

Supplementary Information

A Novel Mesoporous Hydrogen-Bonded Organic Framework with High Porosity and Stability

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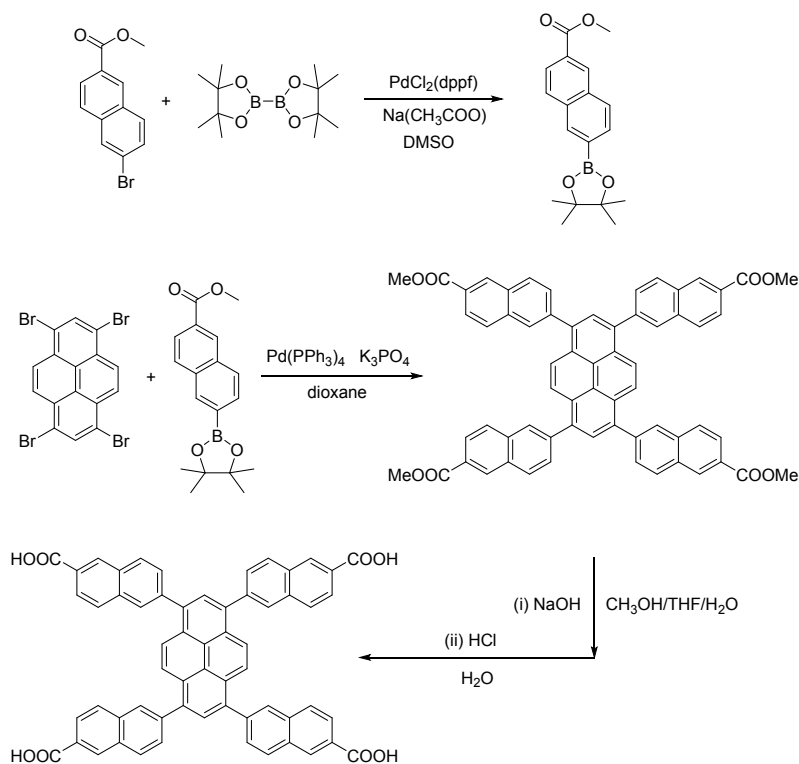
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Chemical Communications

Material characterization.

TGA data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 5 °C min⁻¹ under air atmosphere. Gas adsorption/desorption isotherms were measured by the volumetric method using a Micromeritics ASAP2020 surface area and pore analyzer. The PXRD patterns were recorded on a Rigaku Smartlab3 X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at room temperature. Simulation of the PXRD pattern 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.ccdc.cam.ac.uk/mercury/>. The scanning electron microscope (SEM) images were recorded in HITACHI SU3050.

Synthesis of H₄PTTNA.



Scheme S1 Synthesis procedure for H₄PTTNA.

A. Methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate

To a 500 mL three-necked, round-bottomed flask, methyl 6-bromo-2-naphthoate (14.00 g, 52 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (15 g, 60.00 mmol), NaOAc 8g and PdCl₂(dppf) (600 mg) was added. The flask was connected to Schlenk line and evacuated air and refilled with the nitrogen. 350 mL of dimethyl sulfoxide (DMSO) was degassed (two hours) and added through a canula. The flask was equipped with a water condenser and reflux under the nitrogen for 24 h. After cooling to room temperature, 150 mL of H₂O was added and then extract with CHCl₂. The organic phase was dried with MgSO₄. After removed the CHCl₂ solvent, the crude product was column chromatographed over silica gel using pure petroleum to give the product as white solid in ~87% yield (14.00 g) based on methyl 6-bromo-2-naphthoate. ¹H NMR (400 MHz, DMSO-d₆): δ 8.62 (s, 1H), δ 8.41 (s, 1H), 8.09 (d, 2H), 7.97~7.90 (m, 3H), 4.01 (s, 3H), 1.42 (s, 12H).

B. Tetramethyl 6,6',6'',6'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-naphthoate)

To a 500 mL three-necked, round-bottomed flask, 1,3,6,8-tetrabromopyrene (2.0 g, 3.86 mmol), methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (6.03 g, 19.31 mmol), K₃PO₄ (15.0 g) and Pd(PPh₃)₄ (300 mg) was added. The flask was connected to Schlenk line and evacuated air and refilled with the nitrogen. 300 mL of dioxane and 10 mL H₂O was degassed (one hour) and added through a canula. The flask was equipped with a water condenser and reflux under the nitrogen for 72 h. The solvent was evaporated on rotary evaporator. 300 mL of H₂O was added and then extract with CHCl₃ (3 × 200 mL). The organic phase combined and dried with MgSO₄ for 10 min and evaporated to dry. The solid residue was dissolved in a small amount of 2:1 CHCl₃-hexane mixture, and then separated by column chromatography (CH₂Cl₂ to CH₂Cl₂/EA = 10:1). Tetramethyl 6,6',6'',6'''-(pyrene-

1,3,6,8-tetrayl)tetrakis(2-naphthoate) was isolated as a yellow solid (2.9 g, 80% yield based on 1,3,6,8-tetrabromopyrene). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.58 (s, 4H), 8.16 (s, 4H), 8.00-8.05 (m, 14H), 7.87-7.90 (m, 8H), 3.92 (s, 12H).

C. 6,6',6'',6'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-naphthoic acid) (H₄PTTNA)

Tetramethyl 6,6',6'',6'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-naphthoate) (2.0 g) was suspended in a mixture of THF (90 mL) and MeOH (90 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF and MeOH were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 2. The solid was collected by filtration, washed with water, and dried to give the product as yellow solid (1.65 g, 88 % yield based on Tetramethyl 6,6',6'',6'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-naphthoate)). ¹H NMR (400 M Hz, DMSO-*d*₆): δ 13.18 (s, 4H), 8.75 (s, 4H), 8.40 (s, 4H), 8.35 (d, 4H), 8.30 (s, 6H), 8.14 (d, 4H), 8.06 (d, 4H), 8.00 (d, 4H).

Preparation of HOF-14 for single crystal x-ray diffraction analysis.

H₄PTTNA (10 mg, 0.0113 mmol) was dissolved in 0.2 mL of DMSO in a 5 mL uncapped vial. The vial was put in a 20 mL vial containing 10 mL THF and the large vial was sealed. The yellow needle like crystals of HOF-14 suitable for single crystal X-ray diffraction analysis were grown by slow vapor diffusion for about 3 weeks at room temperature.

Preparation of powdery HOF-14 with micron-size.

H₄PTTNA (200 mg, 0.226 mmol) was dissolved in 15 mL of DMSO to which 100 mL THF was added and stirred for 5 minutes. The mixture stands at room temperature for 12 hours to afford yellow block crystals of HOF-14 (182.3 mg, Yield: 91.2%).

Single-Crystal X-ray Crystallography.

The crystal data of HOF-14 were collected by Advanced Light Source on beamline 12.2.2 at Lawrence Berkeley National Laboratory. The structure of the two MOFs were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the *SHELXTL* software package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of the ligands were calculated in ideal positions with isotropic displacement parameters. There is large solvent accessible pore volume in the crystals of HOF-14, which are occupied by highly disordered solvent molecules. No satisfactory disorder model for these solvent molecules could be assigned, and therefore the *SQUEEZE* program implemented in *PLATON* was used to remove the electron densities of these disordered species. Thus, all of electron densities from free solvent molecules have been “squeezed” out. The details of structural refinement can be found in Supplementary Tables S1 and cif file.

Gas Sorption Measurements.

The gas isotherms were measured using ASAP 2020 from Micromeritics Co. Ltd. The as-prepared sample was washed with acetone for 3 times. Then the sample was allowed to soak in acetone for 24 h with the supernatant being replaced by fresh acetone several times during the process to exchange and remove nonvolatile solvates (DMSO). After removal of acetone by centrifugation, the samples were activated under vacuum at room temperature, and then dried again in the “outgas” function of instruments at 100 °C for 10 hours prior to gas adsorption.

Fitting of pure-component isotherms.

The pure-component adsorption isotherm data measured at 298 K were fitted with the

single-site Langmuir-Freundlich equation

$$N = N^{\max} \times \frac{bp^{1/n}}{1 + bp^{1/n}}$$

Here, p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), N is the adsorbed amount per mass of adsorbent (mol kg^{-1}), N^{\max} is the saturation capacities (mol/kg), b is the affinity coefficient ($1/\text{kPa}$), and n represent the deviations from an ideal homogeneous surface.

Isosteric heat of adsorption.

The isosteric heat of adsorption represents the strength of the interactions between adsorbate molecules and the adsorbent lattice atoms and can be used as a measure of the energetic heterogeneity of a solid surface. The isosteric heat of adsorption at a given amount can be calculated by the Clausius–Clapeyron equation as

$$Q_{st} = -RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_{n_a}$$

where Q_{st} is the isosteric heat of adsorption (kJ mol^{-1}), P is the pressure (kPa), T is the temperature, R is the gas constant, and n_a is the adsorption amount (mmol g^{-1}).

Calculations of adsorption selectivity.

The selectivity of preferential adsorption of component **1** over component **2** in a mixture containing **1** and **2**, perhaps in the presence of other components too, can be formally defined as

$$S_{ads} = \frac{q_A / q_B}{y_A / y_B}$$

In the equation, q_A , and q_B represent the molar loadings, expressed in mol kg^{-1} , within the HOF that is in equilibrium with a bulk fluid mixture with mole fractions y_A , and $y_B = 1 - y_A$.

The molar loadings, also called *gravimetric uptake capacities*, are usually expressed with the units mol kg⁻¹. The IAST calculations of 50/50 mixture adsorption taking the mole fractions $y_A = 0.5$ and $y_B = 1 - y_A = 0.5$ for a range of pressures up to 100 kPa and 298 K were performed.

Regeneration of HOF-14.

100 mg used HOF-14 was dissolved in 6 mL DMSO to get a clear solution, to which 50 mL THF was added and stirred for 1 minutes. The mixture stands at room temperature for 12 hours to afford light yellow crystalline HOF-14.

Table S1 Crystal data and structure refinement for **HOF-14**.

HOF-14 (CCDC: 1955714)	Before squeeze	After squeeze
Empirical formula	C ₆₀ H ₃₄ O ₈	C ₆₀ H ₃₄ O ₈
Formula weight	882.87	882.87
Measurement temperature	100.0 K	100.0 K
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>
<i>a</i> (Å)	35.192(2)	35.192(2)
<i>b</i> (Å)	32.9021(18)	32.9021(18)
<i>c</i> (Å)	3.7820(2)	3.7820(2)
α (°)	90	90
β (°)	92.815(2)	92.815(2)
γ (°)	90	90
Volume(Å ³)	4373.8(4)	4373.8(4)
<i>Z</i>	2	2
Calculated density(g/cm ³)	0.670	0.670
Absorption coefficient (mm ⁻¹)	0.047	0.047
Independent reflections ($I > 2\sigma(I)$)	3945 [$R(\text{int}) = 0.0594$]	3945 [$R(\text{int}) = 0.0577$]
<i>F</i> (000)	916	916
Reflections collected	25210	25210
Completeness to theta = 133.12°	99%	99%
θ range for data collection	3.478-51.416	3.478-51.416
Data/restraints/parameters	3945/216/236	3945/214/236
Limiting indices	$-41 \leq h \leq 41$	$-41 \leq h \leq 41$
	$-39 \leq k \leq 39$	$-39 \leq k \leq 39$
	$-4 \leq l \leq 4$	$-4 \leq l \leq 4$
Goodness-of-fit on F^2	3.431	1.243
R_1^a, wR_2^b [$I > 2\sigma(I)$]	$R_1 = 0.2867, wR_2 =$ 0.6503	$R_1 = 0.1458, wR_2 =$ 0.3867
R_1^a, wR_2^b (all data)	$R_1 = 0.3042, wR_2 =$ 0.6695	$R_1 = 0.1581, wR_2 =$ 0.04128
Largest diff. peak and hole (e/Å ³)	1.88 and -0.91	0.75 and -0.75

$$^a R_1 = \Sigma(|F_0| - |F_C|) / \Sigma|F_0|.$$

$$^b wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2 / \Sigma w(F_0^2)]^{1/2}.$$

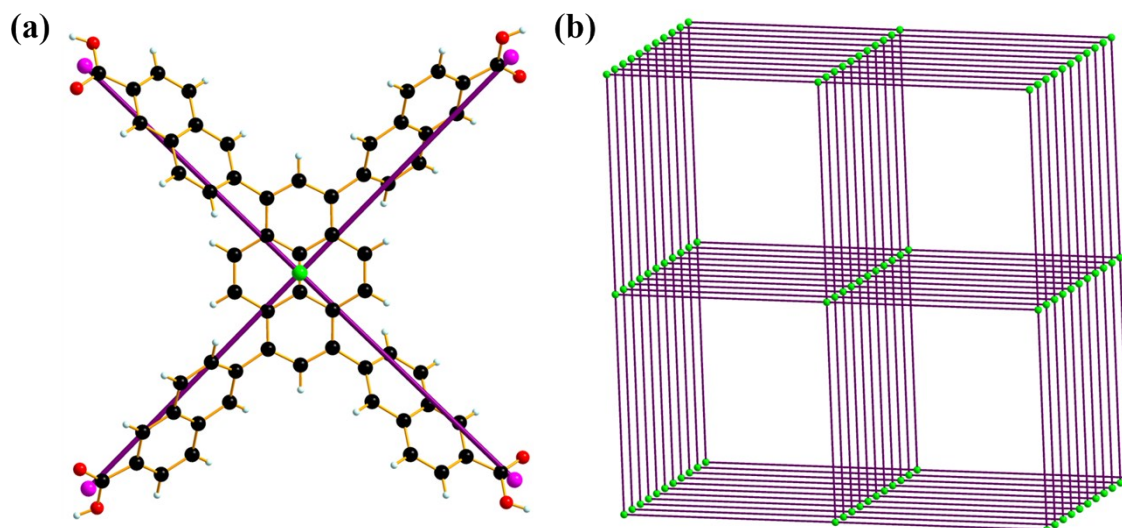


Fig. S1 (a) simplified four-connected node of H₄PTTNA, (b) the *sql*-a topology network.

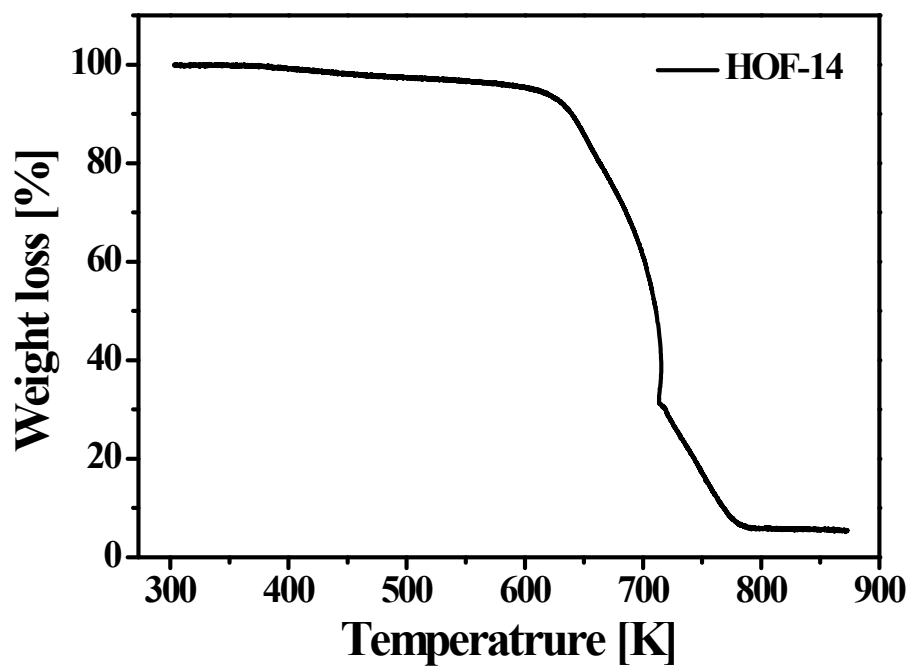


Fig. S2 Thermogravimetric analysis (TGA) of activated HOF-14.

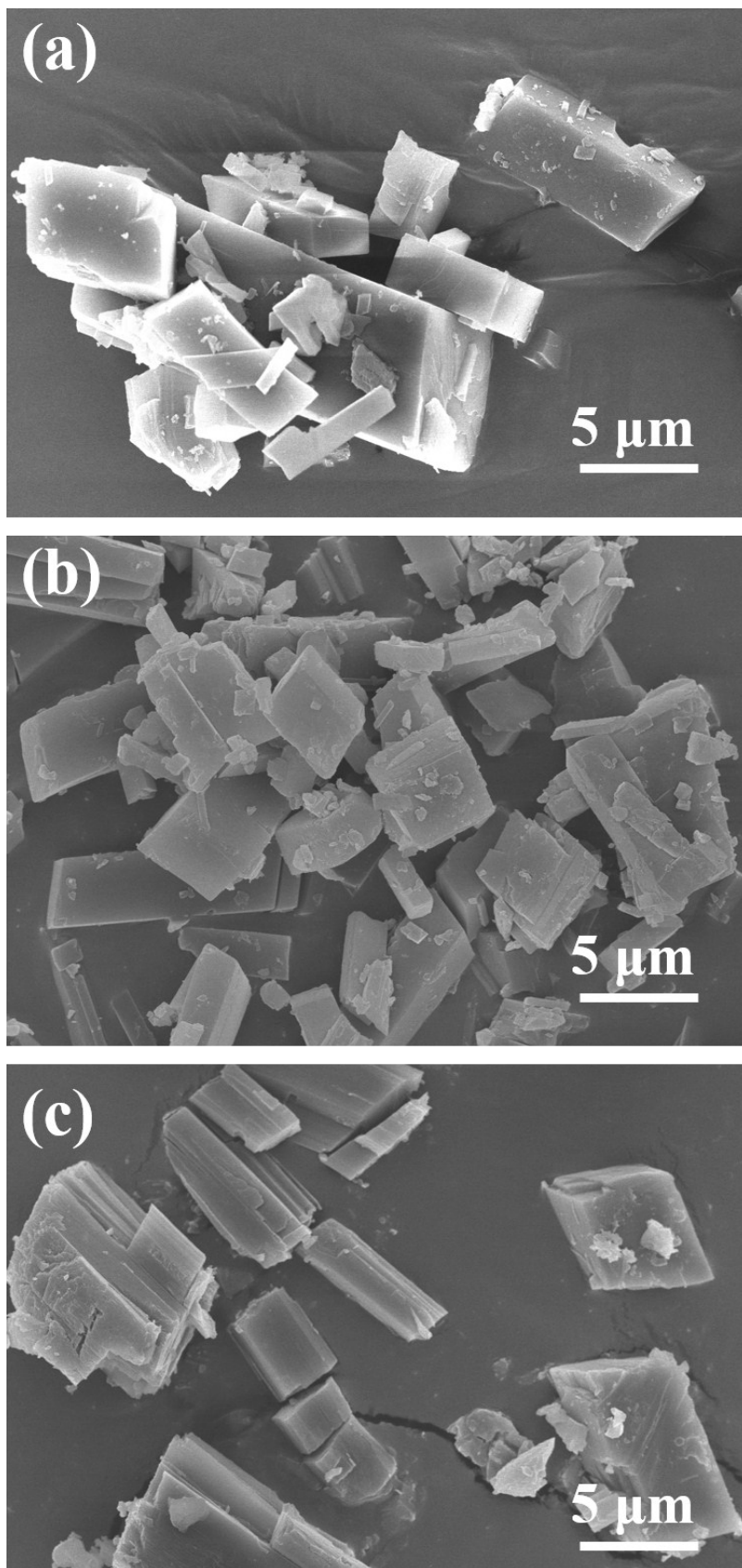


Fig. S3 SEM images of HOF-14. (a) original sample, (b) after HCl aqueous solution (12 M) treatment for 12 h, and (c) after NaOH aqueous solution (pH = 10) treatment for 12 h.

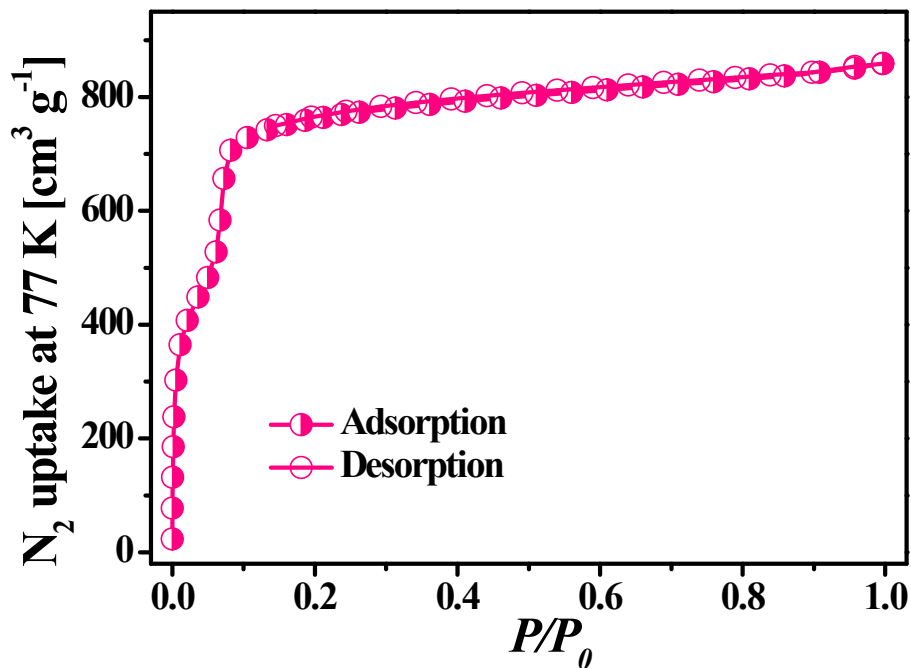


Fig. S4 N₂ adsorption isotherms of regenerated HOF-14 at 77 K.

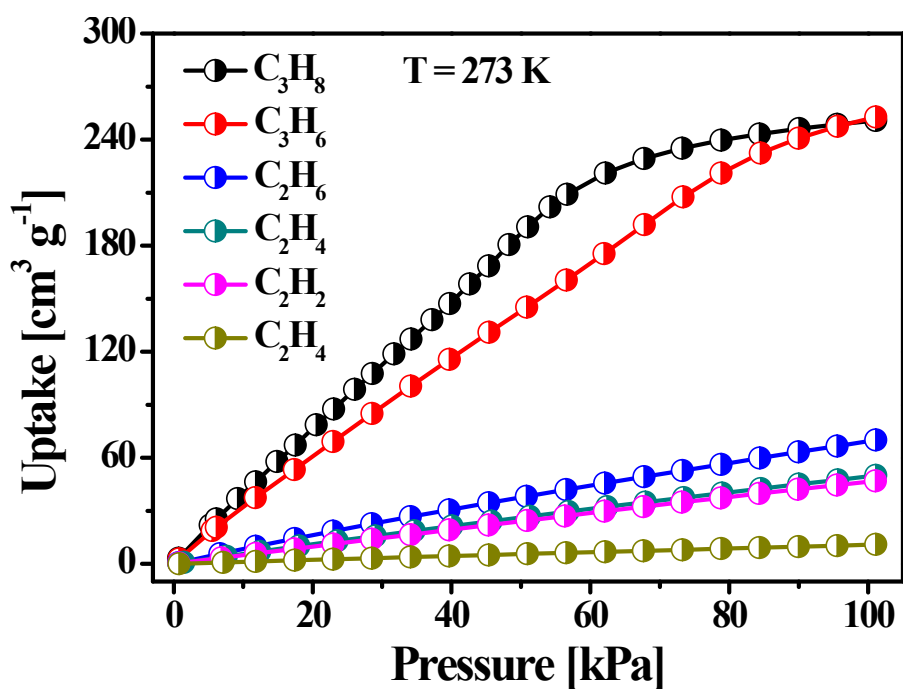


Fig. S5 Single-component sorption isotherms for CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ of HOF-14 at 273 K.

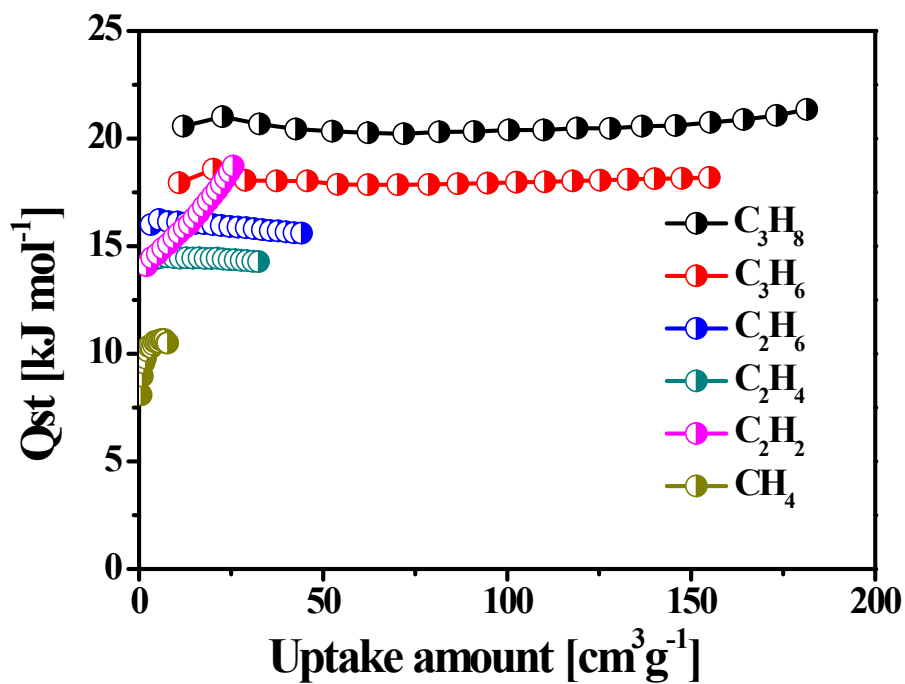


Fig. S6 Isosteric heats (Q_{st}) of different gas in HOF-14.

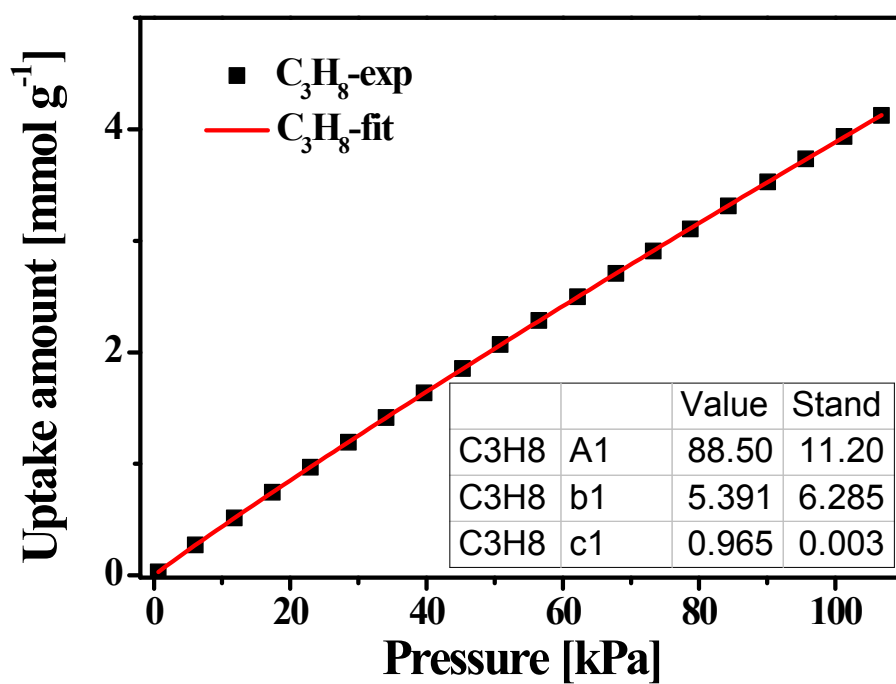


Fig. S7 Single-site Langmuir-Freundlich fits of C_3H_8 adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.

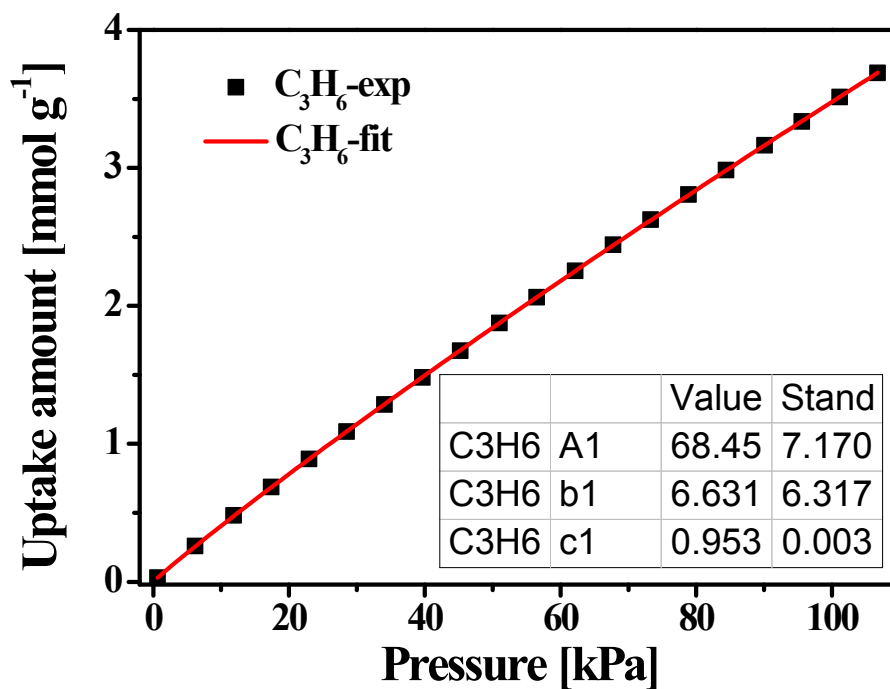


Fig. S8 Single-site Langmuir-Freundlich fits of C_3H_6 adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.

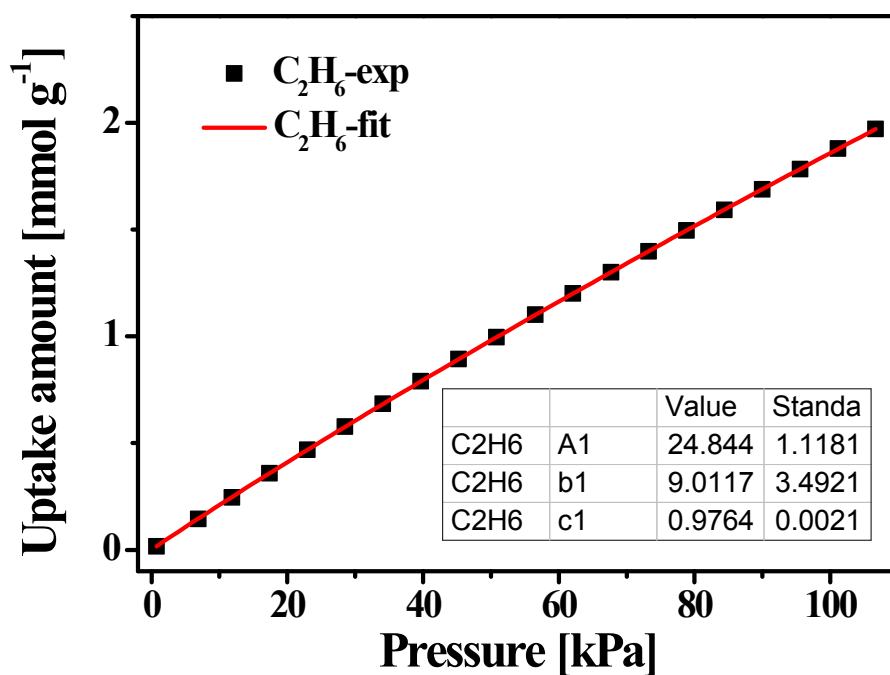


Fig. S9 Single-site Langmuir-Freundlich fits of C_2H_6 adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.

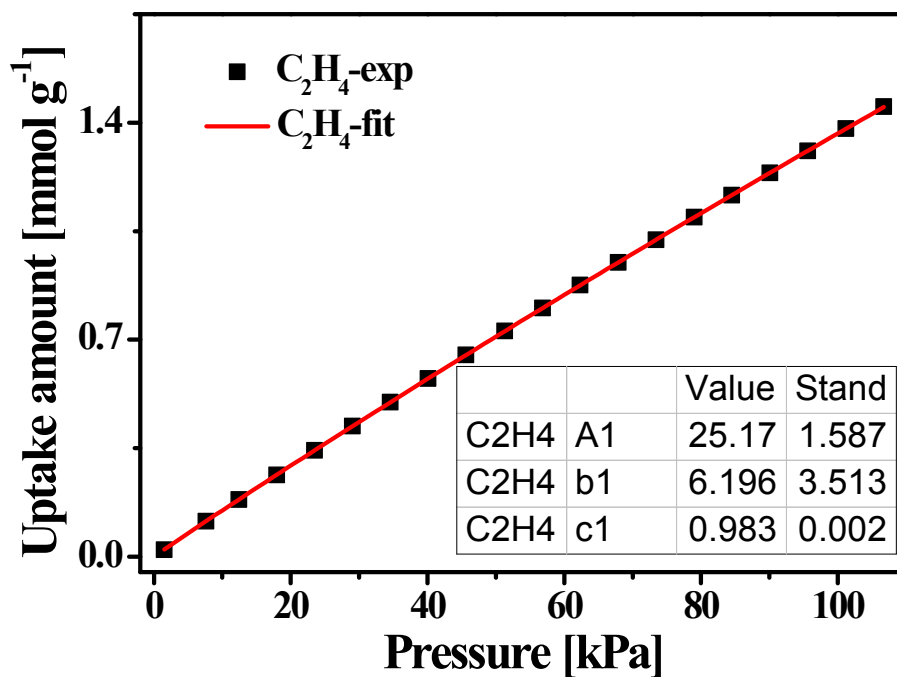


Fig. S10 Single-site Langmuir-Freundlich fits of C_2H_4 adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.

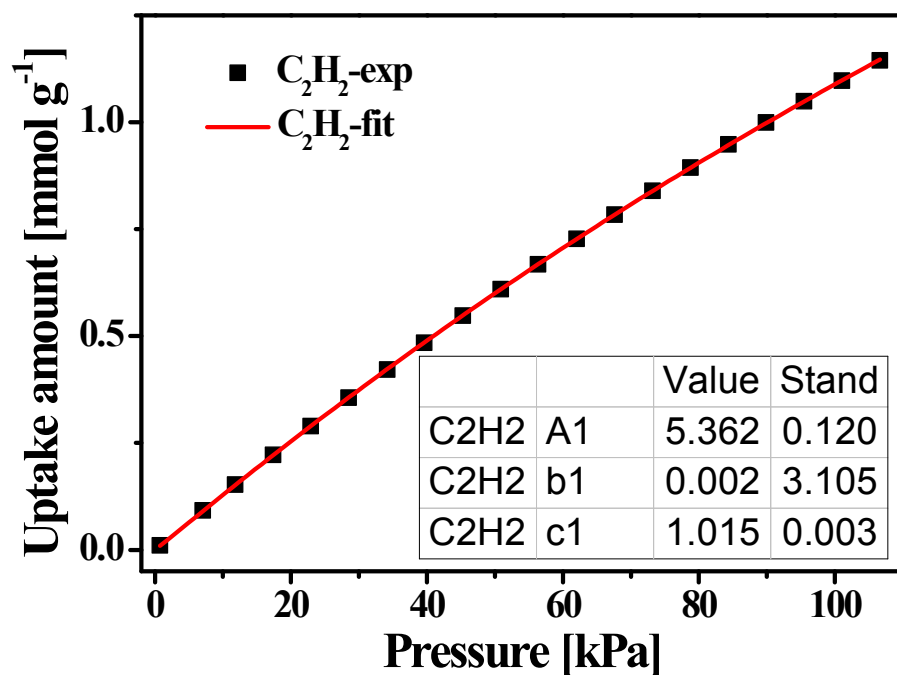


Fig. S11 Single-site Langmuir-Freundlich fits of C_2H_2 adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.

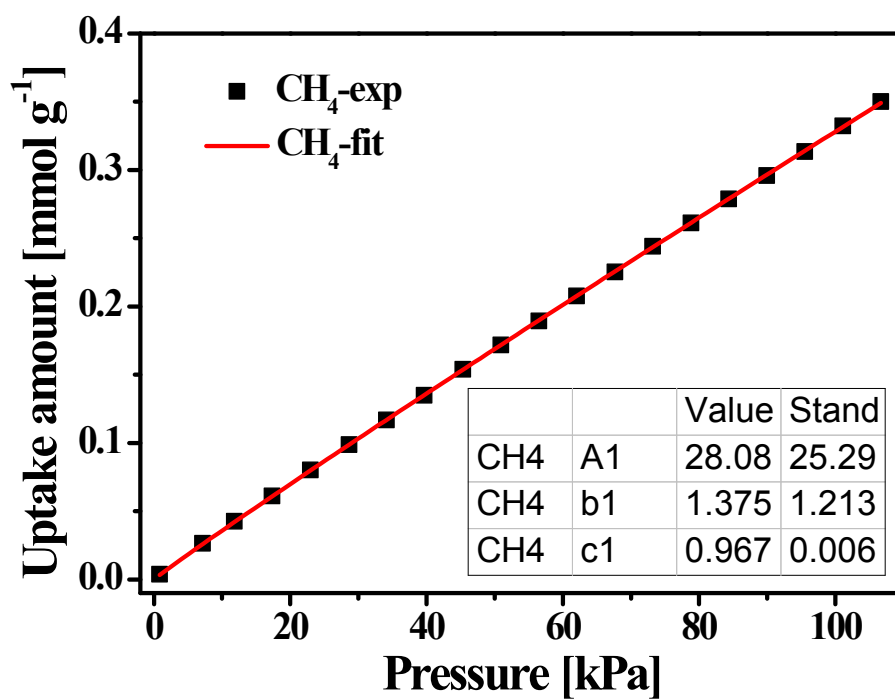


Fig. S12 Single-site Langmuir-Freundlich fits of CH₄ adsorption isotherm on HOF-14 at 298 K, inset table shows the fitting results.