Supporting Information

A microporous hydrogen-bonded organic framework for sustainable adsorption and separation of CO_2

Xin-Yu Yan [a], Wen-Qing An [a, b], Ming-Xuan Ren [a], Ming-Zhi Zhuo [a], Zhaojun Chen [a, *], Ming-Xue Wu [a, *]

[a] School of Chemistry and Chemical Engineering, Qingdao University, Qingdao, 266071, Shandong, China

[b] School of Materials Science and Engineering, Qingdao University, Qingdao, 266071, Shandong, China

1. Materials and characterization

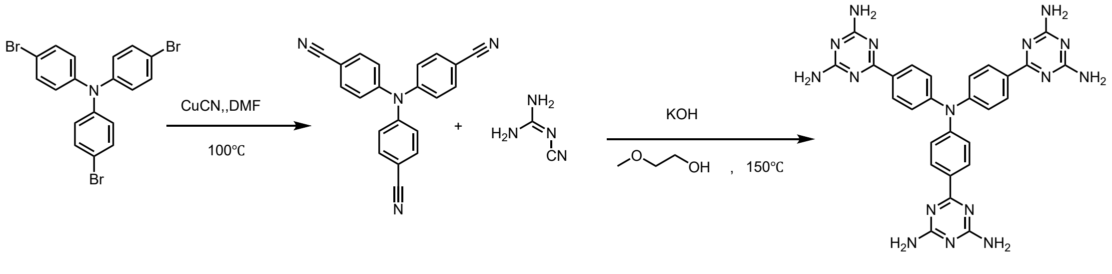
1.1 Materials

All reagents and solvents were obtained directly from commercial suppliers without further purification. Tris(4-bromophenyl)amine (≥ 98%), Copper (I) cyanide (≥ 99%), cyanoguanidine (≥ 98%), Potassium hydroxide (≥ 85%), 2-methoxyethanol (≥ 99%), N,N-Dimethylformamide (≥ 99.5%) were obtained from Energy Chemical., Ethanol absolute (≥ 99.7%) was of analytical grade (Sinopharm Chemical Reagent Co., Ltd. (China)). Ethyl Acetate (≥ 99.5%) and Isohexane (AR) were of analytical grade (Shanghai Titan Scientific Co., Ltd. (China)).

1.2 Characterization

Powder X-ray diffraction (XRD) data were collected using a PANalytical X-ray Diffractometer (X'Pert3 Powder) with Cu Kα radiation (λ = 1.54178 Å). ^{1}H NMR was collected on a Bruker AVANCE III 400 MHz NMR spectrometer. Thermogravimetric analyses (TGA) were performed using a Mettler Toledo TGA 2 in the temperature range of 30-900 °C under flowing Ar with a heating rate of 10 °C min^{-1}. The Kubo-X1000 surface area analyzer was used to measure gas adsorption isotherms. The dynamic adsorption experiment of CO_2 used a fixed-bed adsorption method. The breakthrough experiments for CO_2/N_2 (10/90, v/v) mixtures were carried out at BSD-MAB.

2. Synthesis and characterization of the organic linker



Scheme S1 The synthetic route to the organic building block.

Tris(4-bromophenyl)amine (200 mg, 0.4 mmol) was mixed with CuCN (300 mg, 3.37 mmol) in anhydrous DMF (15 mL) in a 100 mL Schlenk reaction flask. The system was heated under reflux in a nitrogen atmosphere for 48 hours. After cooling the reaction mixture to room temperature, it was poured into deionized water (50 mL) to form a suspension, and ethylenediamine (5 mL) was added. The suspension was vigorously stirred at 100 °C for 60 minutes and then filtered through a Büchner funnel. The collected precipitate was extracted with dichloromethane (3 × 50 mL). The organic fractions were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Final purification was achieved through silica gel column chromatography using a 1:1 hexane/dichloromethane mobile phase, yielding tri(4-cyanophenyl)amine (67 mg, 48%).

The reaction was carried out by combining tris(4-cyanophenyl)amine (200 mg, 0.6 mmol), cyanoguanidine (304 mg, 3.6 mmol), and potassium hydroxide (70 mg, 1.2 mmol) in 2-methoxyethanol (20 mL) under a nitrogen atmosphere. The mixture was gradually heated to 150 °C with stirring and held at this temperature for 12 h. After cooling, the reaction solution was poured into hot deionized water (100 mL) to afford a fluorescent yellow precipitate. The solid was collected by vacuum filtration, washed thoroughly with hot water (3 × 100 mL), and dried under reduced pressure for 48 hours to give the pure product (320 mg, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30-8.25 (m, 6H), 7.26-7.18 (m, 6H), 6.78 (s, 12H).

3. Fitting of pure component isotherms

At 298 K, experimental data were conducted for the isotherms of pure CO_2 and N_2. These data from the pure component isotherms were analyzed and fitted the using the Langmuir-Freundich isotherm model.

$$n(P) = \frac{q \times (k \times P)^n}{1 + (k \times P)^n} \quad (1)$$

As illustration of the goodness of the fits, **Figure S5** presented a comparison of component loadings at 298 K in HOF with the isotherm fits. The fits were good over the entire pressure range.

4. Prediction of the Gas Adsorption Selectivity by IAST

The Ideal Adsorbed Solution Theory (IAST) enables prediction of binary mixture adsorption from pure-component isotherms. For this system, the Langmuir-Freundlich model provided optimal fitting of experimental data. These fitted parameters were subsequently employed in IAST calculations to determine mixed-gas adsorption selectivity. The formula is:

$$S_{A/B} = \left(\frac{x_A}{y_A}\right) / \left(\frac{x_B}{y_B}\right) \quad (2)$$

where x_i and y_i are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases.

5. Pseudo-First Order Model

The dynamic adsorption experiment of CO_2 was conducted as follows: 100 mg of HOF material was weighed and placed in a U-tube, its weight was measured after vacuuming, and then it was connected to a fixed bed for carbon dioxide adsorption testing. At different adsorption time intervals, the weight of the carbon dioxide-loaded material was measured until the weight reaches a stable value. The CO_2 adsorption capacity was estimated by the increase in weight, and the capacity was determined through at least three parallel experiments. A pseudo-first-order model was used to help understand the adsorption kinetics.The pseudo-first order model:

$$Q_t = Q_e(1 - e^{-kt}) \quad (4)$$

Where Q_e (mmol/g) and Q_t (mmol/g) refer to the adsorption capacity at equilibrium and at time t (min); k (min^{-1}) is the adsorption rate constants for the pseudo-first-order.

6.Column Breakthrough Experiments

The column breakthrough experiments for CO_2/N_2 (10/90, v/v) mixtures were carried out at BSD-MAB . In the separation experiment, the activated sample (0.944 g) was loaded into a fixed-bed column with an inner diameter of 6 mm. The column was first heated at 100 °C for 2 h for activation before testing. After activation, the sample was purged with helium at a flow rate of 10 mL/min for 60 min at 298 K. Subsequently, the helium flow was shut off, and a carbon dioxide/nitrogen mixture (10/90, v/v) was introduced into the column at a flow rate of 5 mL/min. The column effluent was monitored by a mass spectrometer (MS).

7. Computational calculations

We employed a combined computational strategy based on density functional theory (DFT) and grand canonical monte carlo (GCMC) methods to investigate the HOF framework using Materials Studio (MS). Geometric optimization was first carried out in the Forcite module with a 1×1×1 unit cell containing CO_2 and N_2 molecules. The convergence criteria were set to 0.001 kcal/mol/Å for force and 2×10^{-5} kcal/mol for energy, with both cell parameters and atomic coordinates allowed to relax. Electrostatic interactions were treated with the Ewald summation method at a medium accuracy of 1×10^{-4} kcal/mol, while van der Waals interactions were computed using atom-based summation with a cutoff radius of 12.5 Å and a buffer width of 0.5 Å. The optimized structure agreed well with experimental XRD data, confirming the stability of the hydrogen-bonded network. Adsorption behaviors of CO_2 and N_2 were then studied via GCMC simulations in the grand canonical ensemble using a 1×1×1 supercell. The Metropolis algorithm was applied with 1×10^6 to 1×10^7 steps for each simulation. Two types of conditions were considered: pressure swing adsorption from 0 to 100 kPa at 298 K, and constant-pressure adsorption at 100 kPa across 25-100 °C. The Universal Force Field was used with atom-based summation for both electrostatic and van der Waals interactions, employing consistent cutoff (12.5 Å) and buffer width (0.5 Å) settings to ensure accuracy and computational efficiency.

Based on the results of the grand canonical Monte Carlo (GCMC) simulation and density functional theory (DFT) calculations, gas molecules tend to deposit in the central part of the pores. The interaction energy between the gas molecules and the framework can be calculated using the following formula:

$$E_\mathrm{a} = [E(HOF) + E(gas)] - E(HOF + gas) \quad (4)$$

where E_a is the interaction energy between the framework and the gas molecules, *E(HOF)* is the energy of the framework, *E(gas)* is the energy of the gas molecules, and *E(HOF +gas)* is the total energy of the framework and gas molecules.

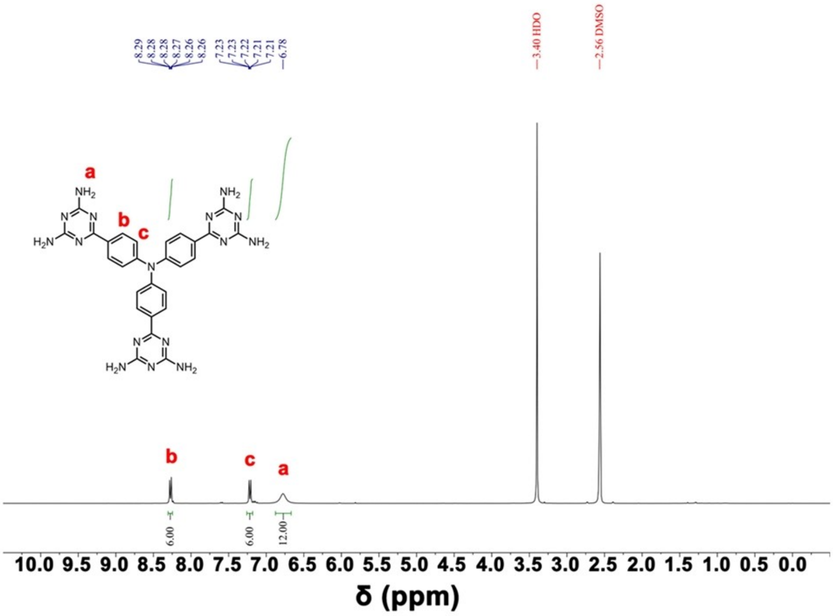


Figure S1. The ^{1}H-NMR spectrum of HOF building block.

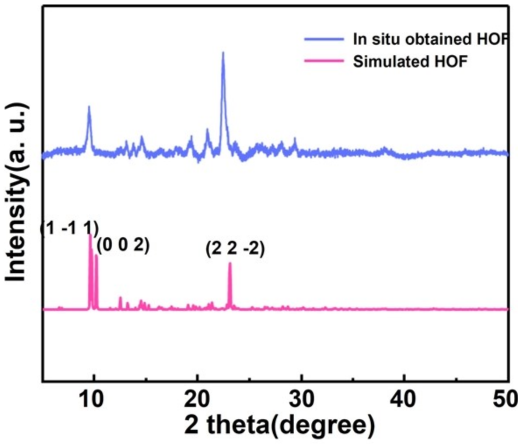


Figure S2. PXRD patterns of HOF obtained from simulation and experiment.

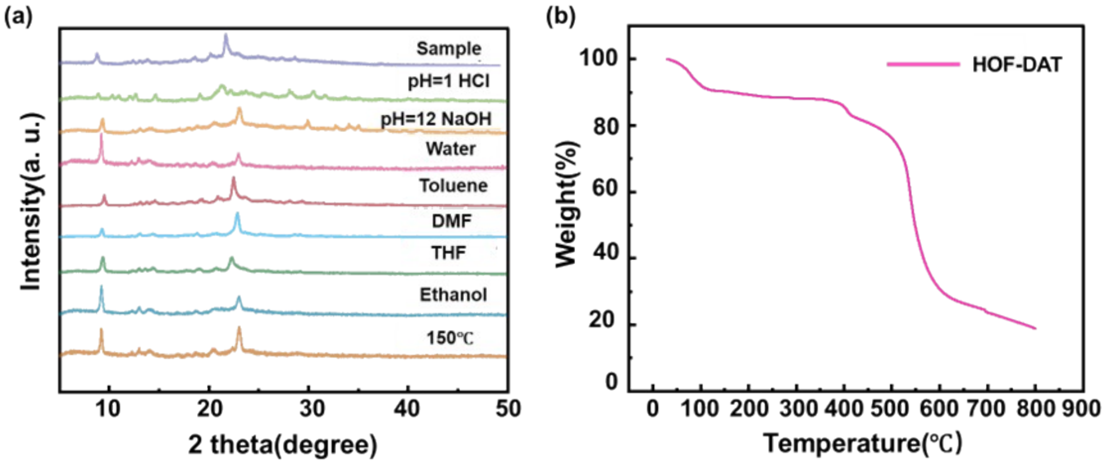


Figure S3. (a) PXRD patterns of HOF after soaking in various solvents and drying at 150 °C for 24 h. (b) The TGA curves of HOF.

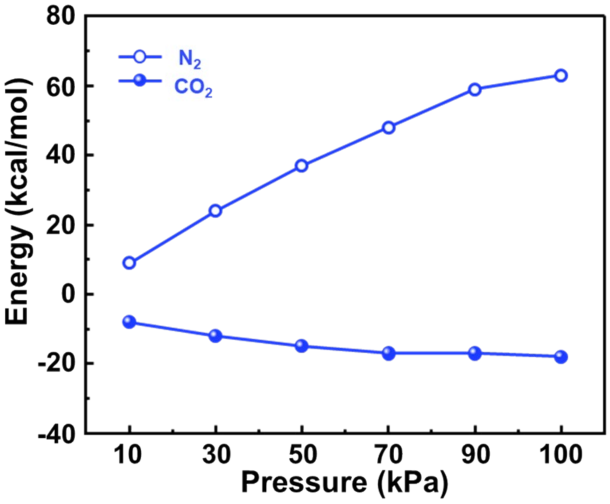


Figure S4. The average total energy of CO_2/N_2 adsorption by HOF at different pressures.

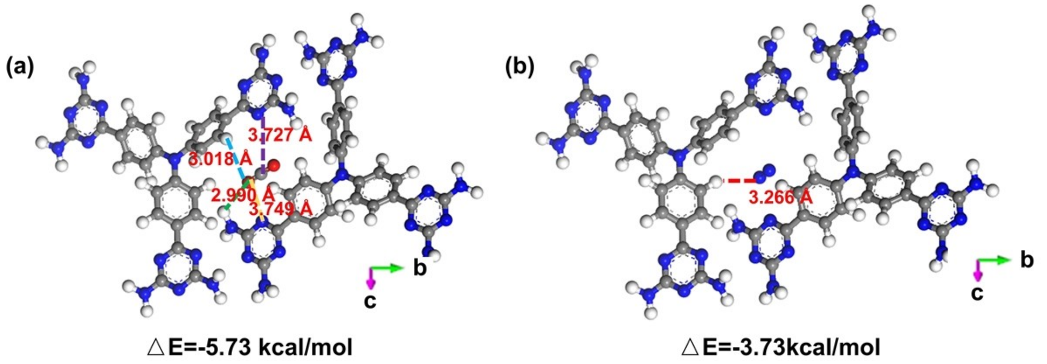


Figure S5. Theory calculation of the preferential binding sites for (a) CO_2 and (b) N_2 in HOF.

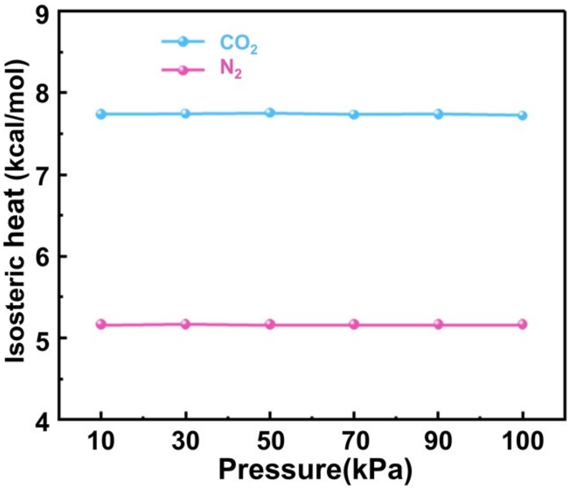


Figure S6. Isosteric heat of adsorption for CO_2 and N_2 by HOF at 298 K.

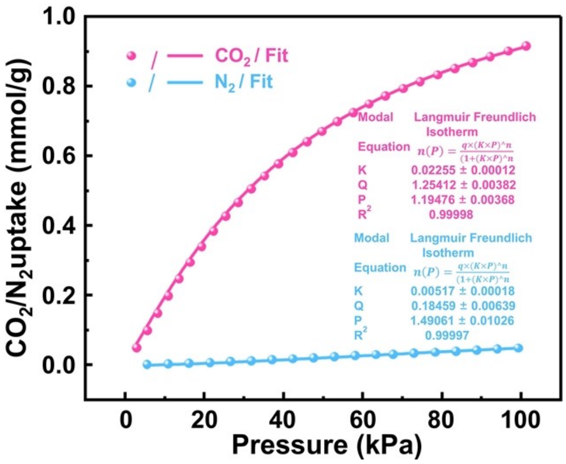


Figure S7. CO_2 and N_2 adsorption isotherm at 298 K.

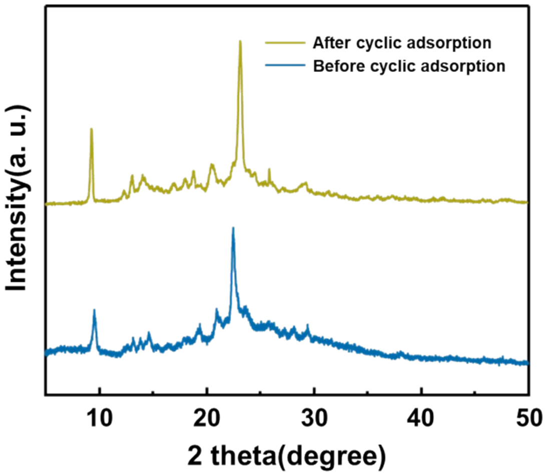


Figure S8. PXRD patterns of HOF obtained before and after cyclic adsorption.

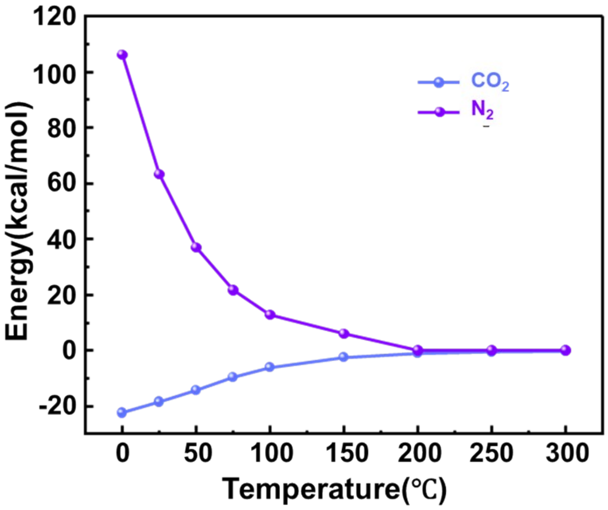


Figure S9. The adsorption average total energy of CO2/N2 at different temperatures were simulated by MS at 100 kPa.

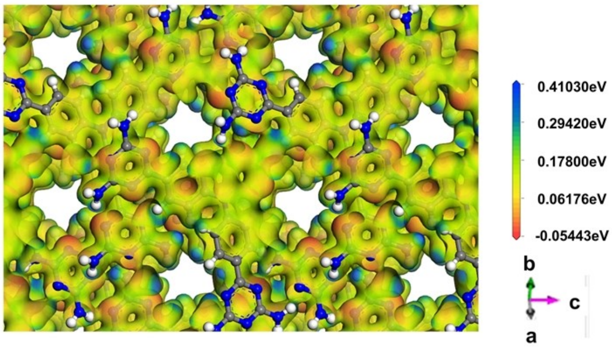


Figure S10. Calculated electrostatic potential surface of HOF.

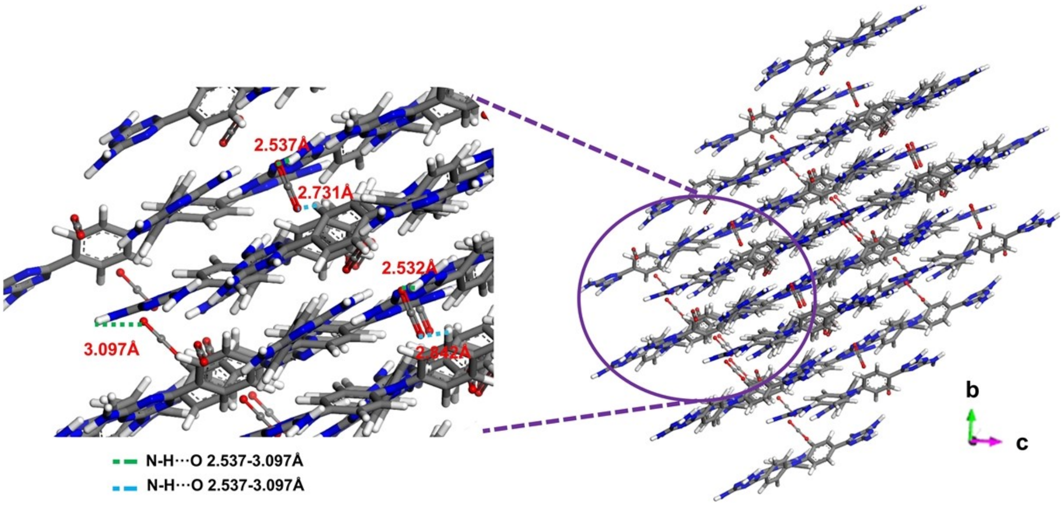


Figure S11. The adsorption sites of CO2 molecule in HOF.

Table S1. Crystal data collection and structure refinement for HOF.

Identification code	HOF
Empirical formula	$C_{108}H_{96}N_{64}$
Formula weigh	2288.96
Temperature/K	298
Crystal system	triclinic
Space group	*P*-1
a/Å	13.3518
b/Å	13.9183
c/Å	17.4294
α/°	93.183
β/°	91.532
γ/°	104.633
Volume/Å	3126.30
Z	1
CCDC No.	2298082

Table S2. Comparison of CO_2 adsorption capacities observed in this work with reported references.

Materials	CO_2 uptake (mmol/g)	Ref.
Me3TFB-BD-COF	0.41	28
COF-709	0.44	12
TCPP-1,3-DPP	0.52	29
HOF-6a	0.53	30
HOF-21n	0.53	20
Ni-MOF/IL-2	0.54	31
SOF-9a	0.55	32
Ni-MOF/IL-4	0.62	31
Me3TFB-(NH2)2BD	0.72	28
TF-COF	0.76	33
Ni-MOF/IL-3	0.92	31
HOF	0.92	This work
InDCPN-I-MOF	0.9375	34
UMC-1	1.13	35
FDU-HOF-2	1.15	36

HOF-21m	1.25	20
HOF-11a	1.33	38
mCB-MOF-1′	1.35	37
BTBA-1a	1.57	15
HOF-ZSTU-4a	1.64	39

Note: References are cited in the main text.