

Electronic Supporting Information (ESI)

Rational design and synthesis of amino-functionalized hydrogen-bonded network with ACO zeolite-like topology for gas storage

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CONTENTS

- S1. Materials and Physical Measurements**
- S2. Synthesis of $[\text{In}_8(\text{AHImDC})_{12}] \cdot 6\text{H}_2\text{O}$**
- S3. Fourier Transform Infrared (FT-IR) Spectra**
- S4. X-ray Single Crystal Structure Determination**
- S5. Selected bond lengths and angles**
- S6. Powder X-ray Diffraction (PXRD) Data**
- S7. Thermal Stability**
- S8. Gas Sorption Measurements**
- S9. Isothermic Heat of Adsorption (Q_{st}) Calculations**
- S10. Reference**

Materials and Physical Measurements

Reagents and solvents were purchased from Aladdin and J&K company. All chemicals were of reagent grade and used without any further purification. Elemental analyses (C, H, N) were recorded on Perkin-Elmer 240 element analyzer. The FT-IR spectra were performed on AVATAR360 spectrometer with KBr pellets in the 4000-400 cm^{-1} region. Thermogravimetric analyses (TGA) were carried under N_2 atmosphere on NETZSH STA 449F3 analyzer with a heating rate of 10 $^\circ\text{C}/\text{min}$. The gas sorption isotherms were recorded Volumetrically Autosorb IQ surface area analyzer (ASAP 2020).

Synthesis of $[\text{In}_8(\text{AHImDC})_{12}] \cdot 6\text{H}_2\text{O}$

In a 20 mL scintillation vial, ADCIm (26.6 mg, 0.2 mmol) and $\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (31.8 mg, 0.1 mol) were dissolved in DMF (6 mL). The reaction mixture was heated at 125 $^\circ\text{C}$ for seven days and then cooled down to room temperature with 5 $^\circ\text{C}/\text{h}$ to produce flaxen polyhedral crystals. Yield 43.1% (based on the In). Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{38}\text{N}_{36}\text{O}_{55}\text{In}_8$: C, 23.52; H, 1.24; N, 16.46. Found: C, 23.46; H, 1.33; N, 16.41. FT-IR (4000-400 cm^{-1}): 3428(m), 1661(s), 1574(m), 1479(s), 1389(m), 1254(m), 1100(s), 787(s), 724(m), 667(m).

Fourier Transform Infrared (FT-IR) Spectra

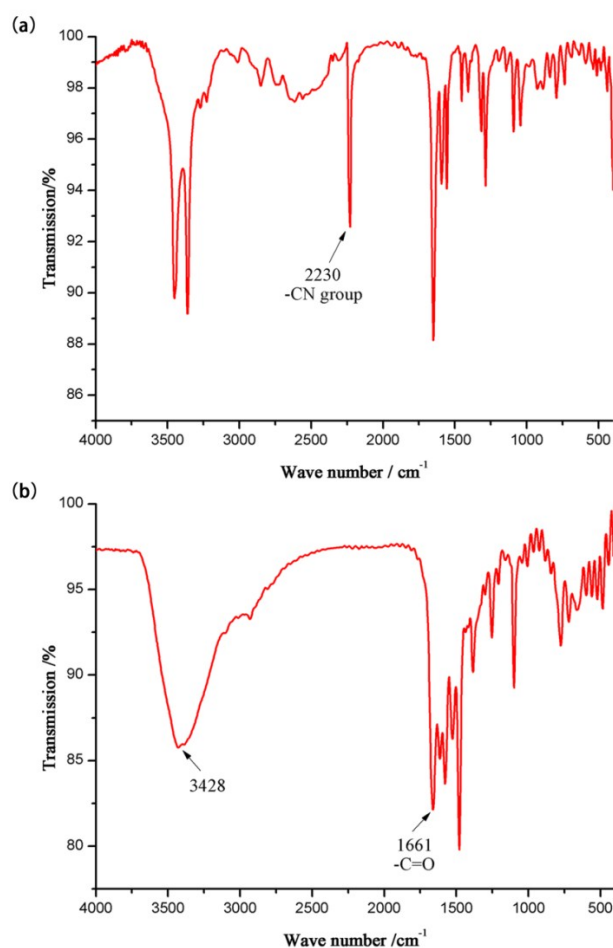


Figure S1. IR spectra: (a) 2-amino-4,5-dicyanoimidazole; (b) as-synthesized **1**.

Powder X-ray Diffraction (PXRD) Data

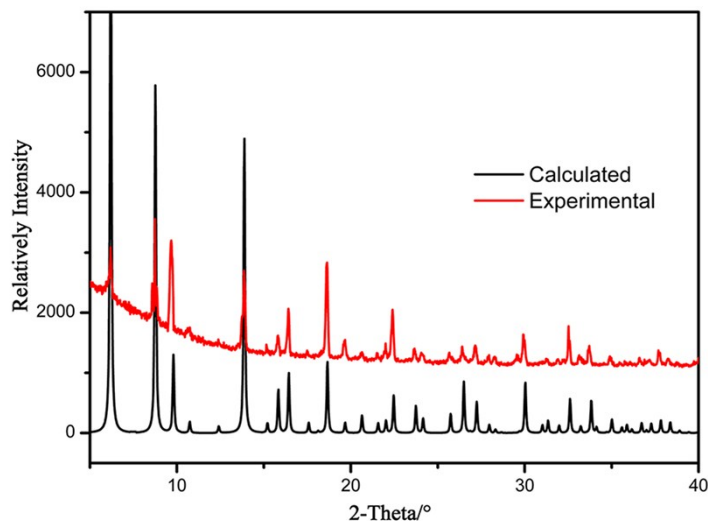


Figure S2. Calculated and experimental powder X-ray diffraction patterns for as-synthesized **1**.

X-ray Single Crystal Structure Determination

Single crystal suitable for X-ray diffraction was attached to a glass fiber, and the intensity data were collected on a Bruker Smart Apex II CCD diffractometer (graphite monochromated Mo/K α radiation, $\lambda = 0.71073\text{\AA}$). The structure was resolved with direct methods using the SHELXTL-97¹ package and refined with full-matrix least squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of organic ligands were generated geometrically calculated position with isotropic displacement parameters set to $1.2 \times U_{\text{eg}}$ of the attached atoms, while the hydrogen atoms of guest molecules were found in the Fourier difference map. In this structure, free solvent molecules were removed using the SQUEEZE routine of PLATON and the structure was then refined again using the data generated. Detail of the Crystallographic parameters, data collection and structural refinements are listed in Table S1. Selected bond lengths and angles are summarized in Table S2. CCDC 1450997 contains the supplementary crystal data for complex **1**.

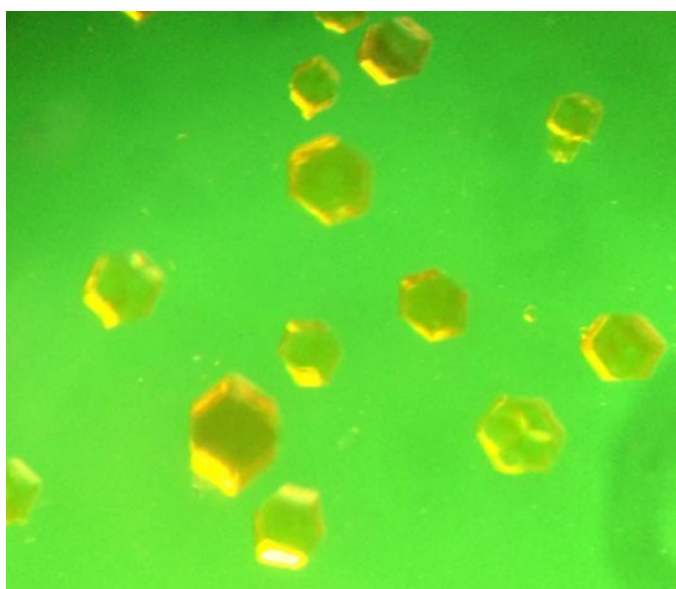


Figure S3. Optical microscope image of as-synthesized **1**

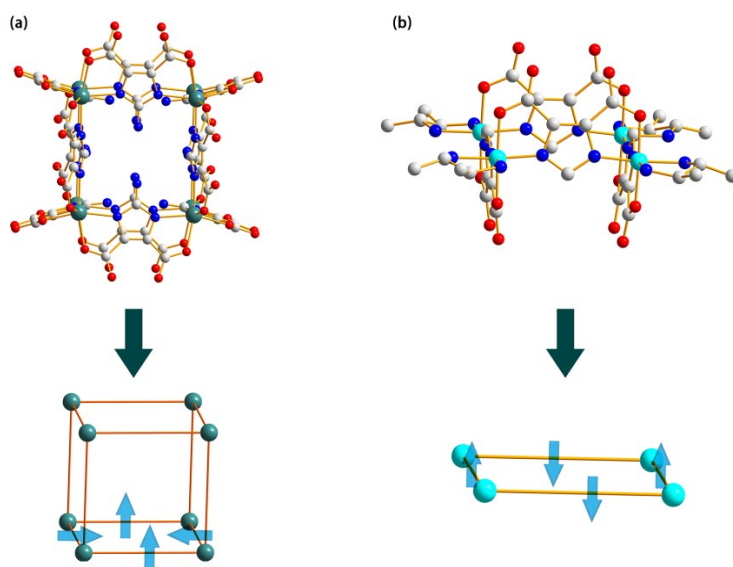


Figure S4. Comparison of the orientation and construction of the ADCIM ligands in **1** with the similar metal-organic squares.

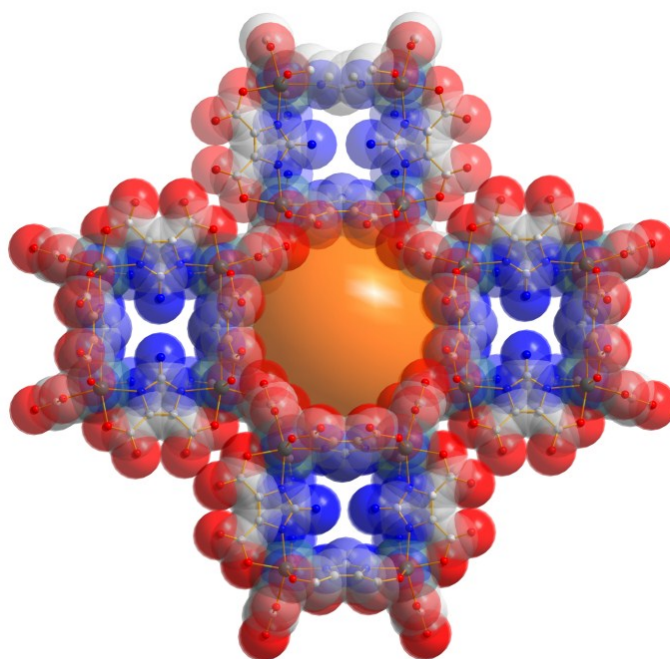


Figure S5. Orange sphere represents the biggest sphere which can be inserted in the larger channel (central atom diameter is 13.1 Å).

Table S1. Crystal data and structure refinement

Empirical formula	$C_{60}H_{37.92}N_{36}O_{55}In_8$
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Formula weight	3061.74
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Pm-3n
Unit cell dimension	a=b=c=20.1628(2) Å
	$\alpha = \beta = \gamma = 90^\circ$
Volume	8203.5(2) Å ³
Z	2
Density (calculated)	1.240 g/cm ³
μ	1.176 mm ⁻¹
No. of measured, independent and observed [$I > 2.0 \sigma(I)$] reflections	198262, 1720, 1394
R _{int}	0.061
R ₁ ($I > 2\sigma$)/ wR ₂ (all data)	0.0912, 0.3045
GOF	1.38

Selected bond lengths and angles

Table S2. Selected bond lengths (Å) and angles (°) for **1**

In(1)-O(2)	2.194(4)	In(1)-N(2)	2.234(8)	In(1)-O(2) ^a	2.194(4)
In(1)-N(2) ^a	2.234(8)	In(1)-O(2) ^b	2.194(4)	In(1)-N(2) ^b	2.234(8)
O(2)-In(1)-N(2)	156.6(2)	O(2)-In(1)-O(2) ^a	87.76(19)		
O(2)-In(1)-N(2) ^a	106.9(2)	O(2)-In(1)-O(2) ^b	87.76(19)		
O(2)-In(1)-N(2) ^b	74.96(19)	N(2)-In(1)-O(2) ^a	74.96(19)		
N(2)-In(1)-N(2) ^a	94.8(2)	N(2)-In(1)-O(2) ^b	106.9(2)		
N(2) - In(1) - N(2) ^b	94.8(2)	O(2) ^a -In(1)-N(2) ^a	156.6(2)		
O(2) ^a - In(1) - O(2) ^b	87.76(19)	O(2) ^a - In(1) - N(2) ^b	106.9(2)		
N(2) ^a - In(1) - O(2) ^b	74.96(19)	N(2) ^a - In(1) - N(2) ^b	94.8(2)		
O(2) ^b - In(1) - N(1) ^b	156.6(2)				

Symmetry transforms used to generate equivalent atoms: (a) z, x, y; (b) y, z, x.

Thermal Stability

The TGA measurements were carried under N₂ atmosphere from room temperature up to 700°C using the NETZSH STA 449F3 analyzer with a heating rate of 10°C/min.

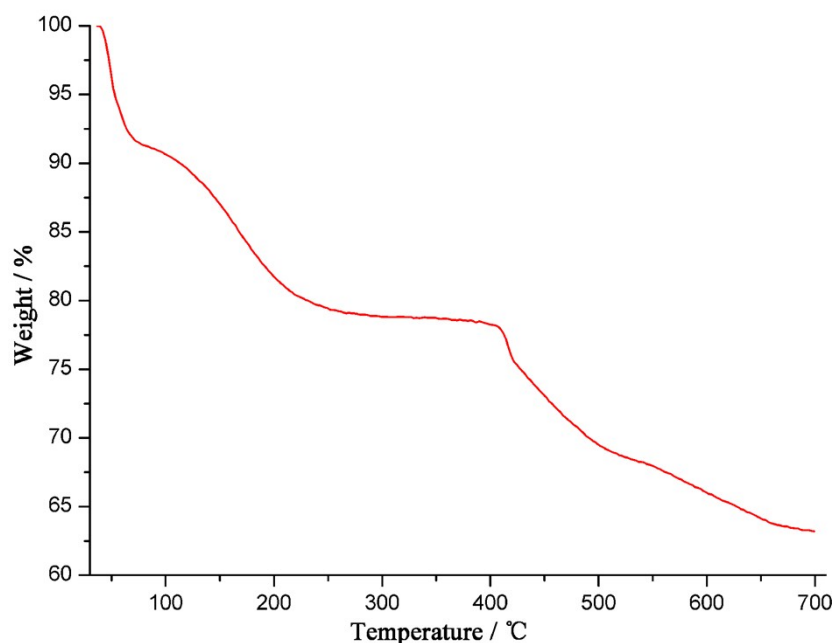


Figure S6. TGA curve of Compound 1.

Gas Sorption Measurements

The N₂ adsorption-desorption isotherms were performed on Micromeritics ASAP 2020 surface area analyzer. Prior to the treatment, as-synthesized **1** was soaked in acetone for three days with acetone refreshing every 8 hours. Then the processed samples were charged into sample tube and activated at 100°C for 10 hours by using the degassing port. Degassed samples were prepared for gas sorption measurements. Helium gas (ultra-high purity 99.999%) was used for the determination of the free space (dead volume). N₂ and H₂ (99.999%) sorption isotherms were collected at 77K in liquid nitrogen bath, while CO₂ and CH₄ sorption isotherms were measured at 273K (ice-water mixture bath) and 298K (passive thermostating).

Isosteric Heat of Adsorption (Q_{st}) Calculations

The isosteric heat of adsorption for gases (CO₂, H₂ and CH₄) was calculated by using a virial-type expansion comprising the temperature-independent parameters a_i and b_j.

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j$$

Here, P is pressure (Torr), N is adsorbed amount (mmol/g), T is temperature (K), m and n are the number of coefficients, and a_i and b_j are virial coefficients.

The isosteric heat of adsorption (Q_{st}) is calculated from:

$$Q_{st} = -R \frac{m}{i} \ln N^i$$

Here, R is the universal gas constant.

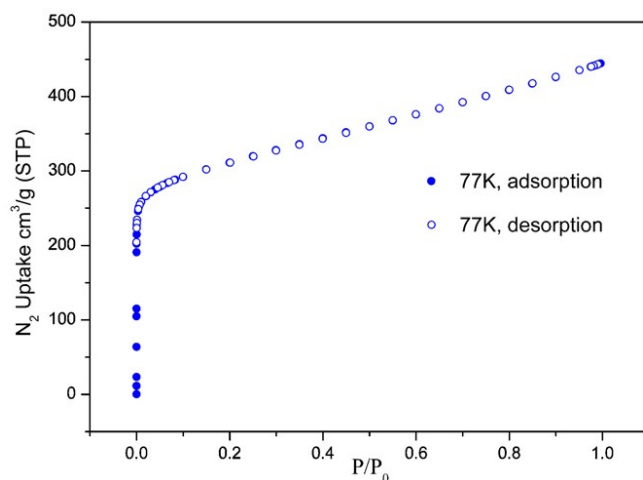


Figure S7 N₂ adsorption (solid circles) and desorption (open circles) isotherms of as-synthesized **1** measured at 77K.

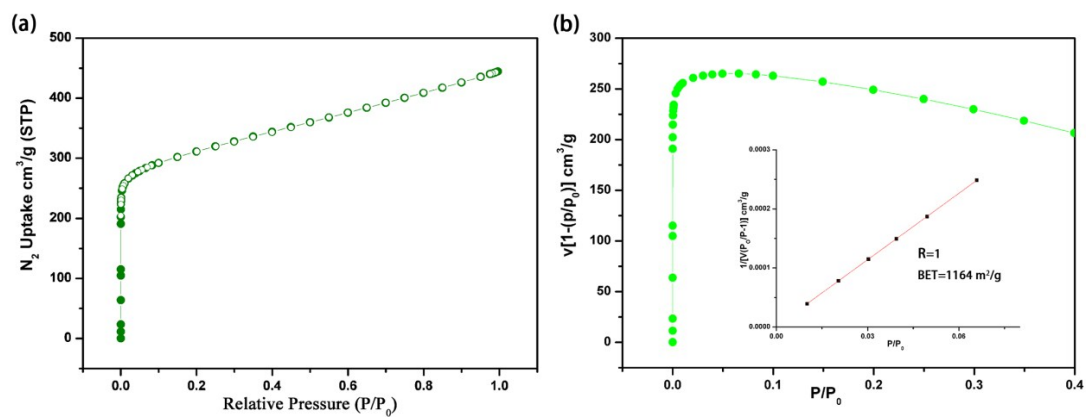


Figure S8. (a) N₂ adsorption (solid circles) and desorption (open circles) isotherms of as-synthesized **1** measured at 77K. (b) $V[1-(P/P_0)]$ vs. P/P_0 for **1**, the values below $P/P_0=0.066$ fits the first consistency criterion for the BET theory (Inset: plot of the linear region for the BET theory).

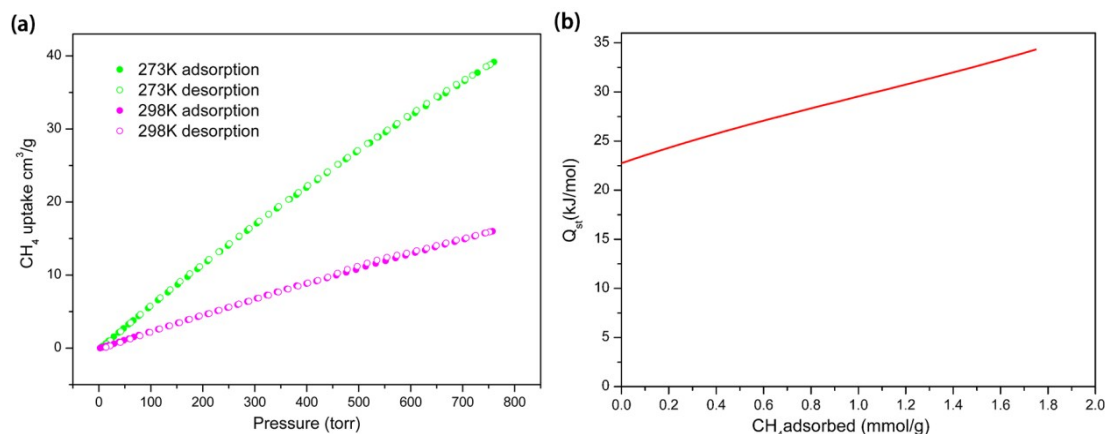


Figure S9. (a) CH₄ adsorption-desorption isotherms for **1** at 273K and 298K; (b) CH₄ adsorption enthalpy.

Table S3. Comparison of sorption data with H-bonded frameworks (MOC-2, Zn₁₄-MBB), amine-functionalized MOFs [Zn₂(atz)₂(ox), Zn₂(datz)₂(ipa), Zn₂(atz)₂(oba)] and some characteristic MOFs (MOF-5, HKUST-1, M-MOF-74, Cu-TPBTM, PCN-61, SYSU, NJU-Bai7).

MOFs	SA _{BET} [m ² /g]	SA _{Langmuir} [m ² /g]	CO ₂ uptake [cm ³ /g, 273 K/1atm]	Q _{st} (CO ₂) [KJmol ⁻¹]	H ₂ uptake [cm ³ /g, 77 K/1atm]	Q _{st} (H ₂) [KJ mol ⁻¹]	Ref
This work	1164	1476	135.8	25.2	232.4	6.4	This work
MOC-2	— ^a	1420	—	—	248.4	6.5	2
Zn ₁₄ -MBB	471	570	56	38	95.1	—	3
Zn ₂ (atz) ₂ (ox)	782	—	97.5	40.8	1.7	—	4
Zn ₂ (datz) ₂ (ipa)	—	643	68.4	28.9	—	—	5
Zn ₂ (atz) ₂ (oba)	—	755	80.6	31.9	—	—	5
ZIF-8	1630	1810	22.76 ^c	—	—	—	6
HKUST-1	1507	2175	114.04 ^d	29.8	284.48	6.8	6,7
MOF-5	3800	4400	20.4 ^c	—	527.75	—	8,9
Mg-MOF-74	1495	1905	178	47	—	—	9
Co-MOF-74	1080	—	154	37	—	—	9
Ni-MOF-74	1070	—	126	41	—	—	9
PCN-305	1720	2599	118.11	23.85	145	6.47	11
PCN-306	1927	2929	116.58	24.0	280	6.37	11
PCN-307	1376	2235	118.11	22.84	293.4	6.24	11
Cu-TPBTM	3160	3570	216.6 ^b	26.3	—	—	12
PCN-61	3000	3500	128 ^b	21.0	257.8	6.36	12,13
SYSU	1100	1216	118	28.2	117	8.4	14
NJU-Bai7	1155	1238	72	40.5	—	—	15

[a] Not reported; [b] Approx. Value was taken from SI; [c] measured at 298K and 1 bar; [d] measured at 295K and 1 bar.

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