Electronic Supporting Information (ESI)

Amino-Functionalized Water Stable Metal–Organic Framework for Enhanced C₂H₂/CH₄ Separation Performance

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Experimental Section

Materials and methods.

All starting chemicals were purchased from commercial sources and were used without further purification. Thermogravimetric analysis was performed on a NETZSCH TG 209 thermobalance in a nitrogen atmosphere, sample was placed in alumina containers and data were recorded at 10 °C/min between 20 and 800 °C. IR spectra (KBr pellet) were obtained from a Vertex 70 spectrometer in the region of 400–4000 cm⁻¹. X-ray powder diffraction (XRPD) was collected on Bruker D8 ADVANCE diffractometer at room temperature using Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org. The elemental analyses (C, H, N contents) were determined on a Vario EL III analyzer. The diffraction data were collected on an Rigaku Oxford XtaLAB PRO diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 273 K. The data were processed using CrysAlis^{pro 1}. The structure was solved and refined using Full-matrix least-squares based on F2 with program SHELXS-97 and SHELXL-97² within Olex2³. Further details of crystal data and structure refinement for NbU-9-NH₂ were collected in Table S1. Selected bond lengths and angles of NbU-9-NH₂ were given in Table S2. Full crystallographic data for NbU-9-NH₂ have been deposited with the CCDC (No.: 1957343). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.4

- 1. CrysAlisPro Version 1.171.35.19. (2011). Agilent Technologies Inc. Santa Clara, CA, USA.
- 2. Sheldrick, G. M. (2008). A short history of SHELX. Acta Cryst. A64, 112-122.

3. Dolomanov et al. (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 42, 339-341.

4. The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Pure gas adsorption

Gas sorption isotherms were performed on Micromeritics (3FLEX) aparatus. Prior to gas measurement, the Methanol-exchanged samples were degassed at 100°C under dynamic vacuum for 24h to give fully activated samples.

Breakthrough tests

The gas-separation properties of NbU-9(591 mg) and NbU-9-NH₂ (640 mg) were examined by breakthrough experiments using 50:50 (v/v) gas mixtures flowed through the activated samples packed into the same glass column (0.46 cm inner diameter, 5.0 cm in length). The gas mixture was dosed into the column at a flow rate of 3 mL min⁻¹. The relative amounts of the gases passing through the column were monitored using gas chromatography (Agilent 7890B) with a thermal conductivity detector (TCD) once every 30 seconds. The concentration of the outlet gas was normalized after calibration with the standard gases.

Synthesis of NbU-9-NH₂·S:

Solid Ni(NO₃)₂·6H₂O (0.147 g, 0.5 mmol) was added without stirring to an EtOH/H₂O (10 mL, v/v=5:5) solution containing 2-amino terephthalic acid (0.018g, 0.1mmol), 4'-(4-carboxyphenyl)-4,2':6',4"-terpyridine (Hctpd, 0.2 mmol, 0.072 g) and NaOH (0.016 g, 0.4 mmol). The mixture was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 180 °C within 500 min, maintained at this temperature for 3600 min and then cooled to 30 °C within 2880 min. Green block crystals of $[Ni_2(\mu_2-OH_2)(ctpd)_2(NH_2-bdc)] \cdot (EtOH)_2 \cdot (H_2O)_2$ (NbU-9-NH₂·S) were obtained by filtration. Elemental analysis for NbU-9-NH₂·S: calcd.: C 58.67%, H 4.40%, N 8.55%; found: C 58.75%, H 4.44%, N 8.57%.

Synthesis of NbU-9·S: The synthesis of **NbU-9**·S was carried out as described in the reference 18: A mixture of Ni(NO₃)₂·6H₂O (0.05 mmol, 0.015 g), 1,4-H₂bdc (0.025 mmol, 0.004 g), Hctpd (0.025 mmol, 0.009 g), water (2 mL), DMF (4 mL) (DMF = N,N'-dimethylformamide), NH₃·H₂O(0.6 mL) and acetonitrile (0.25 mL) was sealed in a Teflon-lined autoclave and heated at 120 °C for 3 days, then followed by slow cooling to room temperature. The resulting green block crystals were filtered off (yield: ca. 40% based on Ni). Elemental anal. found:C, 62.17; H, 3.42; N, 8.38%. Calcd. for C52H34Ni2N6O9: C, 62.19;H, 3.41; N, 8.37%.

| | NbU-9-NH ₂ |
|-------------------|--------------------------|
| Empirical formula | $C_{52}H_{34}N_7Ni_2O_9$ |
| Formula weight | 1018.28 |

| Table S1 Crystal data and structure refinement for NbU-9-NE | I ₂ |
|---|----------------|
|---|----------------|

| Tomporaturo/V | 202 | | |
|---|--|--|--|
| | 293 | | |
| Crystal system | monoclinic | | |
| Space group | I2/a | | |
| a/Å | 15.1556(7) | | |
| b/Å | 14.7793(8) | | |
| c/Å | 25.9554(13) | | |
| $\alpha/^{\circ}$ | 90 | | |
| β/° | 100.382 | | |
| γ/° | 90 | | |
| Volume/Å ³ | 5718.5 | | |
| Ζ | 4 | | |
| $\rho_{calc}g/cm^3$ | 1.183 | | |
| µ/mm⁻¹ | 0.713 | | |
| F(000) | 2092.0 | | |
| Radiation | MoKa ($\lambda = 0.71073$) | | |
| 2θ range for data collection/° | 7.14 to 48.812 | | |
| Index ranges | $-17 \le h \le 17, -17 \le k \le 17, -30 \le l \le 28$ | | |
| Reflections collected | 26717 | | |
| Independent reflections | 4697 [$R_{int} = 0.0647, R_{sigma} = 0.0386$] | | |
| Data/restraints/parameters | 4697/0/326 | | |
| Goodness-of-fit on F ² | 1.055 | | |
| Final R indexes [I>= 2σ (I)] | $R_1 = 0.0392, wR_2 = 0.0843$ | | |
| Final R indexes [all data] | R1 = 0.0480, wR2 = 0.0874 | | |
| Largest diff. peak/hole / e Å ⁻³ | 0.34/-0.26 | | |

Table S2 The selected bond lengths [Å] and angles [°] of NbU-9-NH₂.

| NbU-9-NH ₂ | | | | | | |
|---|------------|-------------|------------|--|--|--|
| Ni(1)-O(2) | 2.0770(16) | Ni(1)-O(4) | 2.0498(16) | | | |
| Ni(1)-O(3) | 2.1071(13) | Ni(1)-O(5c) | 2.0475(16) | | | |
| Ni(1)-N(3a) | 2.086(2) | Ni(1)-N(1b) | 2.1167(19) | | | |
| Ni(1c)-O(3)-Ni(1) | 111.59(11) | | | | | |
| Symmetry codes: (a) -1+x,+y,+z; (b) 1-x,1/2+y,1/2-z; (c) 1/2-x,+y,1-z; (d) 1-x,2-y,1-z. | | | | | | |

| | S _{BET} (m ² g ⁻¹) | Pore size (N ₂ , Å) | C ₂ H ₂ uptake (cm ³ g ⁻¹) | CH4 uptake (cm ³ g ⁻¹) | Qst C ₂ H ₂ (kJ mol ⁻¹) | Qst CH ₄ (kJ mol ⁻¹) | Selectivity for C ₂ H ₂ / CH ₄ |
|----------------------------|---|--------------------------------------|---|---|--|--|---|
| SNNU-95 ²⁰ | 206 | 4.2 | 31.1/15.1 | 9.2/1.1 | 47.2 | - | 20.7 |
| ZJU-199 ²⁹ | 987 | - | 169.5/128 | 25.3/14.4 | 38.5 | 19.0 | 27.3 |
| FJI-C4 ²⁶ | 690 | 5.5 | 82.8/72.5 | 32.7/18.4 | 27 | 20.8 | 51 |
| UTSA-50 ²⁷ | 604 | - | 113.9/91 | 29.2/18.8 | 39.4 | 18.6 | 68 |
| SNNU-65-CuIn ²⁸ | 1936 | - | 251.2/153.3 | 24.7/13.8 | 23.4 | 15.8 | 69.5 |
| NbU-9 | 572 | 4.0 | 78.5/55.2 | 27.3/17.5 | 22.8 | 16.8 | 27.0 |
| NbU-9-NH ₂ | 514 | 3.7 | 108.6/80.3 | 30.5/20.5 | 35.0 | 17.6 | 69.4 |

Table S3 Comparison of adsorption data



Fig. S1 The PXRD patterns of NbU-9 and NbU-9-NH₂.



Fig. S2 The TGA of NbU-9-NH₂.



Fig. S3 N₂ adsorption and desorption isotherm for NbU-9 and NbU-9-NH₂, inset: pore size distribution curve obtained by the Horvath–Kawazoe method.



Fig. S4 Vapor adsorption and desorption isotherm for NbU-9 and NbU-9-NH₂ at 298K.



Fig. S5 Gas adsorption-desorption properties of the activated NbU-9-NH₂.



Fig. S6 Gas adsorption-desorption properties of the activated NbU-9.

IAST adsorption selectivity calculation:

The experimental isotherm data for pure C_2H_2 , C_2H_4 , and CH_4 (measured at 273 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * P^c}$$

Where *q* and *p* are adsorbed amounts and pressures of component i, respectively.

Using the pure component isotherm fits, the adsorption selectivity is defined by

$$S_{ads} = \frac{\frac{q_1}{q_2}}{\frac{p_1}{p_2}}$$

Where q_i is the amount of *i* adsorbed and p_i is the partial pressure of i in the mixture. We used the following written codes to simulate the adsorption selectivity of C₂H₂/CH₄, and C₂H₄/CH₄ in Fig. 2:

28 # No. of Pressure Point

y1, y2 # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 101, 102, 103, 104, 105, 106, 107,

- 108, 109 #The unit is same parameter b, kPa
- a1, a2 # fitting parameter Nsat (A1) for both component (Unit: mmol/g)
- b1, b2 # fitting parameter b1 for both components (Unit: kPa⁻¹)
- c1, c2 # fitting parameter c1 for both components
- 0, 0 # fitting parameter Nsat2(A2) for both component(Unit: mmol/g)
- 0, 0 # fitting parameter b2 for both components (Unit: kPa⁻¹)
- 1, 1 # fitting parameter c2 for both components



Fig. S7 The C₂H₂ fit isotherms of NbU-9-NH₂ at 273 K and 298 K by virial equation.



Fig. S8 The C₂H₂ fit isotherms of NbU-9 at 273 K and 298 K by virial equation.



Fig. S9 The C_2H_4 fit isotherms of NbU-9-NH₂ at 273 K and 298 K by virial equation.



Fig. S10 The C_2H_4 fit isotherms of NbU-9 at 273 K and 298 K by virial equation.



Fig. S11 The CH₄ fit isotherms of NbU-9-NH₂ at 273 K and 298 K by virial equation.



Fig. S12 The CH₄ fit isotherms of NbU-9 at 273 K and 298 K by virial equation.



Fig. S13 C₂H₂ adsorption isotherm of NbU-9-NH₂ with fitting by L-F model.



Fig. S14 C_2H_2 adsorption isotherm of NbU-9 with fitting by L-F model.



Fig. S15 C₂H₄ adsorption isotherm of NbU-9-NH₂ with fitting by L-F model.



Fig. S16 C₂H₄ adsorption isotherm of NbU-9 with fitting by L-F model.



Fig. S17 CH_4 adsorption isotherm of NbU-9-NH₂ with fitting by L-F model.



Fig. S18 CH_4 adsorption isotherm of NbU-9 with fitting by L-F model.