Supporting Information

Three Zn(II)/Cd(II)/Mn(II) Coordination Polymers Based on a 2-Hydroxy-*N*-(1*H*-tetrazol-5-yl) Benzamide Ligand: Structures, Magnetic and Photoluminescence Properties

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General procedures

Infrared spectra were recorded using KBr pellets in the range 4000-400 cm^{-1} employing a Nicolet FT-IR 400 system. Thermogravimetric analysis (TGA) was performed in a nitrogen stream using an Pyris Diamond system with a heating rate of 10°C min^{-1}. Powder X-ray diffraction (PXRD) data was recorded by a Bruker D8 ADVANCE automated diffractometer. Elemental microanalyses (EA) were performed on a Perkin-Elmer CHN-2400 analyzer. Photoluminescence (PL) spectra were recorded using a Xe-lamp source and Edinburgh Instruments FLSP920 steady state spectrometer. Variable-temperature magnetic susceptibilities was measured on a Quantum Design MPMS XL-7 SQUID magnetometer in a magnetic field of 1000Oe under the temperature range 2–300K. The adsorption isotherms were measured at 273 K for CO_2 and 77 K for N_2 using a Micrometric ASAP2020M system and ultra-pure gases (99.999%).

Crystallographic data collections and refinements of structure

All crystals were taken from the solution directly without further treatment, transferred to oil and mounted into a capillary glass for single crystal X-ray data collection. Diffraction was measured on a Bruker Smart Apex diffractometer equipped with a Mo-Kα sealed-tube X-ray source (λ = 0.71073 Å, graphite monochromated) at room temperature. The data frames were recorded using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for

absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structures were solved by direct method using SHELXS and refined by full-matrix least-squares on F2 using SHELXL software. For crystal **1-3**, The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL)[1]. Since the solvent water molecules are badly disordered, we cannot find all water molecules and their exact location, as well as the well anisotropic refinement for this badly disordered solvent molecules seems also impossible. Thereby, in 'Mn.cif' file, we only defined partly solvent molecules that are refined by isotropic refinement. We also tried to refine occupancy of O1s in Zn complex, and the result is 0.9698. Since the O1s is disordered and after PACK in XP, we found the O1s and O1s' is very close (1.988 Å), so we set the occupancy of O1s as 0.5. For Cd complex the refine occupancy of O1s is 0.5. Then, we carry out Platon Squeeze program[2] towards these badly disordered solvent molecules, leading to the better *R1* and *ωR2* values, which is reported as 'M-squeeze.cif' (M= Zn, Cd, Mn) file.

For crystal structure of **1**(ZnL$_2$): We obtained *R1*=0.0558, *ωR2*=0.1270 values before SQUEEZE routine and *R1*=0.0488, *ωR2*=0.0846 after SQUEEZE routine of PLATON. The squeezed void volume was 364.6 Å^3, equivalent to 17.8% of the unit cell.

Alert level A (in **1**)

PLAT430_ALERT_2_A Short Inter D...A Contact   O1S   ..   O1S   ..   2.11 Ang.
Author Response: O1S is the oxygen atom of lattice water molecule. Since O1S is badly disordered in the channels of the framework, the distance between them is reasonable.

For crystal structure of **2** (CdL$_2$): We obtained *R1*=0.0354, *ωR2*=0.1115 values before SQUEEZE routine and *R1*=0.284, *ωR2*=0.0727 after SQUEEZE routine of PLATON. The squeezed void volume was 455.0 Å^3, equivalent to 21.2% of the unit cell.

For crystal structure of **3** (MnL$_2$): We obtained *R1*=0.0492, *ωR2*=0.1500 values before SQUEEZE routine and *R1*=0.389, *ωR2*=0.0981 after SQUEEZE routine of PLATON. The squeezed void volume was 443.9 Å^3, equivalent to 20.7% of the unit cell.

Alert level A (in **3**)

PLAT430_ALERT_2_A Short Inter D...A Contact   O1SA   ..   O1SA   ..   2.43 Ang.
Author Response: O1S is the oxygen atom of lattice water molecule. Since O1S is badly disordered in the channels of the framework, the distance between them is reasonable.

According to Platon calculation, for $C_{64}H_{48}N_{40}O_{20}Zn_4$($C_{64}H_{48}N_{40}O_{20}Cd_4$ and $C_{64}H_{48}N_{40}O_{20}Mn_4$), the total potential solvent accessible void is 364.6 e-/ $Å^3$(455.0 and 443.9 e-/ $Å^3$). So for each [ML_2]·xH_2O, the total potential solvent accessible void is 91 e-/ $Å^3$ (114 and 111 e-/ $Å^3$). Since one hydrogen bonded water molecule has ~40 e-/ $Å^3$ volume. The solvent accessible void may correspond to 2~3 water molecules, which is agreed with the elemental analysis and TGA results.

Gas sorption study

The desolvated samples **1a**, **2a** and **3a** were prepared under vacuum at 90ºC overnight after soaking in DMA for 12h and then in MeOH for 3days.Then **1a**, **2a** and **3a** were subjected to gas adsorption using N_2 at 77K and CO_2 at 273 K. As shown in Fig. S11, N_2 sorption behaviour of **1a**, **2a** and **3a** give a typical Type II isotherm, which is usual for a nonporous solid. The N_2 was adsorbed with an approximate value of 5.2 mL/g of the desolvated sample for **1a** (23.5mL/g for **2a** and 19.5mL/g for **3a**), at 750mmHg (77K), and the estimated BET surface area is 3.21 m^2/g for **1a** (19.88m^2/g for **2a** and 12.45m^2/g for **3a**). These values indicate that the adsorption occurs only on the surface of the solid. As shown in Fig. S12, CO_2 was adsorbed with an approximate value of 1.4 mL/g for **1a** (13.1mL/g for **2a** and 2.4mL/g for **3a**), at 750mmHg (273K).

Table S1. Selected Bond Lengths (Å) and Bond Angles (° deg) for **1-3**

1			
Zn(1)- O(2)	2.135(3)	O(2)-Zn(1)-O(2)i	86.06(12)
Zn(1)-N(2)	2.070(4)	O(2)-Zn(1)-N(2)i	88.59(13)
Zn(1)-O(2)i	2.135(3)	O(2)-Zn(1)-N(3)ii	176.51(13)
Zn(1)-N(2) i	2.070(4)	O(2)-Zn(1)-N(3)iii	91.10(12)
Zn(1)-N(3)ii	2.140(3)	N(2)-Zn(1)-N(2)i	169.19(12)
Zn(1)-N(3)iii	2.140(3)	N(2)-Zn(1)-N(3)ii	98.48(13)
O(2)-Zn(1)-N(2)	83.51(13)	N(2)-Zn(1)-N(3) iii	89.06(13)
2			
Cd(1)-O(2)	2.306(3)	O(2)-Cd(1)-O(2) i	87.82(10)
Cd(1)-N(2)	2.254(3)	O(2)-Cd(1)-N(2) i	93.86(10)
Cd(1)-O(2) i	2.306(3)	O(2)-Cd(1)-N(3) ii	178.72(10)
Cd(1)-N(2) i	2.254(3)	O(2)-Cd(1)-N(3) iii	91.26(10)
Cd(1)-N(3) ii	2.321(3)	N(2)-Cd(1)-N(2) i	168.13(10)
Cd(1)-N(3) iii	2.321(3)	N(2)-Cd(1)-N(3) ii	101. 67(10)
O(2)-Cd(1)-N(2)	77.51(10)	N(2)-Cd(1)-N(3)iii	86.80(10)
3			
Mn(1)-O(2)	2.173(2)	O(2)-Mn(1)-O(2) i	88.39(9)
Mn(1)-N(2)	2.204(2)	O(2)-Mn(1)-N(2) i	92.79(8)
Mn(1)-O(2) i	2.173(2)	O(2)-Mn(1)-N(3) ii	179.19(8)
Mn(1)-N(2) i	2.204(2)	O(2)-Mn(1)-N(3) iii	91.08(8)
Mn(1)-N(3) ii	2.247(2)	N(2)-Mn(1)-N(2) i	170.89(9)
Mn(1)-N(3) iii	2.247(2)	N(2)-Mn(1)-N(3) ii	98.77(8)

O(2)-Mn(1)-N(2)	80.65(8)	N(2)-Mn(1)-N(3) *iii*	87.73(8)

Symmetry transformations used to generate equivalent atoms:

1, *i*= –x+2,y, -z+1/2   *ii*= –x+2, -y+2, -z+1   *iii*= x, -y+2, z-1/2

2, *i*= –x+2,y, -z+3/2   *ii*= –x+2, -y+1, -z+2   *iii*= x, -y+1, z -1/2

3, *i*= -x+1,y, -z+1/2   *ii*= -x+1,-y+1,-z+1   *iii*= x,-y+1, z-1/2

Table S2. Distances [Å]and angles [˚] of selected hydrogen bonding for complex **1-3**

D-H…A	d(D-H)	d(H..A)	d(D…A)	<D-H…A
1				
O1-H1… N5[i]	0.82	1.84	2.633(6)	162.00
N1-H1N…O1	0.86	1.85	2.571(6)	140.00
2				
O1-H1…N5[ii]	0.82	1.84	2.640(5)	165.00
N1-H1N… O1	0.86	1.84	2.568(5)	141.00
3				
O1-H1…N5[iii]	0.82	1.86	2.639(4)	157.00
N1-H1N…O1	0.86	1.87	2.585(4)	140.00

Symmetry operators:
i=-x+3/2, -y +3/2, -z +1; *ii*=-x +3/2, -y+ 1/2, -z+ 2; *iii*=-x +1/2, -y+1/2, -z +1

[1] G. M. Sheldrick, SHELXTL, Structure Determination Software Suite, Bruker AXS, Madison, WI, 2003.

[2] A. L. Spek, PLATON, A multipurpose crystallographic tool, Utrecht University, The Netherlands, 2001.
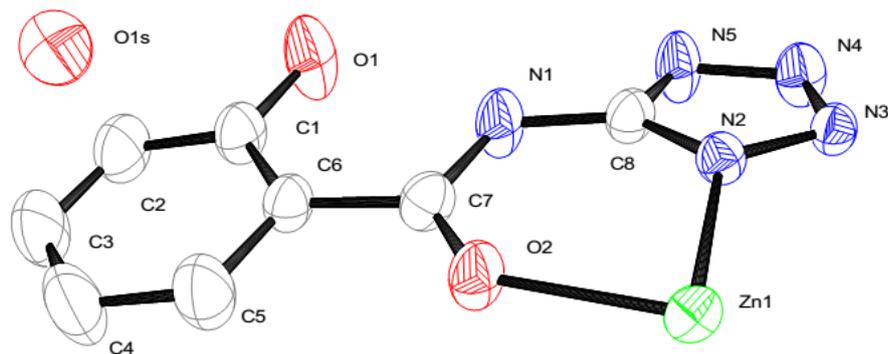
Figure S1. ORTEP drawing of **1** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Atom colours shown as carbon - gray, nitrogen - blue, oxygen - red and zinc- green.
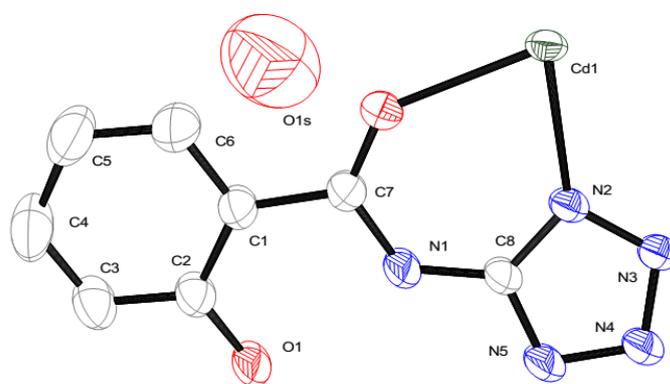
Figure S2. ORTEP drawing of **2** at the 50% probability level. Hydrogen atoms are omitted for clarity. Atom colours shown as carbon - gray, nitrogen - blue, oxygen - red and Cadmium- dark green.
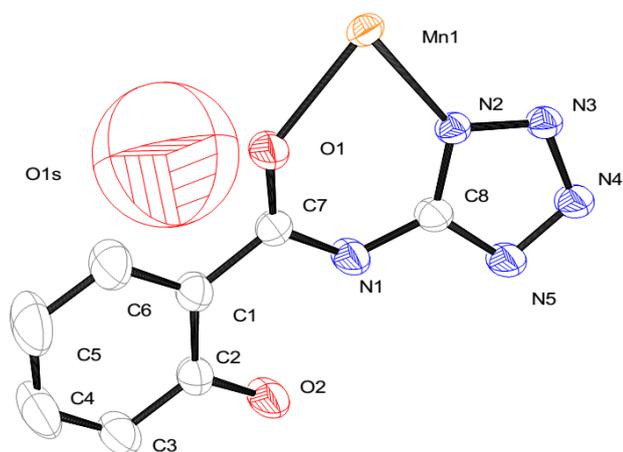

Figure S3. ORTEP drawing of **3** at the 50% probability level. Hydrogen atoms are omitted for clarity. Atom colours shown as carbon - gray, nitrogen - blue, oxygen - red and Manganese- orange.
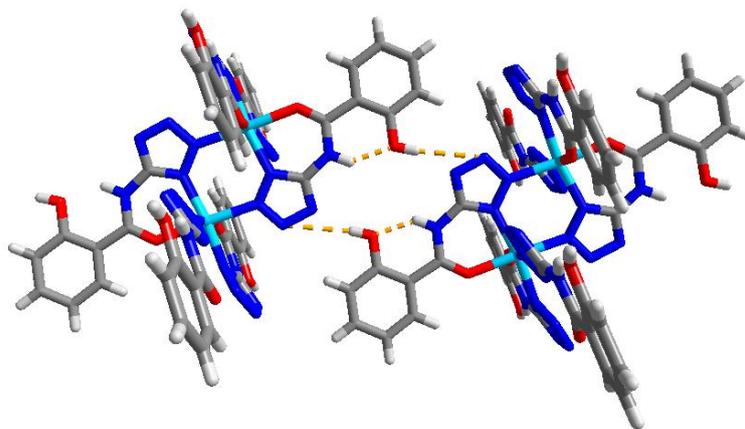
Figure S4. Hydrogen-bonds between the amide, phenol and tetrazole groups in **1**. Yellow dashed lines refer to hydrogen bonds.
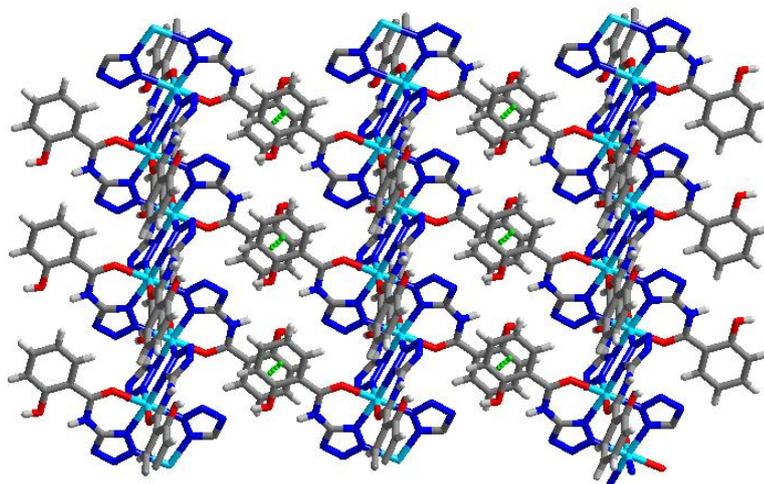
Figure S5. π–π stacking interactions (green dashed lines) between adjacent 1-D chains in **1.**
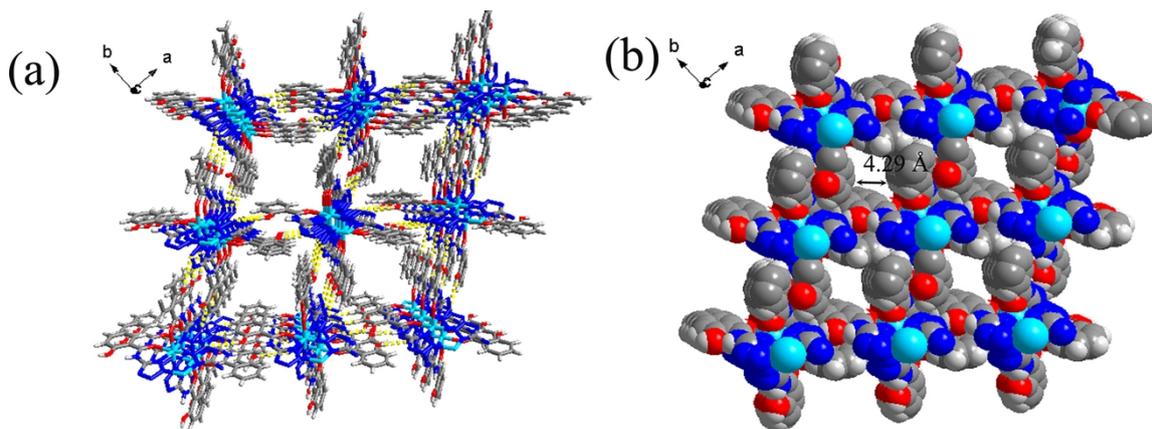
Figure S6. a) X-ray crystal structures of **1** showing 3D network with 1D channels. b) CPK model picture of the **1** illustrating the dimensions of the channel windows (4.29 × 4.29 Å) along the *c* axis. Guest molecules are omitted for clarity.
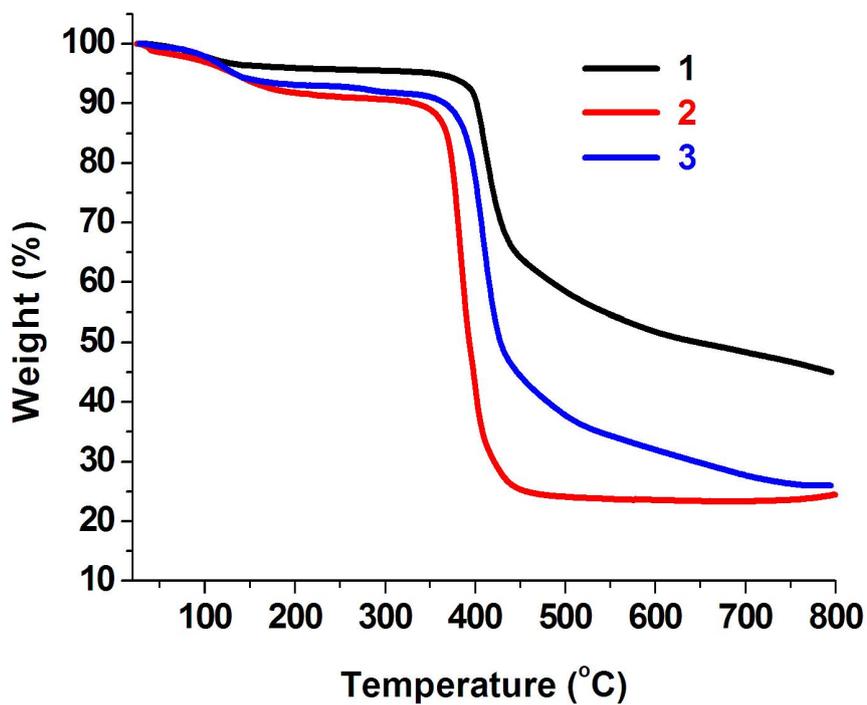

Figure S7. TGA diagrams of compounds **1-3**.
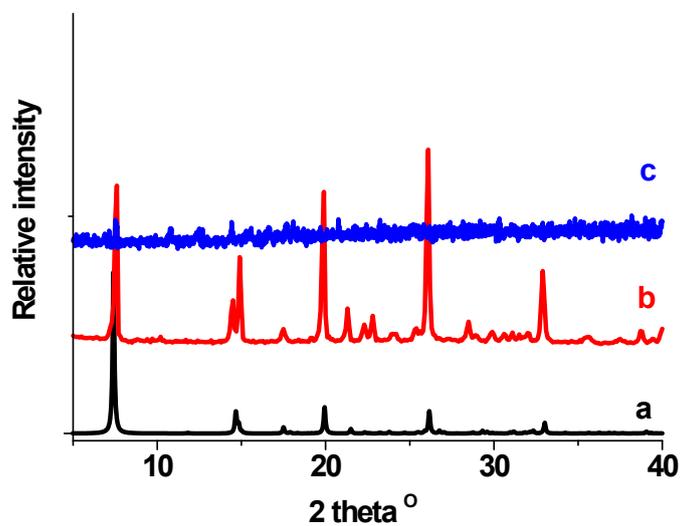
Figure S8. PXRD patterns of **1(Zn)**. (a) Simulated PXRD pattern from the single crystal structure of **1**, (b) as synthesized, **1** and (c) actived **1**.
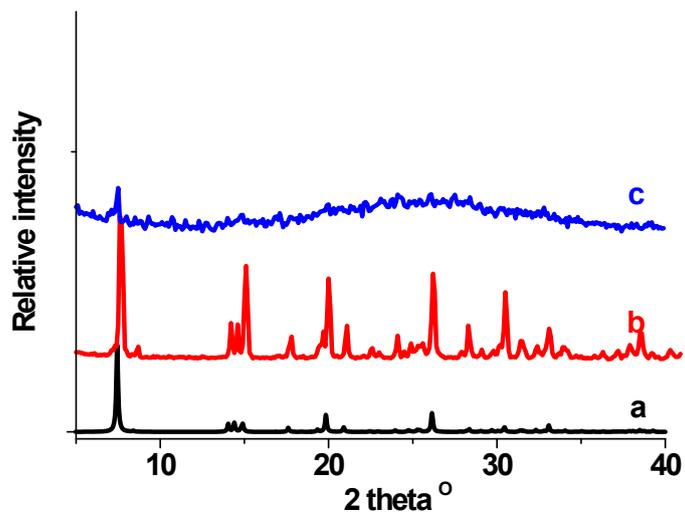

Figure S9. PXRD patterns of **2(Cd).** (a) Simulated PXRD pattern from the single crystal structure of **2,** (b) as synthesized, **2** and (c) actived **2**.

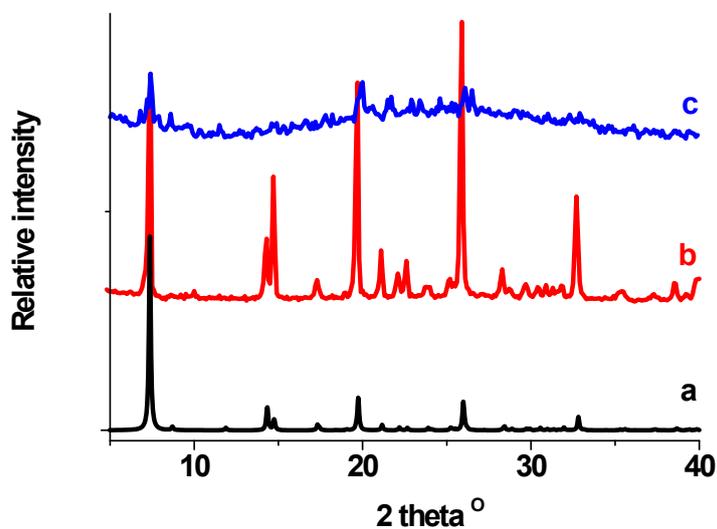Figure S10. PXRD patterns of **3**(**Mn**). (a) Simulated PXRD pattern from the single crystal structure of **3**, (b) as synthesized, **3** and (c) actived **3**.
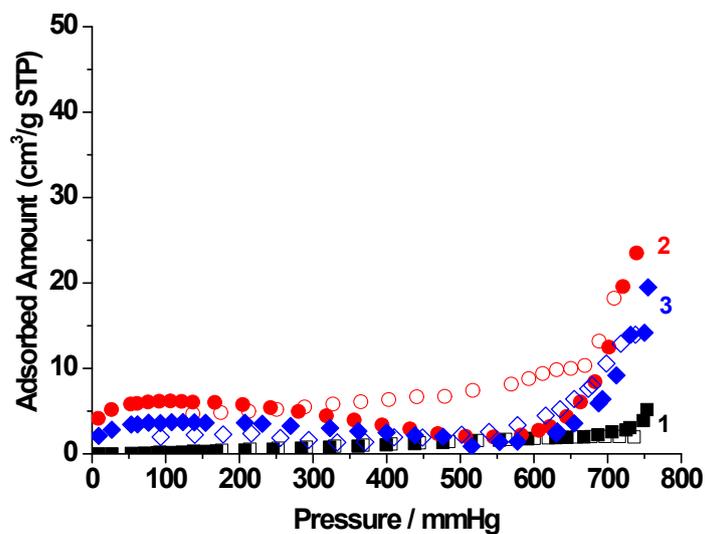

Figure S11. Gas sorption isotherms of N_2(77 K) ; ■ and □ represent the adsorption and desorption of **1** (● and ○ for **2**; ♦ and ◊ for **3**)
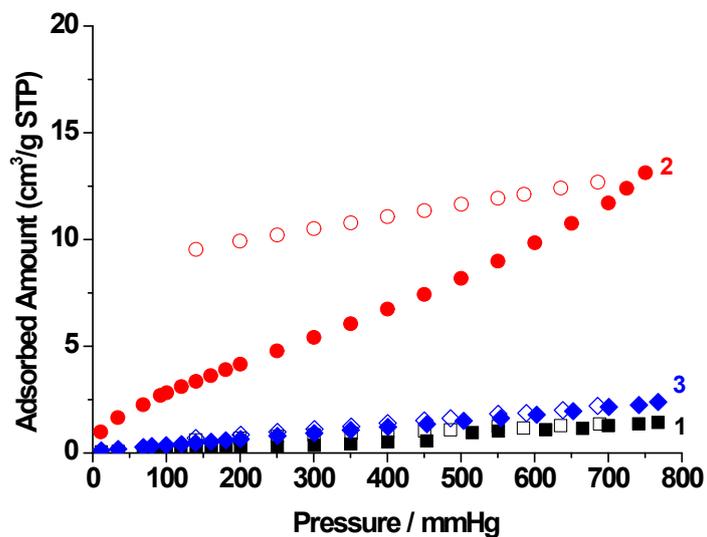
Figure S12. Gas sorption isotherms of CO_2(273 K) ; ■ and □ represent the adsorption and desorption of **1** (● and ○ for **2**; ♦ and ◊ for **3**)
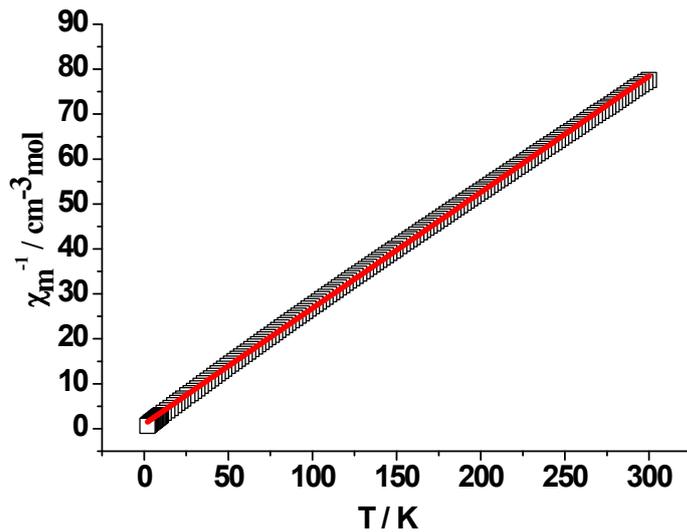

Figure S13. Plots of the χ_M^{-1} vs T for **3**. The solid line shows the Curie–Weiss fitting (2K to 300K).