

Supporting information

A Porous Metal-Organic Framework with Helical Chain Building Units Exhibiting a Facile Transition from Micro- to Meso-porosity

Jinhee Park, Jian-Rong Li, E. Carolina Sañudo, Daqiang Yuan and Hong-Cai Zhou*

Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

Fax: (+01) 979-845-1595, E-mail: zhou@mail.chem.tamu.edu

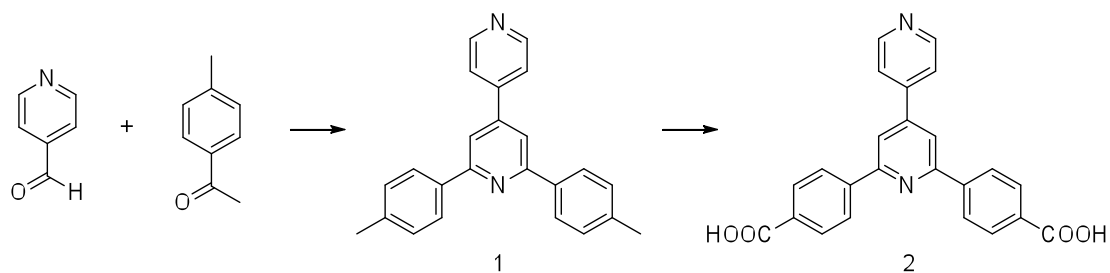
- 1. Materials and Methods**
- 2. Synthesis**
- 3. Single x-ray crystallography**
- 4. PXRD, IR, and TGA**
- 5. Crystal Structure of PCN-122**
- 6. Additional gas adsorption data**
- 7. Magnetic measurements**
- 8. References**

1. Materials and Methods

All chemicals purchased were used as received without further purification. ^1H NMR data in ligand synthesis were recorded on a Mercury 300 spectrometer. FT-IR data were collected by an IRAffinity-1 instrument. To obtain the TGA data, a TGA-50 (SHIMADZU) thermogravimetric analyzer was used with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ under N_2 flow. For a single crystal analysis, a pink block crystal was taken directly from the mother liquor, transferred to oil and mounted into loop. The diffraction data set was collected at 110 K on a Bruker APEX CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71609\text{ \AA}$). The powder X-ray diffraction patterns (PXRD) were collected on a BRUKER D8-Focus Bragg-Brentano X-ray Powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178\text{ \AA}$) at a scan rate of 0.5 s deg^{-1} . The simulated PXRD spectra were obtained by the diffraction-crystal module of the *Mercury* program based on the single crystal data. The program is available free of charge via internet at <http://www.iucr.org>. All gas adsorption measurements were performed by an ASAP 2020 with the extra-pure quality gases

2. Synthesis

Synthesis of 2,6-di-*p*-carboxyphenyl-4,4'-bipyridine (H_2dcbp)



Synthesis of **1**: 4-methylacetophenone (30 mmol, 4.025 g) and 4-pyridinecarboxaldehyde (10 mmol, 1.070 g) were mixed in mortar and powder NaOH (40 mmol, 1.6 g) were added slowly while stirring the solution with spatula. The mixture is crushed together with a pestle for 3 h. The mixture was added to a stirred solution of ammonium acetate (5 g, excess) in ethanol (100 ml). Reaction mixture was heated at reflux for 48 h. The progress of the reaction was monitored by TLC and a white precipitate was observed at the end of the reaction. Upon

cooling to room temp, a precipitate was filtered, washed with ethanol and water three times each and dried to afford the product. ^1H NMR (300 MHz, DMSO- d_6 , δ): 8.77 (d, 2H; ArH), 8.27 (s, 2H; ArH), 8.24 (d, 4H; ArH), 8.09 (d, 2H; ArH), 7.38 (d, 4H; ArH), 2.40 (s, 6H; Ar-CH₃)

Synthesis of 2: The product (1.337 g, 3.9 mmol) of the first step is dissolved in 250 mL of pyridine: water (80:20) solution. And 5 g KMnO₄ is added to the solution. During solution is refluxed, add another portion of KMnO₄ twice in 1 hr interval. The dark solution was filtered and the filtrate was evaporated under reduced pressure. 30 ml water was added and 6 N HCl was dropped until pH 2. The precipitates were filtered out and washed with water several times. Dry the precipitates to afford the product. ^1H NMR (300 MHz, DMSO- d_6 , δ): 8.93 (d, 2H; ArH), 8.54 (d, 4H; ArH), 8.50 (s, 2H; ArH), 8.37 (d, 2H; ArH), 8.15 (d, 4H; ArH)

Synthesis of PCN-121

H₂dcbp (4 mg, 10 μ mole), Co(NO₃)₂·6H₂O (8 mg, 27.5 μ mole) and 8 drops of tetrafluoroboric acid (HBF₄, 48% min w/w aqueous solution) were added to a 0.5 dram vial containing 1.5 mL DMA. The sealed vial was placed in an oven at 85 °C for more than 14 days without disturbing. Crystal synthesis is susceptible to vibration. Therefore, crystal formation should be checked at least after 14 days. Purplish pink block shape crystals were obtained. Calcd (%): C, 30, N, 2, Found (%): C, 43.85, N, 3.63.

For the gas adsorption measurement, sample was washed with fresh DMA and then methanol to remove DMA for 5 min. After draining the methanol, the sample was placed in dichloromethane at RT for 3 hrs. The crystals were dried at 60 °C under reduced pressure for 10 hrs or 10 days.

Synthesis of PCN-122

H₂dcbp (4 mg, 10 μ mole), Co(NO₃)₂·6H₂O (8 mg, 27.5 μ mole) and one drop of concentrated acetic acid were added to a glass tube containing 3 mL DMA. The sealed tube was put in 120 °C oven for 3 days. Pink plate crystals were crystallized out.

3. Single x-ray crystallography

Crystal data for **PCN-121**: $C_{30}H_{26}N_2O_{12}Co_3$, $M = 783.34$, pink block, $0.4 \times 0.34 \times 0.3 \text{ mm}^3$, hexagonal, space group $P6_1$, $a = 24.652(21)$, $c = 19.730(20) \text{ \AA}$, $V = 10383(8) \text{ \AA}^3$, $Z = 6$, $D_c = 0.7515 \text{ g/cm}^3$, $F_{000} = 2382$, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 110(2) \text{ K}$, $2\theta_{\text{max}} = 55.4^\circ$, 125711 reflections collected, 16690 unique ($R_{\text{int}} = 0.0408$). Final $GooF = 0.979$, $RI = 0.0208$, $wR2 = 0.0500$, R indices based on 15571 reflections with $I > 2\sigma(I)$ (refinement on F^2), 427 parameters, $\mu = 0.741 \text{ mm}^{-1}$. CCDC-813603.

Crystal data for **PCN-122**: $C_{24}H_{15}N_2O_{4.5}Co_1$, $M = 462.33$, pink sheet, $0.20 \times 0.18 \times 0.1 \text{ mm}^3$, tetragonal, space group $I4_1cd$, $a = 23.934(4)$, $c = 49.524(9) \text{ \AA}$, $V = 27102.88 \text{ \AA}^3$, $Z = 16$, $D_c = 0.4531 \text{ g/cm}^3$, $F_{000} = 3776$, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 110(2) \text{ K}$, $2\theta_{\text{max}} = 55.4^\circ$, 152492 reflections collected, 15720 unique ($R_{\text{int}} = 0.1264$). Final $GooF = 0.842$, $RI = 0.0466$, $wR2 = 0.0903$, R indices based on 9307 reflections with $I > 2\sigma(I)$ (refinement on F^2), 285 parameters, $\mu = 0.265 \text{ mm}^{-1}$. CCDC-813719.

4. PXRD, IR, and TGA

PXRD

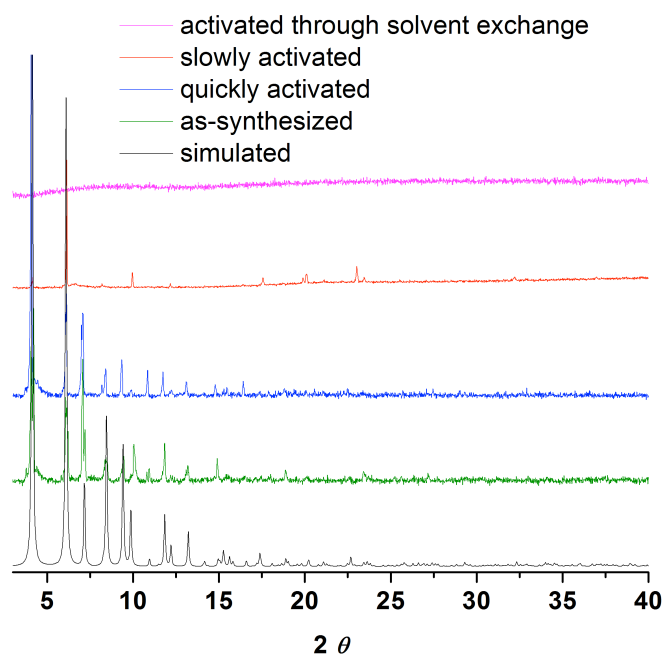


Fig. S1 PXRD of PCN-121.

IR

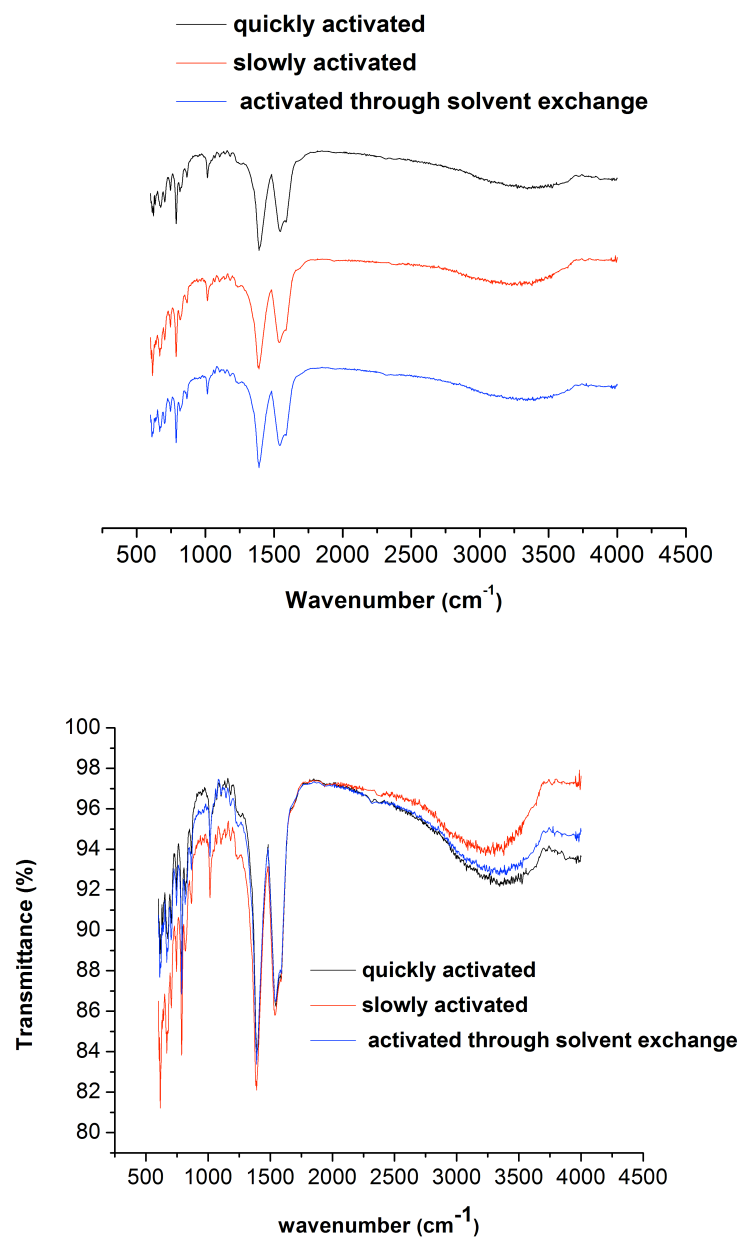


Fig. S2 IR of PCN-121.

TGA

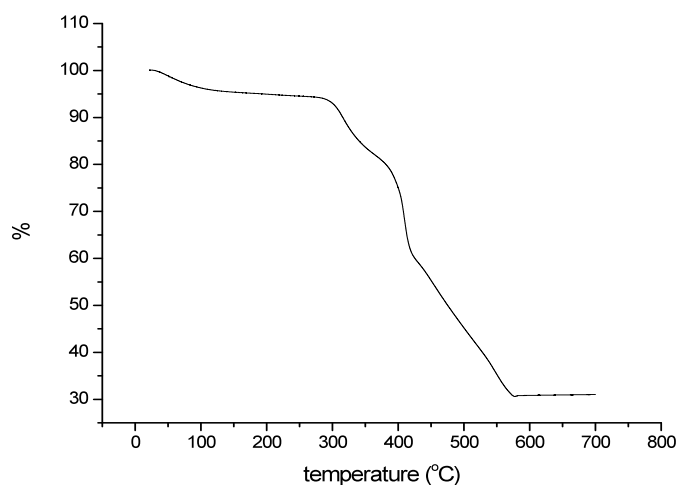


Fig. S3 TGA of PCN-121.

5. Crystal structure of PCN-122

The space group is $I4_1cd$ ($a=b= 23.394$, $c= 49.524$ Å, $V= 27102.9$ Å³). Co1 has an octahedral coordination geometry with mixed functional groups, one pyridyl N atom, four carboxylate oxygen and one aqua ligand (Fig. S4). Co1 is connected with Co1 in the other asymmetric unit through one aqua ligand and two carboxylates of the two different ligands.

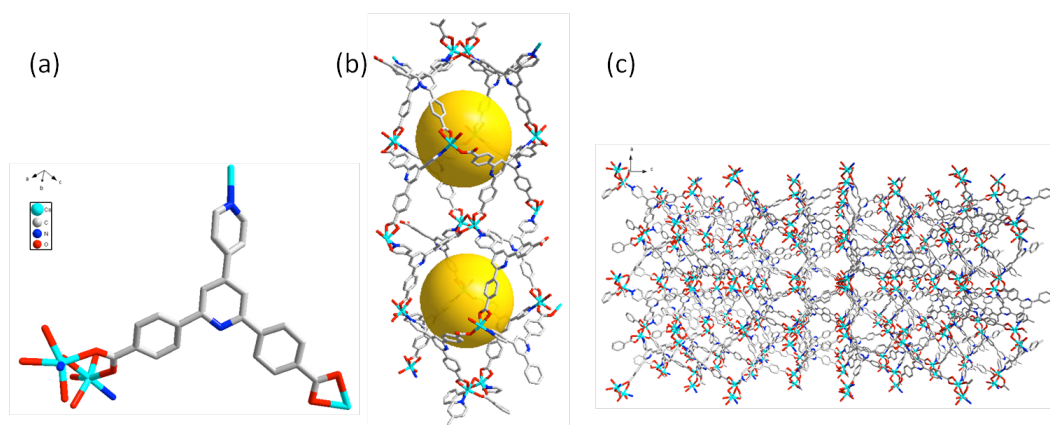


Fig. S4 Views of crystal structure of PCN-122. (a) unsymmetric unit; (b) two different pores of PCN-122. The yellow spheres show the free space of each pore; (c) wire type packing viewed through [0 1 0] direction.

6. Additional gas adsorption data

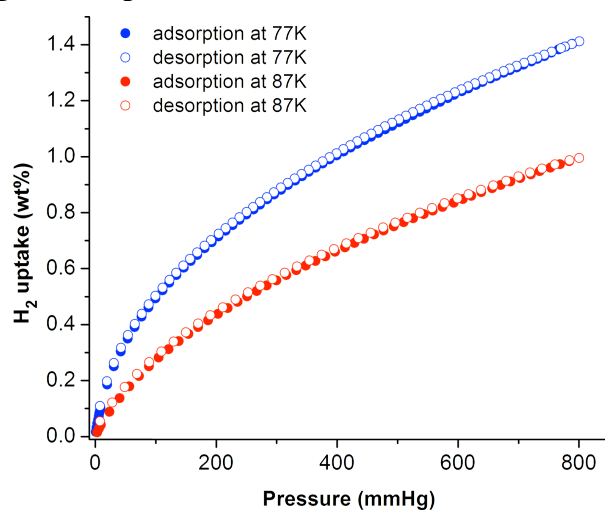


Fig. S5 The low pressure H_2 uptake in PCN-121 at 77K and 87K.

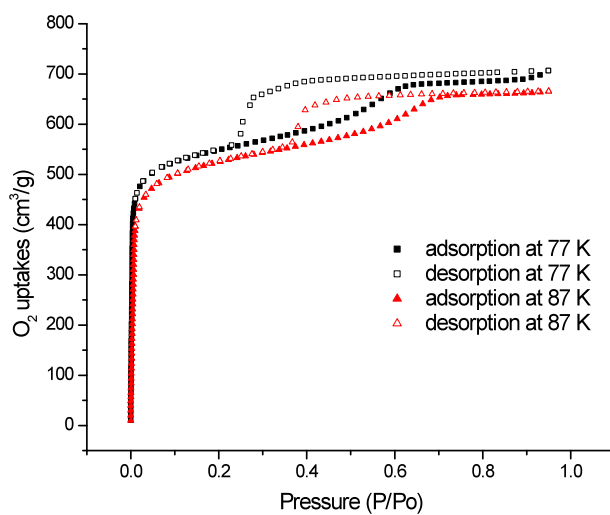


Fig. S6 The O_2 uptake in PCN-121 at 77 K and 87 K.

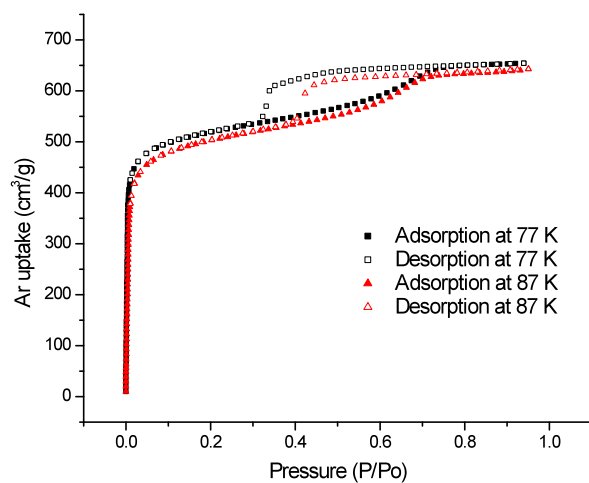


Fig. S7 Ar uptake of PCN-121 at 77 K and 87 K.

7. Magnetic measurements

Magnetic measurements were carried out in the Unitat de Mesures Magnètiques (Universitat de Barcelona) on polycrystalline samples (*circa* 30 mg) with a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants and an experimental correction for the sample holder was applied.

Magnetic susceptibility data were collected for crystalline sample of PCN-121. As shown in Fig. S8(a) the data were not field dependent. The χT product at 300 K has a value of $6.4 \text{ cm}^3 \text{ K mol}^{-1}$, in agreement with the expected for three Co(II) ions in a distorted octahedral coordination environment with strong spin-orbit coupling. As temperature decreases, so does the χT product partly as a result of the depopulation of the $J = 5/2$ state and the preferential population of the $J = 1/2$ on each Co(II) ion. A magnetization vs. field plot at 2 K is shown in Fig. S8(b). At this low temperature, each Co(II) ion behaves as an effective $S = 1/2$. The magnetization does not saturate, and it reaches a value of 2.5 at 5 T, indicating a non-zero spin ground state for the [Co₃] repeating unit of PCN-121 with anisotropy and low lying excited states. This is in agreement with the structural parameters of PCN-121. PCN-121 consists of infinite chains of trinuclear [Co₃] units, where the three Co(II) ions are bridged by a μ_3 -OH and various O atoms from the carboxylate groups. The Co-O-Co angles range from 94.34° (Co1-O8-Co3) to 129.97° (Co2-O1-Co3), thus J13 should be ferromagnetic and J23 antiferromagnetic. The Co1-O1-Co2 angle is 116.89° , thus J12 is expected to be antiferromagnetic.¹ This qualitative interpretation of the exchange interaction in PCN-121 leads to $S = 1/2$ per [Co₃] unit, which is in turn ferromagnetically coupled to its neighbours by the Co1-O4-Co2' and Co1-O5-Co2' exchange pathways, with Co-O-Co angles of 96.24° and 97.23° respectively. Qualitatively, the structural parameters of the [Co₃] polymer in PCN-121 are consistent with weak ferromagnetic coupling between the Co(II) ions to achieve a $S = 3/2$ spin ground state for the repeating unit.

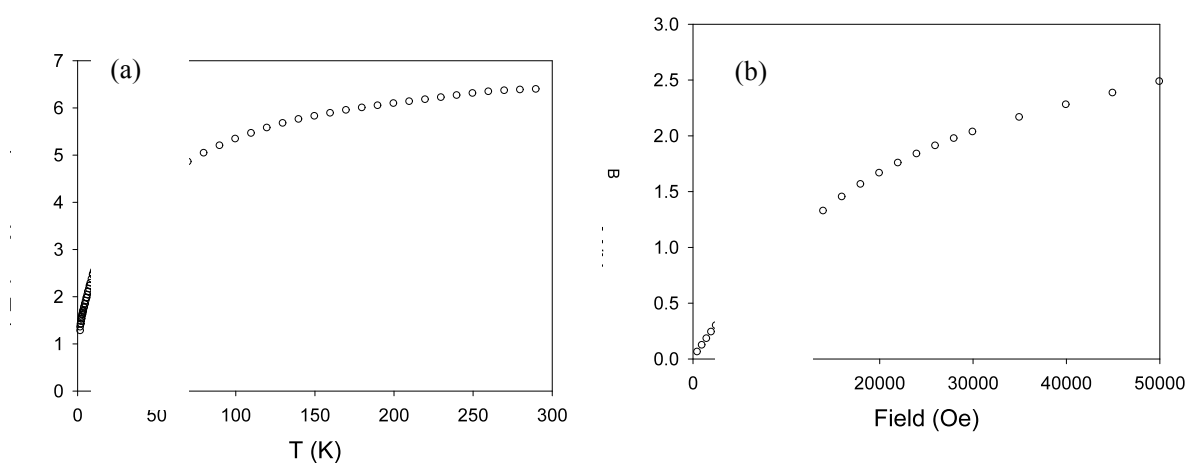


Fig. S8 The results of magnetic property measurements (a) the χT vs. T plot; (b) a magnetization vs. field plot at 2 K of PCN-121.

8. References

1. O. Khan in "Molecular magnetism", VCH, New York, 1993.