

In Situ Generation of Functionality in a Reactive Haloalkane Based Ligand for the Design of New Porous Coordination Polymers

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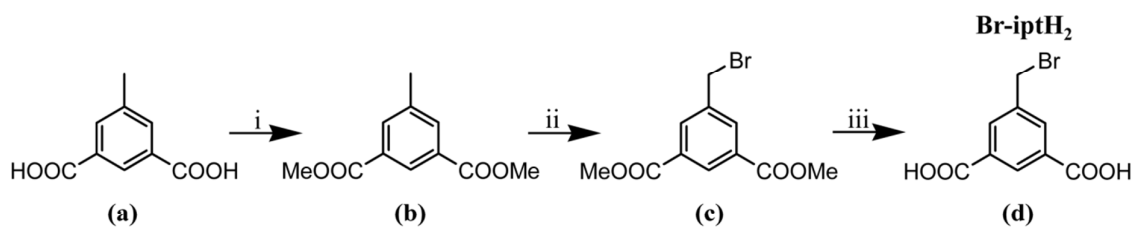
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Materials: All the reagents and solvents were received from Tokyo Kasei Co. and used without further purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 4,4'-bipyridyl and 5-methyl isophthalic acid was received from Wako Pure Chemical Industries Ltd. and TCI, Japan, respectively.

Measurements: ^1H NMR spectra were recorded on a JEOL model JNM-ECS 400 spectrometer, operating at 399.8 MHz, using tetramethylsilane as an internal reference. The samples of **PCP 1** for ^1H NMR spectral measurements were digested in $\text{DMSO}-d_6$ using ethylenediaminetetraacetic acid (EDTA). Infrared spectra were recorded on a Fourier transform infrared spectrometer (JASCO model FT/IR-4200) in ATR mode. Thermogravimetric analyses were recorded on a Rigaku Thermo plus TG-8120 apparatus in the temperature range between 25 °C and 500 °C under a nitrogen atmosphere at a heating rate of 5 °C min^{-1} . Powder X-ray diffraction data were collected with a Bruker D8 Discovery with GADDS equipped with a sealed tube X-ray generator producing $\text{Cu-K}\alpha$ radiation.

Synthesis of Br-iptH₂:



- i. CH_3OH , H_2SO_4 , 80 °C, overnight
- ii. NBS, dibenzoyl peroxide, CH_3CN , 90 °C, 6 hours
- iii. BBr_3 , CH_2Cl_2 , 50 °C, overnight

- (i) To a solution of (a) (1.08 g, 6.0 mmol) in 200 mL MeOH , 4 mL H_2SO_4 was added slowly. The mixture was heated to 80 °C overnight. After cooling to room temperature,

the product was extracted with CH_2Cl_2 and washed with H_2O . The organic layer was collected and dried with MgSO_4 and the solvent was removed with a rotary evaporator to yield **(b)** as a white powder (0.928 g, 86%). ^1H -NMR (400 MHz, CD_2Cl_2): δ 2.42 (s, 3H, CH_3); δ 3.88 (s, 6H, CH_3); δ 8.01 (d, $J = 2$ Hz, 2H, Ar); δ 8.41 (t, $J = 2$ Hz, 1H, Ar). Elemental analysis calculated for $\text{C}_{11}\text{H}_{12}\text{O}_4$: C, 63.45; H, 5.81. Found: C, 63.31; H, 5.69.

- (ii) To a solution of **(b)** (0.832 g, 4.0 mmol) in 100 mL of dehydrated CH_3CN , 0.783 g (4.4 mmol) of NBS and 0.040 g (0.17 mmol) of dibenzoyl peroxide was added. The mixture was refluxed at 90 °C for 6 hours. After cooling to RT, solvent removed by rotary evaporator and the product **(c)** was separated by column chromatography using silica (hexane:ethyl acetate, 9:1). Yield: 0.734 g, 64%. ^1H -NMR (400 MHz, CD_2Cl_2): δ 4.55 (s, 2H, CH_2Br); δ 3.90 (s, 6H, CH_3); δ 8.22 (d, $J = 2$ Hz, 2H, Ar); δ 8.54 (t, $J = 2$ Hz, 1H, Ar). Elemental analysis calculated for $\text{C}_{11}\text{H}_{11}\text{BrO}_4$: C, 46.02; H, 3.86. Found: C, 46.29; H, 3.93.
- (iii) To a solution of **(c)** (0.574 g, 2.0 mmol) in 50 mL of degassed CH_2Cl_2 , 8 mL of BBr_3 (17% in CH_2Cl_2 , 1 mol%) was added drop wise. The solution was then heated under reflux at 50 °C overnight. After cooling to room temperature, the solution was slowly poured into an ice/ H_2O mixture and stirred for 1 hour. The product was then extracted with ethyl acetate and washed with H_2O . The organic layer was collected and the solvent was removed by rotary evaporation to yield **Br-iptH₂** as a light yellow powder. The product was further purified by recrystallization in CH_3CN . Yield: 0.424 g, 82%. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$): δ 4.88 (s, 2H, CH_2Br); δ 8.24 (d, $J = 2$ Hz, 2H, Ar); δ 8.39 (t, $J = 2$ Hz, 1H, Ar). Elemental analysis calculated for $\text{C}_9\text{H}_7\text{BrO}_4$: C, 41.73; H, 2.72. Found: C, 41.79; H, 2.83.

Synthesis of PCPs:

PCP 1: A DMF solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol in 50 mL) was slowly and carefully layered over an aqueous solution of **Br-iptH₂** (1 mmol in 50 mL with 4 mmol of NaHCO_3) using 1:1 H_2O /DMF buffer. Blue hexagonal crystals formed after 10 days. The crystals were collected and washed with H_2O /DMF mixture and then used for single crystal X-ray diffraction. Yield: 38%, relative to Cu(II). Elemental analysis of dried **PCP 1**, calculated for $\text{C}_9\text{H}_8\text{O}_6\text{Cu}$: C, 39.21; H, 2.92. Found: C, 38.88; H, 3.41.

PCP 2: A EtOH solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol in 50 mL) was slowly and carefully layered over an aqueous solution (50 mL with 4 mmol of NaHCO_3) of **Br-iptH₂** (1 mmol) and 4,4'-bipyridine (1.25 mmol) using 1:1 H_2O /EtOH buffer. Blue block shaped crystals formed after 7 days. The crystals were collected and washed with H_2O /EtOH mixture and then used for single crystal X-ray diffraction. Yield: 41%, relative to Cu(II). Elemental analysis of dried **PCP 2**, calculated for $\text{C}_{43}\text{H}_{36}\text{N}_7\text{O}_7\text{Cu}_2$: C, 49.19; H, 3.46; N, 9.34. Found: C, 49.97, H, 3.88; N, 8.91. IR (ATR mode): Bands related to NO_3^- anion: 1075 cm^{-1} (ν_1 , A_1' : symmetric N-O stretch); 821 cm^{-1} (ν_2 , A_2'' : N in and out of NO_3 plane).

Gas Sorption Measurements: The sorption isotherms for N_2 (at 77 K) and CO_2 (at 195 K) gases were measured using an automatic volumetric adsorption apparatus (BELSORP-MAX; Bel Japan, Inc.) A known weight of the as-synthesized samples were placed in the sample cell, then, prior to measurements, the sample were dried under high vacuum at 393 K for 16 h to remove the guest molecules. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.

Single Crystal X-ray Diffraction: X-ray single crystal structural data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo Optic with Mo-K α radiation ($\lambda = 0.71069$ Å) and confocal monochromator. The structures were solved by SIR 92^{S1} and refined by full matrix least square method using SHELXL97^{S2}. All the hydrogen atoms were fixed by HFIX and placed in ideal positions. Potential solvent accessible area or void space was calculated using the PLATON^{S3} multipurpose crystallographic software. All calculations were carried out using SHELXL97^{S2}, PLATON^{S3} and WinGX^{S4} system, Ver 1.70.01.

Table S1: Crystal data and structure refinement parameters for **PCP 1** and **PCP 2**

Parameters	PCP 1	PCP 2
crystal system	trigonal	monoclinic
space group	<i>R</i> -3 <i>m</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	18.268(3)	14.563(3)
<i>b</i> , Å	18.268(3)	34.392(7)
<i>c</i> , Å	30.195(6)	19.462(4)
α , deg	90	90
β , deg	90	101.57(3)
γ , deg	120	90
<i>V</i> , Å ³	8727(4)	9550(4)
<i>Z</i>	18	4
<i>T</i> , K	100	100
μ , mm ⁻¹	1.137	0.484
<i>D</i> _{calcd} , g/cm ³	0.989	0.726
<i>F</i> (000)	2592	2124
reflections [<i>I</i> > 2 σ (<i>I</i>)]	2083	6767
unique reflections	2435	14005
measured reflections	11605	63311
<i>R</i> _{int}	0.043	0.133
GOF on <i>F</i> ²	1.12	0.99
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0784	0.1247
<i>R</i> _w [<i>I</i> > 2 σ (<i>I</i>)]	0.2345	0.3570
$\Delta\rho$ max/min [e Å ⁻³]	1.72, -0.84	1.42, -0.87

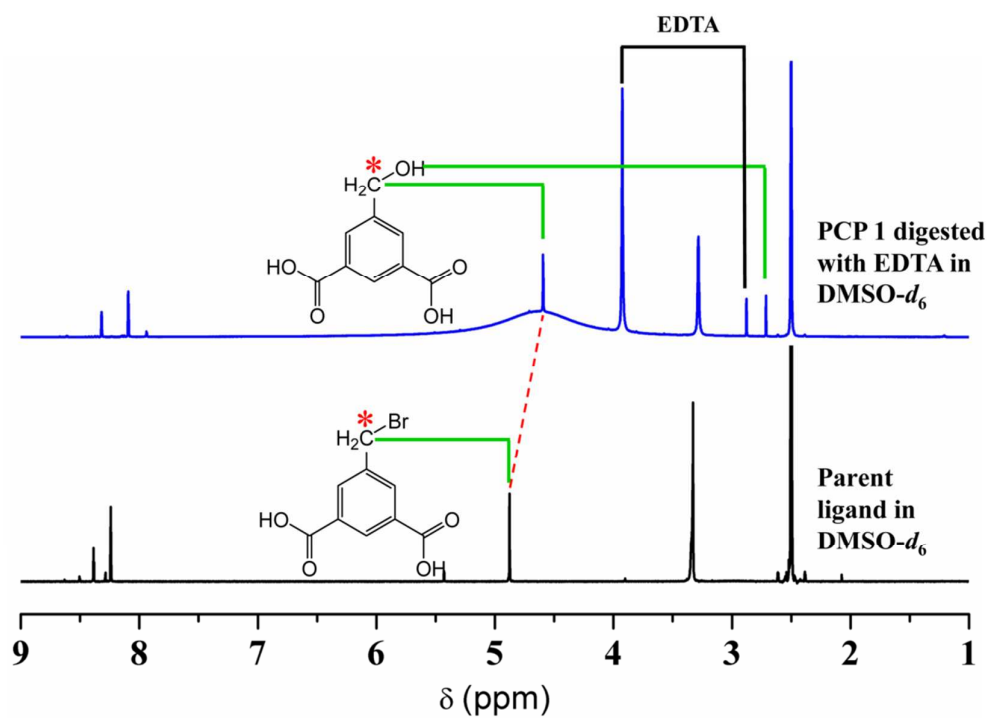


Figure S1: ^1H NMR spectra of **PCP 1** digested in $\text{DMSO-}d_6$ confirms the transformation of $-\text{CH}_2\text{Br}$ group to $-\text{CH}_2\text{OH}$. Peaks at δ 2.5 and δ 3.3 are due to DMSO and H_2O molecules.

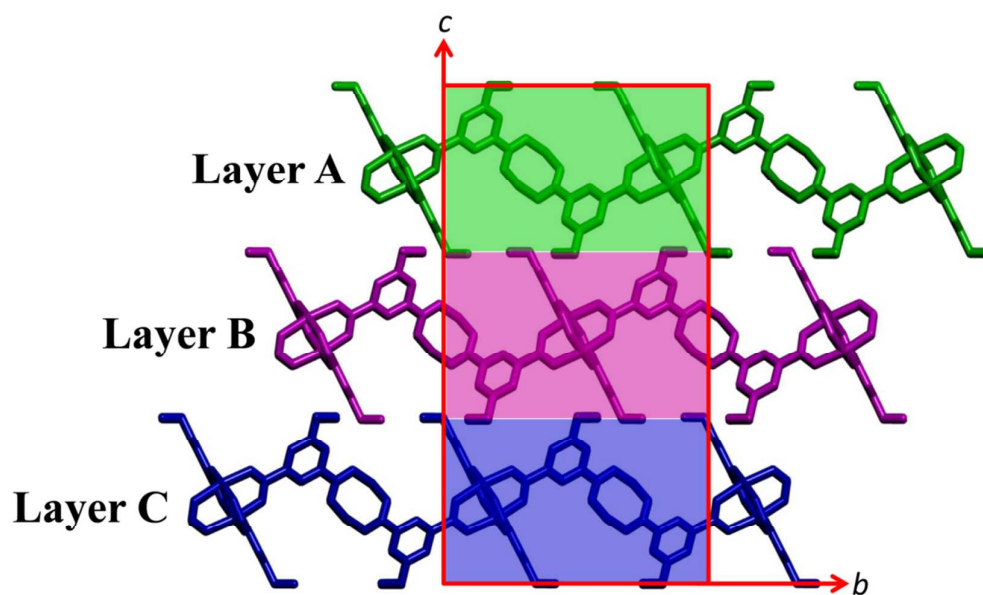


Figure S2: The ABC type packing of layers in **PCP 1**. The three layers are shown in three different colours.

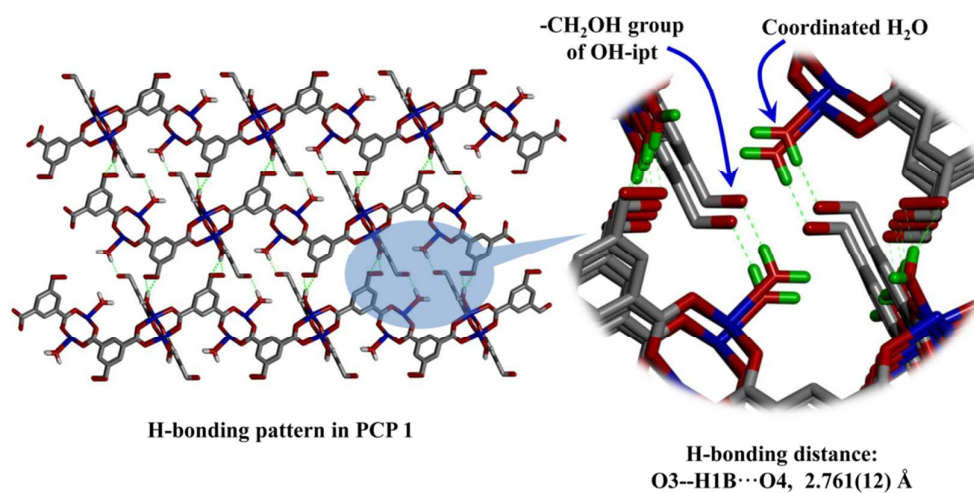


Figure S3: Hydrogen bonding pattern (shown in green dotted lines) between two layers in PCP 1.

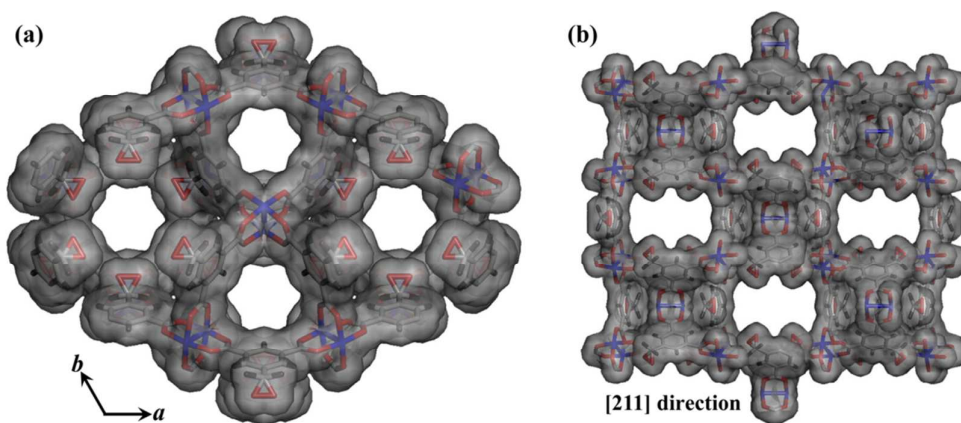


Figure S4: Pore view in PCP 1 considering the van der Waals surface along crystallographic c and $[211]$ direction.

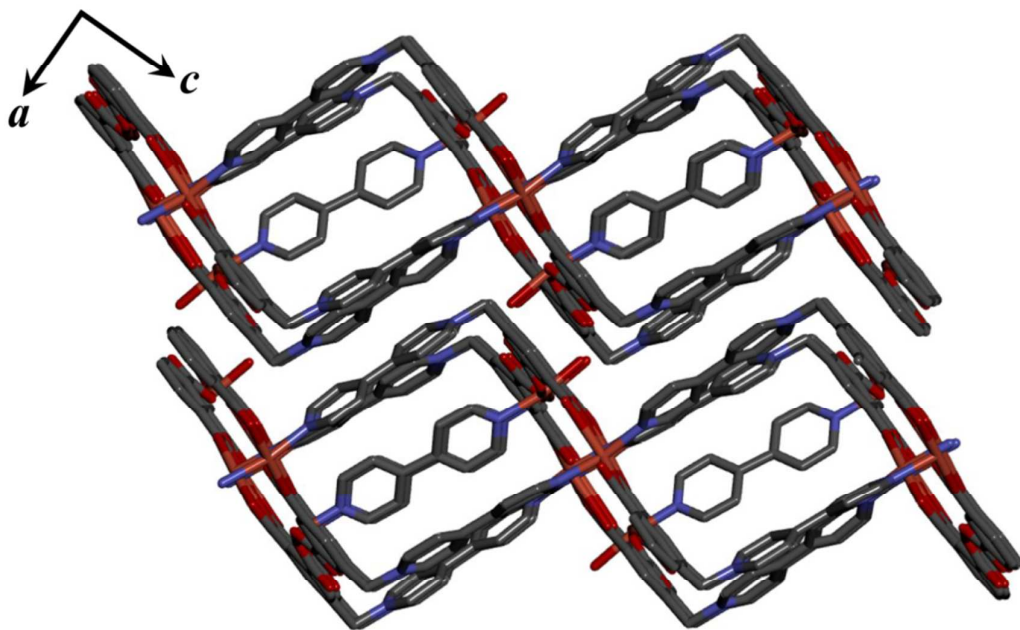


Figure S5: Stacking of 2D layers in **PCP 2** viewed along crystallographic *b* direction.

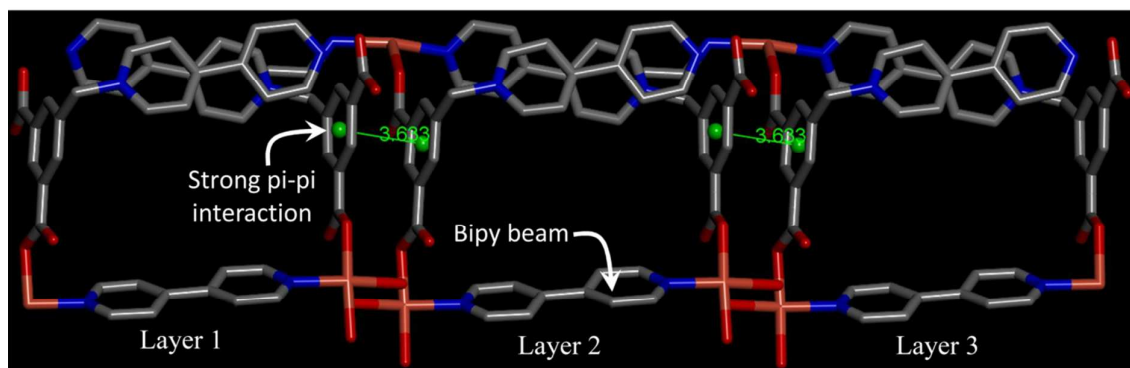


Figure S6: Strong π - π interaction between the isophthalate part of **bpy-ipt** ligand between the 2D layers in **PCP 2**.

1. 1075 (v1, A1': symmetric N-O stretch)
2. 821 (v2, A2'': N in and out of NO₃ plane)

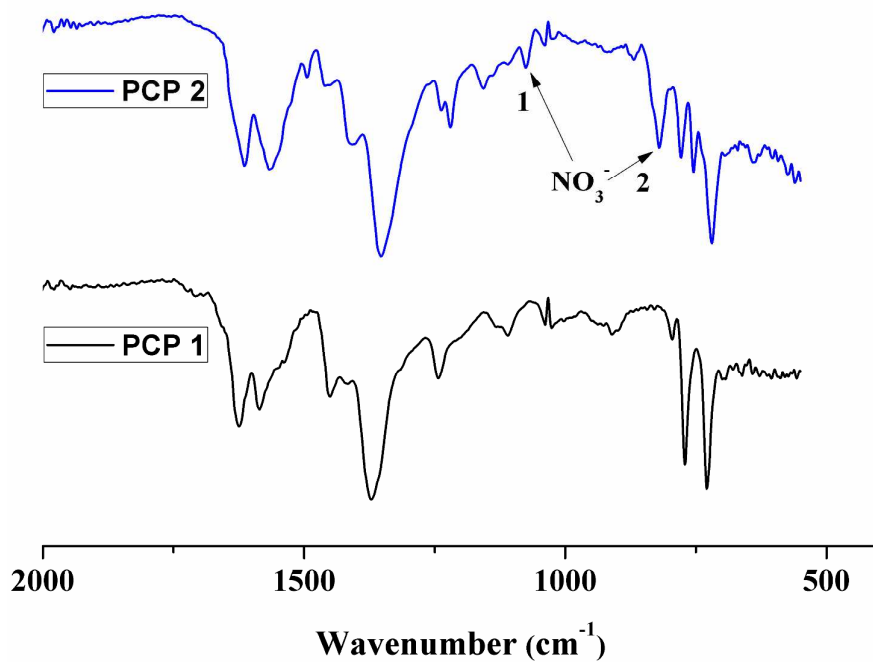


Figure S7: IR plots of **PCP 1** and **PCP 2**.

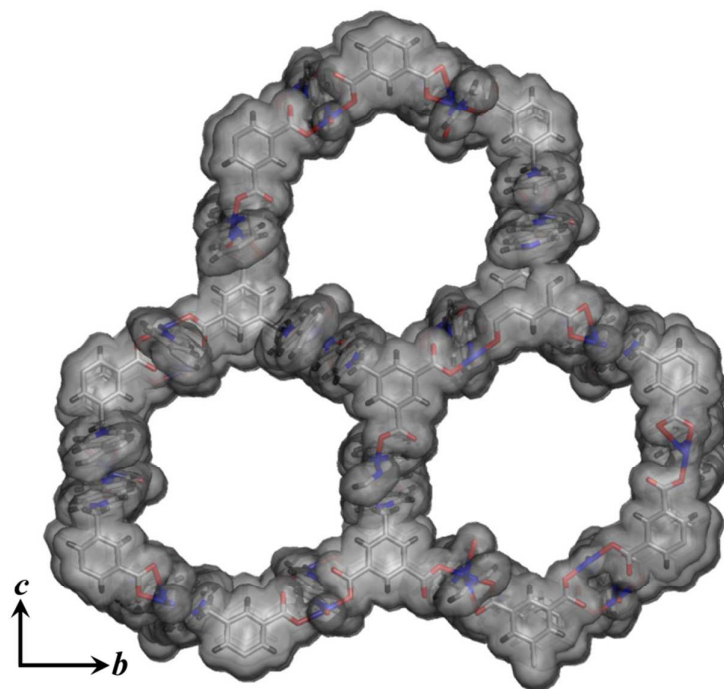


Figure S8: Pore view in **PCP 2** considering the van der Waals surface along crystallographic a direction.

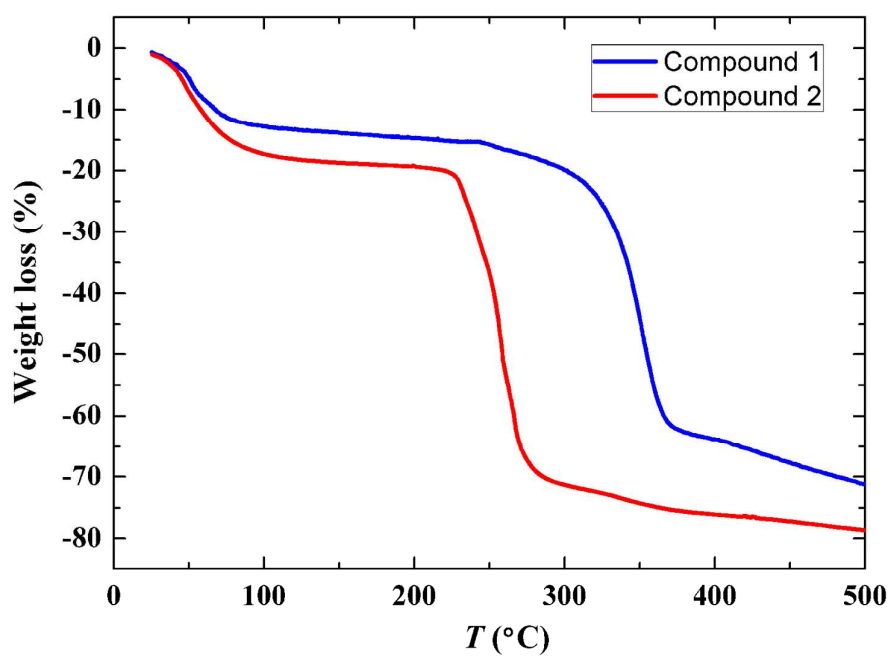


Figure S9: TG analysis plots of **PCP 1** (blue) and **2** (red).

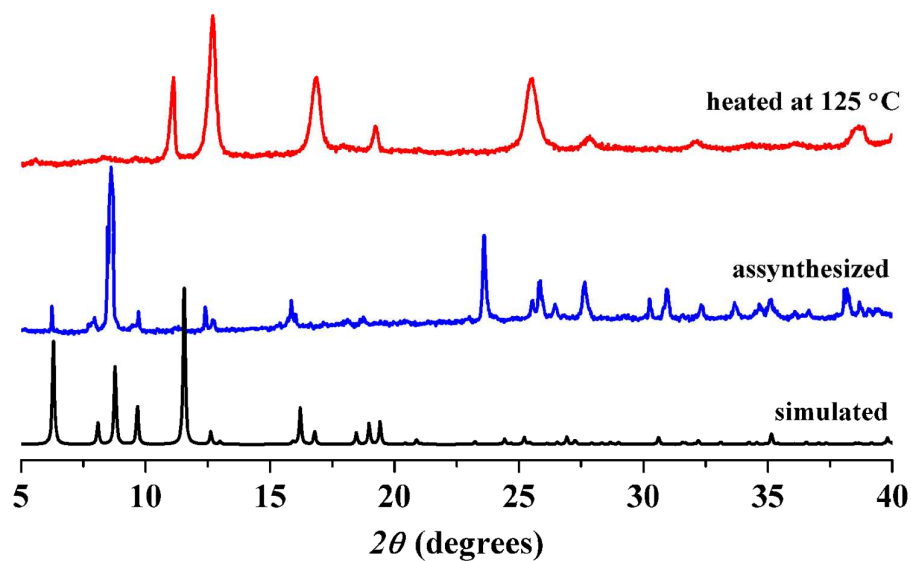


Figure S10: PXRD patterns of **PCP 1** under various states. Very well correspondence between simulated and assynthesized patterns indicate high purity of the samples.

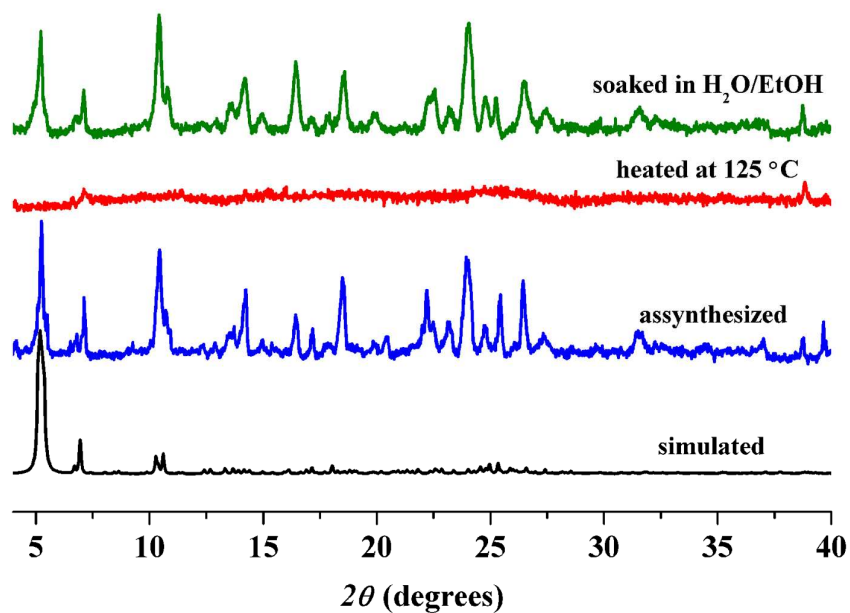


Figure S11: PXRD patterns of **PCP 2** under various states. Very well correspondence between simulated and assynthesized patterns indicate high purity of the samples. The heated PCP is reversible with respect to guest removal.

References:

- S1 Altomare, A.; Casciarano, G.; Giacovazzo, C.; Guadaradi, A. *J. Appl. Crystallogr.* **1993**, 26, 343.
- S2 Sheldrick, G. M. SHELXL 97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
- S3 Spek, A. L. *J. Appl. Crystallogr.* **2003**, 36, 7.
- S4 Farrugia, L. J. WinGX - A Windows Program for Crystal Structure Analysis, *J. Appl. Crystallogr.* **1999**, 32, 837.