Electronic Supporting Information

Highly efficient CO_2 capture and conversion of a microporous acylamide functionalized *rht*-type metal-organic framework

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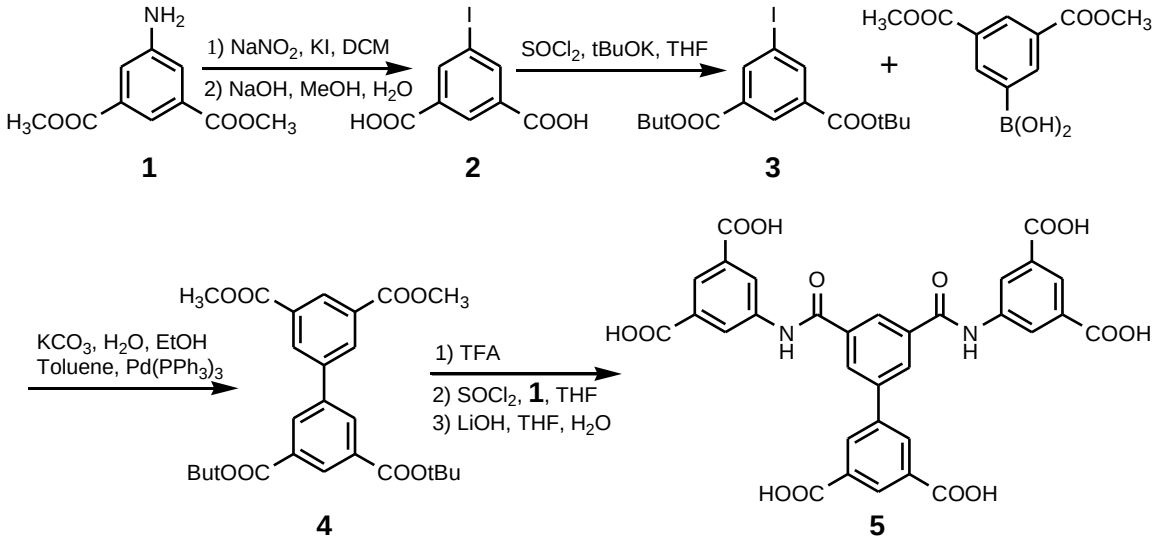
1. Materials and Methods

All chemical reagents were obtained from commercial sources and used without further purification unless otherwise noted. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 analyzer. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane as an internal reference. The IR spectra were recorded in the 400-4000 cm^{-1} on a VECTOR TM 22 spectrometer using KBr pelts. Thermal gravimetric analysis (TGA) were performed under N_2 atmosphere (100 mL min^{-1}) with a heating rate of 5 K min^{-1} using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer using Cu K_α radiation (λ = 1.5418 Å) at room temperature.



Scheme S1. Synthetic route of organic linker, 5,5'-((3',5'-dicarboxy-[1,1'-biphenyl]-3,5-dicarbonyl)-bis(azanediyl))diisophthalic acid, H_6DBDBD (**5**).

2. Synthesis of 5-iodoisophthalic acid (2)

A solution of sodium nitrite (1.0 g, 14.5 mmol) in 20 mL water was added to a solution of dimethyl 5-aminoisophthalate (1.0 g, 4.8 mmol) in 60 mL hydrochloric acid (2 M) cooled below 5 ℃. After stirring for 5h at 0-5 ℃, an solution of potassium iodide (1.5 g, 7.7 mmol) in 10 mL water was added dropwise, and then 100 mL dichloromethane was added. The resulting mixture was stirred overnight at room temprature. The aqueous layer was extracted with dichloromethane, washed with brine and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with petroleum/acetidine (v/v = 5:1) as eluent to give dimethyl 5-iodoisophthalate as a pale yellow solid (1.2 g, 78.1% yield). Dimethyl 5-iodoisophthalate (0.9 g, 2.8 mmol) was then dissolved in MeOH/H_2O (v/v = 1:1, 40 mL), NaOH (1.0 g, 25.0 mmol) was added and the solution was refluxed overnight. The volatiles were removed under vacuum. The residue was dissolved in 100 mL water and then acidified to pH ≈ 2 ~ 3 by 12 M HCl. The precipitate was separated by filtration, washed with water, and dried to give 5-iodoisophthalic acid **2** as a pale yellow solid (0.736g, 89.6% yield).

3. Synthesis of di-tert-butyl 5-iodoisophthalate (3)

$SOCl_2$ (10 mL, 137.5 mmol) was added dropwise to 5-iodoisophthalic acid **2** (0.7g, 2.4 mmol) with 100 μL DMF. The mixture was refluxed overnight and then the excess $SOCl_2$ was removed under vacuum. The resulting solid was dissolved in anhydrous THF and then tBuOK(1.1 g, 9.8 mmol) in 30 mL anhydrous THF was slowly added. After stirring for 24h at room temperature, the solvent was removed under vacuum, and the residue was washed with aqueous hydrochloric acid and water, and then filtered to give di-tert-butyl 5-iodoisophthalate **3** as a pale yellow solid (0.6g, 61.9 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm, Fig. S8a): 8.52 (s, 1H, ArH), 8.44 (s, 2H, ArH), 1.60 (m, 18H, COOtBu).

4. Synthesis of 3,5-di-tert-butyl 3',5'-dimethyl [1,1'-biphenyl]-3,3',5,5'-tetracarboxylate (4)

To a solution of di-tert-butyl 5-iodoisophthalate **3** (0.808 g, 2.0 mmol) in 60 mL toluene, 3,5-bis(methoxycarbonyl)phenylboronic acid (0.714 g, 3.0 mmol) in 12 mL ethanol and Na_2CO_3 (0.74 g, 7.0 mmol) in 4 mL water were successively added, after degassed using N_2 for 10 min, $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) was added. The resulting reaction mixture was stirred at 110 ℃ under N_2 atmosphere overnight. After removal of solvent under vacuum, the residue was dissolved in CH_2Cl_2 and then filtered. CH_2Cl_2 were removed under vacuum, and the crude product was purified by column chromatography on silica gel with dichloromethane as eluent to give 3,5-di-tert-butyl 3',5'-dimethyl [1,1'-biphenyl]-3,3',5,5'-tetracarboxylate **4** as a dark brown solid (0.58 g, 61.6 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm, Fig. S8b): 8.72 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.51 (s, 2H, ArH), 8.42 (s, 2H, ArH), 6.07 (s, 6H, $COOCH_3$), 8.51 (m, 18H, COOtBu).

5. Activation of HNUST-9

The solvent-exchanged HNUST-9 was prepared by immersing the as-synthesized sample in dry methanol for 48 hours to remove the non-volatile solvates (DMF and water), the extract was decanted every 8 hours and fresh methanol was replaced. The completely activated HNUST-9 sample was obtained by heating the solvent-exchanged sample at 100 ℃ under a dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue colour (Fig. S3), indicative of the presence of open copper(II) sites. The completely-activated samples were moisture sensitive and a few minutes of exposure to air could change the sample's color back to pale blue. Anal. Calcd (Found) for [$Cu_3(C_{30}H_{14}N_2O_{14})$]: C, 44.10 (44.06), H 1.739 (1.81), N 3.43 (3.38). Selected IR (KBr, cm^{-1}, Figure S4): 3416, 1652, 1620, 1559, 1370, 1276, 1106, 904, 755, 726, 692.

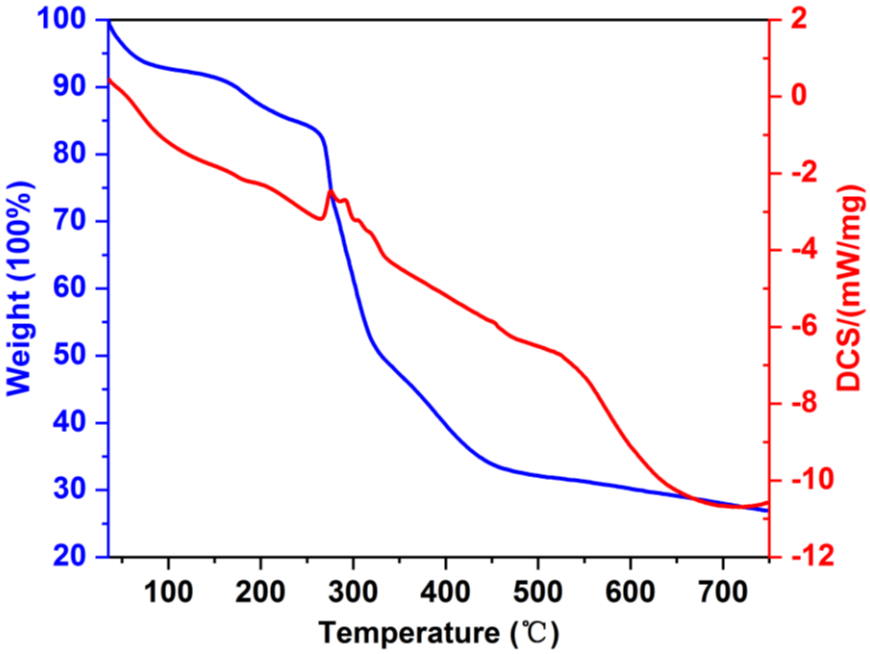


Fig. S1 TGA data of as-synthesized **HNUST-9**.

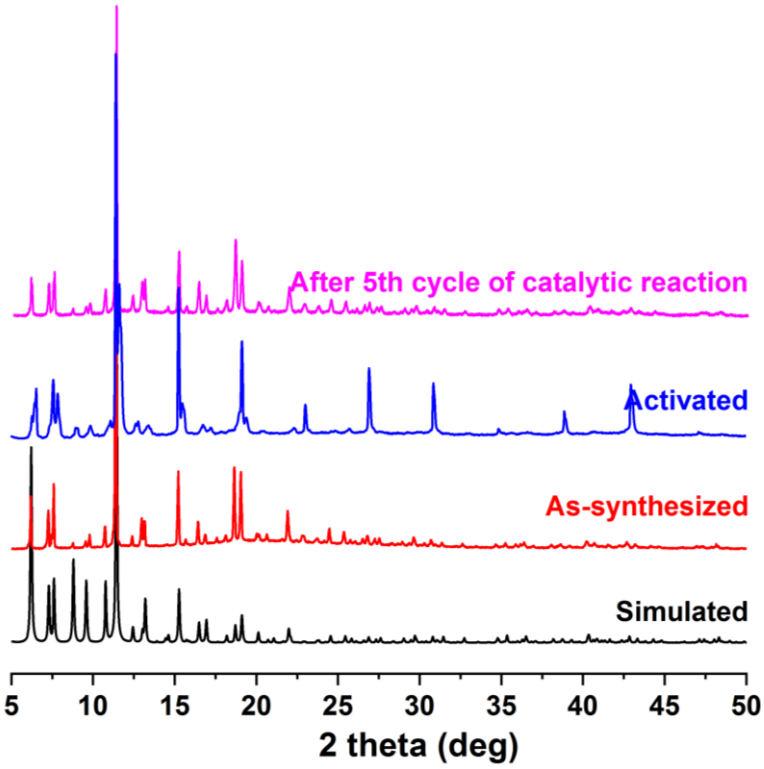


Fig. S2 PXRD patterns of HNUST-9: simulated, as-synthesized, activated, and after the 5th cycle of catalytic reaction, respectively.

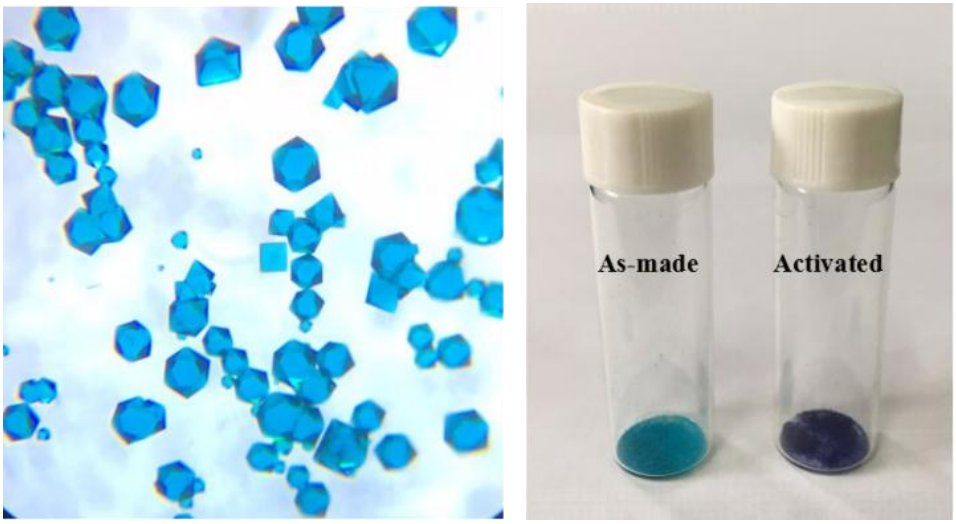


Fig. S3 Left) Photographic image of as-synthesized HNUST-9, the crystal size has been magnified about 80 times; Right) Visual color change of HNUST-9 upon activation.

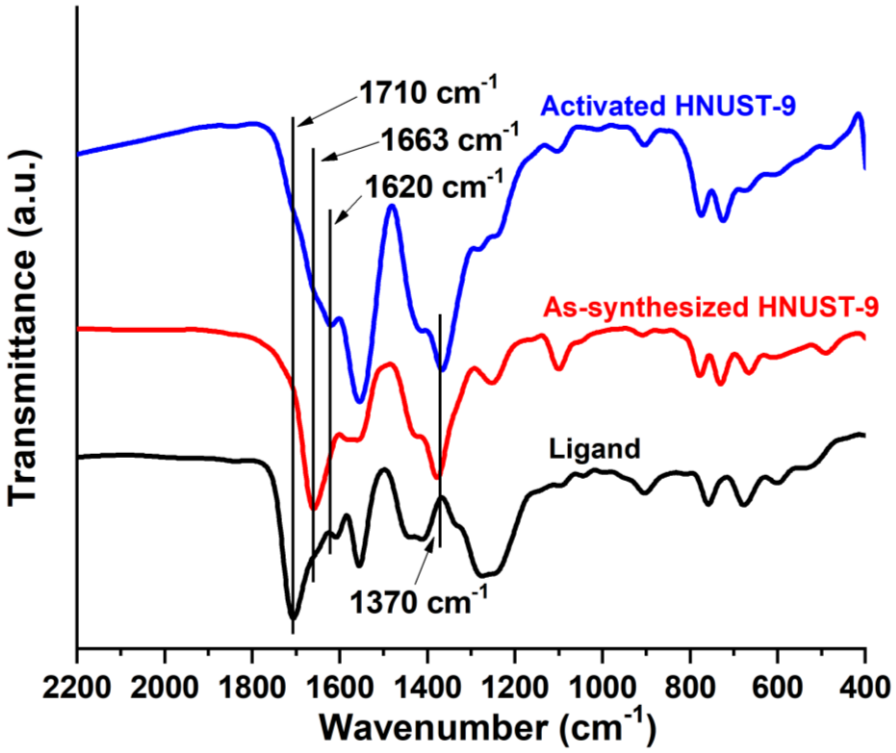


Fig. S4 The IR spectra for HNUST-9. a) Ligand; b) As-synthesized; and c) Activated HNUST-9. Note the absence of the vibration frequencies of the solvent DMF and methanol molecules in the activated samples. The frequencies at 1663 cm^{-1} attributes to the *v*(CO) vibration of the DMF, and the presence of the *v*(OH) stretching frequencies at 1620 cm^{-1} in activated samples may result from the rapid re-adsorption of trace moisture during the IR measurements.

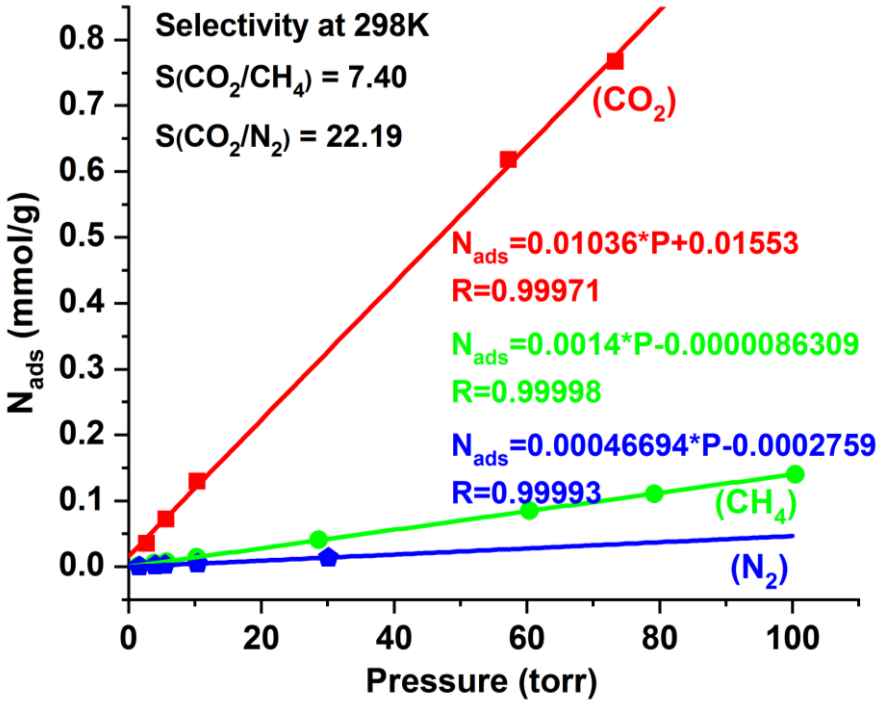


Fig. S5 The fitting initial slope for CO_2, CH_4 and N_2 isotherms for HNUST-9 collected at 298 K (N_{ads} = gases uptake; R = related coefficient). The calculated selectivity of CO_2/CH_4 and CO_2/N_2 for HNUST-9 is about 7.4 and 22.2, respectively.

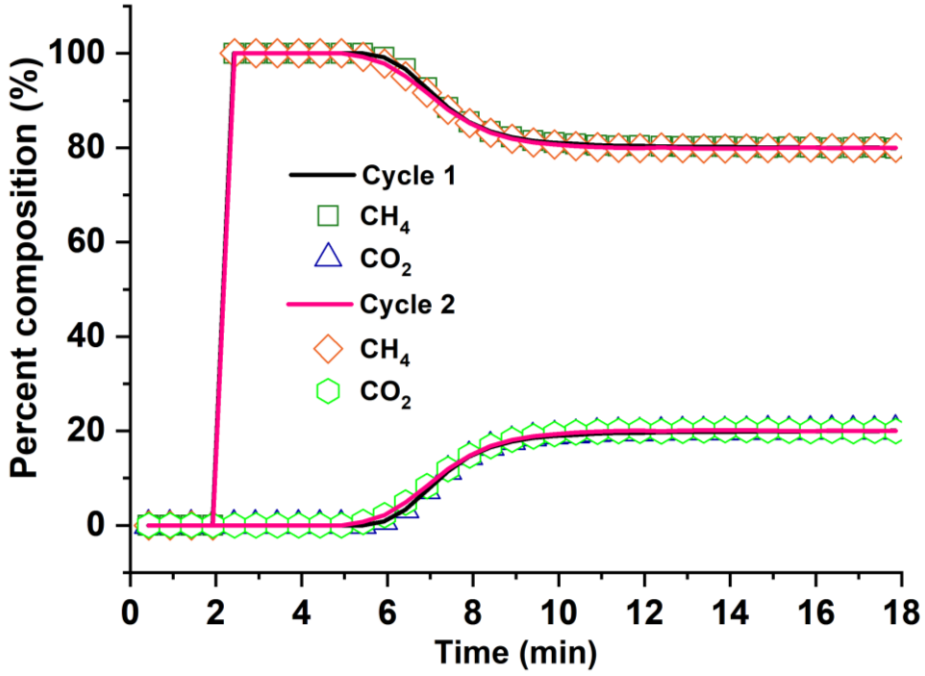


Fig. S6 Repeated CO_2/CH_4 breakthrough experiments of **HNUST-9** after 20 min helium gas blowing at 298 K and 1 bar.

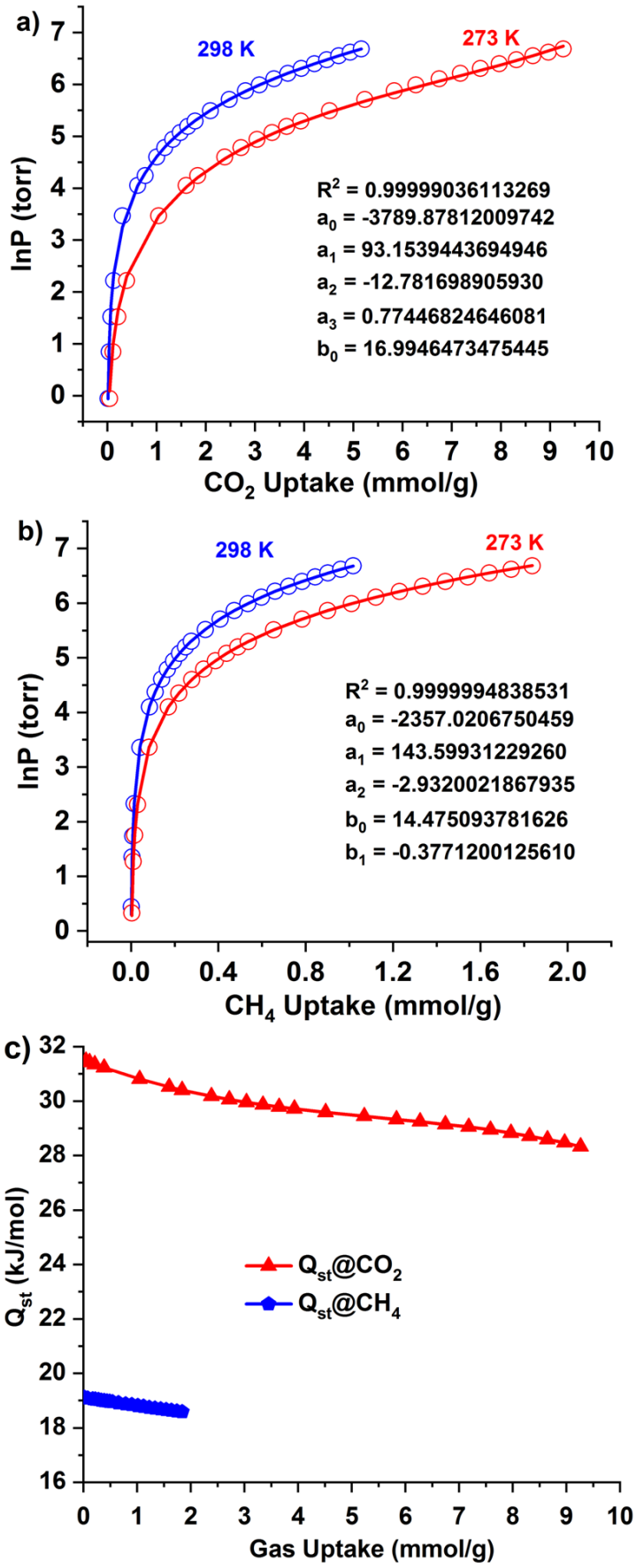


Fig. S7 a-b) Details of Virial equation (symbols) fitting to the experimental CO_2 and CH_4 adsorption data (solid lines) for HNUST-9 collected at 273 K and 298 K; c) The CO_2 and CH_4 isosteric adsorption enthalpies of HNUST-9.

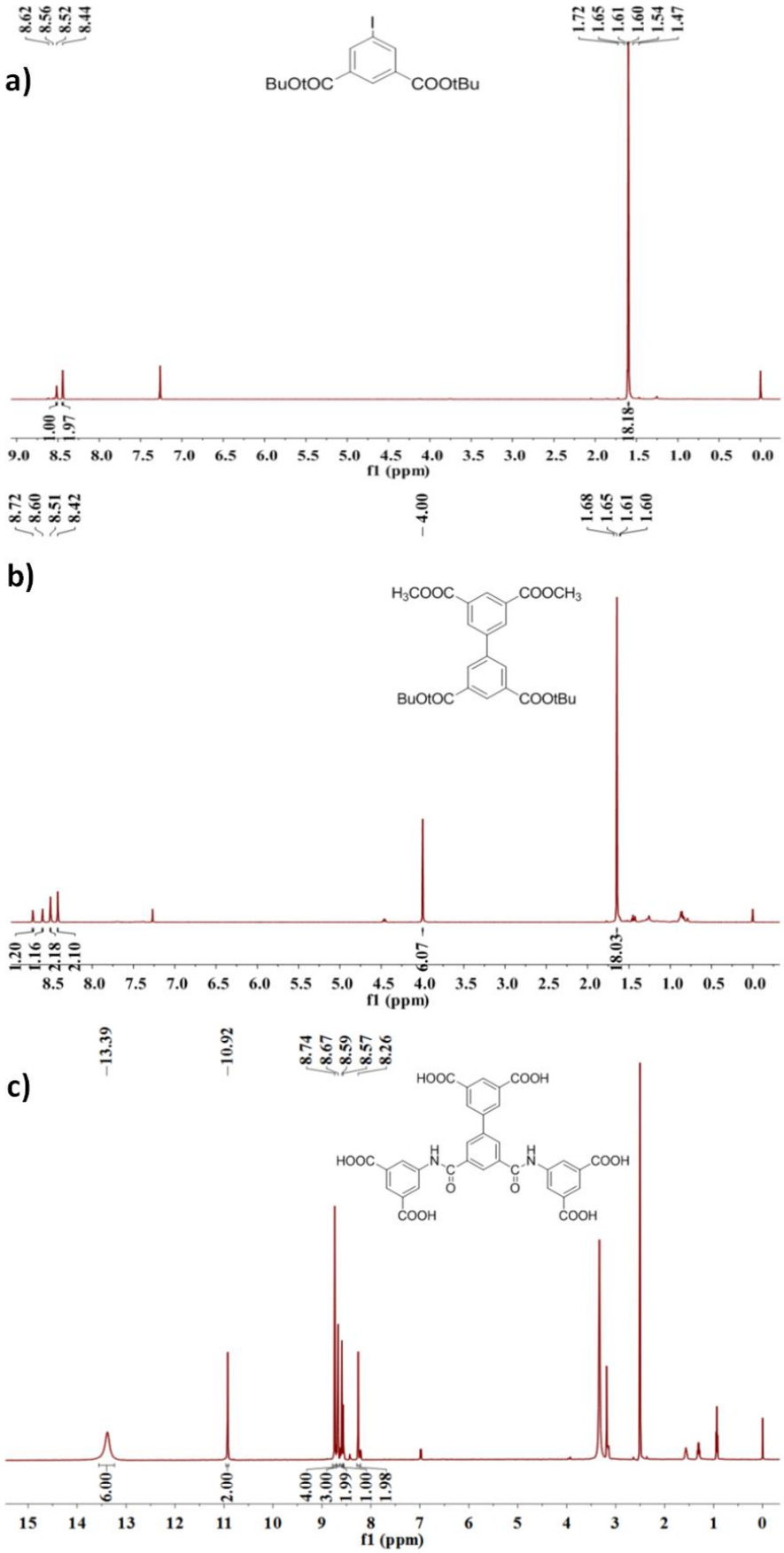


Fig. S8 The ^{1}H NMR spectrum. a) Di-tert-butyl 5-iodoisophthalate in $CDCl_3$; b) 3,5-di-tert-butyl 3',5'-dimethyl [1,1'-biphenyl]-3,3',5,5'- tetracarboxylate in $CDCl_3$; c) H_6DBDBD ligand in DMSO-d_6, H_6DBDBD = 5,5'-((3',5'-dicarboxy- [1,1'-biphenyl]-3,5-dicarbonyl)bis(azanediyl))diisophthalic acid.

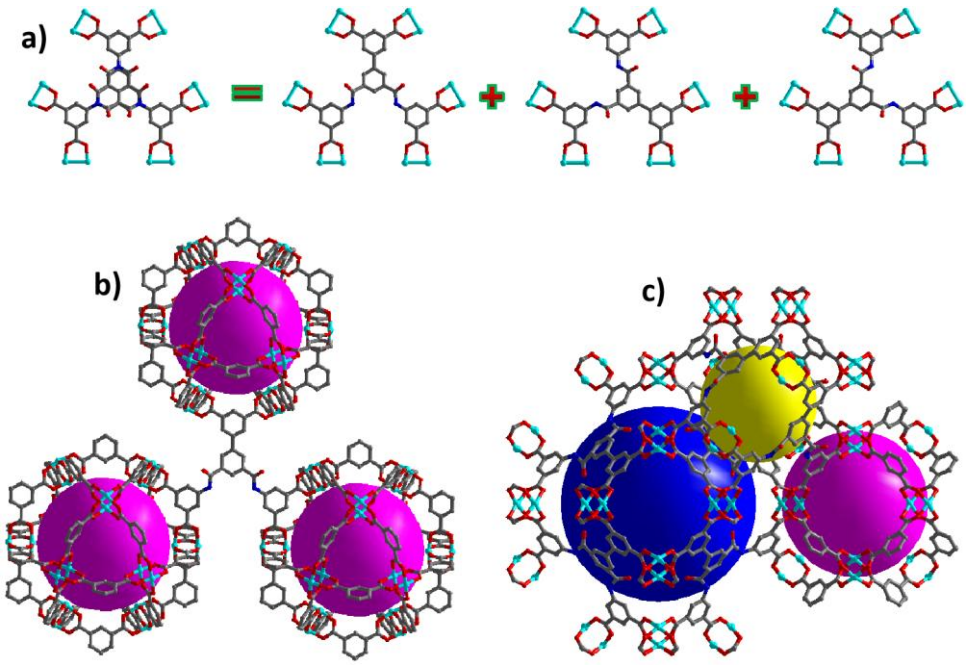


Fig. S9 a) The acylamide and benzene moieties of the DBDBD ligand in the crystal structure of HNUST-9 are disordered over three positions with equal probability; b) A portion of structure of the (3, 24)-connected *rht*-type framework; c) The 3D polyhedra packing in single-crystal structure of HNUST-9. Water molecules and H atoms have been omitted for clarity.

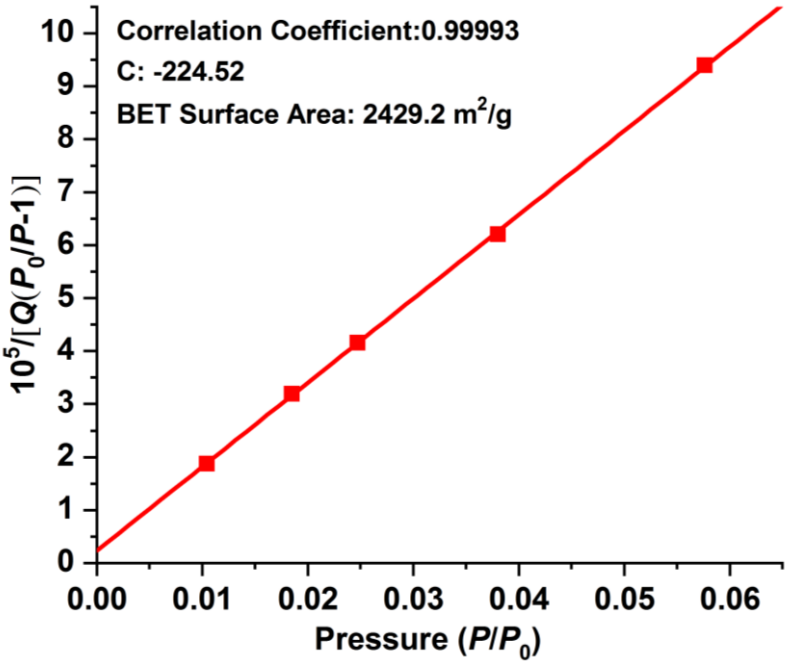


Fig. S10 The BET plots for HNUST-9 in the chosen range (P/P_0 = 0.01-0.06). This range was chosen according to two major criteria established in literatures [(a) J. Rouquerol, P. Llewellyn and F. Rouquerol, *Stud. Surf. Sci. Catal.*, **2007**, *160* ,49-56; (b) K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, **2007**, *129*, 8552 -8556.]: (1) The pressure range selected should have values of $Q(P_0-P)$ increasing with P/P_0. (2) The *y* intercept of the linear region must be positive to yield a meaningful value of the C parameter, which should be greater than zero.

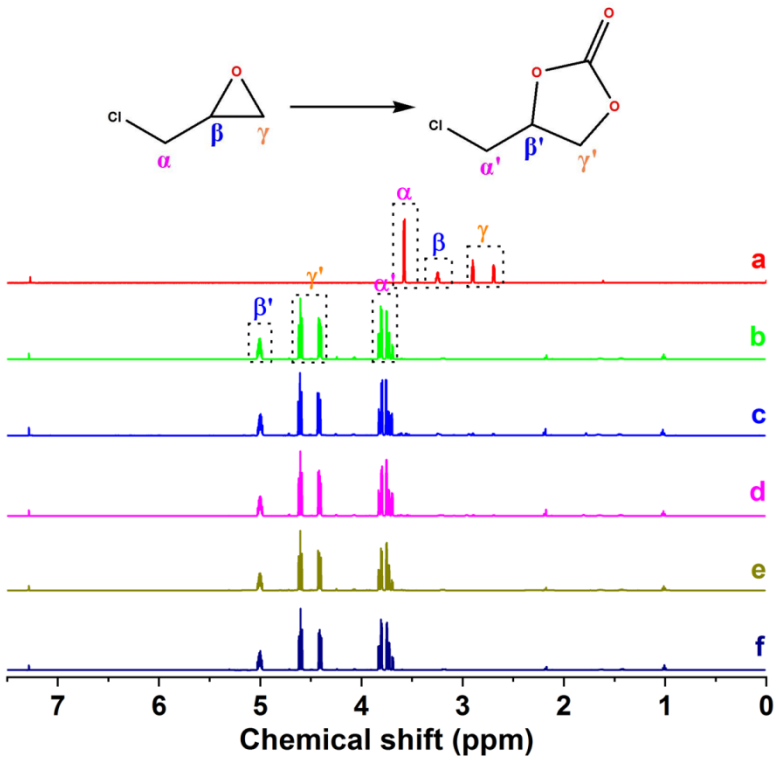


Fig. S11 The ^{1}H NMR spectrum (in $CDCl_3$) of a solution after the cycloaddition of CO_2 with 2-(chloromethyl)oxirane: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle and f) fifth cycle. The yields of the reaction have been calculated by integration of cyclic carbonates protons at the end of the reaction, due to the distinct chemical shifts for the corresponding epoxide protons.

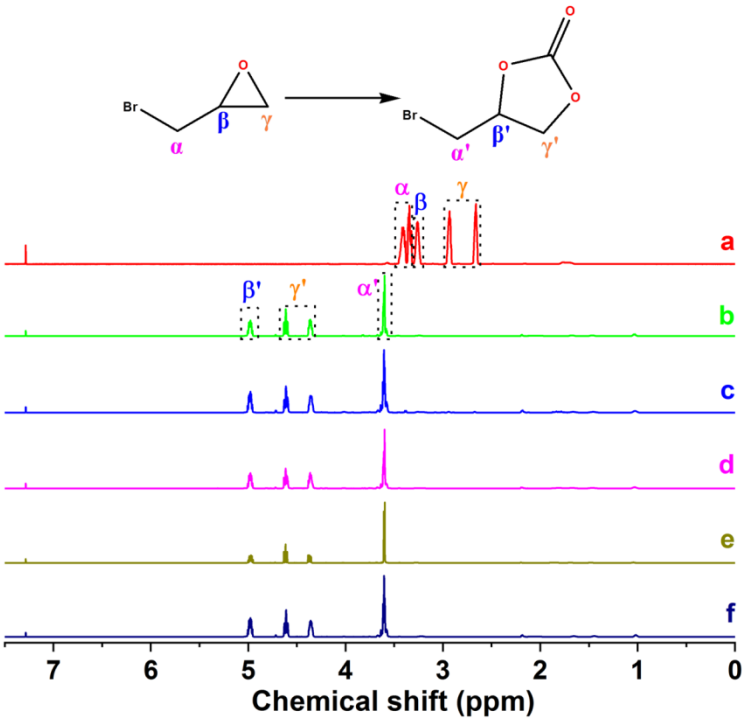


Fig. S12 The ^{1}H NMR spectrum (in $CDCl_3$) of a solution after the cycloaddition of CO_2 with 2-(bromomethyl)oxirane: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle and f) fifth cycle.

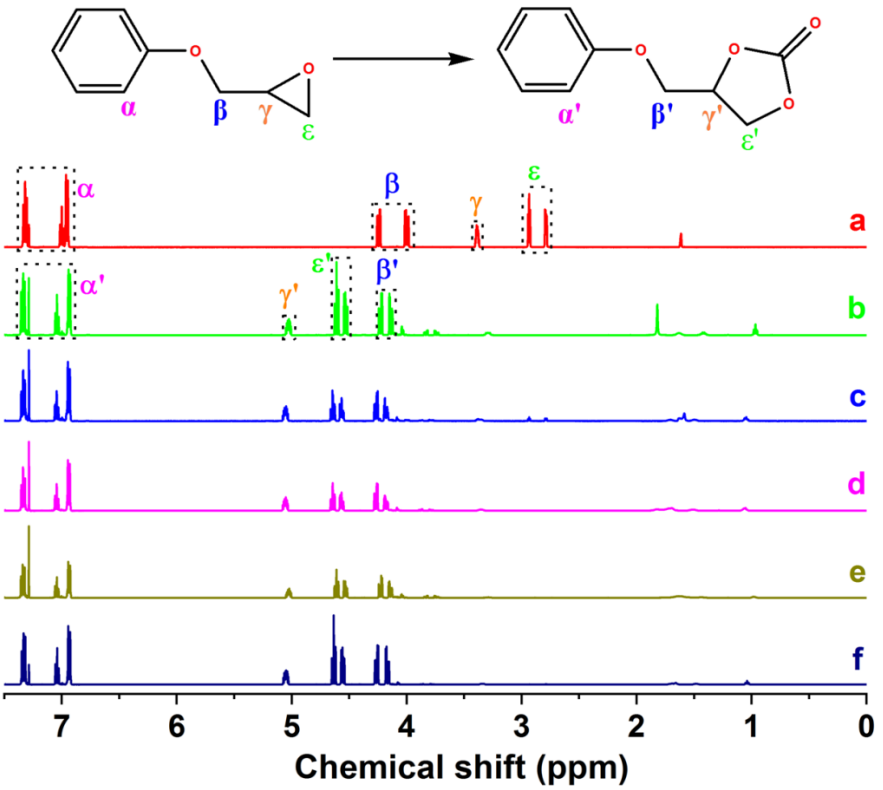


Fig. S13 The ^{1}H NMR spectrum (in $CDCl_3$) of a mixture after the cycloaddition of CO_2 with 2-(phenoxymethyl)oxirane: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle and f) fifth cycle.

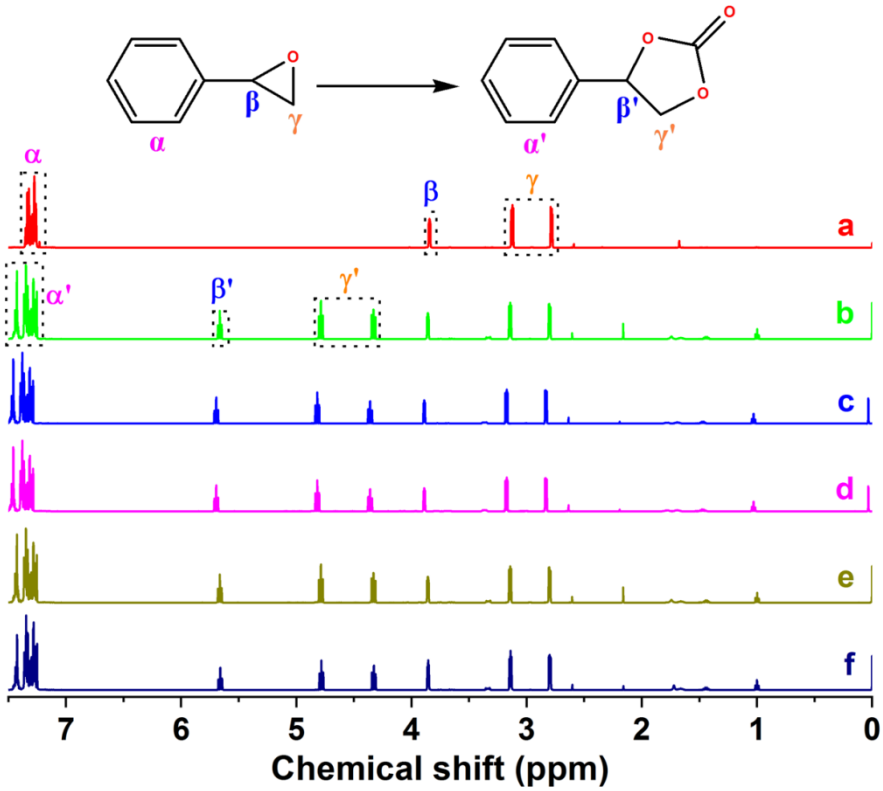


Fig. S14 The ^{1}H NMR spectrum (in $CDCl_3$) of a solution after the cycloaddition of CO_2 with 2-phenyloxirane: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle and f) fifth cycle.

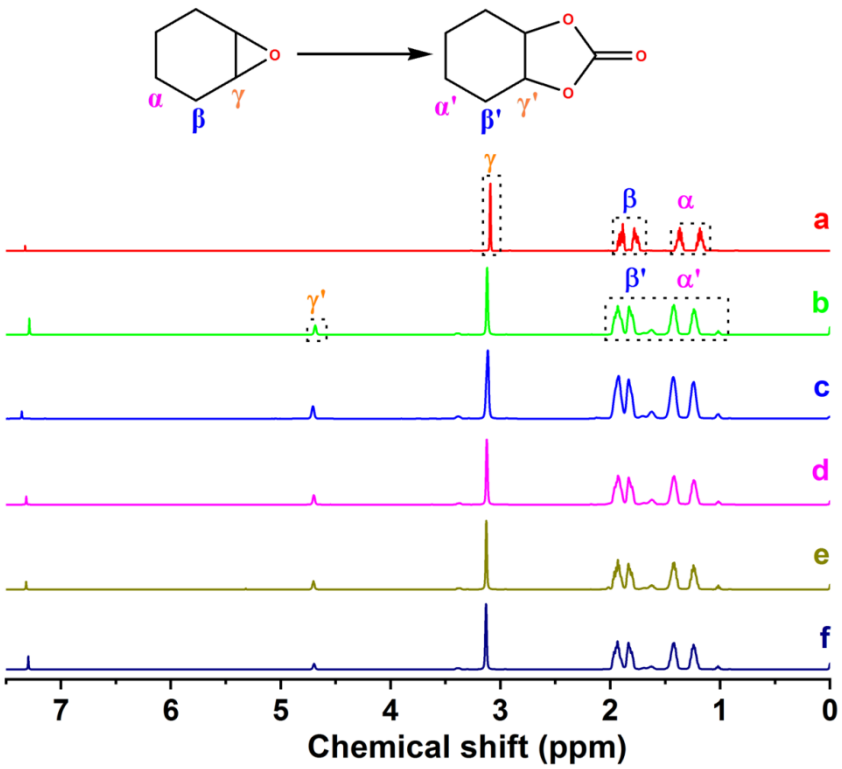


Fig. S15 The ^{1}H NMR spectrum (in $CDCl_3$) of a solution after the cycloaddition of CO_2 with cyclohexene oxide: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle and f) fifth cycle.

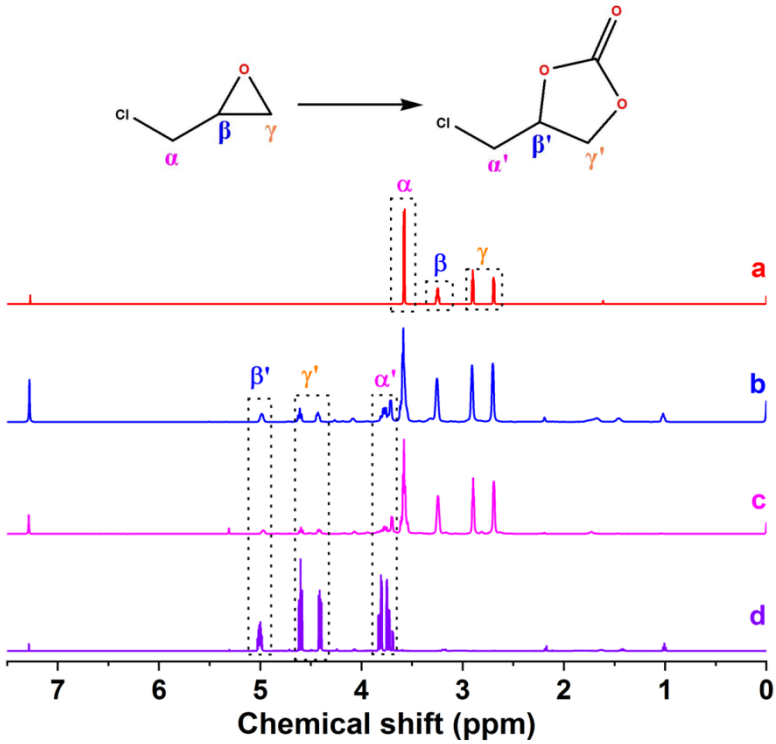


Fig. S16 The ^{1}H NMR spectrum (in $CDCl_3$) of a solution after the controlled experiments for cycloaddition of CO_2 with 2-(chloromethyl)oxirane. a) without catalyst, b) catalyzed by the cocatalyst TBAB alone, c) catalyzed by HNUST-9 only, d) catalyzed by both HNUST-9 and TBAB available at the same conditions.

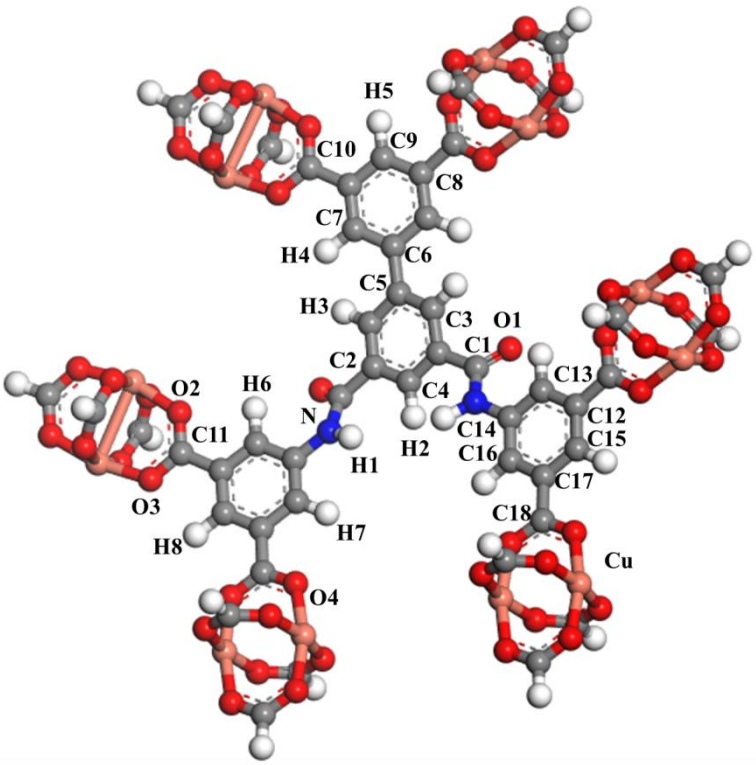


Fig. S17 The atomic schemes in framework of HNUST-9 used for GCMC and First-principles calculations.

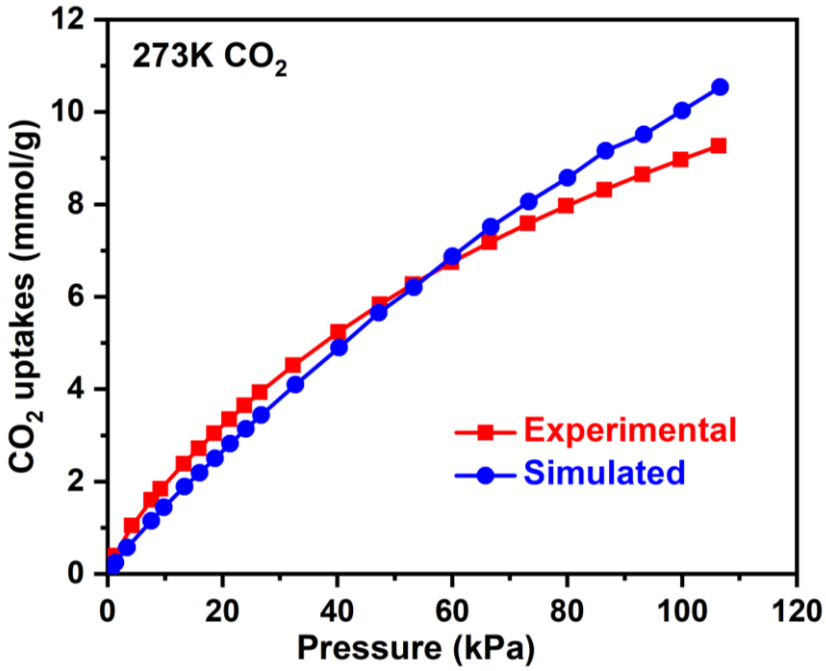


Fig. S18 Comparison of CO_2 adsorption isotherms of HNUST-9 at 273 K up to 1 bar between GCMC simulated and experimental data.

Table S1. Crystal data and structure refinement for HNUST-9.

Identification code	**HUNST-9**
CCDC number	1836745
Empirical formula	C32H20Cu3N2O17
Formula weight	895.14
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Fm-3m
Unit cell dimensions.	$a = b = c = 40.209(9)$ Å, $\alpha = \beta = \gamma = 90$ °
Volume	65010(44) $Å^3$
Z	32
Density (calculated)	0.732 g cm^3
Absorption coefficient	0.813 mm^{-1}
F(000)	14368.0
Crystal size	0.25 × 0.23 × 0.20 mm^3
2theta range for data collection	4.416 to 50.714
Limiting indices	-43 <= *h* <= 48, -48 <= *k* <= 42, -48 <= *l* <= 48
Reflections collected / unique	154811/2940 [R_{int} = 0.1442]
Completeness	99.5% (2theta = 52.00 °)
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data /restraints / parameters	2940/89/123
Goodness-of-fit on F^2	1.189
Final R indices [I>2sigma(I)]	R_1 = 0.0815, wR_2 [a] = 0.2444
R indices (all data)	R_1 = 0.1035, wR_2 [a] = 0.2802
Largest diff. peak and hole	1.41/-0.74 e. $Å^{-3}$

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$; $wR2 = [\Sigma w(\Sigma F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Lennard-Jones parameters of HNUST-9

Atom Type	ε/k_B (K)	σ (Å)	Atom Type	ε/k_B (K)	σ (Å)
H	22.141	2.571	C	52.836	3.431
O	30.192	3.118	N	34.721	3.261
Cu	2.516	3.114			

Table S3. Lennard-Jones parameters and charges of adsorbates

Atom Type	ε/k_B (K)	σ (Å)	q (e)
CO2_O	80.507	3.033	-0.3256
CO2_C	28.129	2.757	0.6512

Table S4. All partial atomic charges for the MOF material HNUST-9 used in GCMC simulations.

Atom Type	q (e)	Atom Type	q (e)
C1	0.698	C10	0.786
C2	-0.077	C11	0.810
C3	-0.107	C12	0.439
C4	-0.109	C13	-0.216
C5	0.087	C14	-0.028
C6	0.027	C15	0.247
C7	0.079	C16	-0.107
C8	-0.071	C17	-0.045
C9	-0.048	C18	0.820
H1	0.319	H5	0.114
H2	0.097	H6	0.178
H3	0.101	H7	0.165
H4	0.112	H8	0.124
O1	-0.511	O3	-0.679
O2	-0.700	O4	-0.713
N	-0.720	Cu	1.076