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Supporting Information

A Robust Aluminum-Octacarboxylate Framework with scu Topology for Selective Capture of Sulfur Dioxide

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Experimental details

Synthesis of 4',4''',4''''',4'''''''-(Ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-3,5-dicarboxylic acid)) (H8ettbpdc)

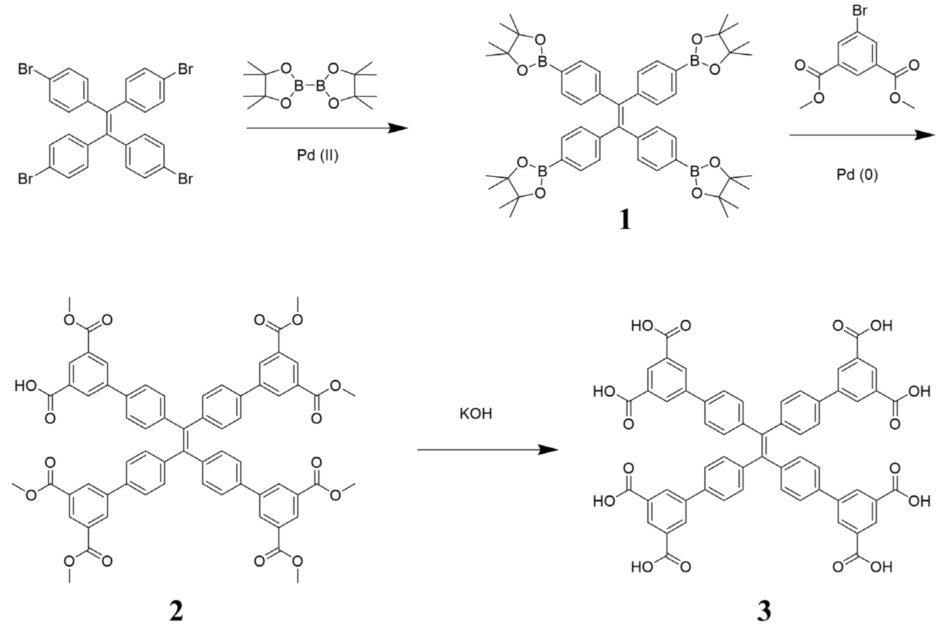


Figure S1. Synthesis of 4',4''',4''''',4'''''''-(Ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-3,5-dicarboxylic acid))

A 100 mL round-bottom flask was charged with 1,1,2,2-tetrakis(4-bromophenyl) ethylene (6.48 g, 10.0 mmol), bis(pinacolato)diboron (15.2 g, 60.0 mmol), [1,1′-Bis(diphenylphosphino)ferrocene] dichloro palladium (II) (1.46 mg, 2.0 mmol), and potassium acetate (7.8 g, 80.0 mmol). The solids were evacuated under high pressure for 15 minutes. Then, dioxane (40 mL) was added and the reaction mixture allowed to reflux for 48 hours under N_2. After the consummation of 1,1,2,2-tetrakis(4-bromophenyl) ethylene, the reaction mixture was cooled to room-temperature and then poured into ice-water to produce a yellow precipitate. The precipitate was filtered and washed several times with water and purified using flash column chromatography with THF/hexane as eluent. The isolate solid was finally recrystallized with dioxane to give **1** as yellow crystals (65% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, J = 7.8 Hz, 8H), 7.01 (d, J = 7.9 Hz, 8H), 1.34 (s, 49H).

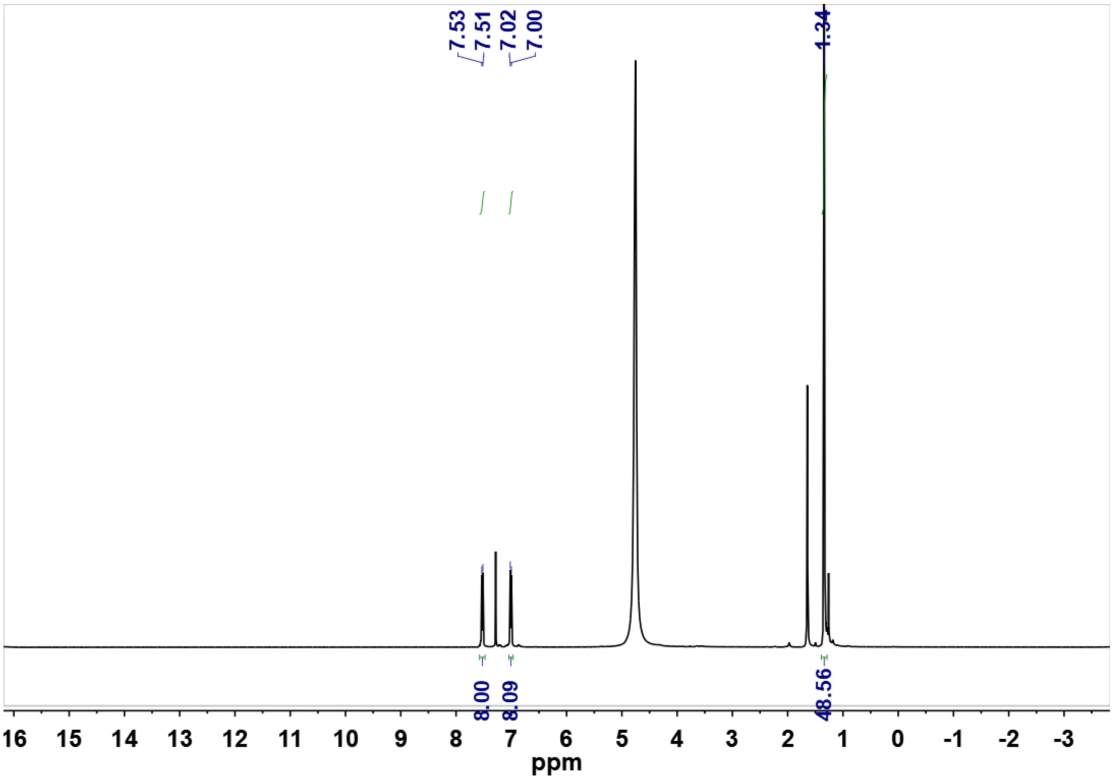


Figure S2. ^{1}H NMR spectrum of compound 1.

Compound **1** (4.2 g, 5.0 mmol), dimethyl 5-bromoisophthalate (6.8 g, 25.0 mmol) and K_2CO_3 (6.9 g, 50.0 mmol) were added to a mixture of toluene and methanol (4 : 1), and the mixture was stirred under N_2 for 15 min. $Pd(PPh_3)_4$ (1.2 g, 1 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80 °C for 3 days under N_2. Afterward it was concentrated under reduced pressure. The crude product was purified by column chromatography to obtain the product **2** as white solid (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 4H), 8.47 (s, 8H), 7.52 (d, J = 8.0 Hz, 8H), 7.26 (d, J = 8.1 Hz, 15H), 3.97 (s, 24H).

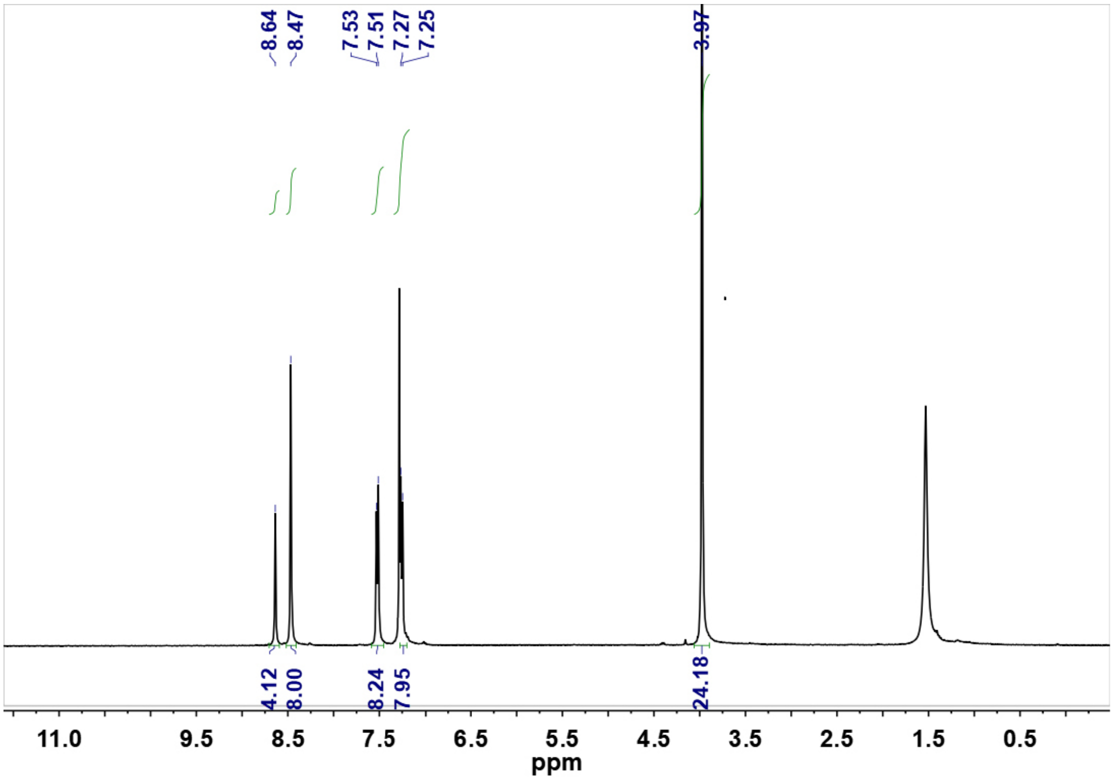


Figure S3. ^{1}H NMR spectrum of compound 2.

Compound **2** (2.7 g, 2.5 mmol) was dissolved in 50 ml of THF, to which 50 ml of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux for 10 h, and then the organic solvent was concentrated under reduced pressure. Then 100 mL of water was added to the resides and aqueous phase was acidified to pH = 2 using 6 M HCl aqueous solution. The resulting precipitate was collected via filtration, washed with water (200 ml) and dried under vacuum to afford **3** as white solid. (92% yield). ^{1}H NMR (400 MHz, DMSO) δ 13.41 (s, 8H), 8.42 (s, 4H), 8.34 (s, 8H), 7.63 (d, J = 8.3 Hz, 8H), 7.23 (d, J = 8.2 Hz, 8H).

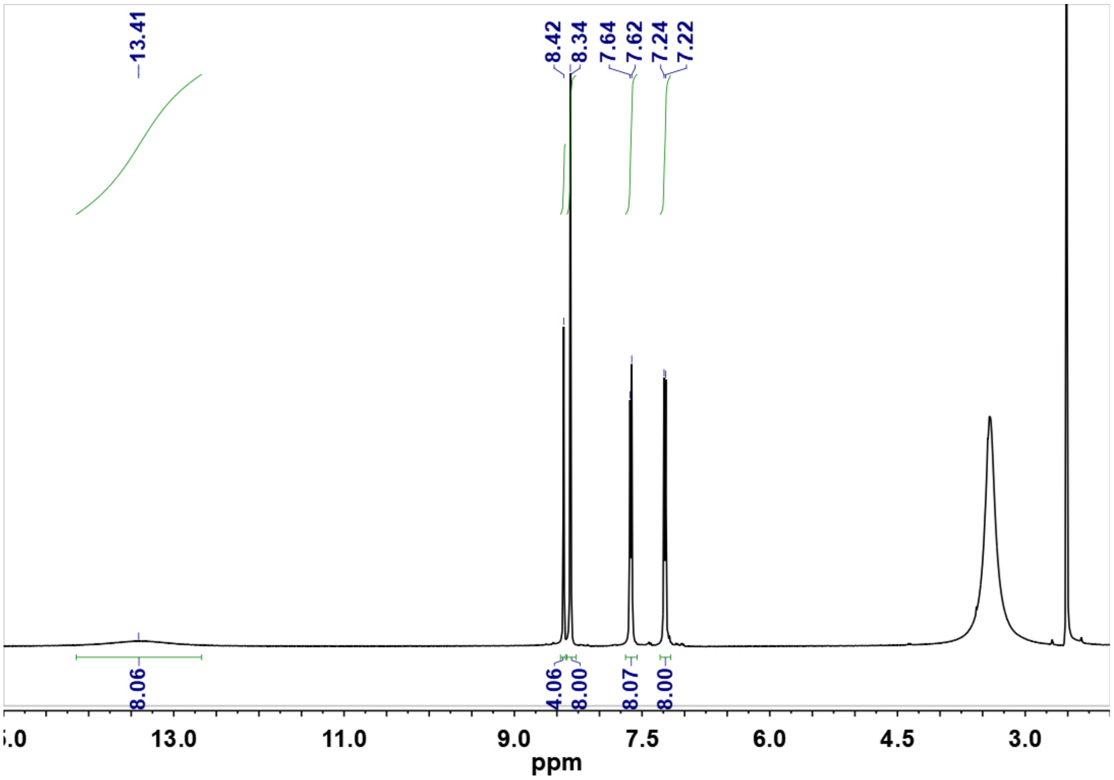


Figure S4. ^{1}H NMR spectrum of compound 3.

Synthesis of HIAM-330: HIAM-330 was prepared via solvothermal reaction. $Al(NO_3)_3{\cdot}9H_2O$ (40 mg) and 4',4''',4''''',4'''''''-(Ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-3,5-dicarboxylic acid)) (20 mg) were added to a mixed solvent of DMF/Acetonitrile/formic acid/ (3.5/1.5/2.5 mL) and the mixture was stirred at room temperature for 1 hour before being transferred to a 20 mL Teflon bomb (Xi'an Taikang Technology Co., Ltd.). The Teflon bomb was placed in an oven preset at 150 °C for 3 days. Colorless crystals were obtained after the reaction was cooled to room temperature.

General characterizations: Single-crystal X-ray diffraction data were collected at 150 K on a Bruker APEX-II CCD diffractometer using GaKα radiation tuned to λ = 1.34139 Å. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance with Cu Kα radiation (λ = 1.5406 Å). Data were collected at room temperature at 2θ = 3-40°. Thermogravimetric analysis was carried out on a TGA550 (TA Instruments) analyzer. For each run, ~5 mg of sample was heated from room temperature to 600 °C at a ramp rate of 10 °C/min.

Adsorption isotherms measurements: Nitrogen adsorption at 77 K was measured on a Micromeritics 3Flex analyzer, The single-component adsorption isotherms of CO_2, CH_4, and N_2 at 288, 298 and 308 K were measured using a Micromeritics 3Flex Analyzer. The SO_2 adsorption isotherms at 288, 298 and 308 K were collected using a BSD-PMC corrosive gas adsorption analyzer (Beishide Instrument Technology (Beijing) Co., Ltd.).

Column breakthrough measurements: All breakthrough tests were performed in dynamic gas breakthrough equipment and conducted using a stainless-steel column (6 mm inner diameter × 100mm) manually packed with 0.33 g and 1.31 g active HIAM-330 powder for SO_2/N_2 and SO_2/CO_2 breakthrough measurements, respectively. The column was first purged with He flow (20 mL min^{-1}) for 6 hours at 423 K. The fixed bed was then cooled to room temperature using a temperature programmed water bath. the breakthrough experiment of SO_2/N_2 was performed with a stream of SO_2/N_2 mixture (2500 ppm SO_2, 75 % N_2 in He, total flow rate: 20 mL/min) and the breakthrough experiment of SO_2/CO_2 was performed with SO_2/CO_2 mixture (2500 ppm SO_2, 15 % CO_2 in He, total flow rate: 20 mL/min) at atmospheric pressure and room temperature. The flow rate of the entering gas mixture was maintained at 20 mL min^{-1}. and the gas concentration of SO_2, N_2 and CO_2 at the outlet was determined by mass spectrometry and compared with the corresponding inlet concentration F_0, where $F/F_0 = 1$ indicates complete breakthrough.

Rietveld refinements of the high-resolution synchrotron PXRD measurements: High-resolution synchrotron powder X-ray diffraction pattern for SO_2-loaded HIAM-330 was collected at the Beamline I11 of Diamond Light Source (DLS) using position sensitive detector (PSD) and a monochromated radiation (λ = 0.824388 Å). The SO_2 dosing procedure °C the lab using a Schlenk line. The powdery sample was ground and packed into 0.7 mm borosilicate capillary and activated under dynamic vacuum at 423K overnight. The packed capillary was then exposed to 1 bar of SO_2 and left for 30 min for equilibration. Diffraction patterns were then collected at room temperature using the high-throughput mode available at I11. Rietveld structure refinement on the high-resolution patterns was carried out using the TOPAS package. Pawley refinement was first conducted to obtain the refined non-structural parameters, including background, peak shape, and lattice parameters. The structure model from the single-crystal diffraction result was used and atom sites were fixed at the beginning of refinement. The atomic displacement parameters (ADPs) are defined using element-wise isotropic parameters. The organic linker was described using a semi-rigid model where the C–C bond distance was allowed to vary within a chemically reasonable range. The phenyl ring moieties were allowed to rotate along their C_2 axis to account for guest-induced re-orientation. The SO_2 molecule was described using the rigid body model with bond distance and angles from the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB). The initial center of masses and orientations of the SO_2 molecules were determined using the simulated annealing (SA) method. All structural and lattice parameters were released to be refined in the final stage, and structure solutions were accepted with good agreement factors.

Adsorption selectivity calculation: The dual site Langmuir-Freundlich isotherm model was adopted to fit the adsorption isotherms of SO_2, CO_2, N_2 and CH_4 on HIAM-330, which was described as follows:

$$q=q_{A,sat}\frac{b_A P^{vA}}{1+b_A P^{vA}}+q_{B,sat}\frac{b_B P^{vB}}{1+b_B P^{vB}} \tag{1}$$

with T-dependent parameters b_A, and b_B

$$b_A=b_{AO}\exp\left(\frac{E_A}{RT}\right);\ b_B=b_{BO}\exp\left(\frac{E_B}{RT}\right) \tag{2}$$

where q represents the adsorption amount of adsorbents with units of mol·kg^{-1}, $q_{A,sat}$ and $q_{B,sat}$ represents the saturated adsorption amount for adsorption sites A and B, respectively, b_A and b_B are constants for species i at adsorption sites A and B, respectively, p is the total pressure of the bulk gas at the adsorption equilibrium, and v_A and v_B are the Freundlich exponent for sites A and B, respectively.

To calculate the adsorption selectivity for the SO_2/CO_2, SO_2/CH_4 and SO_2/N_2 mixtures on HIAM-330, the IAST selectivity is defined by:

$$S_{ads}=\frac{q_1/q_2}{y_1/y_2} \tag{3}$$

where q_1 and q_2 represent the adsorption amounts of SO_2 and CO_2, CH_4 or N_2 upon the sample under equilibrium conditions, which is usually expressed with units of mmol·g^{-1}, y_1 and y_2 are the corresponding mole fractions in the gas phase for the mixtures.

Isosteric heat of adsorption calculation: To determine the affinity between the scaffold and the adsorbates, the Virial equation was employed to calculate the adsorption heat Q_{st} for SO_2 and CO_2 using adsorption isotherm at 273, 283 and 298 K, which was defined as follows:

$$Ln(P)=Ln(N)+\frac{1}{T}\sum_{i=0}^{m} a_i N_i+\sum_{i=0}^{n} b_i N_i \quad (4)$$

$$Q_{st}=-R\sum_{i=0}^{m} a_i N_i \quad (5)$$

where N is the adsorption amount, and m and n determine the number of items required to precisely fit the adsorption isotherms.

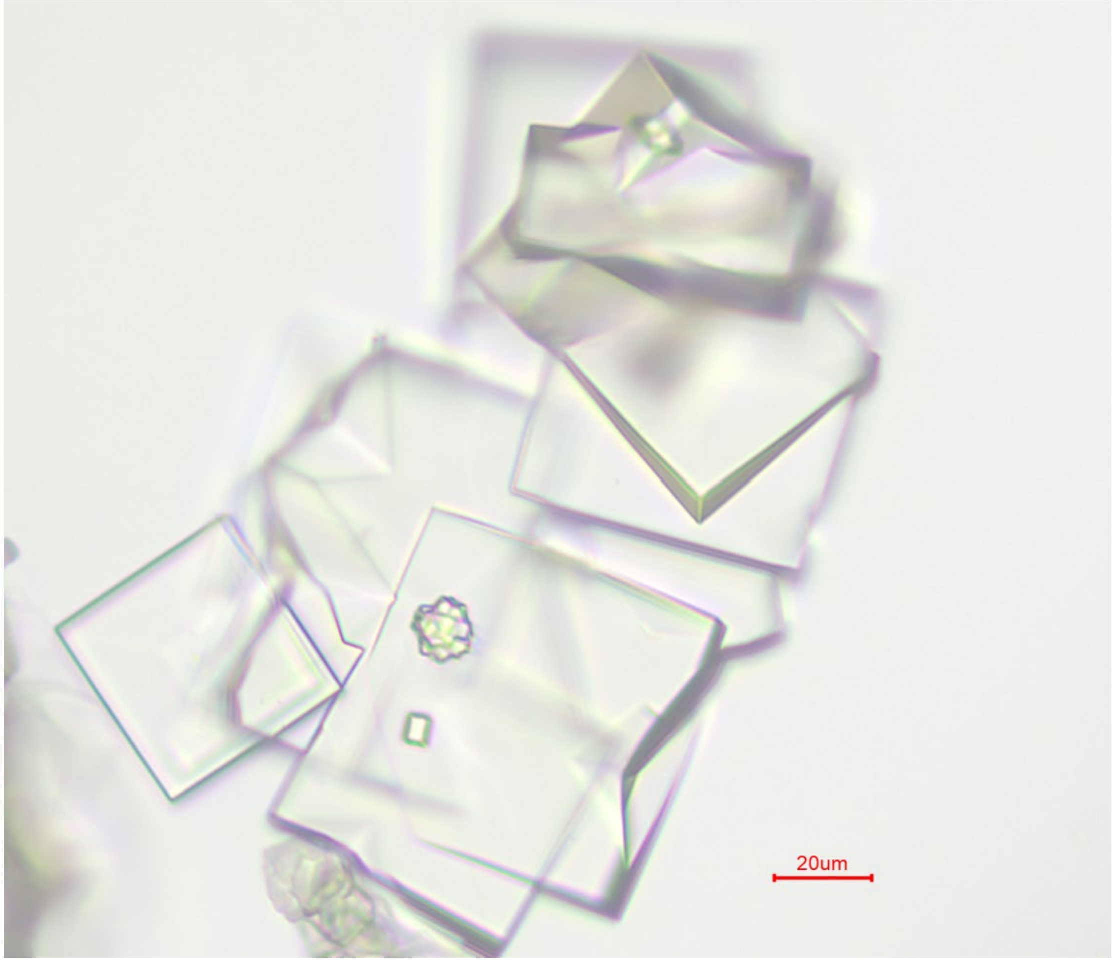


Figure S5. Optical image of the as-synthesized crystals of HIAM-330.

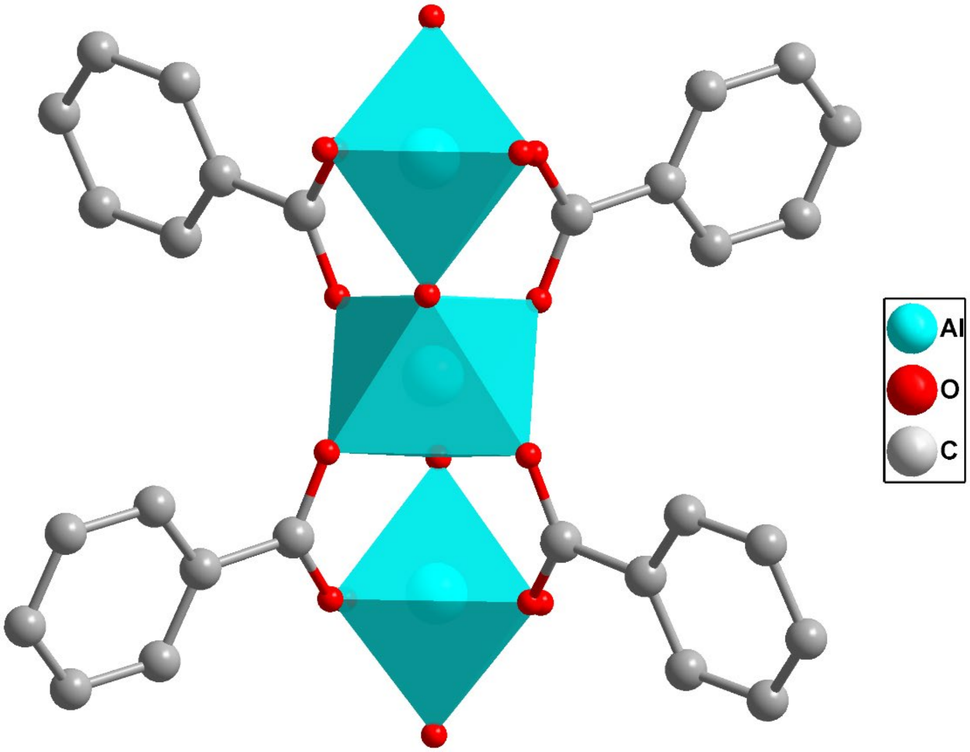


Figure S6. Coordination of trinuclear aluminum cluster in the structure of HIAM-330.

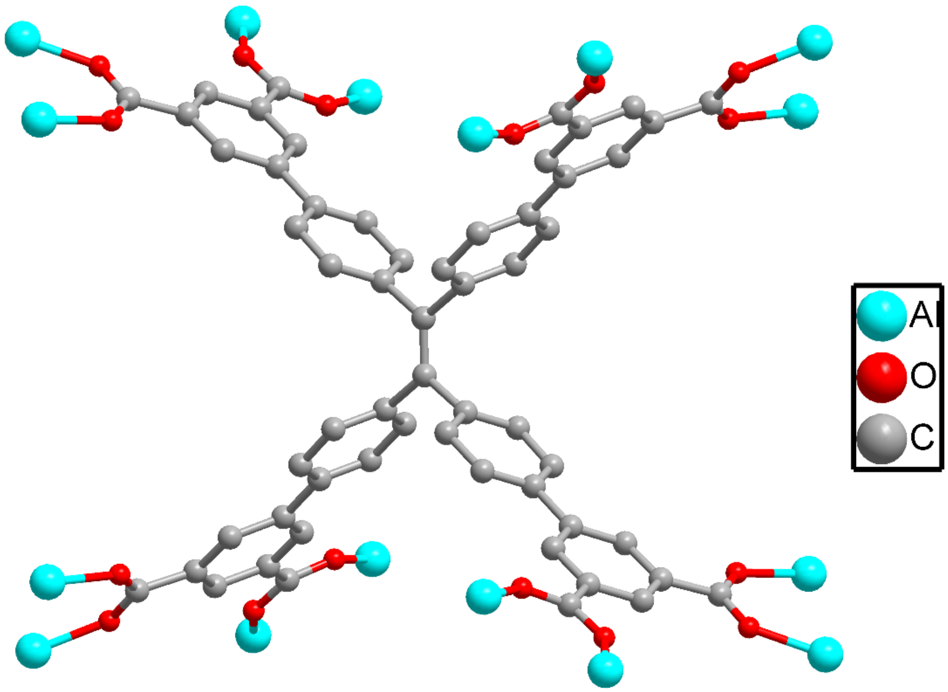


Figure S7. Coordination of octacarboxylate ligand the structure of HIAM-330.

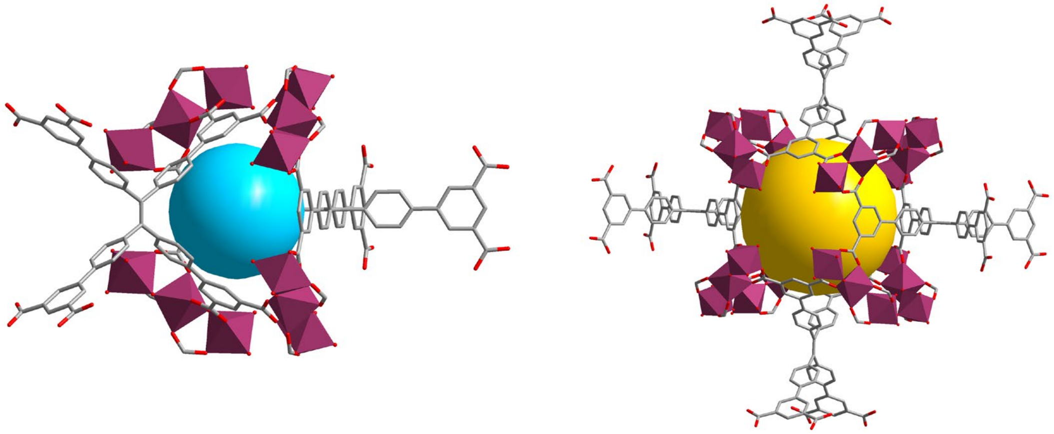


Figure S8. Representation of two types of cages in HIAM-330.

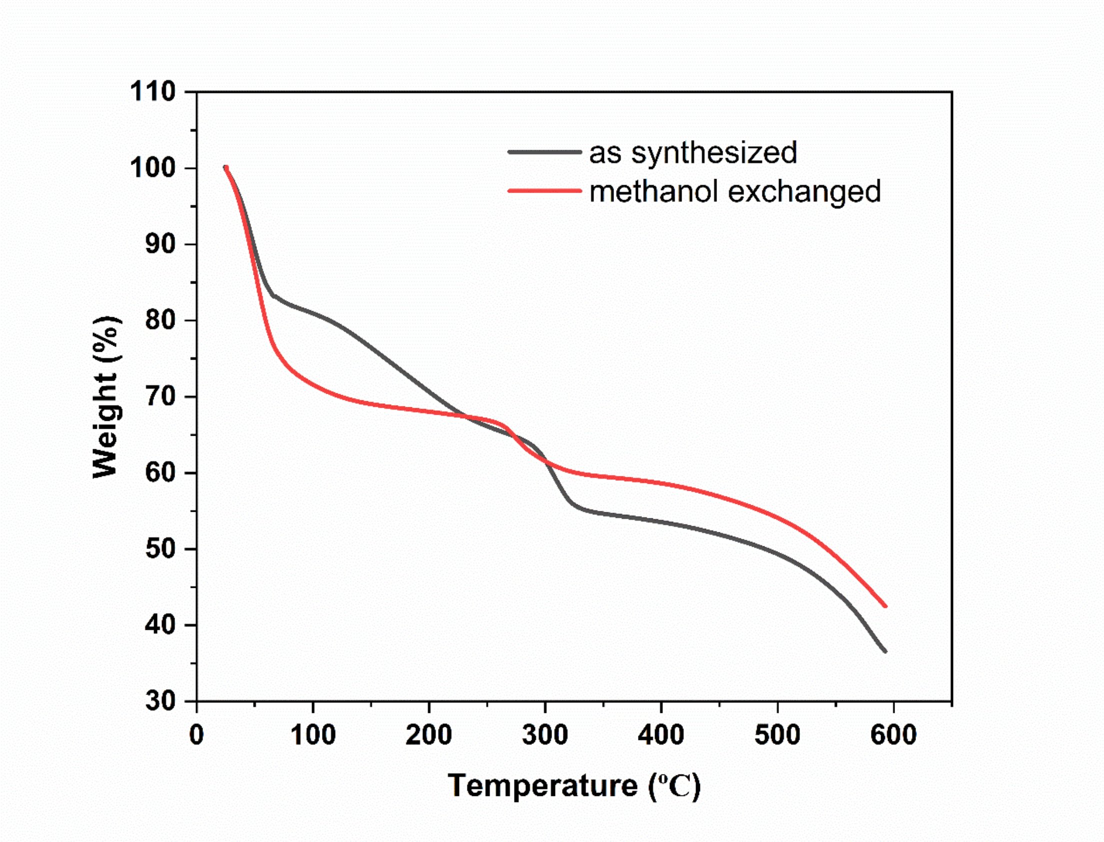


Figure S9. TG curve of as synthesized and methanol exchanged HIAM-330.

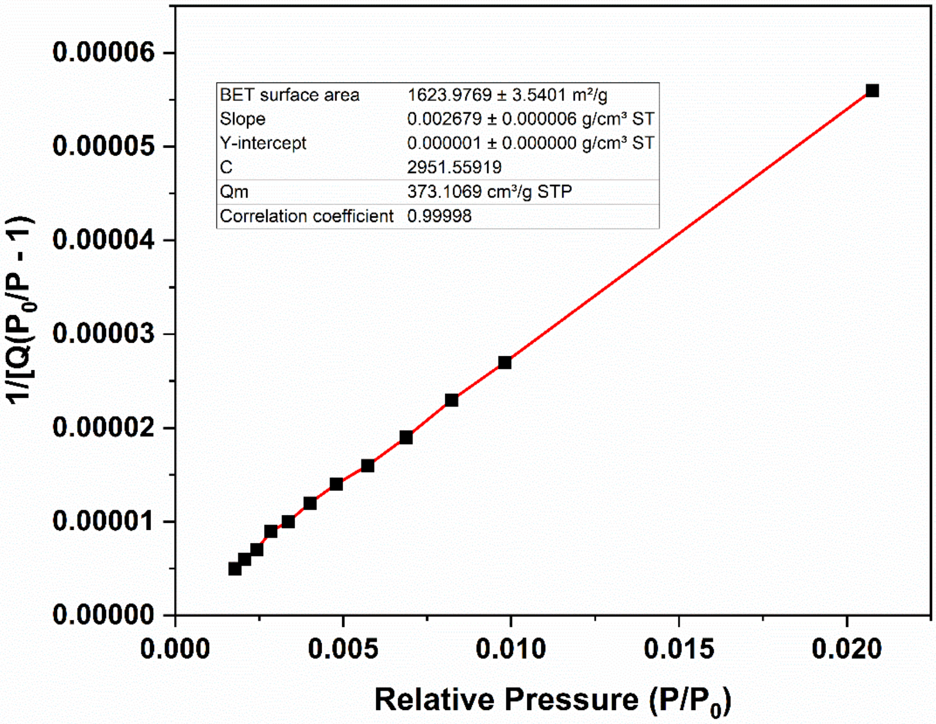


Figure S10. The BET fitting of HIAM-330 obtained from the N_2 adsorption isotherm at 77K.

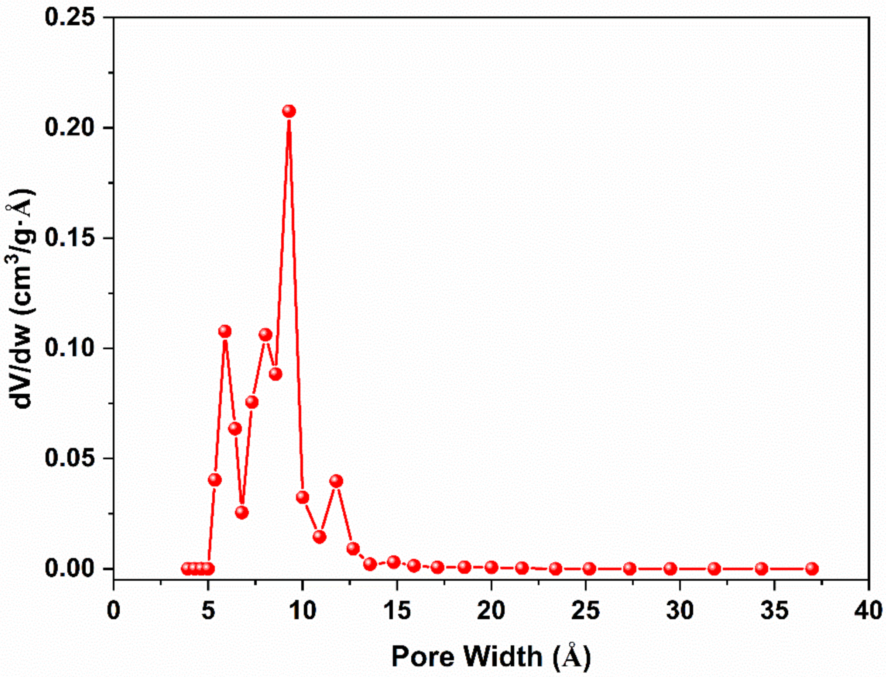


Figure 11. Pore size distribution (DFT model) calculated from N_2 adsorption at 77 K.

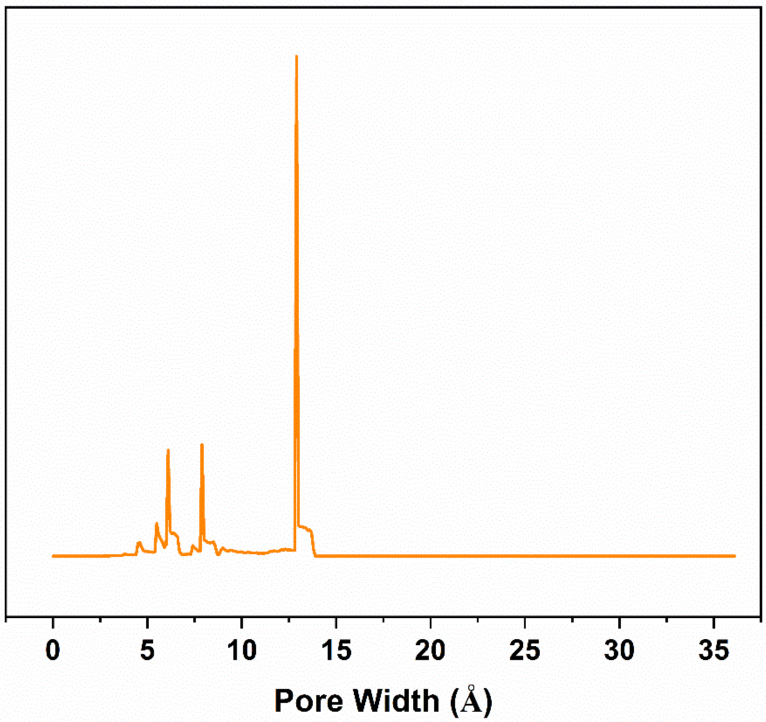


Figure S12. Pore size based on Zeo++ calculation with the crystal structure.

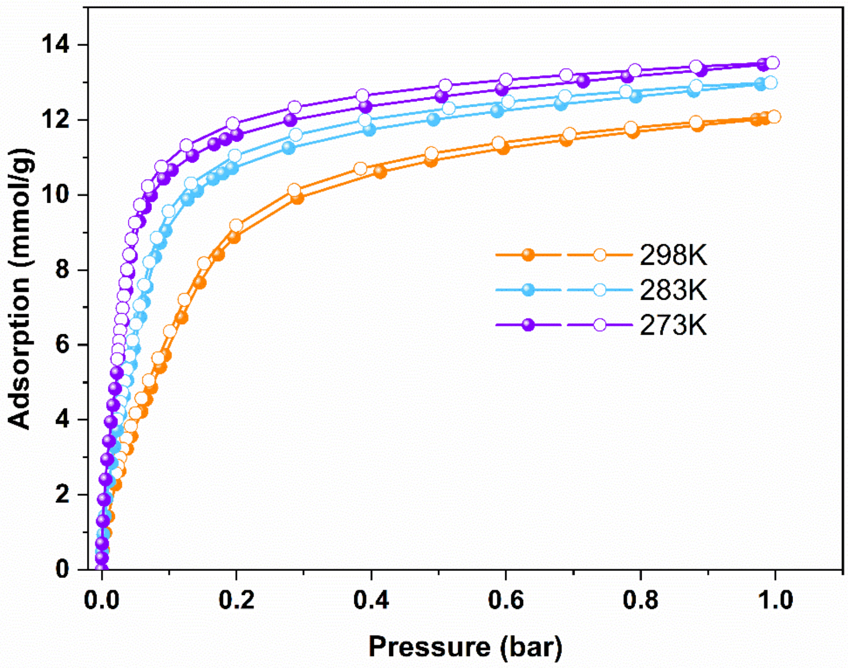


Figure S13. Adsorption isotherms of SO_2 on HIAM-330 at 298, 283, and 273K.

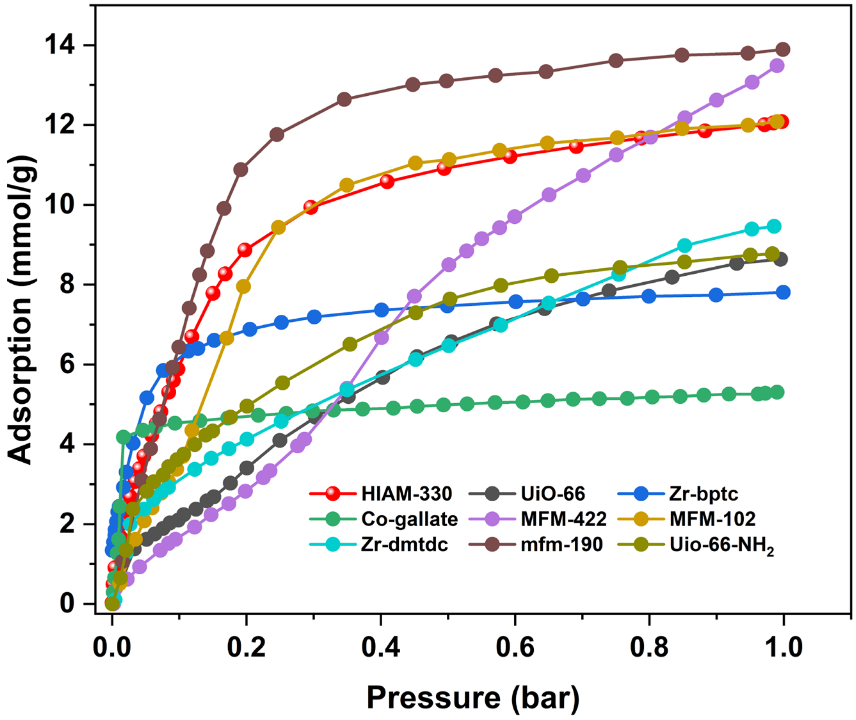


Figure S14. Adsorption isotherms of SO_2 on HIAM-330 and representative adsorbents at 298K and 1 bar.

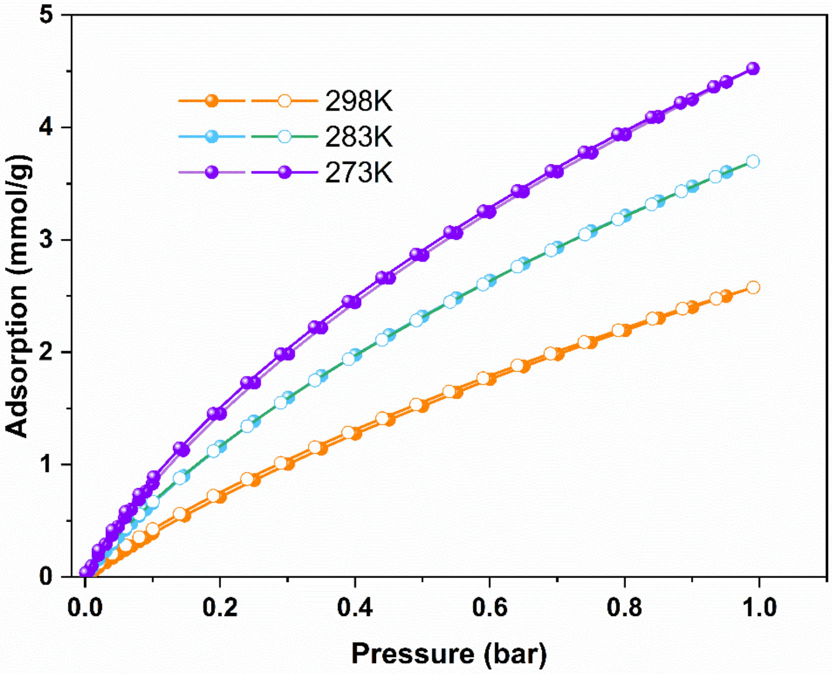
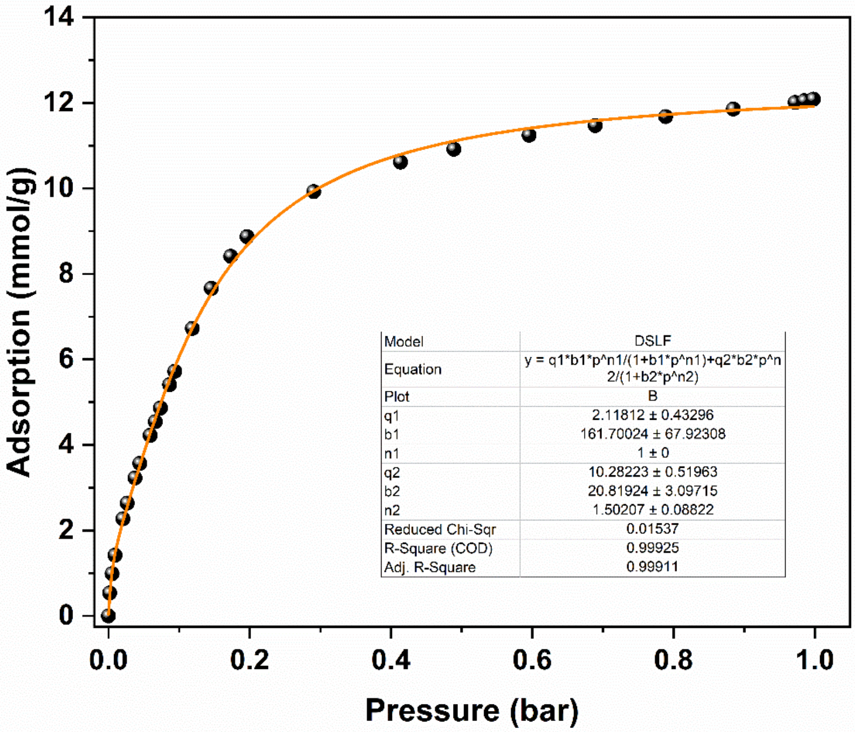
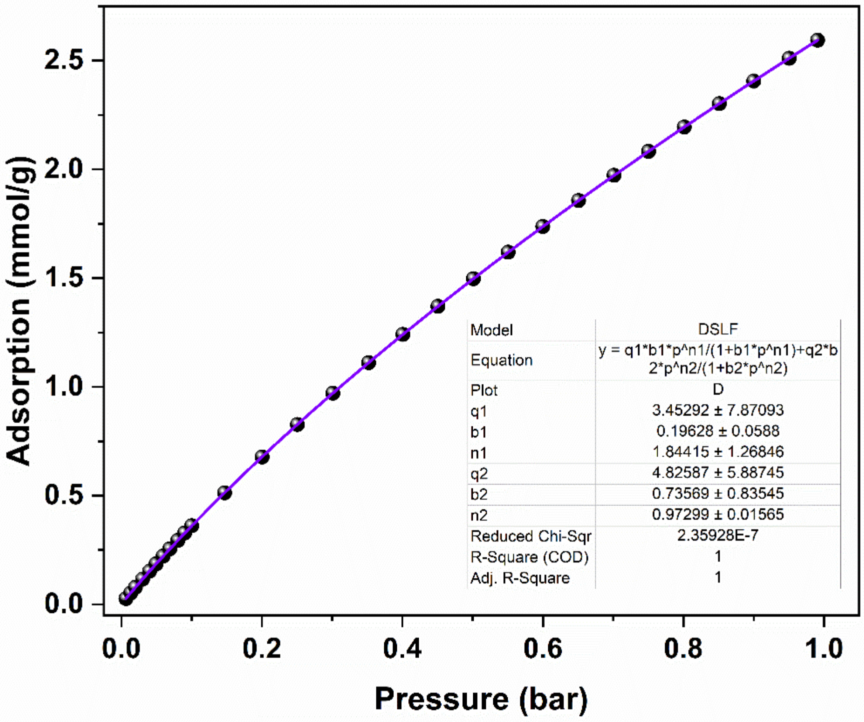


Figure S15. Adsorption isotherms of CO_2 on HIAM-330 at 298, 283, and 273K.



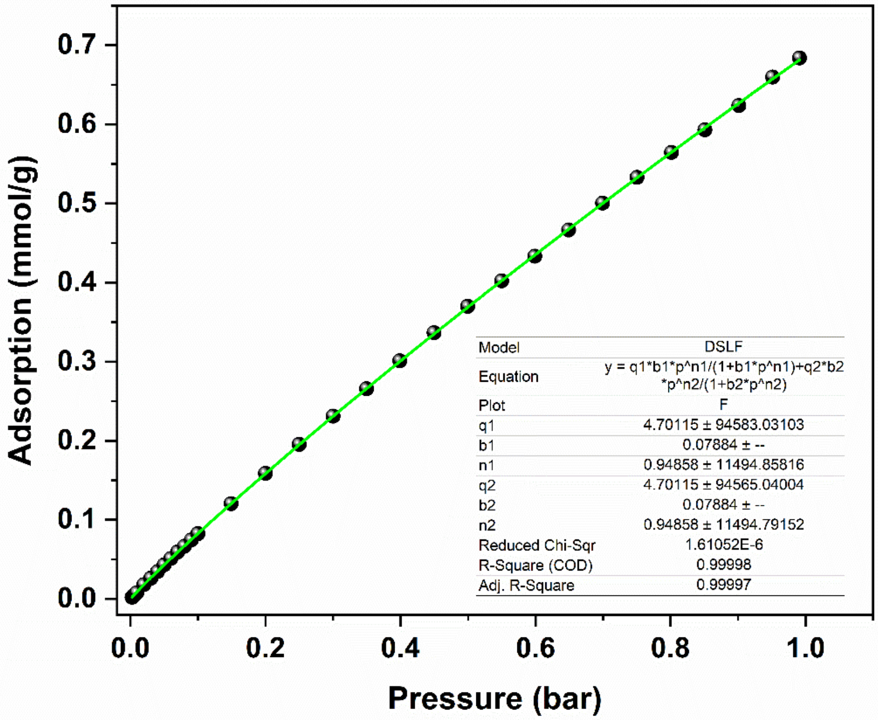
Model	DSLF
Equation	y = q1*b1*p^n1/(1+b1*p^n1)+q2*b2*p^n2/(1+b2*p^n2)
Plot	B
q1	2.11812 ± 0.43296
b1	161.70024 ± 67.92308
n1	1 ± 0
q2	10.28223 ± 0.51963
b2	20.81924 ± 3.09715
n2	1.50207 ± 0.08822
Reduced Chi-Sqr	0.01537
R-Square (COD)	0.99925
Adj. R-Square	0.99911

Figure S16. Fitting (lines) of SO_2 adsorption isotherms (points) of HIAM-330 at 298K.



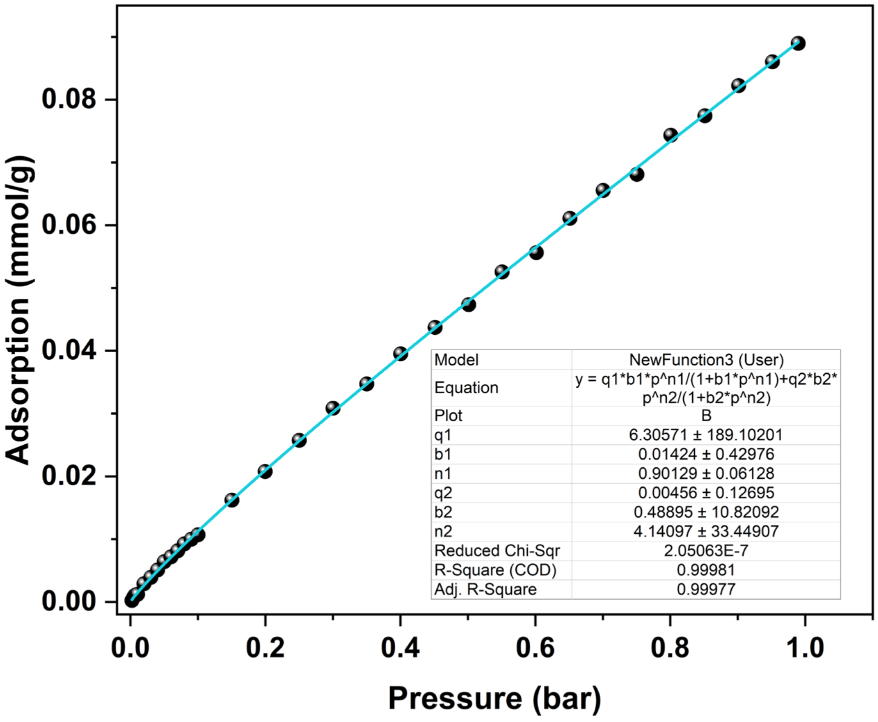
Model	DSLF
Equation	y = q1*b1*p^n1/(1+b1*p^n1)+q2*b2*p^n2/(1+b2*p^n2)
Plot	D
q1	3.45292 ± 7.87093
b1	0.19628 ± 0.0588
n1	1.84415 ± 1.26846
q2	4.82587 ± 5.88745
b2	0.73569 ± 0.83545
n2	0.97299 ± 0.01565
Reduced Chi-Sqr	2.35928E-7
R-Square (COD)	1
Adj. R-Square	1

Figure S17. Fitting (lines) of CO_2 adsorption isotherms (points) of HIAM-330 at 298K.



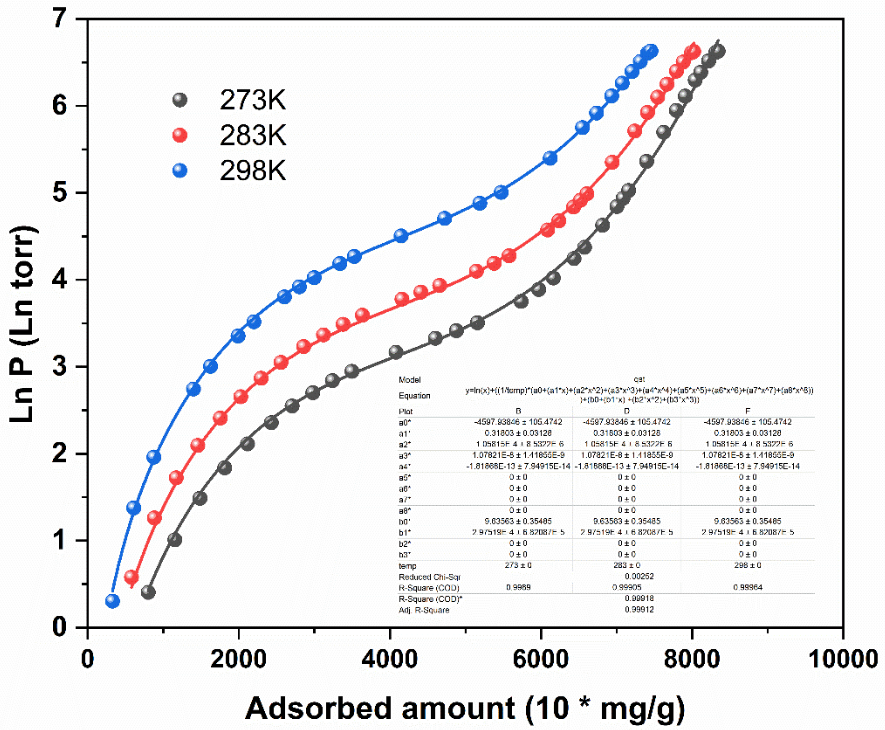
Model	DSLF
Equation	y = q1*b1*p^n1/(1+b1*p^n1)+q2*b2 *p^n2/(1+b2*p^n2)
Plot	F
q1	4.70115 ± 94583.03103
b1	0.07884 ± --
n1	0.94858 ± 11494.85816
q2	4.70115 ± 94565.04004
b2	0.07884 ± --
n2	0.94858 ± 11494.79152
Reduced Chi-Sqr	1.61052E-6
R-Square (COD)	0.99998
Adj. R-Square	0.99997

Figure S18. Fitting (lines) of CH_4 adsorption isotherms (points) of HIAM-330 at 298K.



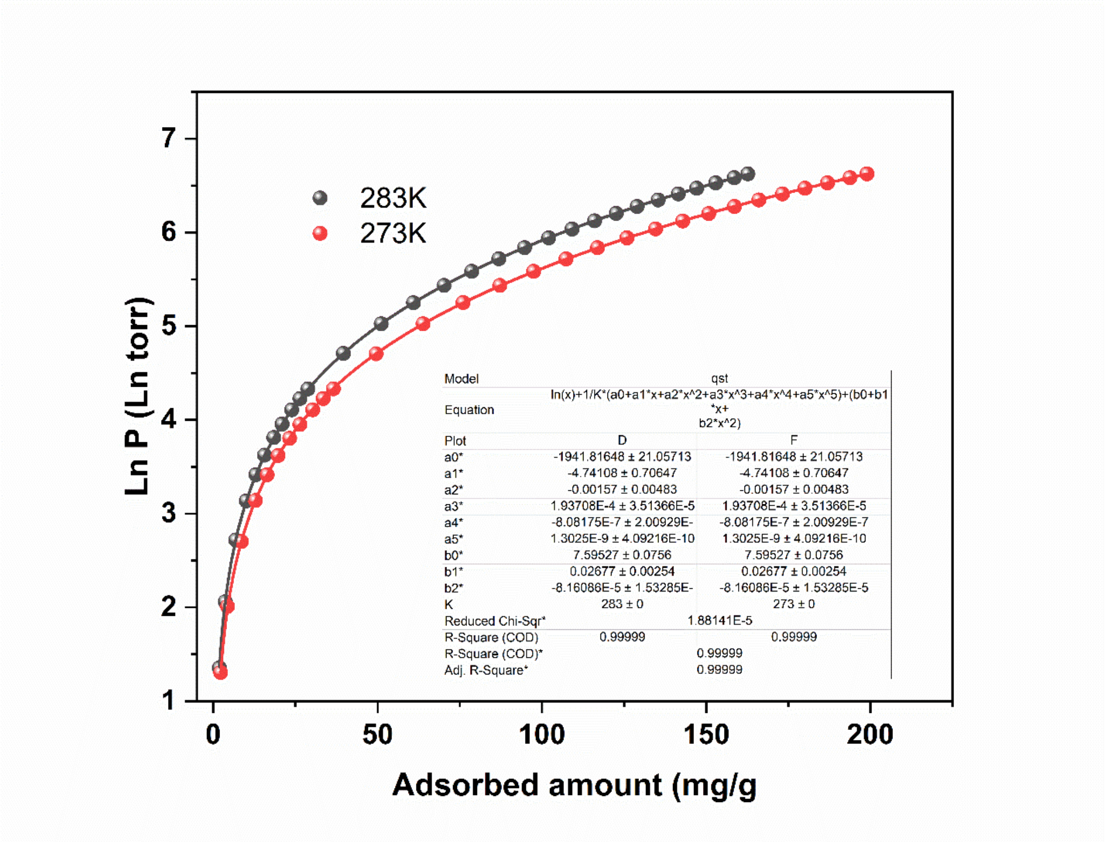
Model	NewFunction3 (User)
Equation	y = q1*b1*p^n1/(1+b1*p^n1)+q2*b2*p^n2/(1+b2*p^n2)
Plot	B
q1	6.30571 ± 189.10201
b1	0.01424 ± 0.42976
n1	0.90129 ± 0.06128
q2	0.00456 ± 0.12695
b2	0.48895 ± 10.82092
n2	4.14097 ± 33.44907
Reduced Chi-Sqr	2.05063E-7
R-Square (COD)	0.99981
Adj. R-Square	0.99977

Figure S19. Fitting (lines) of N_2 adsorption isotherms (points) of HIAM-330 at 298K.



Model	qst		
Equation	y=ln(x)+((1/temp)*(a0+(a1*x)+(a2*x^2)+(a3*x^3)+(a4*x^4)+(a5*x^5)+(a6*x^6)+(a7*x^7)+(a8*x^8)))+(b0+(b1*x) +(b2*x^2)+(b3*x^3))		
Plot	B	D	F
a0*	-4597.93846 ± 105.4742	-4597.93846 ± 105.4742	-4597.93846 ± 105.4742
a1*	0.31803 ± 0.03128	0.31803 ± 0.03128	0.31803 ± 0.03128
a2*	1.05815E-4 ± 8.5322E-6	1.05815E-4 ± 8.5322E-6	1.05815E-4 ± 8.5322E-6
a3*	1.07821E-8 ± 1.41855E-9	1.07821E-8 ± 1.41855E-9	1.07821E-8 ± 1.41855E-9
a4*	-1.81868E-13 ± 7.94915E-14	-1.81868E-13 ± 7.94915E-14	-1.81868E-13 ± 7.94915E-14
a5*	0 ± 0	0 ± 0	0 ± 0
a6*	0 ± 0	0 ± 0	0 ± 0
a7*	0 ± 0	0 ± 0	0 ± 0
a8*	0 ± 0	0 ± 0	0 ± 0
b0*	9.63563 ± 0.35485	9.63563 ± 0.35485	9.63563 ± 0.35485
b1*	2.97519E-4 ± 6.82087E-5	2.97519E-4 ± 6.82087E-5	2.97519E-4 ± 6.82087E-5
b2*	0 ± 0	0 ± 0	0 ± 0
b3*	0 ± 0	0 ± 0	0 ± 0
temp	273 ± 0	283 ± 0	298 ± 0
Reduced Chi-Sqr		0.00252	
R-Square (COD)	0.9989	0.99905	0.99964
R-Square (COD)*		0.99918	
Adj. R-Square		0.99912	

Figure S20. Virial fitting (lines) of SO_2 adsorption isotherms (points) of HIAM-330.



Model	qst	
Equation	ln(x)+1/K*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)+(b0+b1 *x+ b2*x^2)	
Plot	D	F
a0*	-1941.81648 ± 21.05713	-1941.81648 ± 21.05713
a1*	-4.74108 ± 0.70647	-4.74108 ± 0.70647
a2*	-0.00157 ± 0.00483	-0.00157 ± 0.00483
a3*	1.93708E-4 ± 3.51366E-5	1.93708E-4 ± 3.51366E-5
a4*	-8.08175E-7 ± 2.00929E-	-8.08175E-7 ± 2.00929E-7
a5*	1.3025E-9 ± 4.09216E-10	1.3025E-9 ± 4.09216E-10
b0*	7.59527 ± 0.0756	7.59527 ± 0.0756
b1*	0.02677 ± 0.00254	0.02677 ± 0.00254
b2*	-8.16086E-5 ± 1.53285E-	-8.16086E-5 ± 1.53285E-5
K	283 ± 0	273 ± 0
Reduced Chi-Sqr*	1.88141E-5	
R-Square (COD)	0.99999	0.99999
R-Square (COD)*	0.99999	
Adj. R-Square*	0.99999	

Figure S21. Virial fitting (lines) of CO_2 adsorption isotherms (points) of HIAM-330.

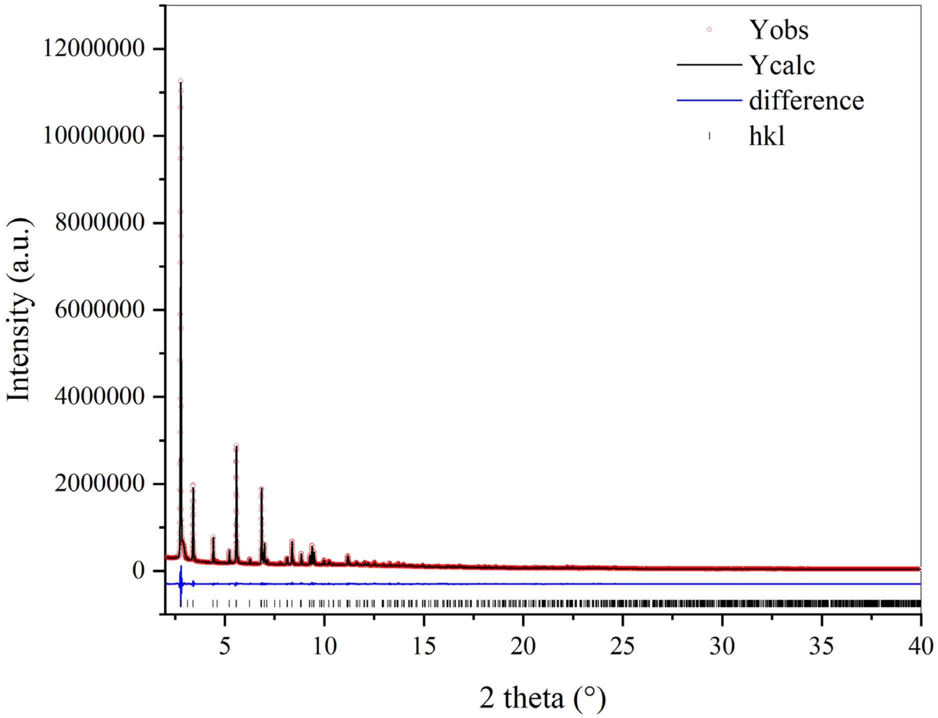


Figure S22. Rietveld refinements of the high-resolution XRD data of SO_2-loaded HIAM-330.

Table S1. Crystal data and structure refinement for HIAM-330

Identification code	HIAM-330
Empirical formula	$C_{29}H_{26}Al_3O_{16}$
Formula weight	711.44
Temperature/K	150.00
Crystal system	tetragonal
Space group	I4/mmm
a/Å	21.5005(6)
b/Å	21.5005(6)
c/Å	28.4908(11)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	13170.5(9)
Z	8
ρ_{calc}g/cm^3	0.718
μ/mm^{-1}	0.553
F(000)	2936.0
Crystal size/mm^3	0.12 × 0.1 × 0.02
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.444 to 102.56
Index ranges	$-24 \le h \le 10$, $-13 \le k \le 23$, $-33 \le l \le 25$
Reflections collected	20369
Independent reflections	3020 [R_{int} = 0.0343, R_{sigma} = 0.0236]
Data/restraints/parameters	3020/0/143
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.0790, wR_2 = 0.2365
Final R indexes [all data]	R_1 = 0.0857, wR_2 = 0.2435
Largest diff. peak/hole / e Å^{-3}	0.91/-0.43