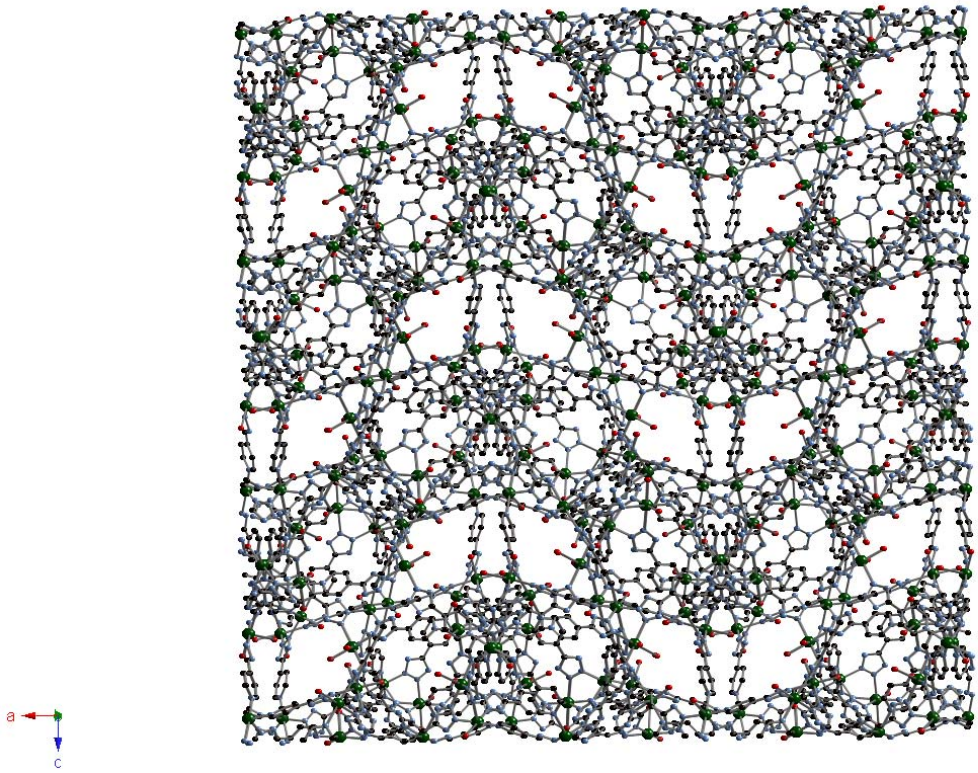

Figure S1. (a) Atom-labeling scheme and 50% thermal ellipsoids for the structure of **[Cd_4(4-pt)$_6$$(OH)_2$$(DMF)_4$] DMF (1•12DMF);** (b) a view of the framework structure of **1** in the *ac* plane.

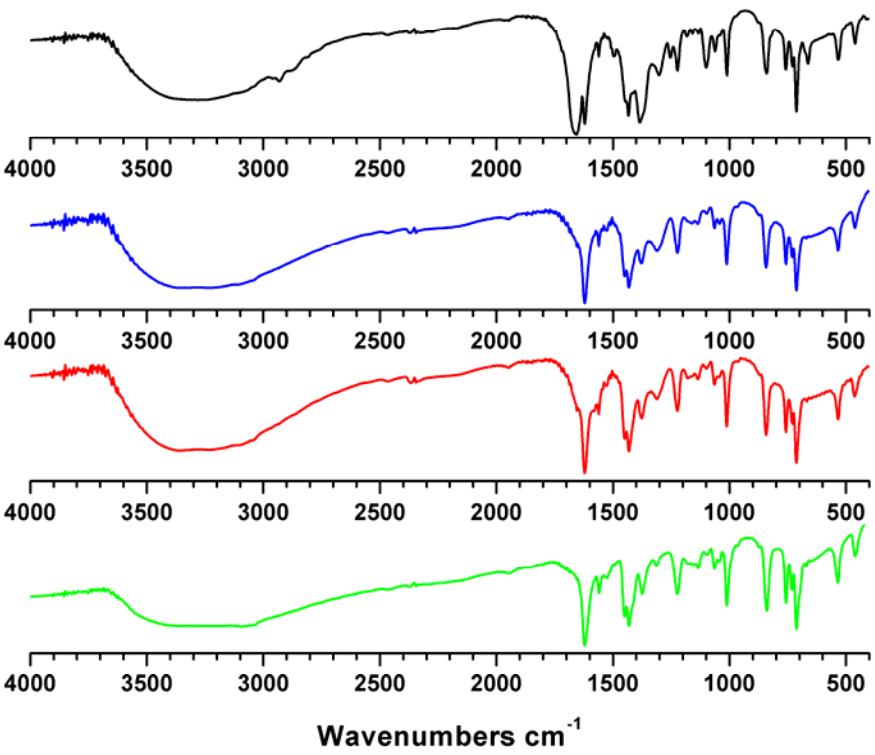

Figure S2. Infrared spectra of **$[Cd_4(4\text{-pt})_6(OH)_2(DMF)_4]$ •12DMF (1•12DMF)** (black), **$[Cd_4(4\text{-pt})_6(OH)_2(DMF)_4]$ •27H_2O (1•**$27H_2O$) (blue), **$[Cd_4(4\text{-pt})_6(OH)_2(DMF)_4]$ (1)** (red), and **$[Cd_4(4\text{-pt})_6(OH)_2(H_2O)_4]$ (1')** (green).

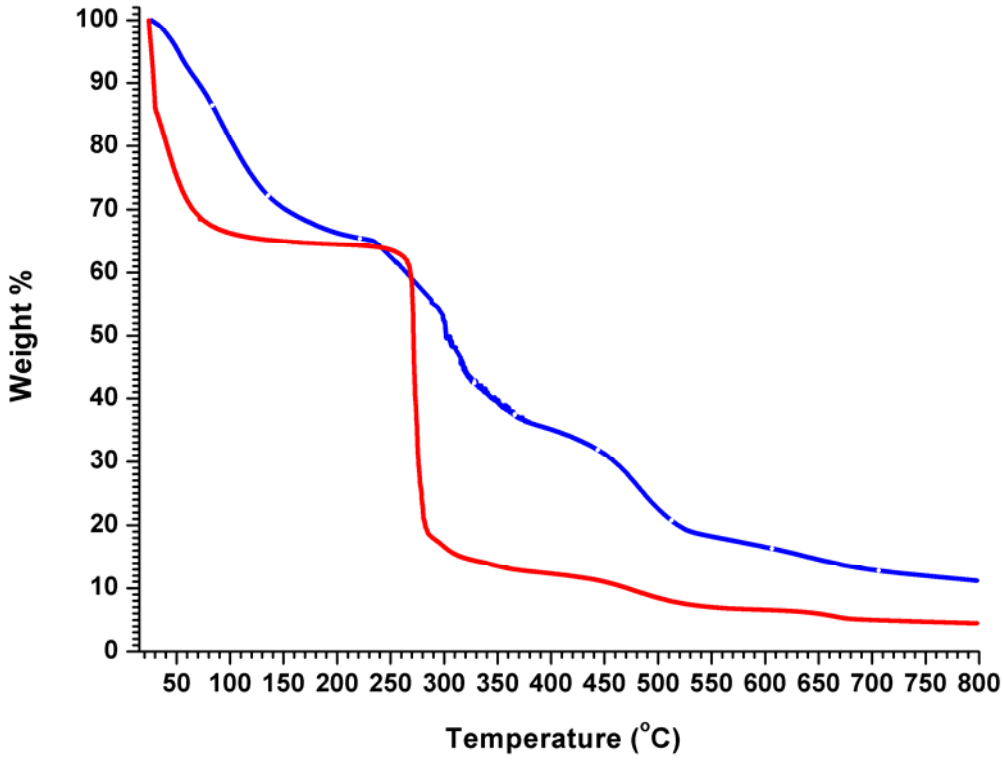

Figure S3. Thermagravimetric profiles for **[Cd_4(4-pt)$_6$$(OH)_2$$(DMF)_4$] •12DMF** (**1**•12DMF) (blue) **and [Cd_4(4-pt)$_6$$(OH)_2$$(DMF)_4$] •27MeOH** (**1**•27MeOH) (red).

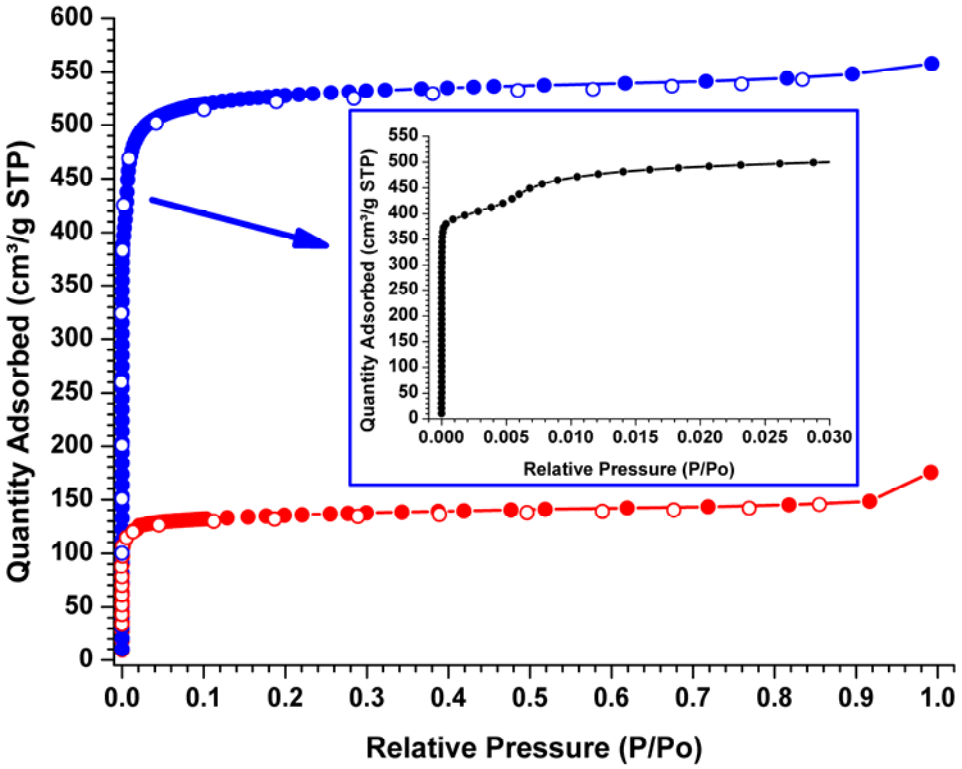

Figure S4. N_2 adsorption isotherms for **[Cd_4(4-pt)$_6$(OH)$_2$(DMF)$_4$] (1)** (red), and **[Cd_4(4-pt)$_6$(OH)$_2$(H_2O)$_4$] (1')** (blue); filled circles for sorption; open circles for desorption. The inset shows the adsorption behavior at low relative pressure P/P_0.

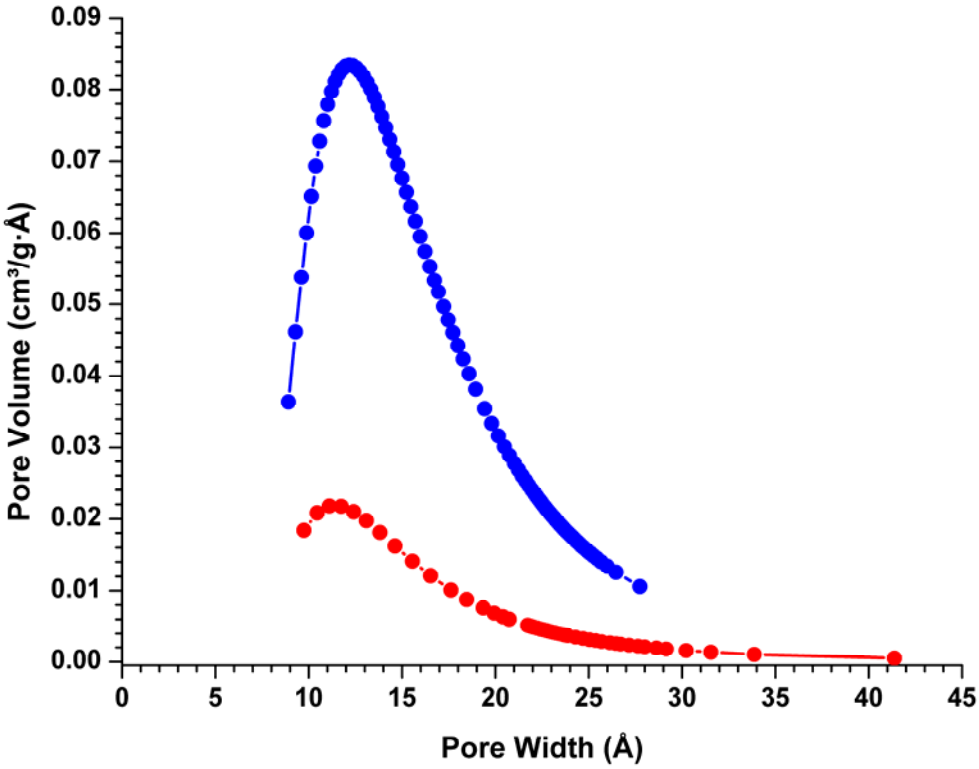

Figure S5. Pore size distributions for **[Cd_4(4-pt)$_6$(OH)$_2$(DMF)$_4$] (1)** (red), and **[Cd_4(4-pt)$_6$(OH)$_2$(H_2O)$_4$] (1')** (blue) based on Dubinin-Astakhov analyses of the N_2 sorption isotherms.

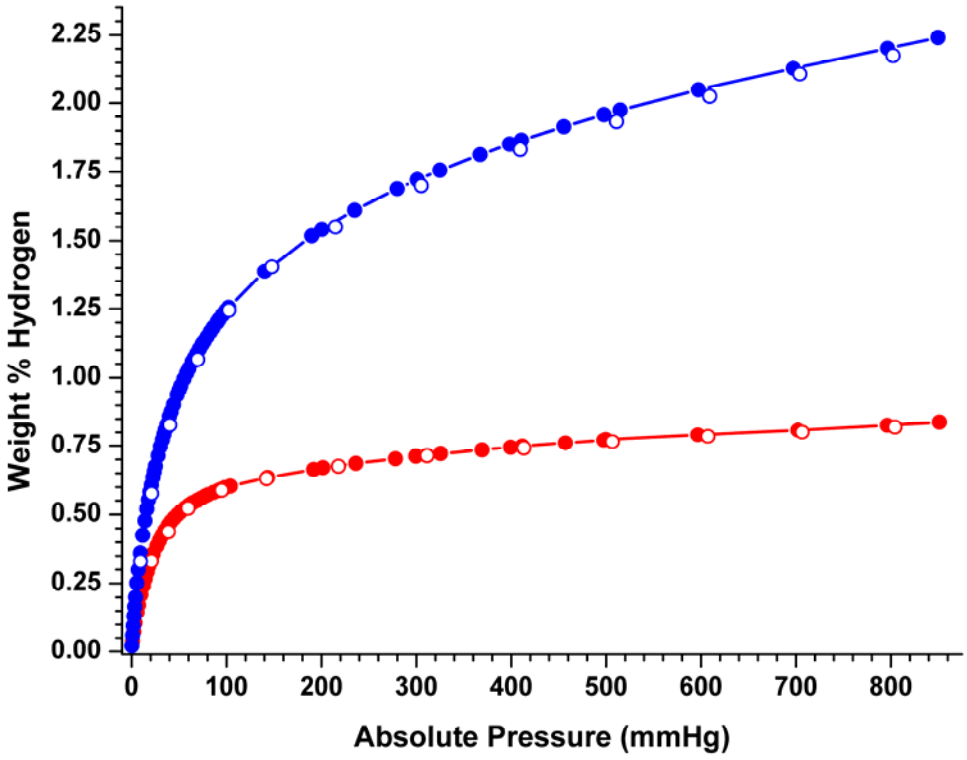

Figure S6. H_2 sorption isotherms for for **[Cd_4(4-pt)$_6$(OH)$_2$(DMF)$_4$] (1**) (red), and **[Cd_4(4-pt)$_6$(OH)$_2$(H_2O)$_4$] (1'**) (blue); filled circles for sorption; open circles for desorption.

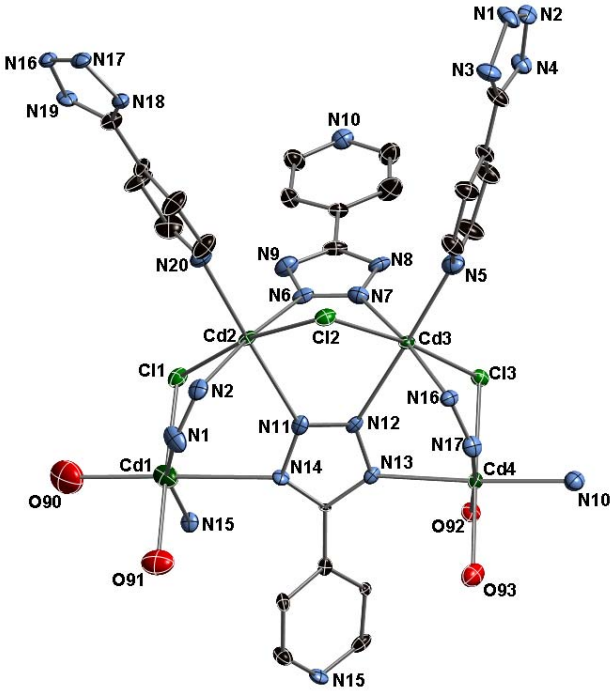

Figure S7. Atom-labeling scheme and 50% thermal ellipsoids for the structure of **$[Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3]$ •8DMF•14MeOH (2•8DMF•14MeOH).**

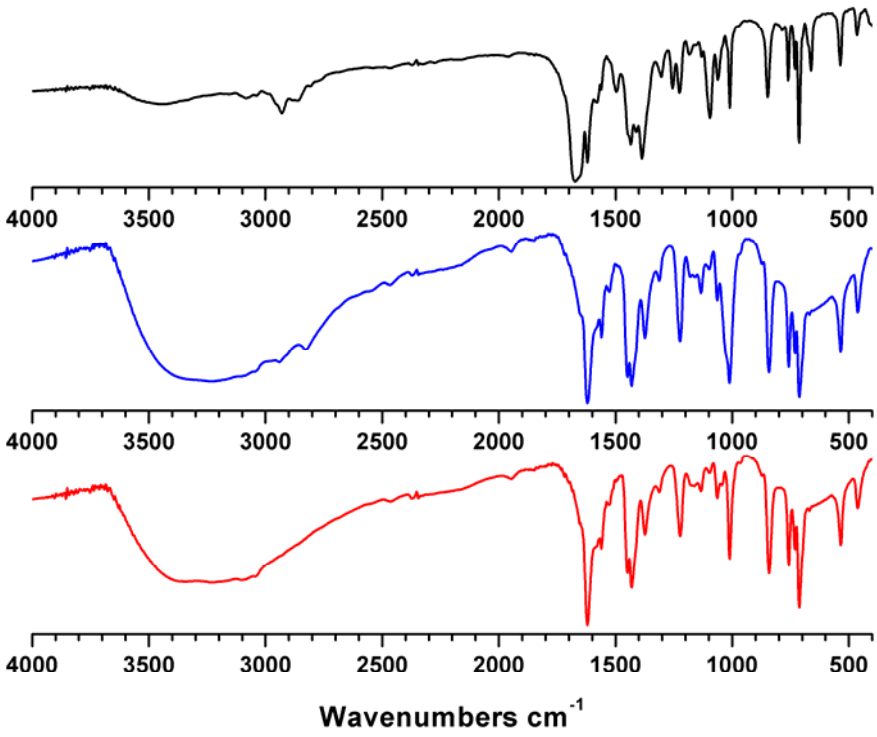

Figure S8. Infrared spectra of **[$Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3$] •8DMF•14MeOH (2•8DMF•14MeOH)** (black), **[$Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3$] (2)** (blue), and **[$Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3$] (2')** (red).

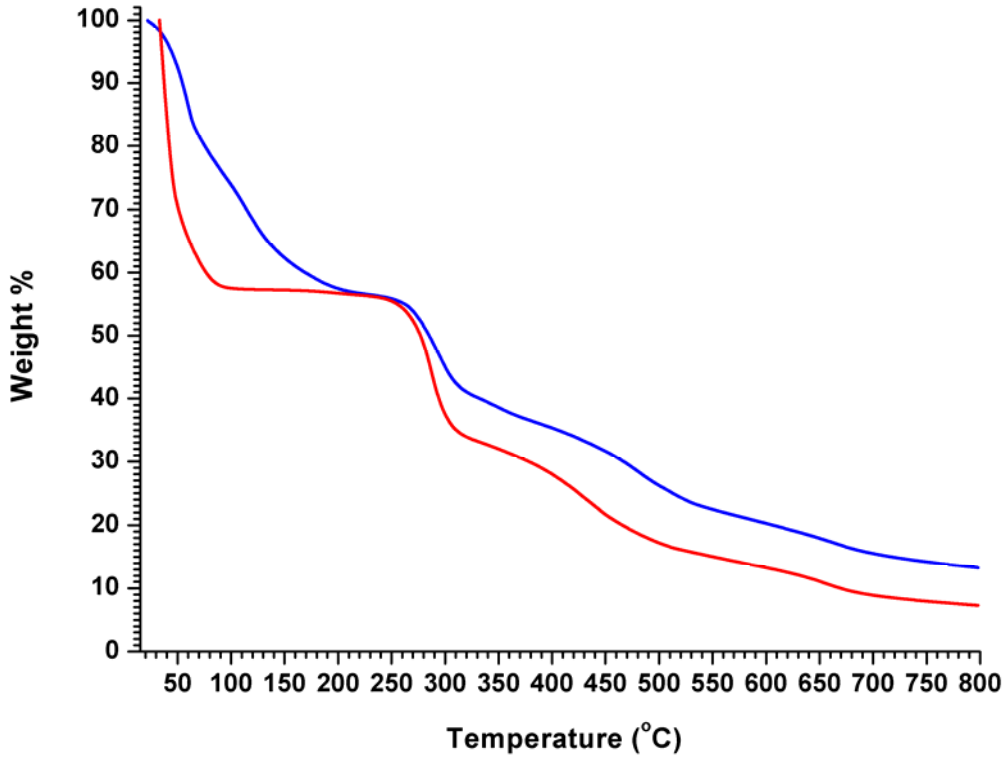

Figure S9. TGA profiles of **[$Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3$]•8DMF•14MeOH (2•8DMF•14MeOH)** (blue) and **[$Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3$]•32MeOH (2•32MeOH)** (red).

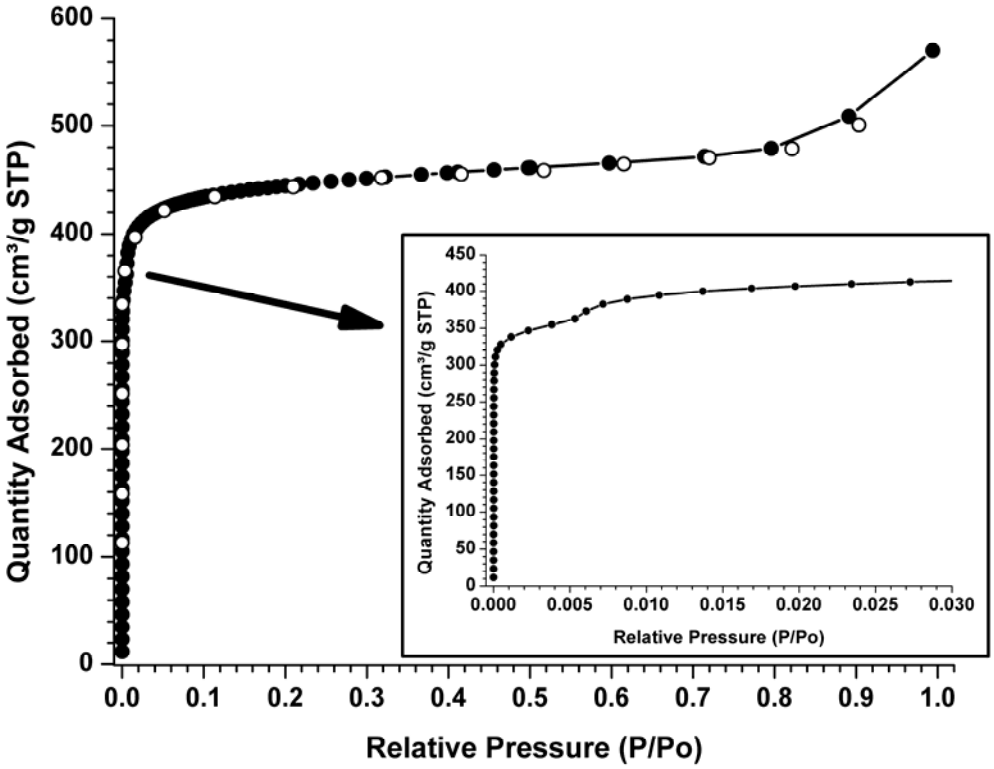

Figure S10. N_2 sorption isotherm for **$[Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3]$ (2').** The inset shows the sorption behavior at low relative pressure P/P_0; filled circles for sorption; open circles for desorption.

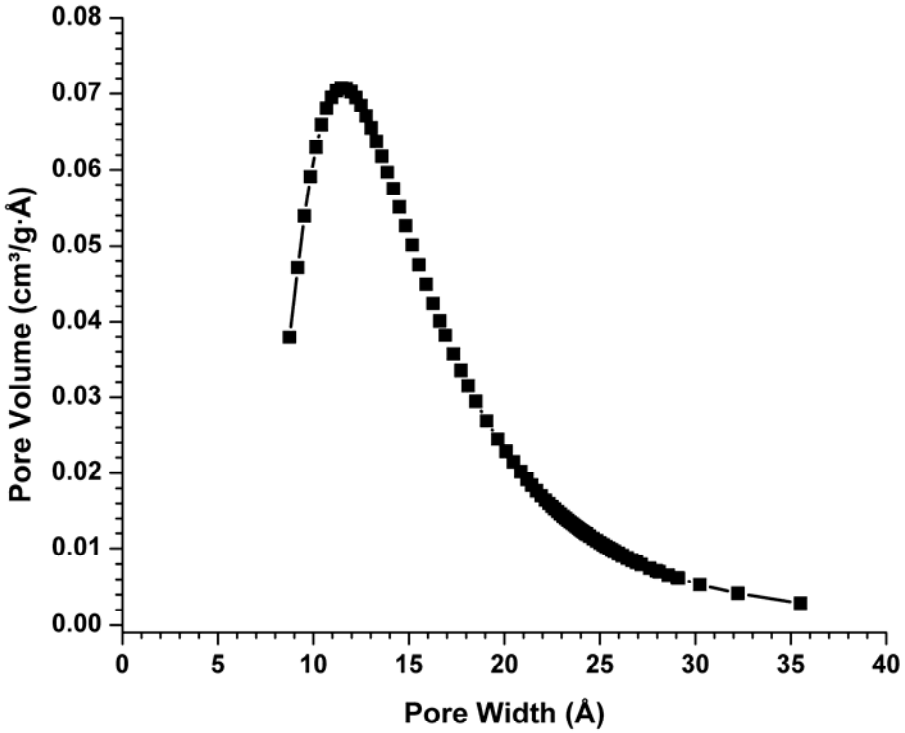

Figure S11. Pore size distribution for **[$Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3$] (2')** based on Dubinin-Astakhov analyses of the N_2 sorption isotherm.

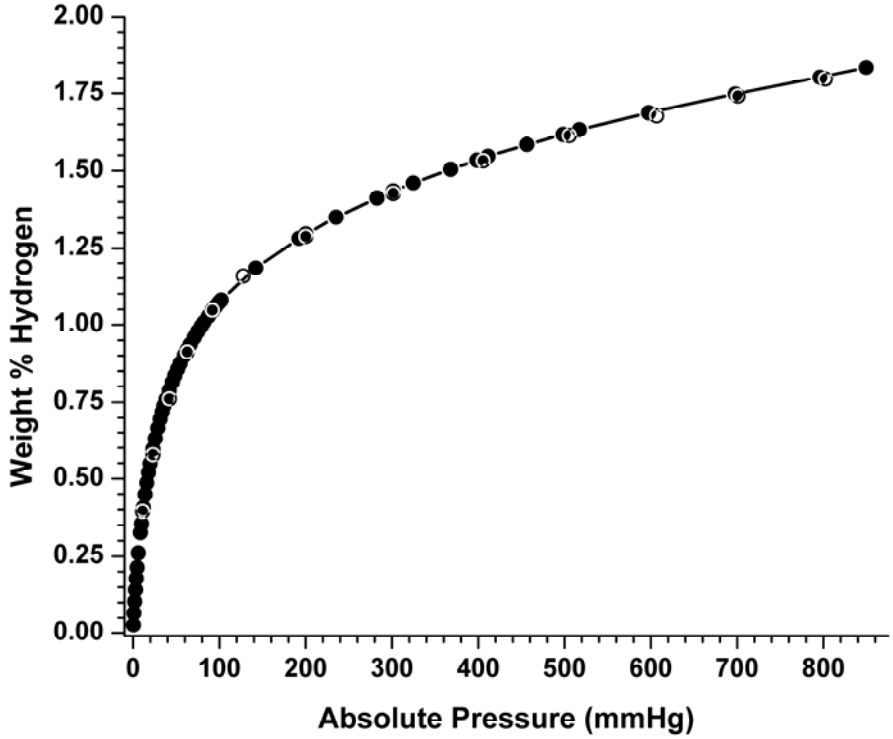

Figure S12. H_2 sorption isotherm for **[$Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3$] (2');** filled circles for sorption; open circles for desorption.

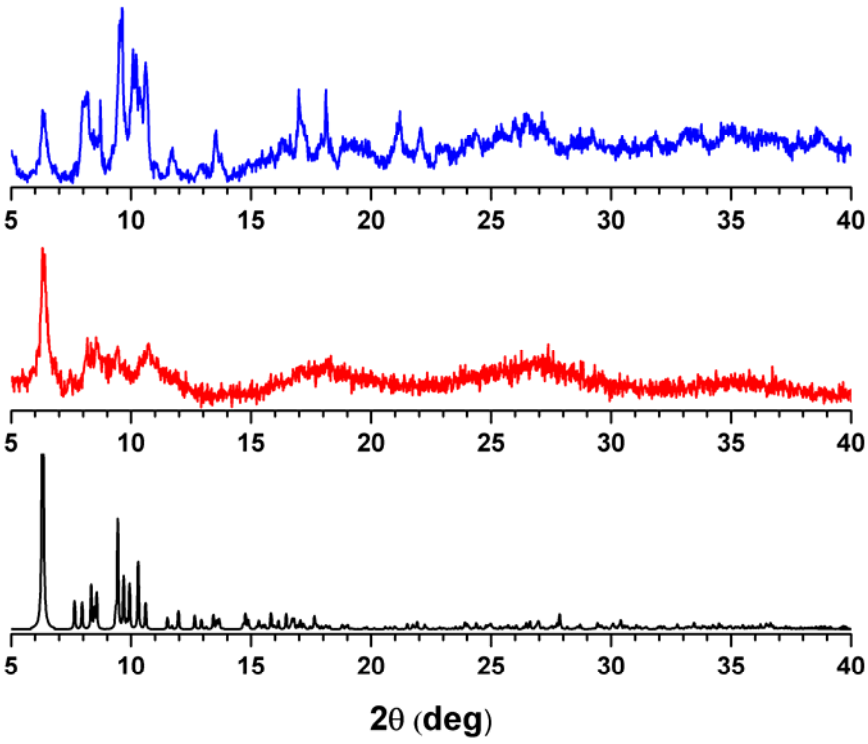

Figure S13. Powder diffraction profiles for **[$Cd_4Cl_3(4\text{-pt})_4(OH)(DMF)_3$] •8DMF•14MeOH (2•8DMF•14MeOH)** (blue), **[$Cd_4Cl_3(4\text{-pt})_4(OH)(H_2O)_3$] (2')** (red), and calculated for **2•8DMF•14MeOH** (black).

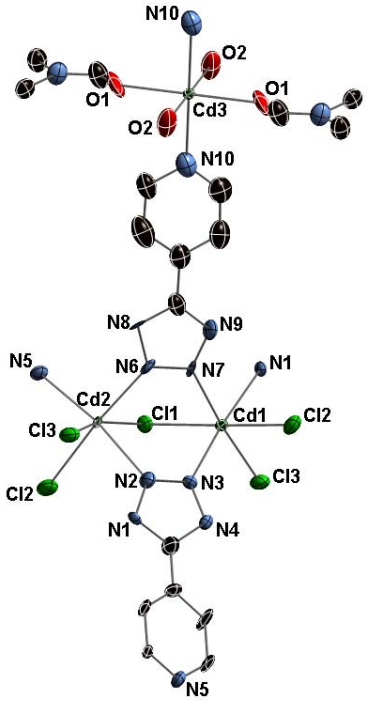

Figure S14. Atom-labeling scheme and 50% thermal ellipsoids for the structure of of **$[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H_2O)_2]$•10DMF (3•10DMF)**.

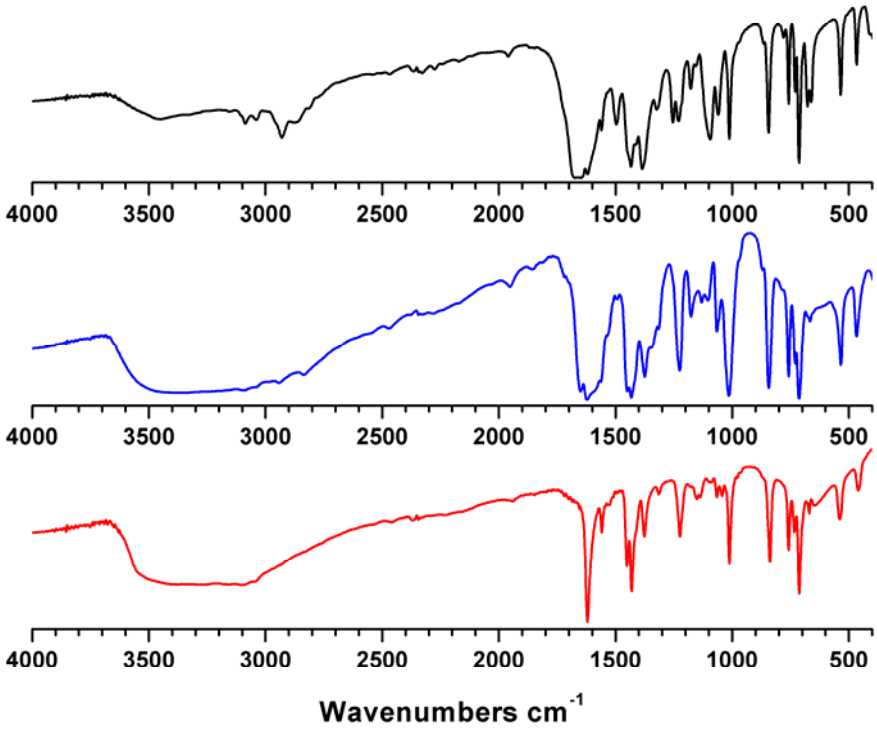

Figure S15. Infrared spectra of **$[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H_2O)_2]$•10DMF (3•10DMF)** (black), **$[Cd_5Cl_6(4\text{-pt})_4(DMF)_2(H_2O)_2]$ (3)** (blue), and **$[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]$ (3')** (red).

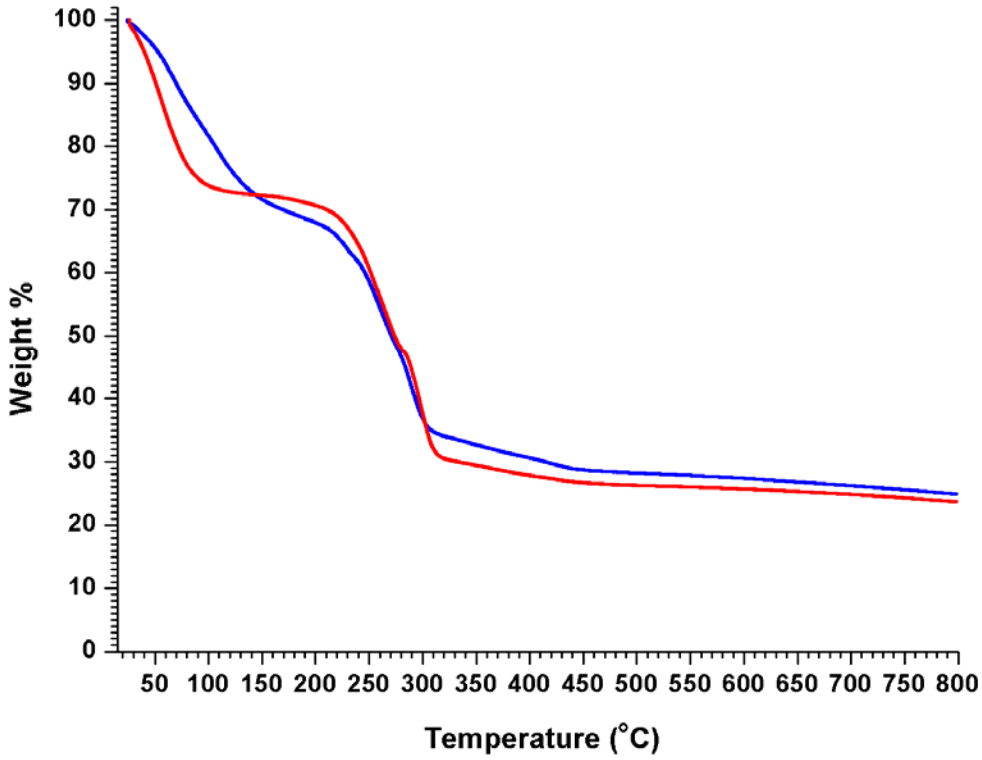

Figure S16. TGA profiles **[Cd_5Cl_6(4-pt)$_4$(DMF)$_2$(H_2O)$_2$] •10DMF (3•10DMF)** (blue) and **[Cd_5Cl_6(4-pt)$_4$(DMF)$_2$(H_2O)$_2$]•9MeOH (3•9MeOH)** (red).

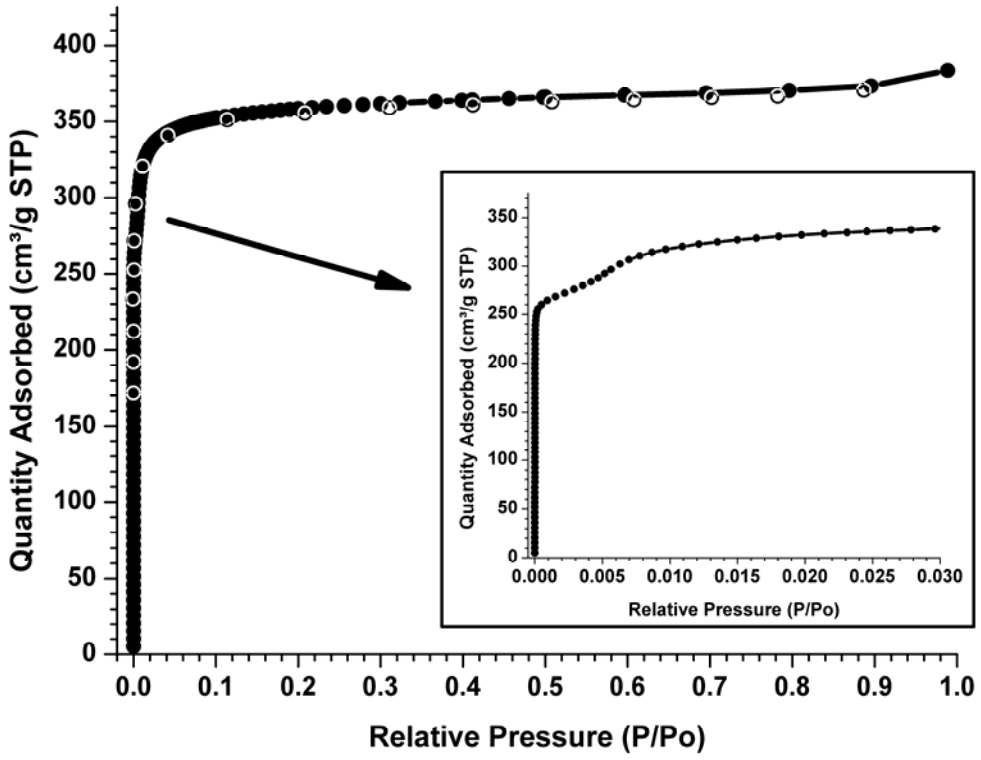

Figure S17. N_2 sorption isotherm for **[$Cd_5Cl_6(4\text{-pt})_4(H_2O)_4$] (3').** The inset shows the sorption behavior at low relative pressure P/P_0; filled circles for sorption; open circles for desorption.

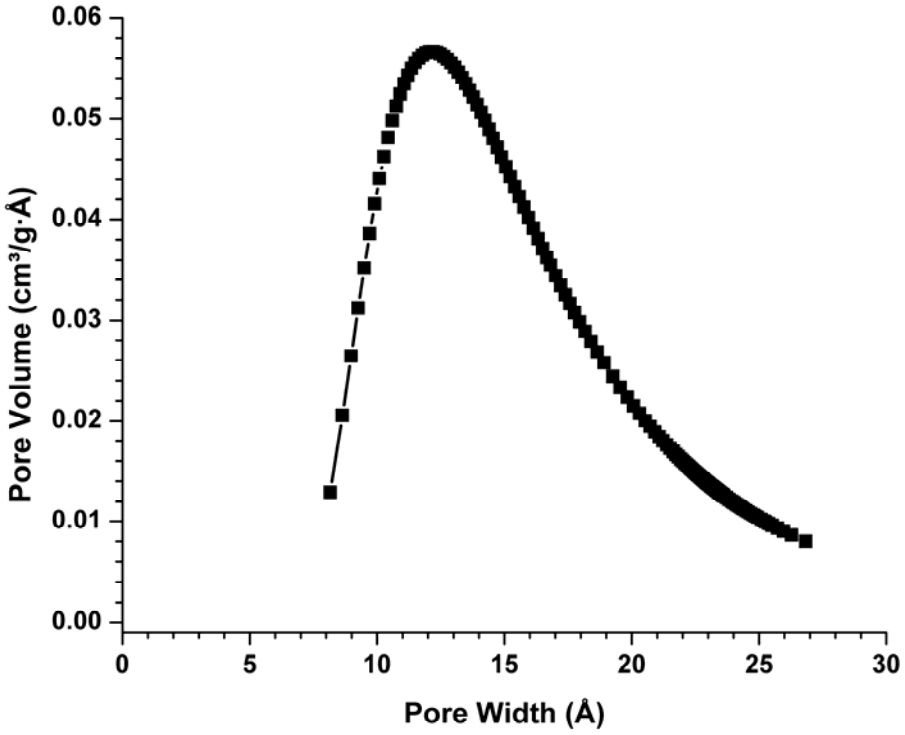

Figure S18. Pore size distribution for **[$Cd_5Cl_6(4\text{-pt})_4(H_2O)_4$] (3')** based on Dubinin-Astakhov analyses of the N_2 sorption isotherm.

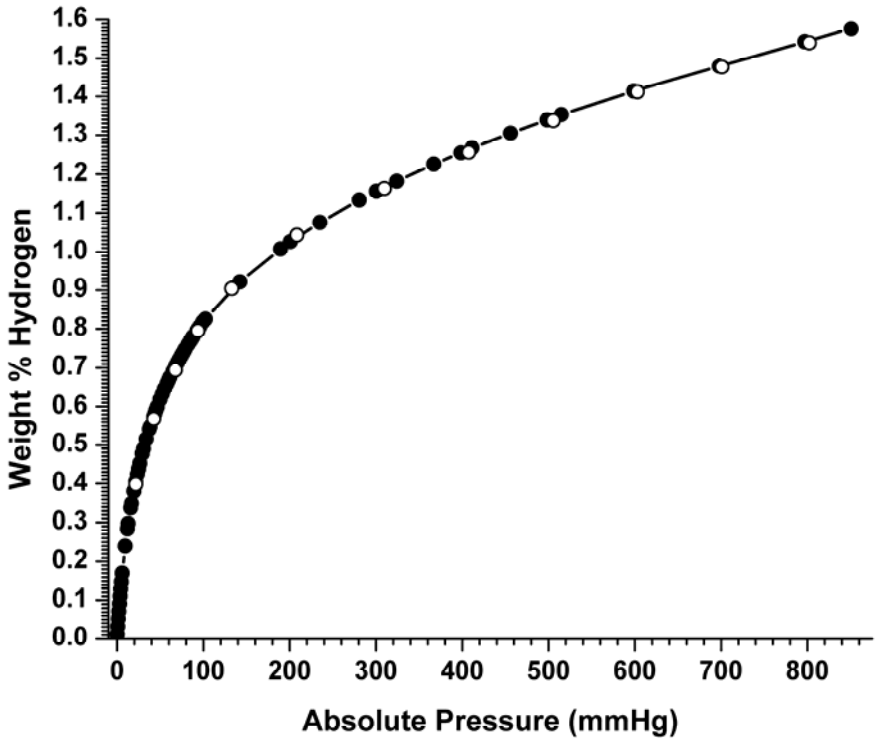

Figure S19. H_2 sorption isotherm for **$[Cd_5Cl_6(4\text{-pt})_4(H_2O)_4]$ (3');** filled circles for sorption; open circles for desorption.

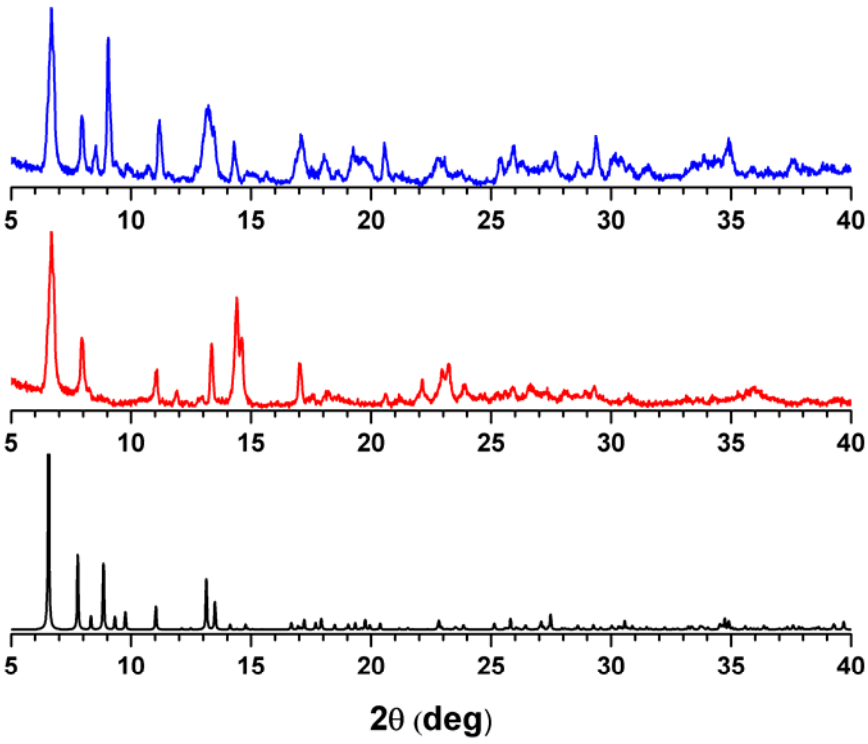

Figure S20. Powder diffraction profiles for **[Cd_5Cl_6(4-pt)$_4$(DMF)$_2$(H_2O)$_2$] •10DMF (3•10DMF)** (blue), **[Cd_5Cl_6(4-pt)$_4$(H_2O)$_4$] (2')** (red), and calculated for **(3•10DMF)** (black).

Supplementary Material (ESI) for Chemical Communications
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