Electronic Supplementary Information for

Selective gas adsorption and unique phase transition properties in a stable magnesium metal-organic framework constructed from infinite metal chains

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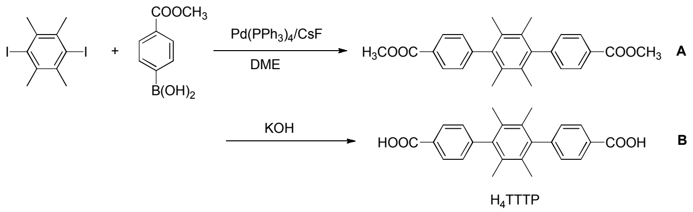
1. Materials and Instrumentation:

All chemicals were obtained commercially and used without further purification. 1,4-diiodo-2,3,5,6-tetramethylbenzene, (4-(methoxycarbonyl)phenyl)boronic acid, $Pd(PPh_3)_4$ and CsF were obtained from Alfa Aesar. N,N'-dimethylformamide (DMF), ethanol, dimethyl ether and dimethyl sulfoxide were purchased from Macron. Thermogravimetric analysis (TGA) was conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer. About 5 mg of sample was heated from 25 ℃ to 600 ℃ at a ramp rate of 5 ℃/min in a N_2 flow. Fourier transform infrared (IR) measurements were performed on a SHIMADZU IR Affinit-1 spectrometer. Nuclear magnetic resonance (NMR) data was obtained on a Mercury 300 spectrometer.

2. Synthesis of 2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (H_4TTTP)



2.1 Synthesis of A

To a 250 mL Schlenk flask, 1,4-dibromo-2,5-dimethylbenzene (1.50 g, 3.89 mmol), 4-(methoxycarbonyl)phenylboronic acid (1.54 g, 8.55 mmol), CsF (5.00 g) and $Pd(PPh_3)_4$ (250 mg) were added. The flask was connected to a Schlenk line and was evacuated then refilled with nitrogen. 150 mL 1,2-dimethoxyethane (DME) was degassed (two hours) and added to the flask through a canula. The flask was equipped with a water condenser and refluxed under nitrogen for 3 days. The solvent was removed on a rotary evaporator. 100 mL H_2O was added and then the mixture was extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$. After removed the CH_2Cl_2 solvent, the crude product was washed with acetone. The white solid pure product **A** was obtained by filtration (Yield 1.14 g, 72.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 12 H), 3.94 (s, 6 H), 7.26 (d, 4 H), 8.10 (d, 4 H).

2.2 Synthesis of B

1.14 g **A** was dissolved in 60 mL of mixed solvent of THF and MeOH (v/v = 1:1), and 20 mL of 2N KOH aqueous solution was added. The mixture was refluxed overnight. After the organic phase was removed, the aqueous phase was acidified with diluted hydrochloric acid to give white precipitate, which was filtered and washed with water several times (Yield: 1.00 g, 96.0%). ^1H NMR (300 MHz, DMSO-d_6): δ 1.80 (s, 12 H), 7.26 (d, 4 H), 8.02 (d, 4 H).

3. Synthesis of PCN-72

H_4TTTP (50 mg, 0.134 mmol) and $Mg(NO_3)_2 \cdot 6H_2O$ (150 mg, 0.586 mmol) were dissolved in a mixed solvent of DMA (10 mL)/ethanol (5 mL)/DMSO (5 mL) in a 20 mL vial. The vial was then sealed and put in the oven at 100 ℃. After 3 days, colorless needle shaped crystals were obtained.

4. X-ray Crystallography

Single crystal X-ray data of PCN-72 was collected on a Bruker Smart Apex diffractometer equipped with low temperature device and a fine-focus sealed-tube X-ray source (Mo−Kα radiation, λ = 0.71073 Å, graphite monochromated). The structure was solved by direct method and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.[1] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters. In these structures, free solvent molecules were removed using the SQUEEZE routine of PLATON and the structures were then refined again using the data generated. The crystal structure can be found at the Cambridge Crystallographic Data Centre with an assigned deposition number: CCDC 943806.

5. PXRD Patterns and Analysis of Phase Transition

In situ synchrotron-based powder diffraction experiments were performed for a sample filled in a polyimide capillary with 0.9 mm diameter at the 17-BM beamline of the Advance Photon Source in Argonne National Laboratory (Argonne, IL, USA). The incident X-ray wavelength was 0.60505 Å through the whole measurement. The data were gathered from 0.7° to 30° with a step interval of 0.013°, using a Perkin-Elmer flat panel area detector (XRD 1621 CN3-EHS) as well as the thermostat ranged from 25°C to 285°C in an atmosphere of He. The raw images were processed within Fit-2D software, which is used for refining the sample-to-detector distance and tilt of the detector relative to the beam based on the data of LaB_6 standard.

The rough cell parameters were indexed by *TOPAS* 4.2 software[2]. It was found to be Orthorhombic *Ima*2 with parameters a = 36.7484, b = 8.8322, c = 7.5844 Å and α=ß =γ= 90° for the sample heated at 100°C. Systematic absences were consistent with the space group *Imam*.

The collected PXRD patterns were analyzed by Le Bail refinement which is coded in *JANA2006*. Intensity data recorded at the 2θ larger than 25° and smaller than 1.4° was deleted without ignoring strong peaks. The background, zero shift, unit cell, and profile parameters, including asymmetry, were refined step by step. The pattern backgrounds were modeled with

20-term Legendre polynomials, and the peak profiles were fitted with pseudo-Voigt profile function as well as Simpson asymmetry correction. The unit cell parameters were started refinements with the rough results from indexing by *TOPAS*.

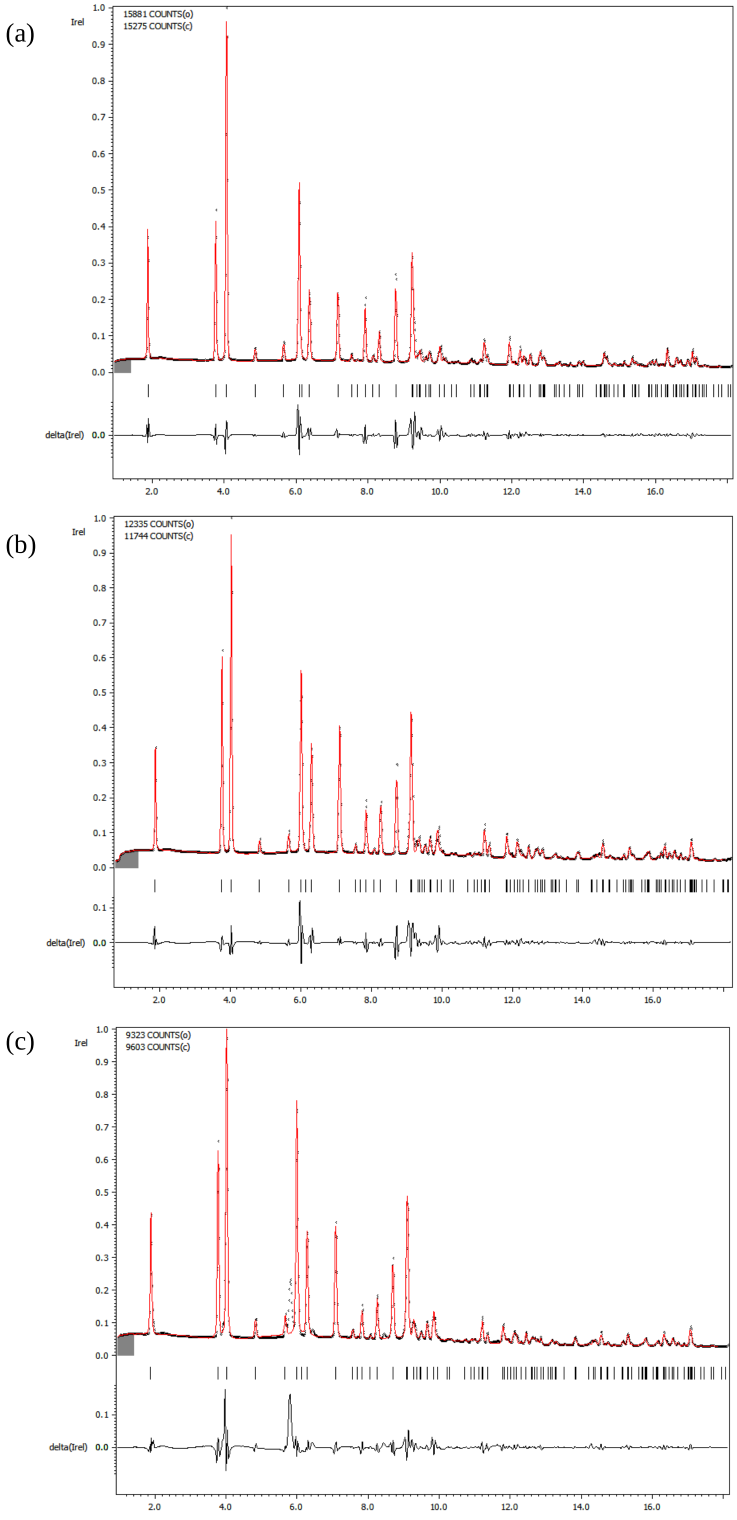


Figure S1. Final Le Bail whole pattern decomposition plots for PCN-72 at (a) 25°C, (b) 200°C, (c) 285°C: observed data (black spots) and calculated profiles (red solid line), relative intensity(*y-axis*) and 2θ (*x-axis*); the difference is drawn as black curves below the profiles. Tick marks indicate the calculated peak positions of the corresponding compound.

Table S1. The summary of the cell and refinement parameters from the synchrotron powder X-ray diffraction before phase transition

Compound	Single Crystal	Powder		
Temperature	-100°C	25°C	200°C	285°C (just reached)
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	*Imma*	*Imma*	*Imma*	*Imma*
a (Å)	36.85(2)	36.80(1)	36.68(1)	36.61(1)
b (Å)	7.469(4)	7.50(1)	7.59(1)	7.62(1)
c (Å)	8.756(5)	8.76(1)	8.82(1)	8.85(1)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00	90.00
V ($Å^3$)	2410(2)	2418(1)	2452(1)	2469(1)
Rp	N.A	6.39	6.34	6.82
wRp	N.A	10.35	10.45	12.36
GoF	1.053	2.43	2.49	2.88

6. Hydrogen Adsorption Isotherm

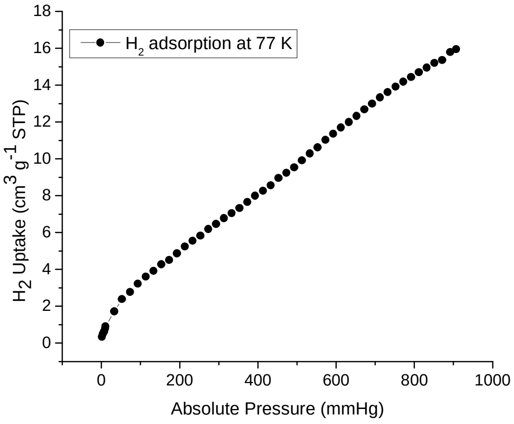


Figure S2. Hydrogen Adsorption of PCN-72 at 77 K

7. IR spectrum of PCN-72

As synthesized sample was filtered from mother solution (DMF, DMSO and ethanol) and washed with ethanol. The sample was then dried in the air for 30 min. Freestanding film method was used for the IR measurement (peak around 3500 cm^{-1} should be the peak of ethanol residue).

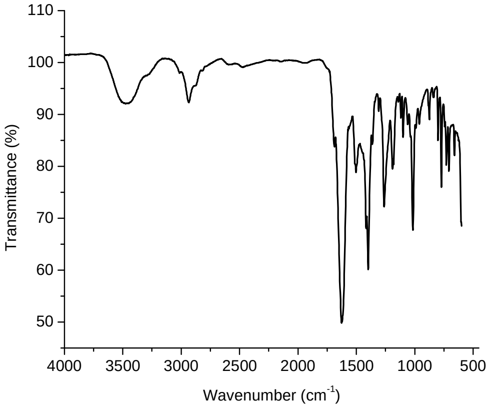


Figure S3. IR Spectrum of PCN-72

References

1. G. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
2. R. W. Cheary, A. A. Coelho. *J. Appl. Crystallogr.* **1992**, *25*, 109.