Electronic supplementary information (ESI)

Single-Crystal to Single-Crystal Transformation of a 2-D Coordination Network to a 3-D Metal-organic Framework Greatly Enahnces Porosity and Hydorgen Uptake

Liang Wen,[a,b] , Peng Cheng,[b] and Wenbin Lin[a,]*

[a]*Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599, USA. E-mail: wlin@unc.edu*

[b]*Department of chemistry and Key Laboratory of Advanced Energy Materials Chemistry (MOE), Nankai University, Tianjin 30071, China.*

Material and Methods: All solvents were purchased from Fisher or TCI and used without further purification. Thermogravimetric analysis (TGA) was performed in air using a Shimadzu TGA-50 equipped with a platinum pan and heated at a rate of 3 °C per minute. Single-crystal X-ray diffraction and Powder X-ray diffraction (PXRD) data were collected on a Bruker SMART APEX II diffractometer using Cu radiation. The PXRD patterns were processed with the APEX 2 package using PILOT plug-in. Nitrogen and hydrogen adsorption experiments were performed with Autosorb-1C from Quantachrome, Inc. The ligand of methanetetra (biphenyl-p-carboxylic acid) (H_4**L**) was synthesized via the literature method.[1]

Procedures for crystal growth:

Synthesis of $[Zn_2L(DMF)_4]\cdot 2DMF\cdot 4H_2O$ (1): A mixture of H_4**L** (5 mg, 0.0063 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (10 mg, 0.0336 mmol) was dissolved in DMF (1 mL) in a screw capped vial. After addition of several drops of HCl (3M, aq.), the vial was capped and placed in an oven at 90 °C for two days. Rod-shaped crystals (2.2 mg, 44%) were obtained after filtration.

Synthesis of [Co_2L(DMF)$_4$]·xSolv (1Co): A mixture of H_4**L** (2.5 mg, 0.0032 mmol) and $Co(NO_3)_2·6H_2O$ (8 mg, 0.028 mmol) was dissolved in DMF (1 mL) in a screw capped vial. After addition of several drops of HCl (3M, aq.), the vial was capped and placed in an oven at 70 °C for one day. Needle-shaped crystals (0.7 mg, 28%) were obtained after filtration.

Transformation of 1 or 1-Co to [Zn_2L(H_2O)$_2$]·xSolv (2) or [Co_2L(H_2O)$_4$]·xSolv (2-Co): A sample of **1** or **1**-Co was soaked in CH_2Cl_2 for 3-8 hours at room temperature. After CH_2Cl_2 was removed, DEF (N,N-diethylformamide) was added to exchange the low boiling point CH_2Cl_2. PXRD results showed that the structures of **2** or **2**-Co did not change upon solvent exchange with DEF.

X-ray Structure Determination

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based X-raydiffractometer system equipped with Cu –target X-ray tube and operated at 1600 watts. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. All of the structures were solved by direct methods and refined to convergence by least squares method on F^2 using the SHELXTL software suit. All non-hydrogen atoms are refined anisotropically. SQUEEZE subroutine of the PLATON software suit was applied to remove the scattering from the highly disordered solvent molecules. The resulting new HKL4 files were used to further refine the structures. Datasets for 1 and 2 were collected to $2\theta = 101^o$ and 71^o respectively.

Table S1. Crystal data and structure refinements for **1** and **2**

MOF	**1**	**2** (Framework)
Empirical formula	C71 H82 N6 O18 Zn2	C53H36O10Zn2
Formula weight	1438.24	963.64

Temperature	296(2) K	100(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system, space group	Orthorhombic, Pnn2	Orthorhombic, $P2_12_12$
Unit cell dimensions	a = 14.3366(7) Å	a = 26.9842(8) Å
	b = 36.0309(18) Å	b = 31.2626(7) Å
	c = 7.0730(3) Å	c = 7.2309(2) Å
	α = β = γ=90 deg	α = β = γ=90 deg
Volume	3653.6(3) Å ^{3}	6100.0(3) Å ^{3}
Z, Calculated density	4, 1.309 Mg/m^3	4, 1.010 Mg/m^3
Absorption coefficient	1.406 mm^{-1}	1.337 mm^{-1}
F(000)	1488	1832
Crystal size	0.31 x 0.15 x 0.04 mm	0.20 x 0.03 x 0.03 mm
Theta range for data collection	2.45 to 50.37 deg.	2.16 to 35.48 deg.
Limiting indices	-14<=h<=14, -35<=k<=36, -6<=l<=6	-15<=h<=15, 0<=k<=23, 0<=l<=5
Reflections collected / unique	3340 / 2722 [R(int) = 0.0394]	2320 / 1931 [R(int) = 0.0377]
Completeness to theta = 50.37	97.8 %	85.8 %
Max. and min. transmission	0.9511 and 0.6665	0.9610 and 0.7759
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3340 /12 / 406	2310 / 70 / 174
Goodness-of-fit on F^2	0.784	1.726
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1540	R1 = 0.0920, wR2 = 0.2399
R indices (all data)	R1 = 0.0737, wR2 = 0.1675	R1 = 0.1047, wR2 = 0.2466
Absolute structure parameter	0.96(8)	0.11(13)
Largest diff. peak and hole	0.037 and -0.027 e.A^-3	1.197 and -0.496 e.A^-3

[a]R(F) =Σ||Fo| - |Fc||/Σ|Fo|. b RW(F2) = [Σ{w(Fo2 - Fc2)2}/Σ{w(Fo2)2}]0.5; w-1 = σ2(Fo2) + (aP)2 + bP, where P= [Fo2 +2Fc2]/3 and a and b are constants adjusted by the program.

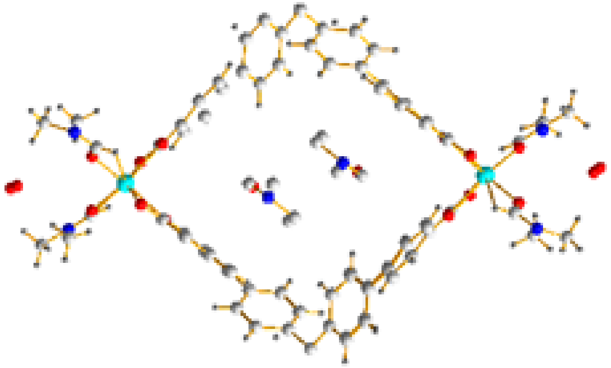

Fig. S1. The solvent molecules of **1** in a unit cell.

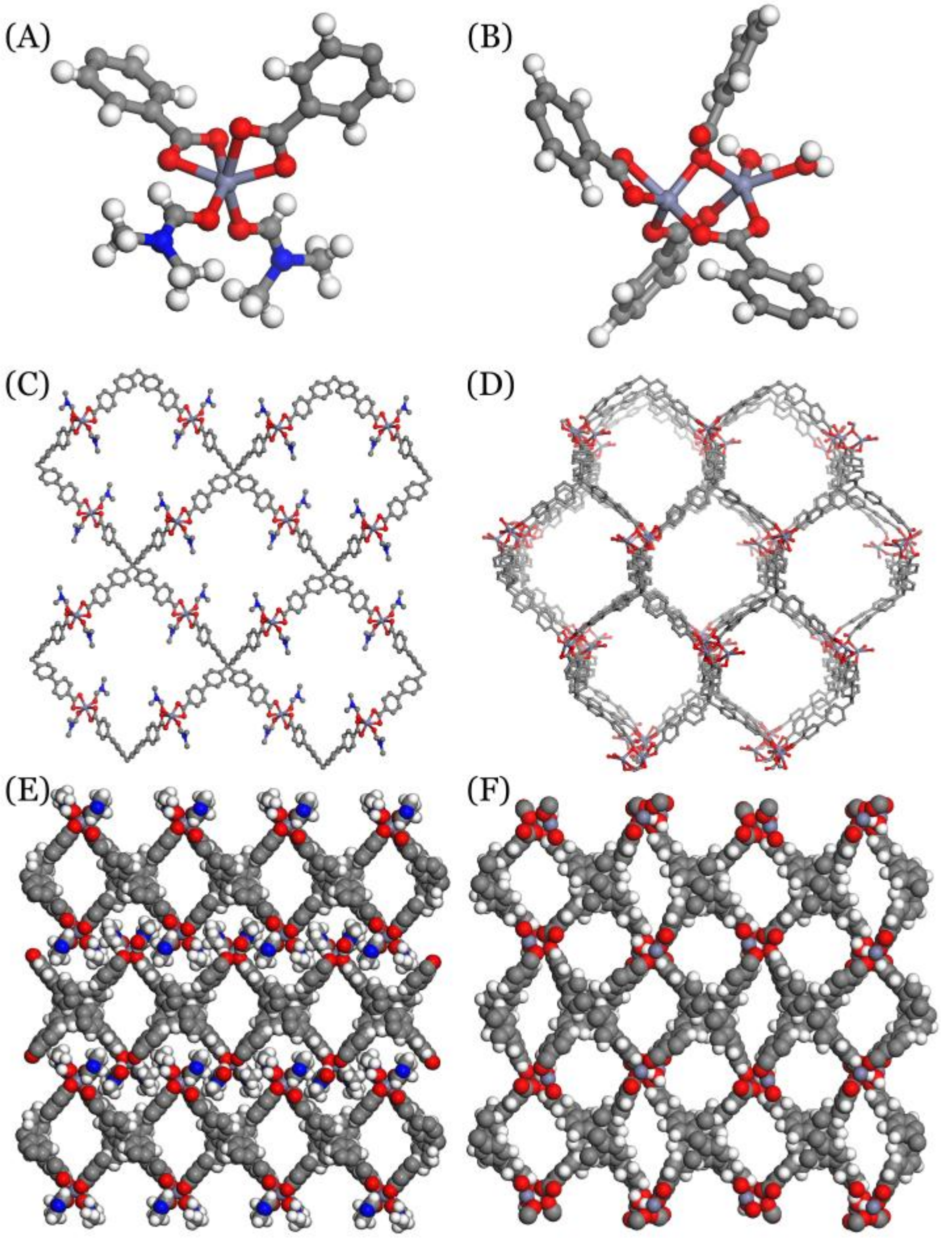

Fig. S2. (A) Coordination environments of Zn ions in **1**. (B) Coordination environments of Zinc ions in **2**. (C) 2D layers of **1** viewed along the *b* axis. Three folds of interpenetrated layers were omitted for charity. (D) 3D porous framework of **2** viewed along the *b* axis. Three folds of interpenetrated frameworks were omitted for charity. (E) Packing of **1** as viewed along the c axis. (F) 3D porous framework of **2** as viewed down the c axis.

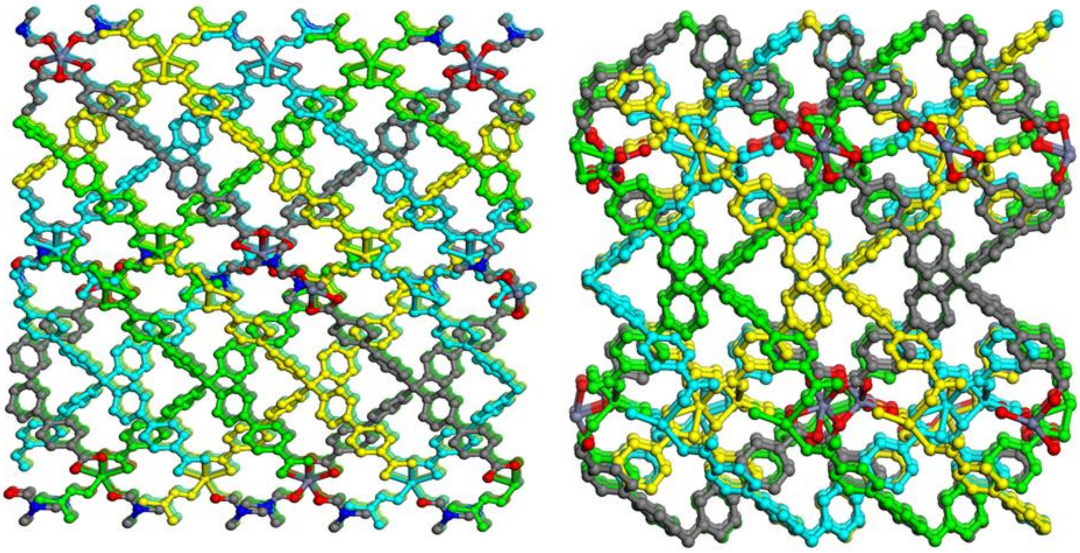

Fig. S3. Four-fold interpenetrated structure of **1** (left) and **2** (right) in the *bc* plane.

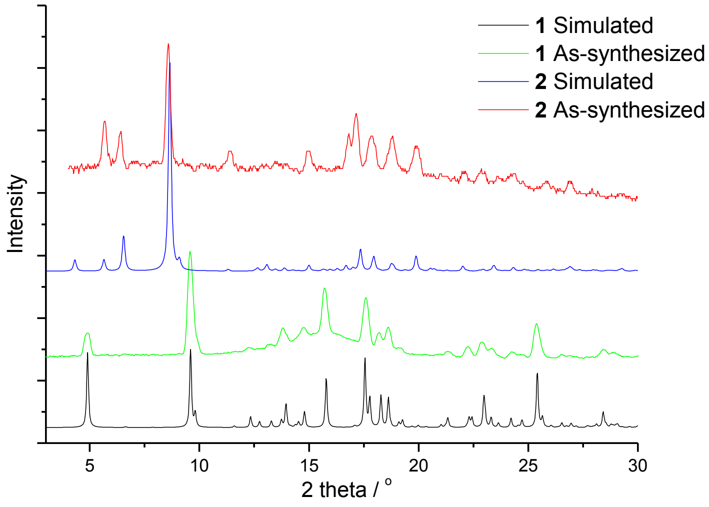

Fig. S4. Powder X-ray diffraction patterns of fresh crystals of **1**, **2** and their calculated

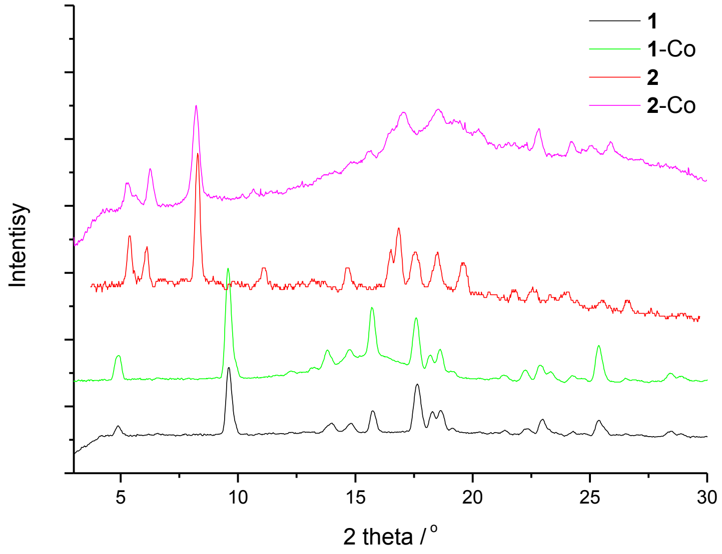

Fig. S5. Powder X-ray diffraction patterns of fresh crystals of **1**, **1**-Co, **2** and **2**-Co.

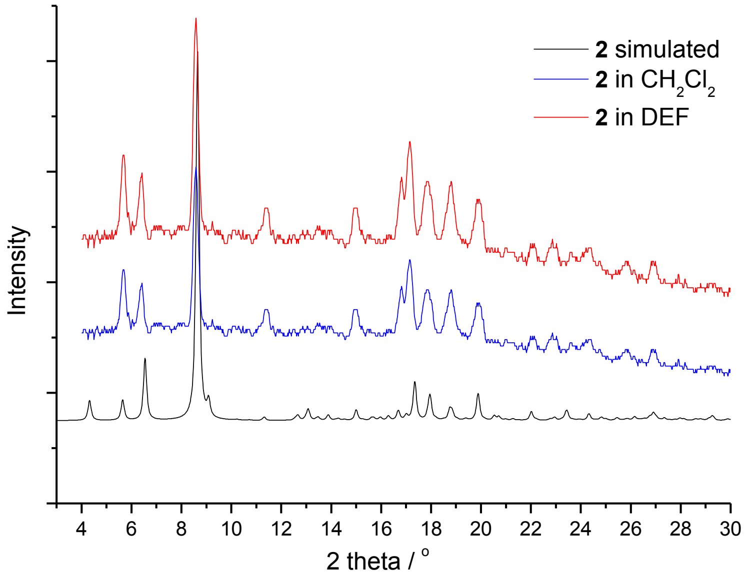

Fig. S6. Powder X-ray diffraction patterns of **2** in CH_2Cl_2, **2** in DEF and calculated PXRD pattern of **2.**

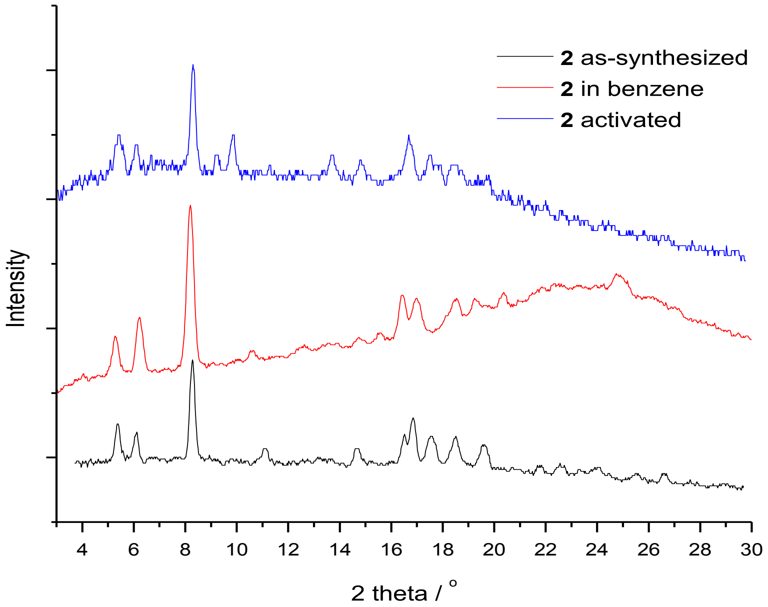

Fig. S7. Powder X-ray diffraction patterns of fresh crystals of **2**, **2** after soaked in benzene and **2** after activation.

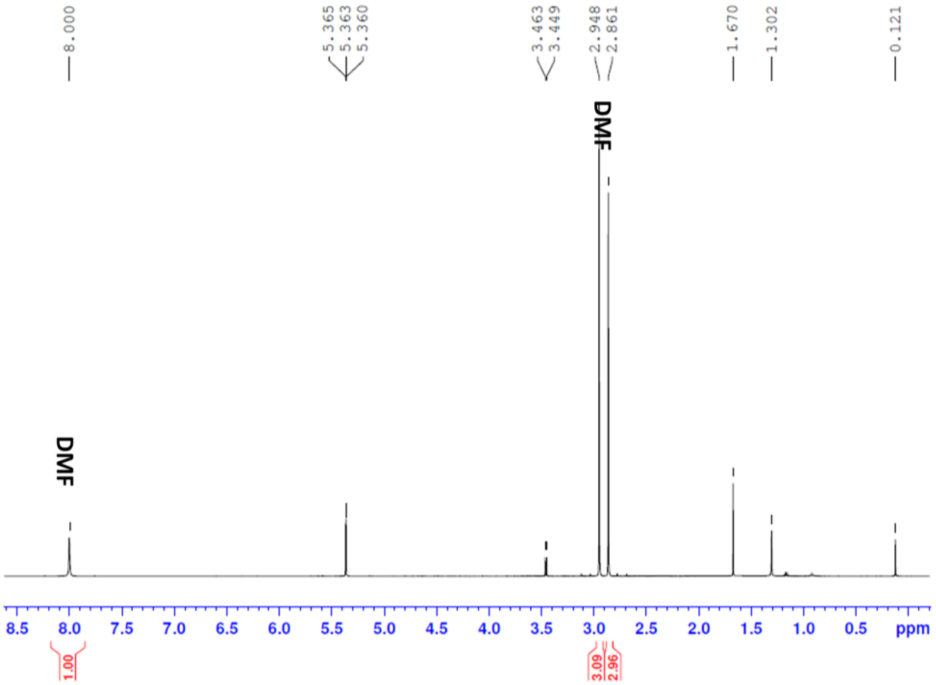

Fig. S8. ^{1}H NMR spectrum of the exchanged solvents after the transformation of **1** to **2**. **1** was washed with MeOH five times and dried in air for 10 minutes, and then soaked in CD_2Cl_2 in an NMR tube overnight before the ^{1}H NMR spectrum was taken. The signals due to DMF are clearly visible in the ^{1}H NMR spectrum, indicating the replacement of DMF molecules by water molecules in the coordination spheres.

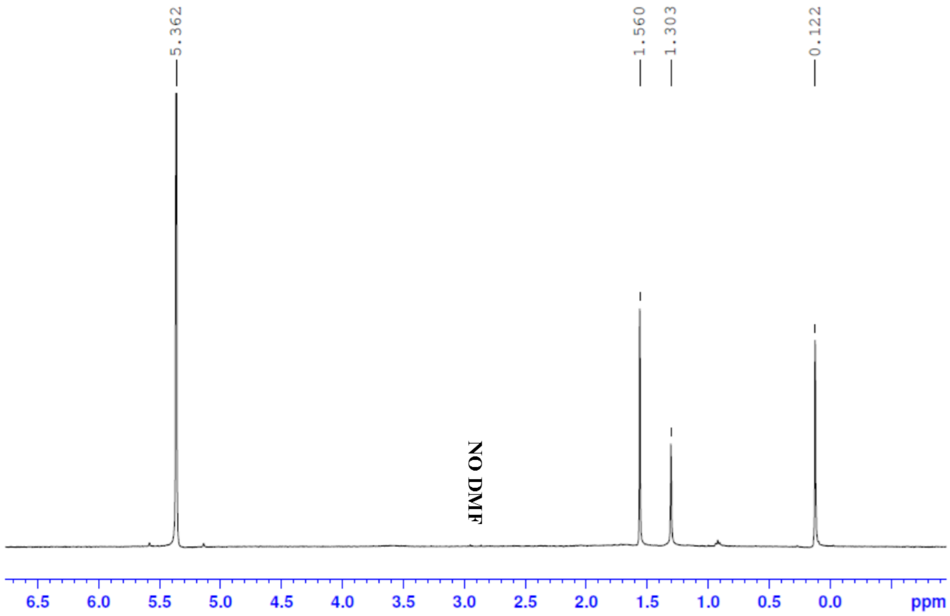

Fig. S9. ^{1}H NMR spectrum of the exchanged solvents from **2**. In this experiment, 1 was soaked in CH_2Cl_2 overnight then washed with CH_2Cl_2 for 5 times. After being dried in air for 5 minutes, the sample was soaked in CD_2Cl_2 before taking the ^{1}H NMR spectrum. The absence of DMF peaks indicated that DMF molecules have been replaced by water molecules in the coordination spheres.

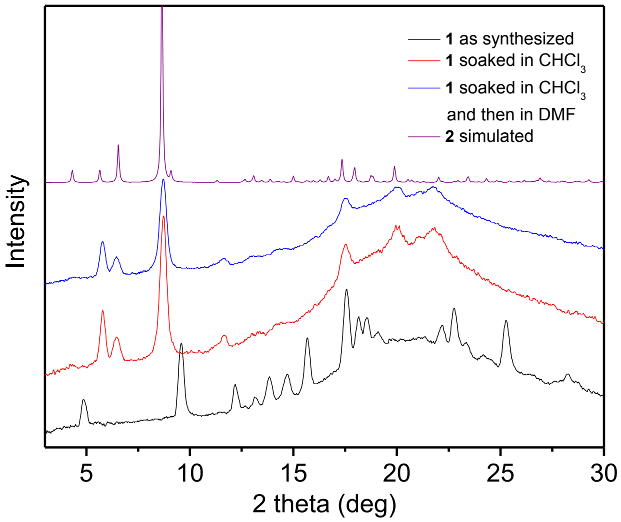

Fig. S10. PXRD patterns of as-synthesized **1**, **1** soaked in $CHCl_3$ overnight, **1** soaked in $CHCl_3$ overnight and then in DMF one day, and **2** (simulated from CIF file).

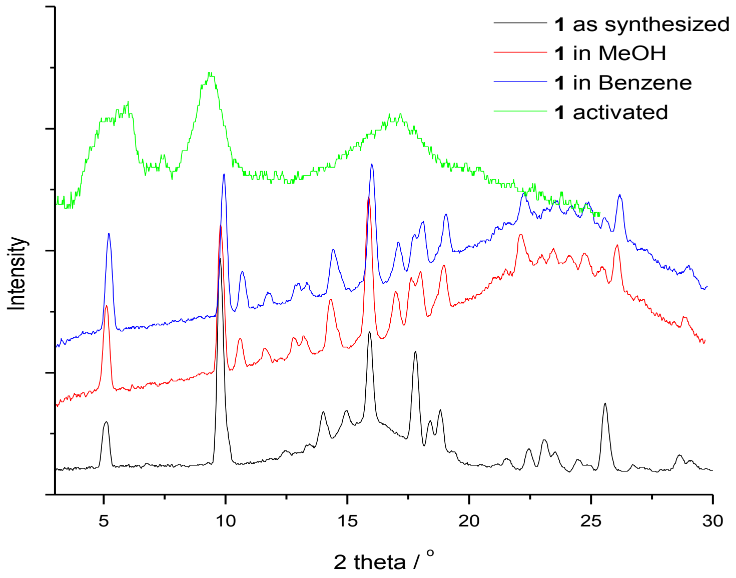

Fig. S11. Powder X-ray diffraction patterns of fresh crystals of **1**, **1** in MeOH, **1** in benzene and **1** after activation.

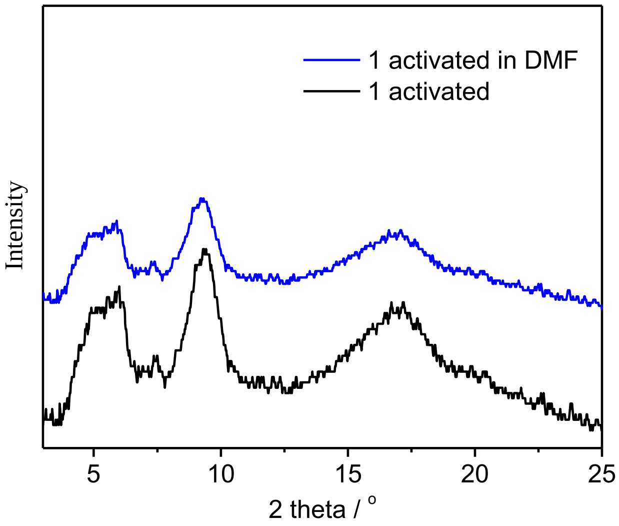

Fig. S12. PXRD patterns of **1** after activation and **1** after activation and then treated in DMF for one day.

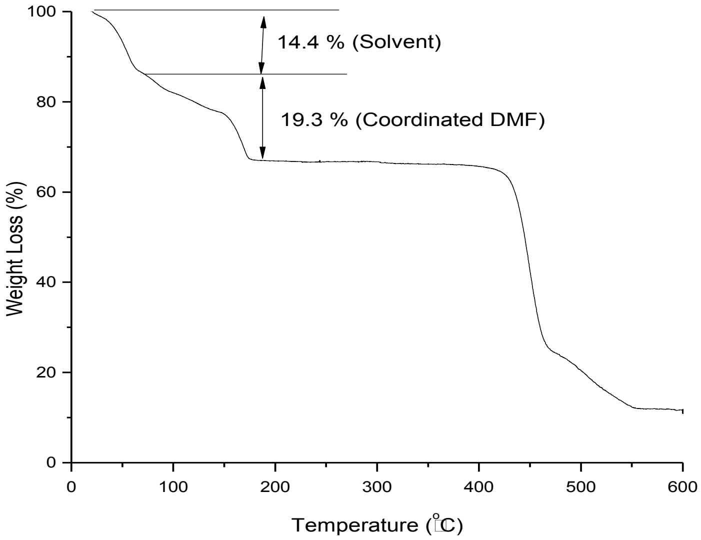

Fig. S13. The TGA curve of **1.**

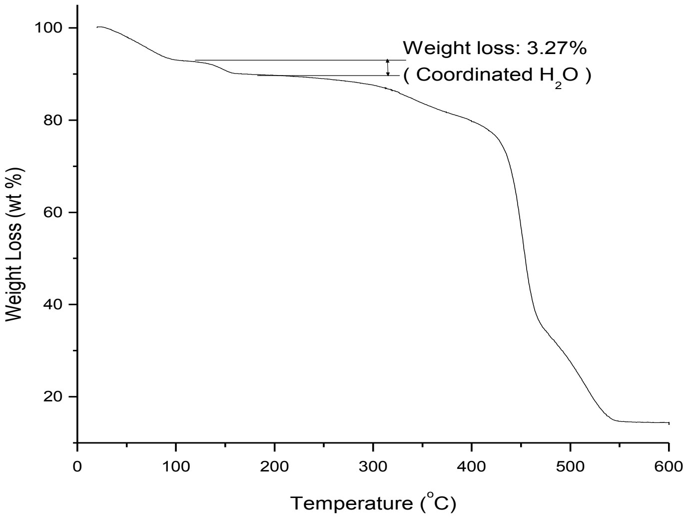

Fig. S14. The TGA curve of **2.**

ICP-MS analysis of 2 and 2-Co obtained from SC→SC transformation from 1 and 1-Co:

Samples **1** and **1-Co** were put together into a glass vial and soaked in 3 mL of methylene chloride. Photos of the samples were taken during the transformation process, and no changes of morphology were observed for the crystals. After 8 hours, the Zn and Co crystals handpicked based on their different colors and separately washed with DEF. The Zn and Co crystals were separately digested in concentrated nitric acid (228 μL) for 2 h then diluted to 8 mL. The metal content of the samples were determined by ICP-MS.

Table S2 Gas uptake data of **1** and **2** at 77 K

MOF	gas	amount of gas adsorb			surface area
		cm^3/g (STP)	mmol/g	wt%	BET/Langmuir
L2Zn1	N2	87.80	3.92	10.98	177.3/310.3 m^2/g
	H2	36.74	1.64	0.33	
L2Zn2	N2	397.04	17.72	49.62	1170/1467 m^2/g
	H2	195.55	8.73	1.75	

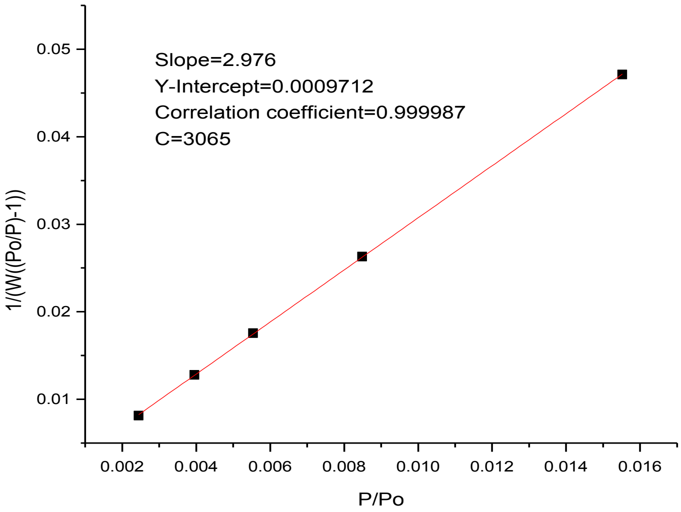

Fig. S15. Multipoint BET plot of **2** (S_{BET}=1170 m^2/g).

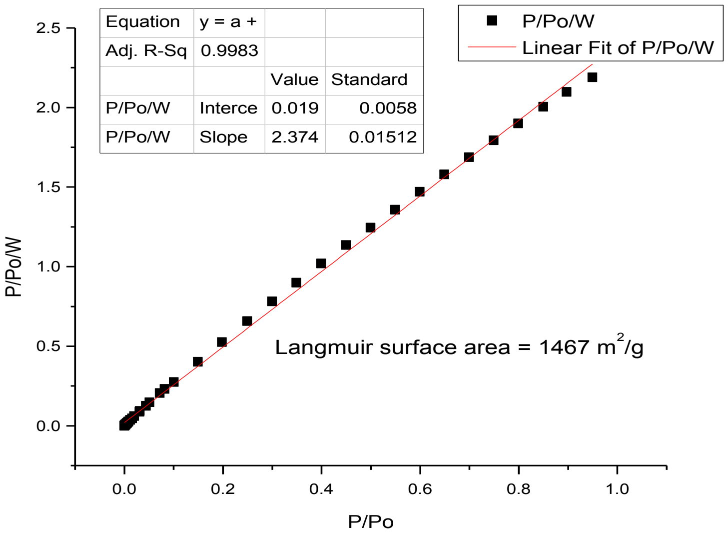

Fig. S16. Langmuir plot of **2**

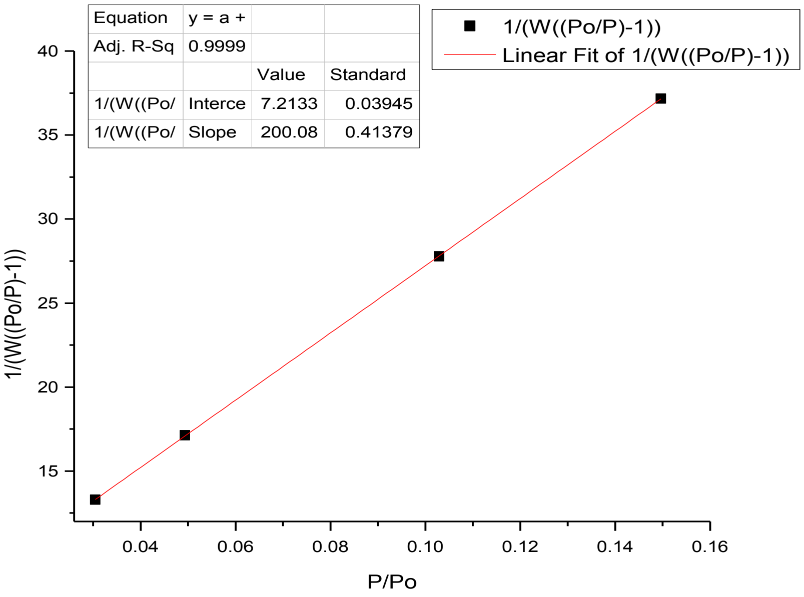

Fig. S17. Multipoint BET plot of **1.**

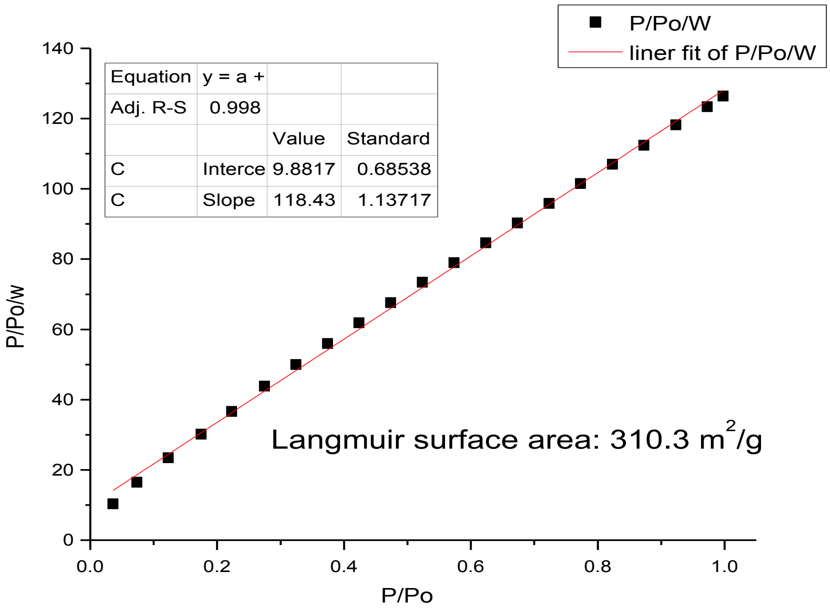

Fig. S18. Langmuir plot of **1.**

Reference:

1. L. Ma, A. Jin, Z. Xie and W. Lin, *Angew. Chem. Int. Ed.*, 2009, **48**, 9905-9908.