Supporting Information

A highly stable amino-coordinated MOF for unprecedented block off N_2 adsorption and extraordinary CO_2/N_2 separation

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1. Materials and methods

All reagents and solvents were commercially available and used without further purification. The organic linker (2E, 2E')-3, 3'-(5-amino-1, 3-phenylene) diacrylic acid was synthesized according to previously reported procedure.[1] ^{1}H NMR spectra were recorded on a Bruker Advance DMX 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Infrared spectrum (IR) was performed on Thermo Fisher Nicolet iS10 spectrometer using KBr pallets. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10^{o}C/min in N_2 atmosphere. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 3-50° range on an X'Pert PRO diffractometer with Cu Kα (λ = 1.542Å) radiation at room temperature.

2. Single-crystal X-ray crystallography.

Crystallographic measurements for **ZJU-198** were taken on an Oxford Xcalibur Gemini Ultra diffractometer equipped with an Atlas detector using graphite-monochromatic Mo Kα radiation (λ = 0.71073Å) at 293 K. The determination of the unit cell and data collection for the crystal of **ZJU-198** was performed with CrysAlisPro. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure of **ZJU-198** was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package. The solvent molecules in the

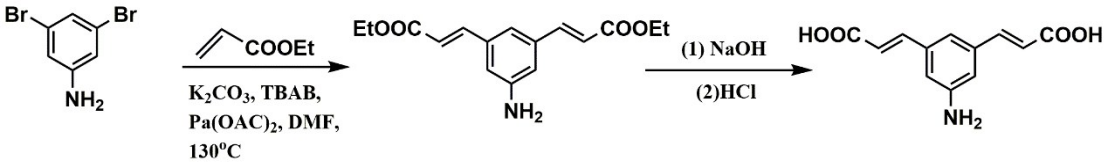
compound are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules. The new resulting files were used to further refine the structure. The composition of the as-synthesized **ZJU-198** was figured out based on the elemental analysis, TGA and single crystal structure. Crystallographic data are summarized in Table S2.

3. Gas Sorption Measurements.

All gas sorption isotherms were obtained from the Micromeritics ASAP 2020 surface area analyzer. Before the gas sorption measurements, the fresh sample of **ZJU-198** was guest–exchanged with dry acetone at least 10 times, then filtered and degassed at 298 K for two days, 323 K for 12 hours and at 373 K for 5 hours under high vacuum to obtain the activated **ZJU-198a**. The measurements were maintained at 77 K with liquid nitrogen and at 196 K with drikold. The adsorption isotherms of CO_2 and N_2 gases were obtained at 273 K, 298 K, 308 K and 318 K, respectively.

4. Synthesis of the organic linker 5-amino-H_2L.

5-amino-H_2L was synthesized via Heck cross-coupling, followed by hydrolysis and acidification as shown in Scheme S1.



Scheme S1. Synthetic routes to the organic linker 5-amino-H_2L.

As shown in Scheme S1, the 3, 5-dibromoaniline (11.87 g, 40 mmol), ethyl

acrylate (9 mL, 100mmol), tetrabutyl ammonium bromide (TBAB) (3.22 g, 10 mmol), K_2CO_3 (10.35 g, 75 mmol), $Pd(OAc)_2$ (1.122 g, 5 mmol), and DMF (100 mL) were mixed in a 250 mL round-bottomed flask. The mixture was heated at 130^oC, under stirring for 24 h. Then, the mixture was extracted with water and ethyl acetate. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was subjected to chromatography on silica gel. The solvent was removed under reduced pressure to give a white power **1**. The white power **1** was then suspended in a mixture of THF (20 mL) and H_2O (50 mL), to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF was removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water, and dried to give 5-amino-H_2L (4.5 g). Yield: 38%. ^1H NMR (500 MHz, d6-DMSO, ppm): δ= 12.35 (s, 2H), 7.45 (d, 2H), 7.20 (s, 1H), 6.85 (s, 2H), 6.45 (d, 2H), 5.33 (s, 2H).

5. Synthesis of ZJU-198.

A mixture of the organic linker 5-amino-H_2L (8 mg, 0.014 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (15.0 mg, 0.051 mmol) was dissolved into a 13 mL mixed solvent (DMF/H_2O/acetonitrile, 2 mL/4 mL/7 ml) in a screw-capped vial (20 mL), at 80^oC for 1 d. Colorless layer-shaped crystals were obtained as **ZJU-198. ZJU-198** has a formula as ZnL•DMF, which was obtained based on the single-crystal X-ray structure determination, elemental analysis and TGA.

Anal. Calcd for C_{12} H_7 N O_4 Zn: C, 46.25; H, 4.009; N, 7.08; found: C, 46.26; H, 3.985; N, 7.17.

6. The TGA curves of ZJU-198.

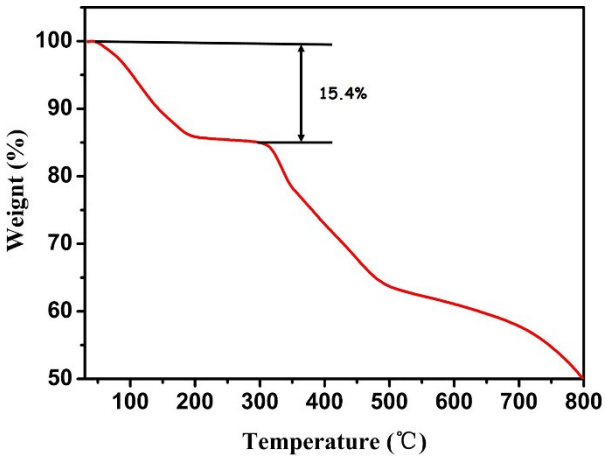


Figure S1. Thermogravimetric analysis (TGA) curves of as-synthesized **ZJU-198**. It's demonstrated the remarkable thermostability of **ZJU-198**, with no decomposition of framework occurring up to at least 300°C.

7. The IR spectra of the ligand 5-amino-H_2L and ZJU-198.

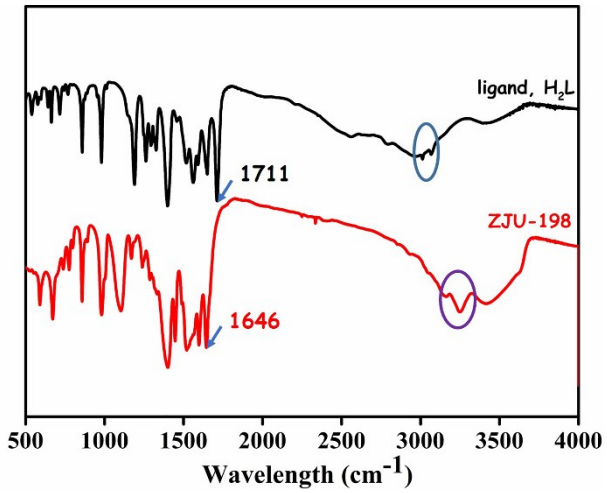


Figure S2. Infrared spectrum (IR) curves of ligand (H_2L), as-synthesized **ZJU-198**. It's clear to see that the adsorption peak of carbonyl changes from 1711 cm^{-1} of ligand to 1646 $cm^{-1}$of **ZJU-198** and the double-peak of amino varies from 3075 cm^{-1} to 3254 cm^{-1} during the deprotonation process.

8. The adsorption isotherms for ZJU-198a.

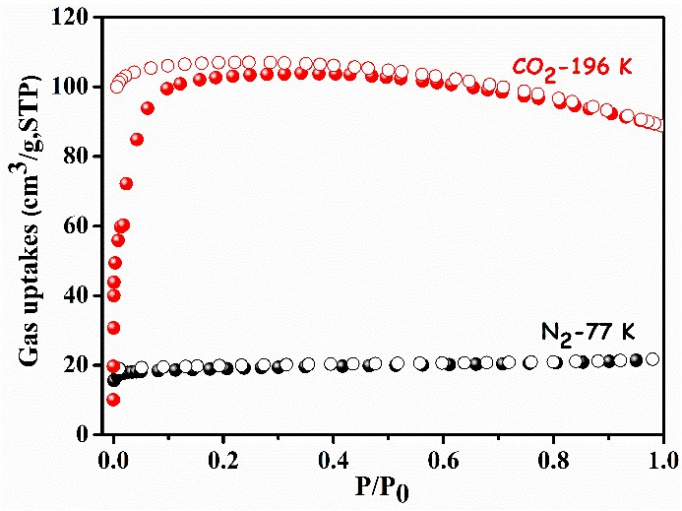


Figure S3. The CO_2 adsorption isotherms for **ZJU-198a** at 196 K and N_2 adsorption isotherms for **ZJU-198a** at 77 K.

9. The CO_2 adsorption isotherms for ZJU-198a.

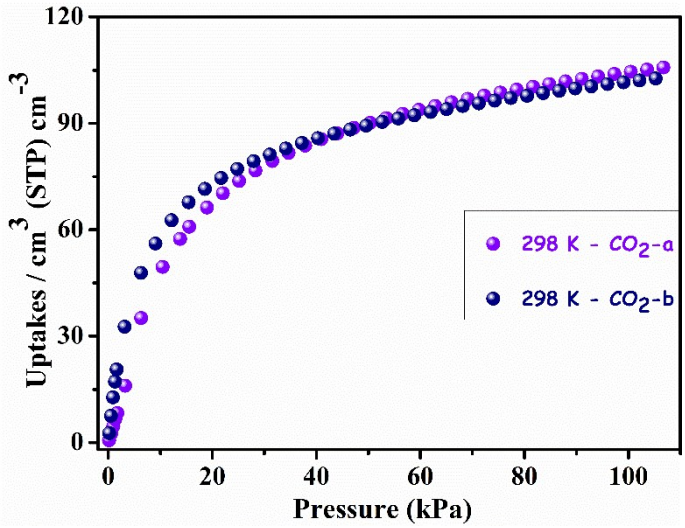


Figure S4. The CO_2 adsorption isotherms for **ZJU-198a** at 298 K. 298 K-CO_2-a is the CO_2 adsorption isotherms of the fresh **ZJU-198a**, 298 K-CO_2-b is the CO_2 adsorption isotherms of **ZJU-198a** after soaking the bulk material in deionized water for 30 minutes.

10.Breakthrough test of ZJU-198.

The breakthrough experiments were accomplished by a dynamic gas breakthrough equipment[2]. The experiment was conducted using a stainless steel column (4.6 mm inner diameter × 50 mm). The weight of sample powder packed in the column was 0.613 g. The column packed with sample was firstly activated with He flow (15 ml min^{-1}) for 12 h at room temperature (25 °C). After activation, the mixed gas (CO_2/N_2: 15/85, v/v) flow was introduced at 2.30 ml min^{-1}. Outlet gas from the column was monitored using gas chromatography (GC-2010 plus, SHIMADZU) with a thermal conductivity detector (TCD). After the breakthrough experiment, the sample was regenerated with He flow (12.5 ml min^{-1}) for about 20 hours at 35 °C. A GC-2010 plus (SHIMADZU) was used for the measurement of CO_2 and N_2 levels. The gas mixture was separated by a capillary column (Agilent GS-GASPRO, Φ0.32 × 60 M) at 333 K with a He flow rate of 8 ml/min. The concentration of CO_2 or N_2 in the outlet gas was monitored by a TCD at 443 K.

Table S1. Breakthrough calculations for separation of CO_2/N_2 mixture containing 15 mol% CO_2 at 298 K.

	Dimensionless breakthrough time τ_{break}	adsorbed during 0 - τ_{break}* mmol g^{-1}
CO_2	48.693	1.223

∗ The amount of CO_2 captured during the time interval 0 to 100% C_A/C_0. All experiments were conducted using a stainless steel column (4.6 mm inner diameter × 50 mm) at a flow rate of 2.30 ml/min.

Table S2. Crystallographic data and structure refinement results for **ZJU-198**.

	ZJU-198
Empirical formula	C_{12} H_7 N O_4 Zn
Formula weight	294.56 g/mol
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	P b c a
a (Å)	7.1952(5)
b (Å)	19.7441(16)
c (Å)	20.4254(14)
α (°)	90
β (°)	90
γ (°)	90
V (Å3)	2901.69(37)
Z	8
Density (calculated g/cm-3)	1.349
Absorption coefficient (mm-1)	1.696
F(000)	1184.0
GOF	1.037
R1, wR2 (I>2σ (I)) a	0.0893, 0.2027
R1, wR2 ((all data) a	0.1194, 0.2188
Largest diff. peak and hole (e/Å-3)	1.027, -0.940

Reference

1. G. Q. Kong, Z. D. Han, Y. He, S. Ou, W. Zhou, T. Yildirim, R. Krishna, C. Zou, B. L. Chen, C. D. Wu, *Chemistry*, 2013, **19**, 14886.

2. X. L. Cui, K. J. Chen, H. B. Xing, Q. W. Yang, R. Krishna, Z. B. Bao, H. Wu, W. Zhou, X. L. Dong, Y. Han, B. Li, Q. L. Ren, M. J. Zaworotko, B. L. Chen, *Science*. 2016, **353**: 141.