

**[Supporting Information]**

**A novel MOF with mesoporous cages for kinetic trapping of Hydrogen**

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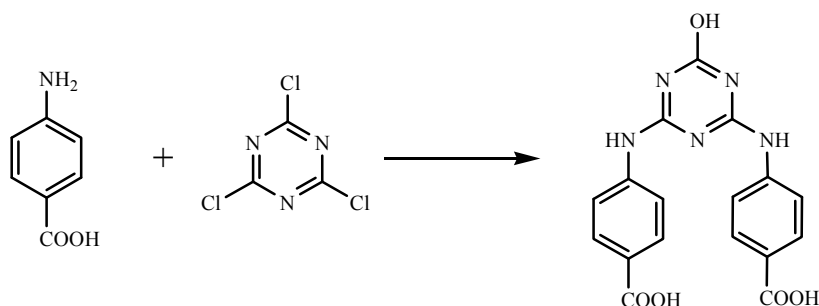
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**Experimental General Information.** Commercially available reagents were used as received without further purification. Elemental analyses (C, H, and N) were obtained by Atlantic Microlab, Inc.. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. The powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8 Discover diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ) at a scan rate of  $50 \text{ s deg}^{-1}$ . Powder samples were dispersed on low-background quartz discs (G. M. Associates, Inc., Oakland, California) for analyses. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via internet at <http://www.iucr.org>. FT-IR data were recorded on an IRAffinity-1 instrument. Thermogravimetric analysis (TGA) was obtained under  $\text{N}_2$  atmosphere on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$ .

**Synthesis of  $\text{H}_2\text{HTDBD}$ , 4,4'-(6-hydroxy-1,3,5-triazine-2,4-diyl)bis(azanediyl)dibenzoic acid.** To a stirred solution of 1.4 g (10.0 mmol) of 4-aminobenzoic acid in 20.0 ml of water and 3.0 ml of 5 N sodium hydroxide is added 0.7 g (8.3 mmol) of sodium bicarbonate, followed by a solution of 0.6 g (3.3 mmol) of cyanuric chloride in 5.0 ml of 1,4-Dioxane. The mixture is stirred at room temperature for 10 minutes, then overnight at  $110 \text{ }^\circ\text{C}$ . After cooling to room temperature, the solution was acidified with 20 % hydrochloric acid to a pH value to 3. The solution was centrifuged and washed with water and get the

product, 0.8 g (66 %).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ ):  $\delta$  7.80 (d, 4H), 7.90 (d, 4H), 9.85 (s, 2H), 10.91 (s, 1H), 12.61 (s, br, 2H).



**Synthesis of PCN-105,**

**$\text{Cd}_4\text{Na}(\text{H}_2\text{O})_2(\text{HTDBD})_3(\text{TDBD})\cdot 10(\text{DMF})\cdot 6(\text{EtOH})\cdot 3(\text{H}_2\text{O})$ .**  $\text{H}_2\text{HTDBD}$  (7.0 mg, 0.02 mmol),  $\text{Cd}(\text{NO}_3)_2\cdot 4(\text{H}_2\text{O})$  (5.0 mg, 0.02 mmol) and NaOH (0.4 mg, 0.01 mmol) were dissolved in a 20 mL vial with *N,N*-dimethylformamide (DMF, 10.0 mL)/ ethanol (EtOH, 2.0 mL)/  $\text{H}_2\text{O}$  (0.5 mL). Subsequently, 1-amino-2-propanol (0.02 mL) with DMF (2.0 mL) in a 5 mL vial was placed into the above vial to slowly diffuse to the mixture. The reaction was held at 60 °C for 4 days to produce colorless block crystals, PCN-105 (0.03 g, 0.01 mmol, 50 % yield based on  $\text{H}_2\text{HTDBD}$ ) with a formula of  $\text{Cd}_4\text{Na}(\text{H}_2\text{O})_2(\text{HTDBD})_3(\text{TDBD})\cdot 10(\text{DMF})\cdot 6(\text{EtOH})\cdot 3(\text{H}_2\text{O})$ . This formula was derived from crystallographic data, elemental analysis (calculated for  $\text{C}_{110}\text{H}_{159}\text{N}_{30}\text{O}_{41}\text{Cd}_4\text{Na}$ : C, 43.60; H, 5.29; N, 13.87; Na, 0.76; Cd, 14.84. Found: C, 43.71; H, 5.47; N, 13.66; Na, 0.69; Cd, 14.93 %) and TGA.

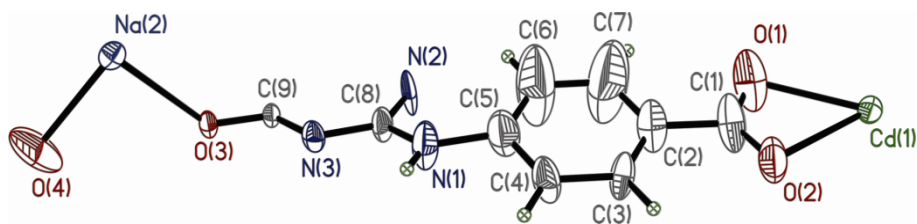
**X-ray Crystallography.** Single crystal X-ray data of PCN-105 were collected on a Bruker Smart Apex diffractometer equipped with a low temperature device and a fine-focus sealed-tube X-ray source (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, graphite monochromated). The structure was solved by direct methods and refined by

full-matrix least-squares on  $F^2$  with anisotropic displacement using the *SHELXTL* software package.<sup>31</sup> 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 highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these residual solvent molecules were removed from the data set using the *SQUEEZE* routine of *PLATON* and refined further using the data generated.<sup>32</sup> The contents of the solvent region are not represented in the unit cell contents in the crystal data.

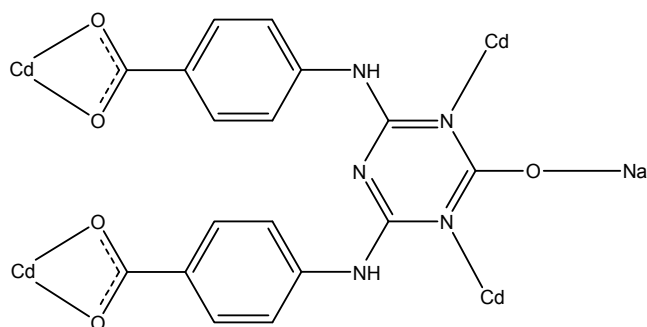
**Gas Sorption Measurements.** Gas sorption isotherm measurements were performed on an ASAP 2020 Surface Area and Pore Size Analyzer. Before the measurements, the samples of PCN-105 were soaked in methanol for 7 days and  $\text{CH}_2\text{Cl}_2$  for 7 days; during the exchange methanol and  $\text{CH}_2\text{Cl}_2$  was refreshed 7 times, respectively. The wet sample was then evacuated at 60°C for 6 h to remove the included solvent molecules and yield an activated sample. UHP-grade  $\text{N}_2$ ,  $\text{O}_2$  and Ar source was used in the sorption measurement. In the hydrogen sorption measurement, high purity hydrogen (99.9995%) was used. The temperature was maintained at 77 K with liquid nitrogen or 87 K with liquid argon throughout the entire measurement.

**Table 1. Crystal data and structure refinement for PCN-105.**

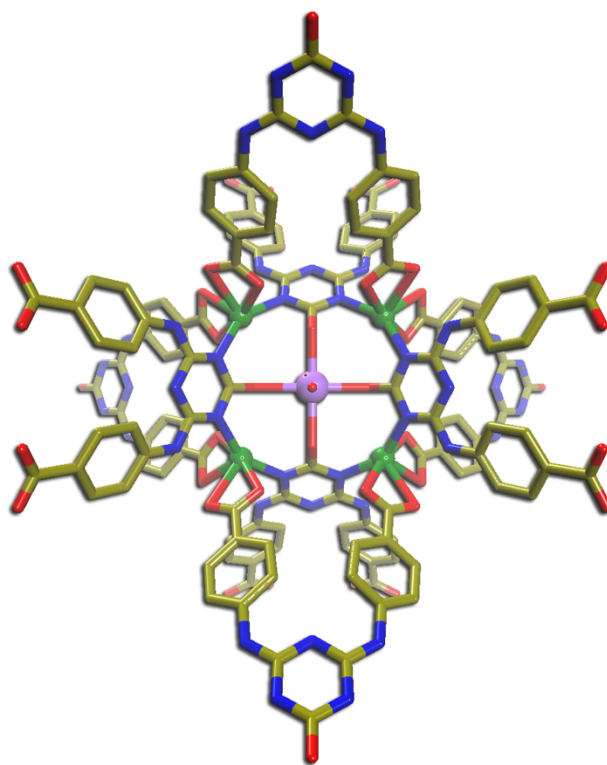
Identification code	pcn-105	
Empirical formula	$C_{68}H_{40}Cd_4N_{20}NaO_{22}$	
Formula weight	1961.79	
Temperature	208(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Fm-3c	
Unit cell dimensions	$a = 45.300(5)$ Å	$\alpha = 90^\circ$ .
	$b = 45.300(5)$ Å	$\beta = 90^\circ$ .
	$c = 45.300(5)$ Å	$\gamma = 90^\circ$ .
Volume	$92960(18)$ Å <sup>3</sup>	
Z	24	
Density (calculated)	0.841 Mg/m <sup>3</sup>	
Absorption coefficient	0.587 mm <sup>-1</sup>	
F(000)	23208	
Crystal size	0.32 x 0.30 x 0.25 mm <sup>3</sup>	
Theta range for data collection	1.27 to 24.99°.	
Index ranges	$-53 \leq h \leq 53$ , $-53 \leq k \leq 47$ , $-53 \leq l \leq 52$	
Reflections collected	114738	
Independent reflections	3557 [R(int) = 0.0676]	
Completeness to theta = 24.99°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8671 and 0.8343	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3557 / 0 / 121	
Goodness-of-fit on F <sup>2</sup>	1.079	
Final R indices [I > 2sigma(I)]	R1 = 0.0712, wR2 = 0.2136	
R indices (all data)	R1 = 0.1022, wR2 = 0.2455	
Largest diff. peak and hole	2.029 and -1.952 e.Å <sup>-3</sup>	



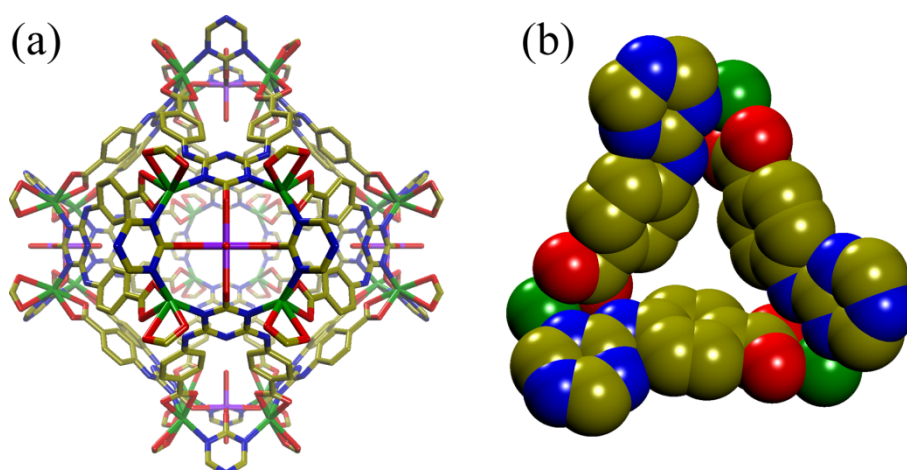
**Fig. S1. Asymmetric structural unit of PCN-105.**



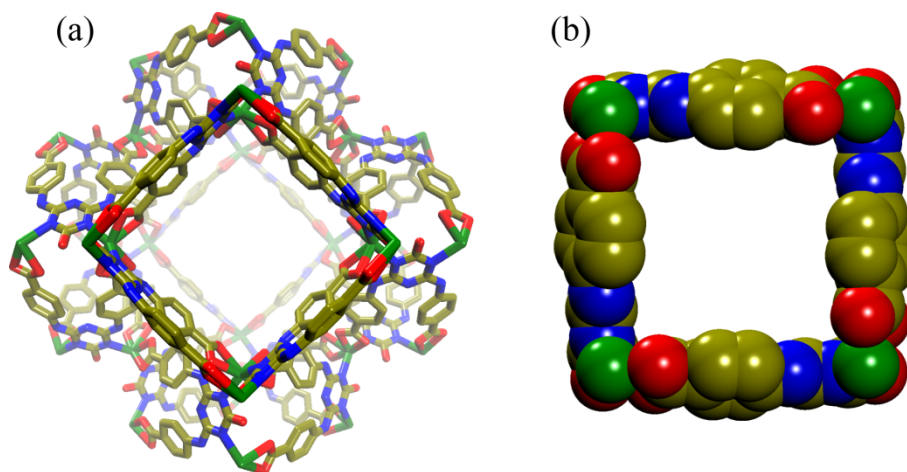
**Fig. S2. Coordinated modes of HTDBD ligand.**



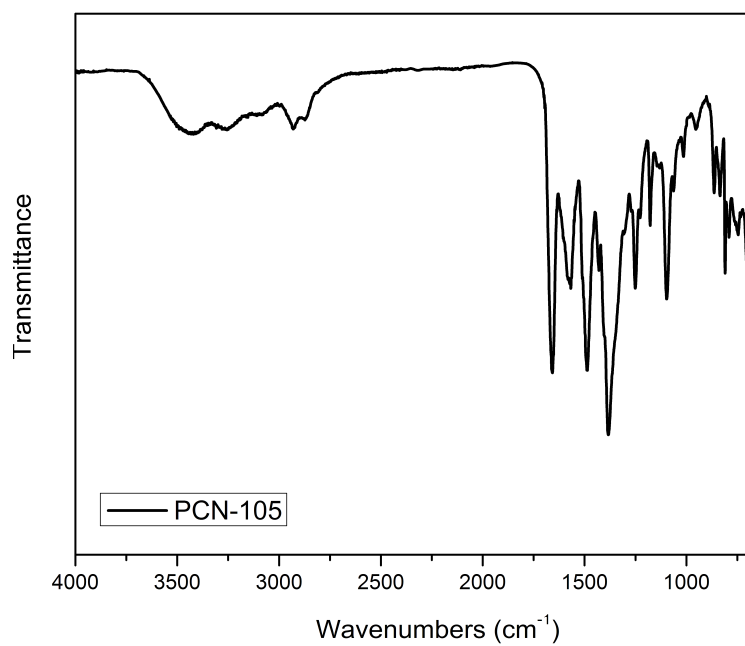
**Fig. S3. A pentanuclear SBU of PCN-105.**



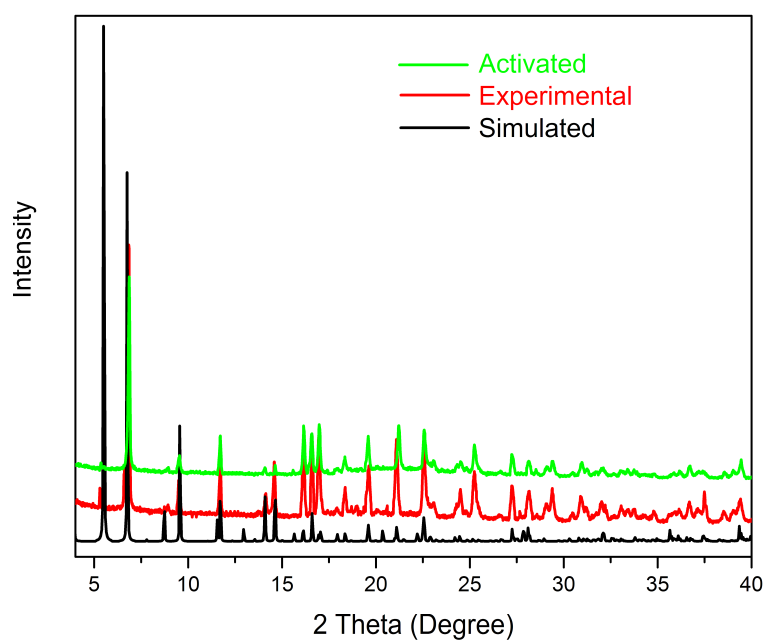
**Fig. S4.** (a) The A cage of 20 Å in PCN-105. (b) A triangular window of A cage with 4 Å.



**Fig. S5.** (a) The B cage of 21 Å in PCN-105. (b) A square window of B cage with 9 Å.

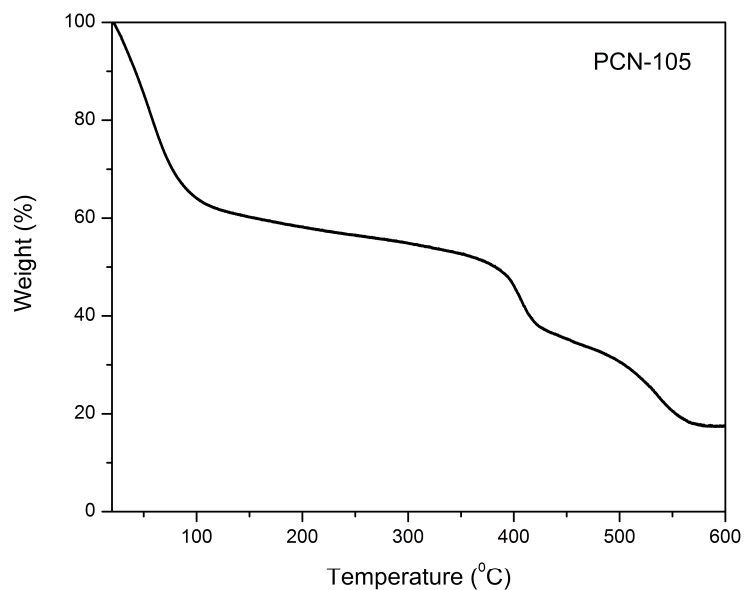


**Fig. S6. IR spectrum of PCN-105.**

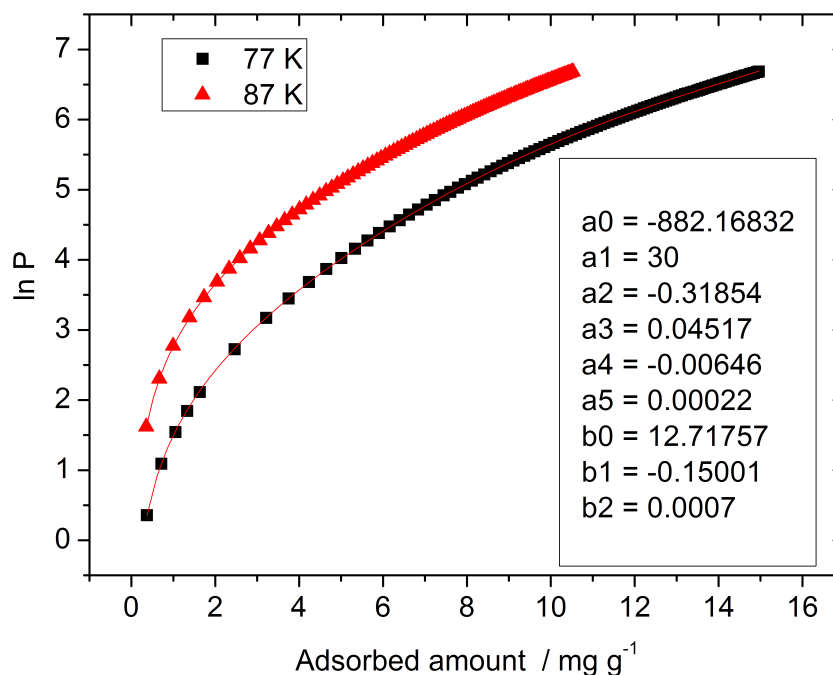


**Fig. S7. PXRD of PCN-105.**

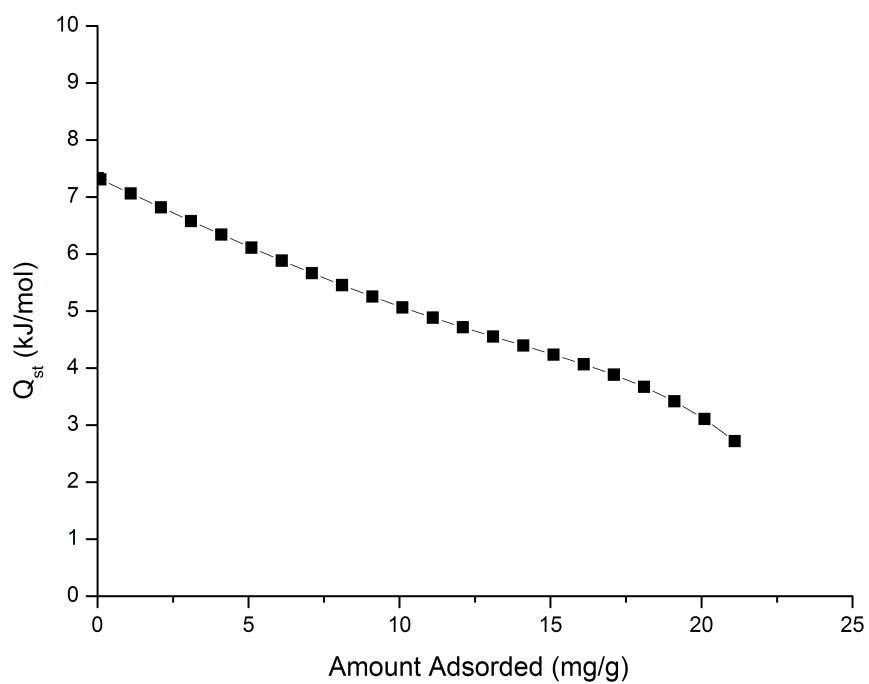




**Fig. S8. TGA of PCN-105.** The TGA curve of PCN-105 showed that the weight loss of 35.97 % between 20 and 100 °C corresponds to the loss of 10 guest DMF, 6 guest EtOH and 3 guest H<sub>2</sub>O (calculated 35.03 %). Decomposition of PCN-105 began at about 350 °C. The residue was CdO and Na<sub>2</sub>O (experimental: 17.52 % and calculated: 17.97 %).



**Fig. S9. H<sub>2</sub> isotherms measured of PCN-105 at 77 K and 87 K.** Inset, the temperature-independent parameters during the non-linear curve fit of H<sub>2</sub> isotherms.



**Fig. S10. Coverage dependence of the isosteric heat of adsorption for H<sub>2</sub> in PCN-105 calculated from fits of its 77 and 87 K isotherms.**