

Supporting Information

A Microporous $Zr_6@Zr$ -MOF for the Separation of Xe and Kr

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Materials and characterizations. All starting chemicals were purchased from commercial companies and could be directly used without further purification. Among them, Zirconium chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, CAS: 13520-92-8) was purchased from Sinopharm, Acetic acid (CH_3COOH , CAS: 64-19-7) was purchased from Sinopharm, 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl) tetrabenzoic acid/ H_4tcpe ($\text{C}_{30}\text{H}_{20}\text{O}_8$, CAS: 1351279-73-6) was purchased from EXTENSION. Thermogravimetric analyses (TGA) were examined by using a TGA550 (TA Instruments) under N_2 atmosphere with a heating rate of 10 K min^{-1} . Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 2\text{-}40^\circ$ range on a Bruker D8 Advance with $\text{Cu K}\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation at room temperature. Xe (99.999%), Kr (99.999%) and mixed gases of 20/80 (v/v) Xe/Kr were purchased from XIANG YUAN Gas Company (China).

Single-crystal X-ray diffraction analysis. Single crystals of HIAM-401 and HIAM-401W were mounted on MicroMesh (MiTeGen) with paratone oil. The data were collected on a 'Bruker D8 VENTURE' diffractometer equipped with copper micro-focus X-ray sources ($\lambda = 1.5406 \text{ \AA}$). The crystals kept at the 200 K during data collection. Using Olex2, the structures were solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL³ refinement package using Least Squares minimization. In the structure of HIAM-401W, six Zr^{4+} ions form an octahedron with the 8 faces each capped by a $\mu_3\text{-O}$. Eight of the edges of the octahedron are bridged by tcpe ligands *via* bidentate carboxylate groups with the remaining coordination sites of Zr^{4+} are completed by acetate anions and H_2O molecules. And the acetate anions are found to be disordered over two part with occupancy of 0.5:0.5. Moreover, the site occupancy of the isolated Zr_6 cluster is 0.7072, and the restraint SIMU was used to refine the acetate anion of the Zr_6 cluster to make the ADP values of the terminal atom (C14) more reasonable. In the structure of HIAM-401, six Zr^{4+} ions form an octahedron with the 8 faces each capped by a $\mu_3\text{-O}$. And six $\mu_3\text{-O}$ atoms are found to be disordered over two parts (with occupancy of 0.5:0.5). Eight of the edges of the octahedron are bridged by tcpe ligands *via* bidentate carboxylate groups with the remaining coordination sites of Zr^{4+} are completed by formate anions and H_2O molecules. And the formate anions and H_2O molecules are found to share the same coordinated site with occupancy of 0.5:0.5. Furtherly, the site occupancy of the isolated Zr_6 cluster is 0.74073. The restraint SIMU were used to refine the disordered $\mu_3\text{-O}$ atoms (O5&O5A, O6&O6A), partially occupied formate anions and H_2O

molecules (O3, O3A and C9), carboxyl group of tcpe ligand (O1 O2 C1), and the acetate anion (O9 C10 C11) of the isolated Zr_6 cluster to make the ADP values of the atoms more reasonable. The hydrogen atoms on the aromatic rings were located at geometrically calculated positions and refined by riding. However, the hydrogen atoms for the coordinated molecules cannot be found from the residual electron density peaks and the attempt of theoretical addition was not done. The free solvent molecules are highly disordered in HIAM-401 and HIAM-401W, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the Solvent Mask routine of Olex2; structures were then refined again using the data generated. The refinement results are summarized in Table S1. Crystallographic data for all of the crystal structures in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-2159612 (HIAM-401) and CCDC-2159615 (HIAM-401W). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Synthesis of $Zr_6@Zr$ -tcpe (HIAM-401). H_4tcpe (450 mg, 0.89 mmol) and $ZrOCl_2 \cdot 8H_2O$ (600 mg, 1.85 mmol) in 80 mL of acetic acid were ultrasonically dissolved in a 200 mL Teflon autoclave. The mixture was heated in an oven at 120 °C for 3 days. Colourless square-block-shaped single crystals were collected through filtration (Yield: 65%). The crystals were exchanged with methanol for 2 days and the subsequent air-dried sample was subject to PXRD and TGA measurements. Elemental analysis (for $[Zr_6O_4(OH)_4(tcpe)_{1.5}(CH_3COO)_3(OH)_3(H_2O)_3]_8 \cdot 0.74[Zr_6O_4(OH)_4(CH_3COO)_4(OH)_8(H_2O)_8]_3$): calculated: C: 29.9%, O: 35.3%, H: 3.2%; experimental: C: 30.1%, O: 33.9%, H: 3.4%.

Gas sorption measurements

An autosorb-iQ surface area analyzer was used to measure N_2 adsorption isotherms. To remove all the guest solvents in the framework, the fresh powder sample of HIAM-401 was first solvent-exchanged with dry methanol at least 8 times within two days and then the exchanged sample was evacuated at room temperature (298 K) for 24 h. N_2 sorption measurements were maintained at 77

K under liquid nitrogen bath. Water bath was used to achieve a constant temperature of 278, 288 and 298 K, respectively, for the adsorption of Xe and Kr.

Fitting of single-component adsorption isotherms of Xe and Kr

The pure component isotherm data for Xe and Kr of HIAM-401 were fitted with the dual-site Langmuir-Freundlich isotherm model

$$q = q_{A,sat} \frac{b_A p^{v_A}}{1 + b_A p^{v_A}} + q_{B,sat} \frac{b_B p^{v_B}}{1 + b_B p^{v_B}} \quad (1)$$

with T-dependent parameters b_A , and b_B

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right) \quad (2)$$

The fitted parameter values are presented in Table S2.

Isosteric heat of adsorption

A virial-type expression of comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for Xe and Kr on HIAM-401. In each case, the data were fitted using equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N_i + \sum_{j=0}^m b_j N_j \quad (3)$$

Here, P is the pressure expressed in mmHg, N is the amount absorbed in mmol g⁻¹, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased till the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit. And the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression:

$$Q_{st} = -R \sum_{i=0}^m (a_i N_i)$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

IAST calculations

We consider the separation of binary Xe/Kr mixtures for HIAM-401. The adsorption selectivity for Xe/K separation is defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (5)$$

In equation (5), q_1 and q_2 are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures p_1 , and p_2 . Figure 3a presents IAST calculations of the adsorption selectivity of 20/80 (v/v) Xe/Kr mixtures for Zr-H₄tpe.

Breakthrough experiments

The breakthrough experiment was performed with an auto mixed-gas breakthrough apparatus (3P MIXSORB S, 3P Instruments) equipped with a mass spectrometer (MKS CIRRUS-3). The measurement was carried out using a stainless-steel column (2.0 mm inner diameter × 160 mm). The weight of HIAM-401 sample packed in the column was: 0.418 g. The mixed gas flows of Xe/Kr = 20/80 was then introduced with a total flow of 1 mL min⁻¹. The downstream was monitored by a 3P mass spectrometer (HPR 20). The standard gases were used to calibrate the concentration of the outlet gas.

Table S1. Crystallographic data and structure refinement results of HIAM-401 and HIAM-401W.

Unit cell parameters	HIAM-401W	HIAM-401
Identification code	HIAM-401W	HIAM-401
Empirical formula	C _{17.71} H ₈ O _{13.5} Zr _{2.53}	C _{389.78} H ₁₉₂ O _{327.86} Zr _{61.33}
Formula weight	667.50	15715.06
Temperature/K	200.0	200.0
Crystal system	cubic	cubic
Space group	Pm-3m	Pm-3m
a/Å	29.9252(15)	29.9798(6)
b/Å	29.9252(15)	29.9798(6)
c/Å	29.9252(15)	29.9798(6)
α /°	90	90
β /°	90	90
γ /°	90	90
Volume/Å ³	26799(4)	26945.5(16)
Z	24	1
ρ_{calc} /g/cm ³	0.993	0.968
μ /mm ⁻¹	5.111	5.121
F(000)	7762.0	7607.0
Crystal size/mm ³	0.1 × 0.1 × 0.1	0.04 × 0.04 × 0.04
Radiation	CuK α (λ = 1.54178)	CuK α (λ = 1.54178)
2 Θ range for data collection/°	6.604 to 144.388	4.168 to 136.638
Index ranges	-36 ≤ h ≤ 26, -32 ≤ k ≤ 36, - 35 ≤ l ≤ 34	-36 ≤ h ≤ 29, -16 ≤ k ≤ 33, - 34 ≤ l ≤ 27
Reflections collected	98433	59176
Independent reflections	5073 [R _{int} = 0.0588, R _{sigma} = 0.0188]	4762 [R _{int} = 0.1084, R _{sigma} = 0.0471]
Data/restraints/parameters	5073/6/209	4762/54/205
Goodness-of-fit on F ²	1.042	1.054

Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0676$, $wR_2 = 0.1700$	$R_1 = 0.0744$, $wR_2 = 0.1882$
Final R indexes [all data]	$R_1 = 0.0689$, $wR_2 = 0.1710$	$R_1 = 0.0841$, $wR_2 = 0.1939$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.18/-0.95	1.25/-1.22

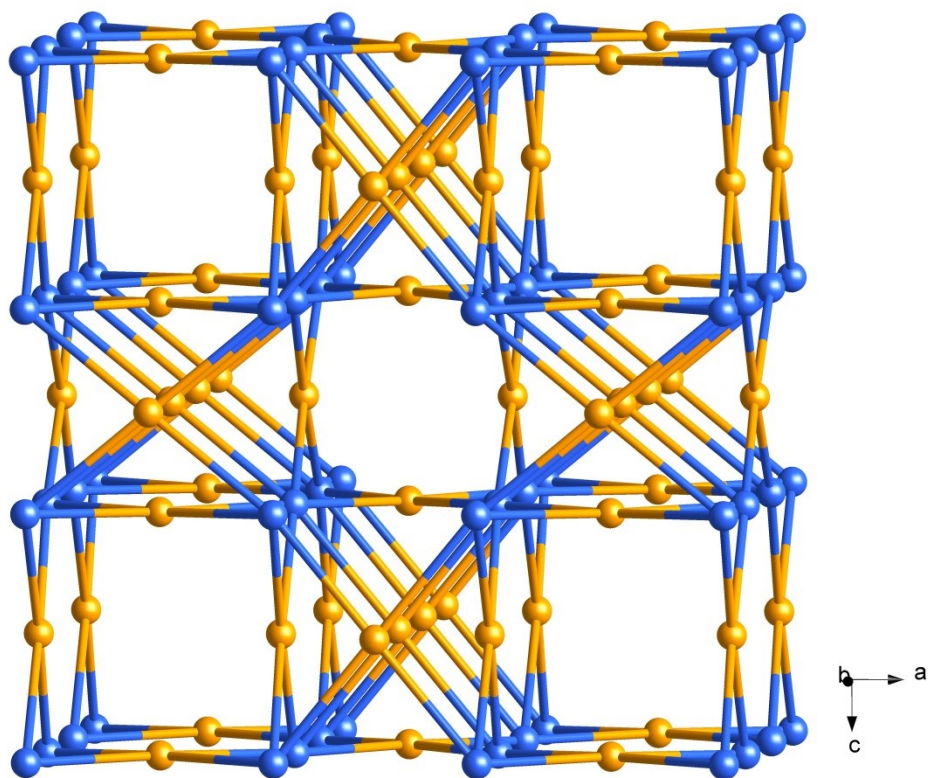


Fig. S1. Schematic illustration of the **she** topology of HIAM 401(The blue and yellow spheres represent Zr_6 clusters and *tcpe* ligands, respectively).

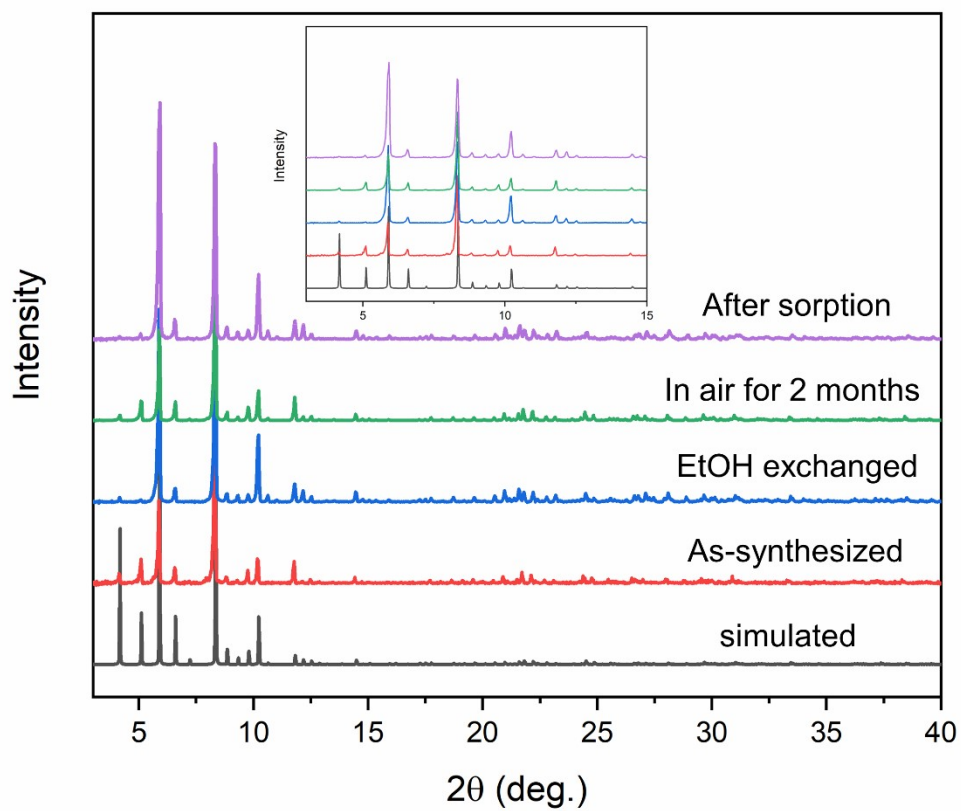


Fig. S2. PXRD patterns of HIAM-401.

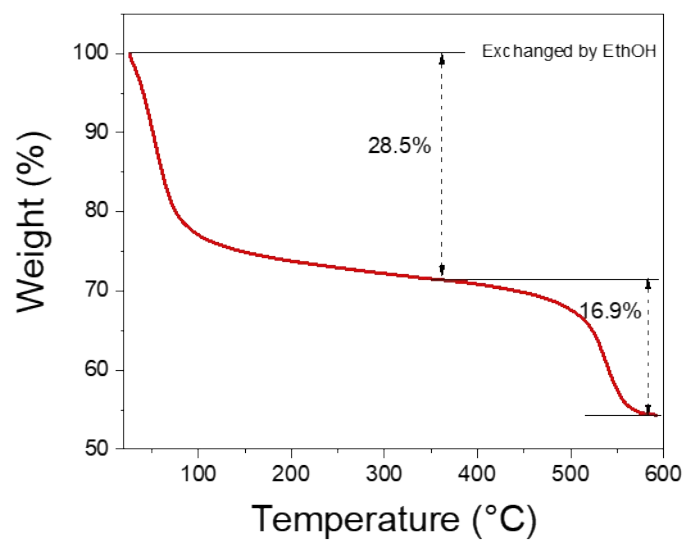


Fig. S3. TGA curves of as-synthesized HIAM-401(red) and after exchanged by EtOH (blue).

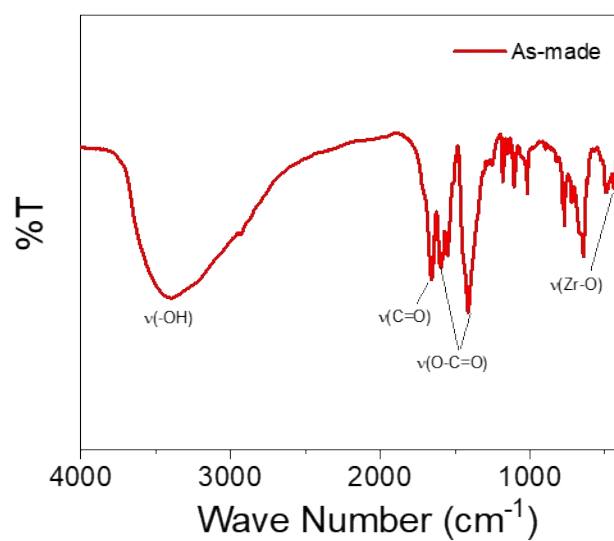


Fig. S4. IR spectrum of HIAM-401.

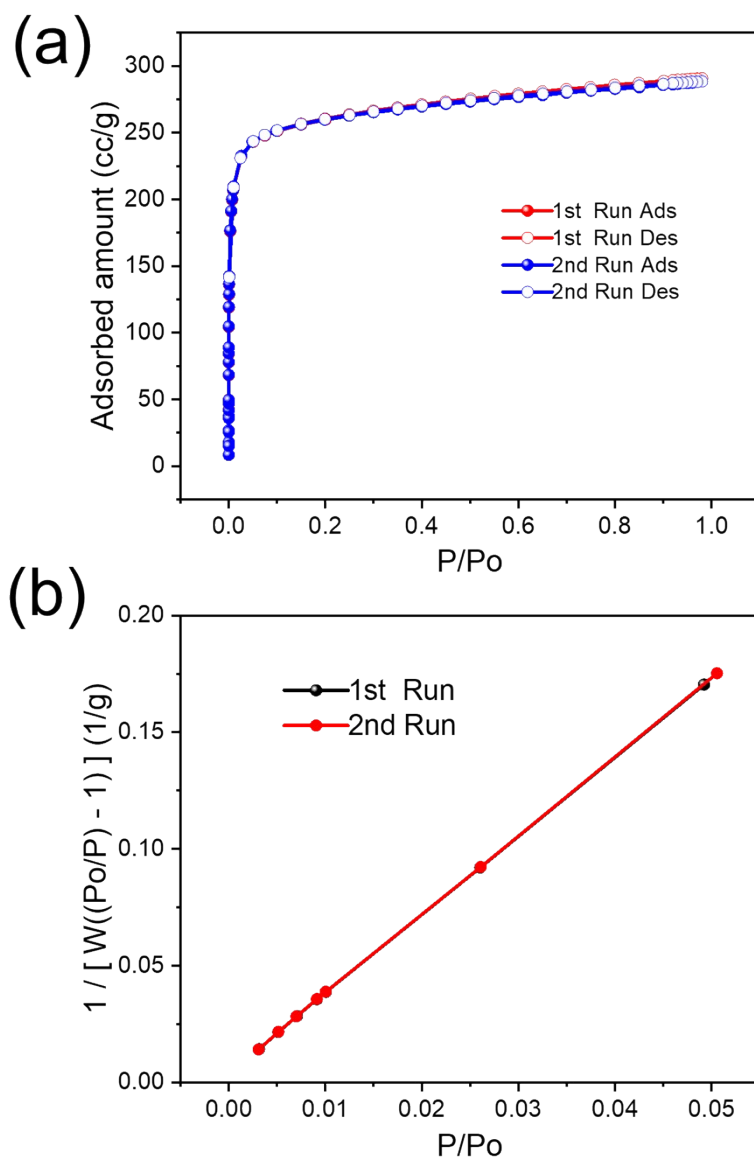


Fig. S5 (a) N₂ adsorption isotherm of HAIM 401 at 77K, (b) the fitting curves of BET plot.

Table S2. Dual-site Langmuir-Freundlich parameter fits for Xe, Kr in HIAM-401. The fits are based on experimental isotherm data at 278 K, 288 and 298K.

Temperature(K)		$q_{sat, A}$	b_A	v_A	$q_{sat, B}$	b_B	v_B	R-Square
		cm ³ ·g ⁻¹	kPa ⁻¹	dimensionless	cm ³ ·g ⁻¹	kPa ⁻¹	dimensionless	
278	Xe	12.98	12.98	0.91	319.16	0.21	0.78	0.99995
	Kr	3.73	1.10	4.63	42.60	0.68	0.99	0.99996
288	Xe	8.98	15.03	0.97	198.88	0.27	0.82	0.99997
	Kr	52.98	0.39	0.97	0.69	25.11	20.88	0.99999
298	Xe	174.44	0.26	0.87	8.99	11.59	0.99	0.99999
	Kr	102.82	0.15	0.96	0.59	127133.61	4.16	0.99996

Table S3. Comparison of the Xe adsorption uptake, Xe/Kr selectivity, and heat of adsorption data of HIAM-401 with some top-performing materials reported

Materials	Xe uptake at 1 bar (cm ³ g ⁻¹)	Q _{st} of Xe (kJ mol ⁻¹)	Ref.
Zr-H ₄ tcpe	66.5	32.7	This work
ZJU-74a-Ni	59.5	41.7	1
ZJU-74a-Pd	48.5	45.5	1
CROFOUR-1-Ni	39.6	37.4	2
CROFOUR-2-Ni	33.6	30.5	2
SBMOF-1	31.4	37.0	3
SBMOF-2	63.4	26.4	4
[Co ₃ (C ₄ O ₄) ₂ (OH) ₂]	30.2	43.6	5
Ni-MOF-74	93.2	22	6
Ca-SINAP-1	69.7	29.2	7
Co ₃ (HCOO) ₆	44.8	28	8
Ag-MOF-303	108.7	28.2	9
Ag@MOF-74Ni	109.5	23.6	10

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