Supporting Information

A Zn(II) Pillared-Layer Ultramicroporous Metal-Organic Framework with Matching Molecular Pockets for C₂H₂/CO₂ Separation

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Experimental Section

Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O, 99%), 5-methyl-isophthalic acid (H₂mipa, 99%), 3, 5-diamino-1,2,4-triazole (Hdatz, 98%), ethanol (EtOH, 99%) were were used as received unless otherwise stated.

Synthesis of Zn-mipa-datz

Zn(NO₃)₂·6H₂O (1 mmol, 0.298 g), 5-methyl-isophthalic acid (H₂mipa, 0.5 mmol, 0.9 g), 3, 5-diamino-1,2,4-triazole (Hdatz, 1 mmol, 0.099 g) were dissolved in 12 mL H₂O/EtOH mixed solution (5/7, v/v). After 30 minutes of sonication treatment, the resulting solution was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 150 °C under autogenous pressure for 72 hours. After slowly cooling down to room temperature, the colorless crystals of **Zn-mipa-datz** were washed with H₂O/EtOH (1:1, v/v) mixed solution three times and dried at room temperature (yield= 52 % based on Zn).

Physical measurement

Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku Mini Flex II X-ray diffractometer (Cu K_{α}, $\lambda = 1.54059$ Å) with a voltage of 40 kV and a current of 15 mA. **Zn-mipa-datz** were subjected to a scanning at 20 from 5°-50° with a scanning rate of 5 °/min.

Thermogravimetric analyses (TGA) were conducted using a METTLER TGA2 instrument in N_2 flow with a heating rate of 10 °C/min to measure the decomposition of materials.

Single X-ray diffraction characterization

Crystal data of **Zn-mipa-datz** were collected at 298 K on a Bruker D8 Venture diffractometer equipped with Ga K α microfocus X-ray generator (λ =1.34139 Å), Photon II detector. The data were empirically corrected for X-ray adsorption with Sadabs,^{1,2} in the Bruker APEX II software suite. The structures were solved by direct method and refined with full-matrix least-squares technique using the SHELXTL program package.^{2,3} Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were generated geometrically (C–H 0.95 Å). The Olex Solvent Mask treatment was applied because the guest molecule is extremely disordered and

cannot be modeled. The crystallographic data of **Zn-mipa-datz** were summarized in Table S1. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2323202, and can be obtained free of charge (http://www.ccdc.cam.ac.uk/data_request/cif).

Modeling Studies

The Grand Canonical Monte Carlo (GCMC) simulations were performed for CO₂ and C₂H₂ adsorption on **Zn-mipa-datz**. The framework of **Zn-mipa-datz** and gas molecules were both treated as rigid bodies. The beneficial adsorption sites were simulated by the simulated by the fixed loading task and Metropolis method at 298 K and 1 bar. The loading steps, equilibration steps and production steps were all set to 2.0 $\times 10^7$. The saturation/maximum uptakes were modeled at 298 K using the fixed pressure task with 1.0×10^5 equilibration steps, followed by 2.0×10^7 production steps for calculating the ensemble averages. The gas-framework interactions were described by the standard universal force field (UFF). The atomic partial charges of the framework were used for the Qeq method, and the guest gas molecules were optimized using the DMol3 method and adopted the ESP-fitted charge. The cut-off radius used for the Lennard–Jones interactions is 18.5 Å.³

Gas adsorption isotherm

The thermodynamic adsorption isotherms for CO_2 and C_2H_2 were conducted on 3FLEX (Micromertics). Prior to each measurement, **Zn-mipa-datz** powder (~100 mg) were evacuated under a dynamic vacuum at 80 °C for 6 hours to remove the guest molecules.

Dynamic breakthrough test

Before the penetration experiment, 1.37 g sample was loaded into a stainless-steel sample column and heated at 80 °C in a 20 mL/min He flow to remove solvent molecules. After activation, the sample column was cooled to room temperature. A mixture of CO_2 (0.5 mL/min) and C_2H_2 (0.5 mL/min) was injected into the sample column, and a TCD-Thermal Conductivity Detector was used. Real-time monitoring of the composition and concentration of the gas at the outlet end of the sample column. In the gas penetration cycle experiment, the sample column was regenerated at 20 mL/min He flow after each penetration experiment.

Calculation of adsorption enthalpy

In order to extract the coverage-dependent isosteric adsorption enthalpy (Q_{st}), the CO₂ and C₂H₂ gas adsorption isotherms at 273 K and 298 K were all fitted using the virial-type expression:

$$\ln(P) = \ln(N) + (\frac{1}{T}) \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$
 (S1)

where *P* is the pressure in kPa, *N* is the amount uptake in mmol/g, *T* is the temperature in K, a_i and b_j are virial coefficients that are independent of temperature, and *m* and *n* are the number of coefficients used to adequately describe the isotherm.

$$Q_{st} = -R\sum_{i=0}^{n} a_i N^i$$
 (S2)

The adsorption enthalpy at zero loading of CO_2 was obtained according to Equation S2 based on the adsorption data collected at 273 and 298 K. Where Q_{st} in kJ/mol, *R* is the universal gas constant.

Calculation of adsorption selectivity

The single-component CO_2 and C_2H_2 adsorption data of **Zn-mipa-datz** at 298 K were fitted by the two-site Langmuir-Freundlich equation, and the correlation coefficient was calculated (Equation S3):

$$q = Q_{A,sat} \frac{b_{A} P^{\nu_{A}}}{1 + b_{A} P^{\nu_{A}}} + Q_{B,sat} \frac{b_{B} P^{\nu_{B}}}{1 + b_{B} P^{\nu_{B}}}$$
(S3)

where, q is the gas adsorption capacity of the adsorbent (unit: mmol/g); Q_A , _{sat} and Q_B , _{sat} were the saturated absorption at sites A and B (unit: mmol/g), respectively. P is the gas pressure in the equilibrium state (unit: kPa); b_A and b_B were the affinity coefficients at sites A and B, respectively (unit: kPa^{-vi}). v is the Freundlich index.

The adsorption selectivity of adsorbent *i* relative to adsorbent *j* was established by using ideal adsorption solution theory (IAST) and calculated as follows:

$$S_{i'_j} = \frac{x_i y_j}{x_j y_i}$$
(S4)

Among them, x_i and x_j represent the equilibrium adsorption capacity of adsorbent *i* and

j in the adsorbent (unit: mmol/g), respectively. y_i and y_j represent the molar ratio of adsorbent *i* and *j* in the adsorbent mixture, respectively.

Kinetic adsorption measurements and calculation

Time-dependent adsorption determination of CO_2/C_2H_2 was performed with an automatic volumetric adsorption apparatus BELSORP-HP/MAXII at 298 K. Prior to adsorption measurement, the samples were activated at 80 °C for 6 h under high vacuum. The resulting curves were used to calculate the diffusional time constants by using the following Equation S5:

$$\frac{M_t}{M_e} = 1 - exp(-kt)$$
(S5)

Where M_t is the mass uptake at time t, M_e is the mass uptake at equilibrium, and k is the kinetic rate constant. After normalization of kinetic adsorption data, t (min) and M_t/M_e were taken as x and y axes, respectively.



Figure S1 TGA curve of as-synthesized Zn-mipa-datz powder.



Figure S2 Virial fitting of CO₂ adsorption data for Zn-mipa-datz at 273 and 298 K.



Figure S3 Virial fitting of C₂H₂ adsorption data for Zn-mipa-datz at 273 and 298 K.



Figure S4 Dual-site Langmuir-Freundlich fitting of CO₂ adsorption isotherm at 298 K for **Zn-mipa-datz**.



Figure S5. Dual-site Langmuir-Freundlich fitting of C_2H_2 adsorption isotherm at 298 K for Zn-mipa-datz.



Figure S6. Adsorption kinetics profiles (point) and linear fittings (line) of C_2H_2 (black) and CO_2 (red) for **Zn-datz-mipa** at 298 K.



Figure S7. Moisture stability tests of Zn-mipa-datz. The PXRD patterns of the Zn-mipa-datz stay unchanged after breakthrough tests and the subsequent 5-months moisture exposure (*ca*. 35% RH).

| Compounds | Zn-mipa-datz |
|----------------------------------|-----------------------------|
| Empirical formula | $C_{13}H_{14}N_{10}O_4Zn_2$ |
| Formula weight | 505.08 |
| Temperature (K) | 298 |
| Crystal system | monoclinic |
| Space group | C2/m |
| <i>a</i> (Å) | 18.279(2) |
| <i>b</i> (Å) | 26.478(5) |
| <i>c</i> (Å) | 13.2955(17) |
| α (°) | 90 |
| eta (°) | 133.43 |
| $V(Å^3)$ | 4673.5(12) |
| Ζ | 8 |
| $D_{\rm c}$ (g/cm ³) | 1.436 |
| Reflections collected | 29553 |
| <i>R</i> _{int} | 0.0506 |
| $R_1 [I > 2\sigma(I)]^{[a]}$ | 0.0361 |
| $wR_2 [I > 2\sigma(I)]^{[b]}$ | 0.1004 |
| R_1 (all data) | 0.0418 |
| wR_2 (all data) | 0.1047 |
| GOF | 1.070 |

Table S1. Summary of the single-crystal diffraction data of Zn-mipa-datz.

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$.

| Compound | Zn-mipa-datz |
|---------------------------------|--------------|
| Topology | рси |
| Pore size (Å) | 5.3 |
| Density (g/cm ³) | 1.436 |
| Volume ratio (%) ^[a] | 30.7 |
| Pore volume | 0.214 |
| (calculated) | |
| Pore volume | 0.206 |
| (measured) ^[b] | |

Table S2. Summary of the structural information and adsorption data of Zn-mipa-datz.

[a] Volume ratio estimated by PLATON software⁴ without consideration of the solvent in the pore.

[b] The measured pore volume (cm³/g) calculated from the uptake at $P/P_0 = 0.95$ assuming the liquid CO₂ filling in the pore.

Table S3. Comparison of **Zn-datz-mipa** with other benchmark materials for C_2H_2/CO_2

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|-----|----------|--|
| COL | anrotion | |
| SCI | Jarahon. | |
| | | |

| | C ₂ H ₂ | CO ₂ | IAST | $Q_{ m st}$ | $Q_{ m st}$ | | |
|-----------------------|-------------------------------|-----------------|----------------------------------|-------------------|-------------|-----|--|
| | uptake | uptake | (C ₂ H ₂ / | (C_2H_2) | (CO_2) | | |
| Adsorbent | (<i>a</i>) 1 bar | @ 1 bar | CO ₂) | kJ/mo | kJ/mol- | Ref | |
| | (mmol/ | (mmol/ | (50/50 | l ⁻¹) | 1) | | |
| | g) | g) |) | | | | |
| UTSA-300 | 3.08 | 0.15 | 743 | 57.6 | | 5 | |
| CPL-1-NH ₂ | 1.84 | 0.21 | 119 | 50.0 | 33.0 | 6 | |
| SIFSIX-dps-Cu | 4.57 | 0.61 | 1786.6 | 60.5 | | 7 | |
| GeFSIX-dps-Cu | 4.04 | 0.45 | 171.9 | 56.3 | | | |
| ZNU-9 | 7.94 | 4.32 | 10.3 | 33.1 | 26.6 | 8 | |
| ZNU-8 | 5.05 | 2.22 | 3.74 | 27.2 | 23.4 | 0 | |
| BSF-2 | 1.85 | 1.33 | 5.1 | 37.3 | 28.7 | 9 | |
| BSF-3 | 3.59 | 2.11 | 16.3 | 42.7 | 22.4 | 10 | |
| BSF-10 | 2.9 | 1.15 | 5.86 | 34.8 | 22.9 | 11 | |
| ZNU-1 | 3.4 | 1.7 | 56.6 | 54.0 | 44.0 | 12 | |
| PCP-31 | 2.23 | 1.56 | 7 | 53 | 30 | 13 | |
| PCP-32 | 3.79 | 1.56 | 8 | 36 | 26 | 10 | |
| UTSA-74a | 4.82 | 2.85 | 9 | 32 | 25 | 14 | |
| SIFSIX-Cu-TPA | 8.27 | 4.79 | 5.3 | 39.1 | 25.7 | 15 | |
| SIFSIX-21-Ni | 4.02 | 1.3 | 27.7 | 37.9 | 19.8 | 16 | |
| TIFSIX-2-Ni-i | 4.2 | 4.5 | 6.1 | 40 | 34 | 17 | |

| MPM-1-TIFSIX | 4.53 | 3.88 | 0.83 | 30.1 | 48.4 | 18 |
|--|------|------|------|-------|-------|--------------|
| SIFSIX-17-Ni | 3.3 | 2.3 | 11.7 | 44.2 | 40.2 | 19 |
| TIFSIX-17-Ni | 3.26 | 2.1 | 20.9 | 48.3 | 37.8 | |
| SNNU-45 | 5.98 | 4.3 | 8.5 | 39.9 | 27.1 | 20 |
| CuI@UiO-66- (COOH) ₂ | 2.3 | 0.88 | 185 | 74.5 | 28.9 | 21 |
| FeNi-M'MOF | 4.29 | 2.72 | 24 | 27 | 24.5 | 22 |
| NKMOF-1-Ni | 2.72 | 2.28 | 25 | 60.3 | 40.9 | 23 |
| IPM-101 | 2.55 | 3.04 | 12.3 | 43.7 | 30.7 | 24 |
| [Ni ₃ (HCOO) ₆] | 2.38 | 1.73 | 22 | 40.9 | 24.5 | 25 |
| [Ni(dpip)]·2.5DMF· H ₂ O | 3.73 | 2.62 | 1.9 | 41.7 | 30.3 | 26 |
| ATC-Cu | 5.0 | 4.0 | 53.6 | 79.1 | | 27 |
| Zn ₂ (Pydc)(Ata) ₂ | 2.1 | 1.47 | 3.9 | 43.1 | 32.1 | 28 |
| sql-16-Cu-NO ₃ | 1.55 | 0.74 | 78 | 38.6 | 25.6 | 29 |
| Zn-datz-mipa | 2.23 | 1.98 | 2.5 | 29.11 | 27.36 | This work |

Table S4. Comparison of Zn-datz-mipa with TIFSIX-2-Cu-i, SIFSIX-3-Ni for C_2H_2/CO_2 separation.

| Adsorbent | C ₂ H ₂ uptake @ 1 bar (mmol/g) | CO ₂ uptake @ 1 bar (mmol/g) | IAST (C ₂ H ₂ /CO ₂) (50/50) | $Q_{\rm st}$ (C ₂ H ₂ kJ/mol ⁻ ¹) | $Q_{\rm st}$ (CO ₂ kJ/mol ⁻ ¹) | Ref |
|---------------|--|--|--|---|---|--------------|
| TIFSIX-2-Cu-i | 4.1 | 4.3 | 10.7 | 46.3 | 35.8 | 30 |
| SIFSIX-3-Ni | 3.3 | 2.7 | 0.07 | 36.7 | 50.9 | |
| Zn-datz-mipa | 2.23 | 1.98 | 2.5 | 29.11 | 27.36 | This work |

Table S5. Comparison of **Zn-datz-mipa** with **Zn-atz-ipa** and **Zn-atz-ox** for C_2H_2/CO_2 separation.

| Adsorbent | C ₂ H ₂ uptake @ 1 bar (mmol/g) | CO ₂ uptake @ 1 bar (mmol/g) | IAST (C ₂ H ₂ /C O ₂) (50/50) | $\begin{array}{c} Q_{\rm st} \\ ({\rm C_2H_2} \\ \rm kJ/mo \\ l^{-1}) \end{array}$ | $\begin{array}{c} Q_{\rm st} \\ ({\rm CO}_2 \\ \rm kJ/mol^- \\ {}^1) \end{array}$ | Ref |
|--------------|--|--|--|--|---|-----------|
| Zn-atz-ipa | 1.99 | 1.90 | | 37.5 | 31.5 | 31 |
| Zn-atz-ox | 2.74 ^[a] | 3.61 ^[b] | 1.1 ^[a] | 42.9 ^[a] | 40.8 | 32 |
| Zn-datz-mipa | 2.23 | 1.98 | 2.5 | 29.11 | 27.36 | This work |

[a] Adopted from ref *Science* **2010**, *330*, 650-653, [b] At 293 K.

Table S6. Dual-site Langmuir-Freundlich fitting parameters of CO_2 and C_2H_2 adsorption isotherm 298 K for **Zn-mipa-datz**.

| Site A | | | | Site B | | |
|-------------------------------|----------------------|-------------------------------|----------|--------------------------------|--------------------------------|---------|
| | $Q_{A,sat}$ (mmol/g) | b_A (kPa ^{vi}) | v_A | Q _{B,sat} (mmol/g) | b_B (kPa ^{-vi}) | v |
| CO ₂ | 2.60429 | 0.03923 | 0.94805 | 3.33126e ⁻¹⁷ | 13.62790 | 2.03802 |
| C ₂ H ₂ | 1.98463 | 0.04824 | 0.791239 | 0.95796 | 0.24129 | 1.11718 |

Table S7. Selectivity and gas adsorption enthalpy of Zn-mipa-datz.

| Compounds | $Q_{ m st}{}^{[a]}$ | | IAST selectivity ^[b] |
|--------------|---------------------|----------|---------------------------------|
| Compounds | CO ₂ | C_2H_2 | C_2H_2/CO_2 |
| Zn-mipa-datz | 27.36 | 29.11 | 2.5 |

[a] Gas adsorption enthalpy (Q_{st} , kJ mol⁻¹).

[b] Calculated from IAST theory with a ratio of 50:50 at 298 K and 100 kPa.

References

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

[2] Sheldrick, G. M. A short history of SHELX. Acta Crystallogr. A 2008, 64, 112-

122.

[3] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3-8.

[4] Spek, A. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. 2003, 36, 7-13.

[5] Lin, R.-B.; Li, L.; Wu, H.; Arman, H.; Li, B.; Lin, R.-G.; Zhou, W.; Chen, B. Optimized Separation of Acetylene from Carbon Dioxide and Ethylene in a Microporous Material. *J. Am. Chem. Soc.* **2017**, *139*, 8022-8028.

[6] Yang, L.; Yan, L.; Wang, Y.; Liu, Z.; He, J.; Fu, Q.; Liu, D.; Gu, X.; Dai, P.; Li, L.; Zhao, a. X. Adsorption site selective occupation strategy within a metal–organic framework for highly efficient sieving acetylene from carbon dioxide. *Angew. Chem. Int. Ed.* **2021**, *133*, 4620-4624.

[7] Wang, J.; Zhang, Y.; Su, Y.; Liu, X.; Zhang, P.; Lin, R.-B.; Chen, S.; Deng, Q.; Zeng, Z.; Deng, S.; Chen, B. Fine pore engineering in a series of isoreticular metal-organic frameworks for efficient C2H2/CO2 separation. *Nat. Commun.* 2022, *13*, 200.
[8] Zhang, Y.; Sun, W.; Luan, B.; Li, J.; Luo, D.; Jiang, Y.; Wang, L.; Chen, B. Topological Design of Unprecedented Metal-Organic Frameworks Featuring Multiple Anion Functionalities and Hierarchical Porosity for Benchmark Acetylene Separation. *Angew. Chem. Int. Ed.* 2023, *62*, e202309925.

[9] Zhang, Y.; Yang, L.; Wang, L.; Cui, X.; Xing, H. Pillar iodination in functional boron cage hybrid supramolecular frameworks for high performance separation of light hydrocarbons. *J. Mater. Chem. A* **2019**, *7*, 27560-27566.

[10]Zhang, Y.; Hu, J.; Krishna, R.; Wang, L.; Yang, L.; Cui, X.; Duttwyler, S.; Xing, H. Rational design of microporous MOFs with anionic boron cluster functionality and cooperative dihydrogen binding sites for highly selective capture of acetylene. *Angew. Chem. Int. Ed.* **2020**, *132*, 17817-17822.

[11]Sun, W.; Jin, Y.; Wu, Y.; Lou, W.; Yuan, Y.; Duttwyler, S.; Wang, L.; Zhang, Y. A new boron cluster anion pillared metal organic framework with ligand inclusion and its selective acetylene capture properties. *Inorg. Chem. Front.* **2022**, *9*, 5140-5147.

[12] Wang, L.; Sun, W.; Zhang, Y.; Xu, N.; Krishna, R.; Hu, J.; Jiang, Y.; He, Y.; Xing, H. Interpenetration Symmetry Control Within Ultramicroporous Robust Boron Cluster Hybrid MOFs for Benchmark Purification of Acetylene from Carbon Dioxide. *Angew. Chem. Int. Ed.* **2021**, *60*, 22865-22870.

[13]Duan, J.; Higuchi, M.; Zheng, J.; Noro, S.-i.; Chang, I. Y.; Hyeon-Deuk, K.; Mathew, S.; Kusaka, S.; Sivaniah, E.; Matsuda, R.; Sakaki, S.; Kitagawa, S. Density Gradation of Open Metal Sites in the Mesospace of Porous Coordination Polymers. *J. Am. Chem. Soc.* **2017**, *139*, 11576-11583.

[14]Luo, F.; Yan, C.; Dang, L.; Krishna, R.; Zhou, W.; Wu, H.; Dong, X.; Han, Y.; Hu, T.-L.; O'Keeffe, M.; Wang, L.; Luo, M.; Lin, R.-B.; Chen, B. UTSA-74: A MOF-74 Isomer with Two Accessible Binding Sites per Metal Center for Highly Selective Gas Separation. *J. Am. Chem. Soc.* **2016**, *138*, 5678-5684.

[15]Li, H.; Liu, C.; Chen, C.; Di, Z.; Yuan, D.; Pang, J.; Wei, W.; Wu, M.; Hong, M. An Unprecedented Pillar-Cage Fluorinated Hybrid Porous Framework with Highly Efficient Acetylene Storage and Separation. *Angew. Chem. Int. Ed.* **2021**, *133*, 7625-

7630.

[16]Kumar, N.; Mukherjee, S.; Harvey-Reid, N. C.; Bezrukov, A. A.; Tan, K.; Martins, V.; Vandichel, M.; Pham, T.; van Wyk, L. M.; Oyekan, K. Breaking the trade-off between selectivity and adsorption capacity for gas separation. *Chem* **2021**, *7*, 3085-3098.

[17] Jiang, M.; Cui, X.; Yang, L.; Yang, Q.; Zhang, Z.; Yang, Y.; Xing, H. A thermostable anion-pillared metal-organic framework for C2H2/C2H4 and C2H2/CO2 separations. *Chem. Eng. J.* **2018**, *352*, 803-810.

[18]Forrest, K. A.; Pham, T.; Chen, K.-J.; Jiang, X.; Madden, D. G.; Franz, D. M.; Hogan, A.; Zaworotko, M. J.; Space, B. Tuning the Selectivity between C2H2 and CO2 in Molecular Porous Materials. *Langmuir* **2021**, *37*, 13838-13845.

[19] Mukherjee, S.; Kumar, N.; Bezrukov, A. A.; Tan, K.; Pham, T.; Forrest, K. A.; Oyekan, K. A.; Qazvini, O. T.; Madden, D. G.; Space, B.; Zaworotko, M. J. Amino-Functionalised Hybrid Ultramicroporous Materials that Enable Single-Step Ethylene Purification from a Ternary Mixture. *Angew. Chem. Int. Ed.* **2021**, *60*, 10902-10909.

[20] Li, Y. P.; Wang, Y.; Xue, Y. Y.; Li, H. P.; Zhai, Q. G.; Li, S. N.; Jiang, Y. C.; Hu, M. C.; Bu, X. Ultramicroporous building units as a path to Bi-microporous metal– organic frameworks with high acetylene storage and separation performance. *Angew. Chem. Int. Ed.* **2019**, *131*, 13724-13729.

[21]Zhang, L.; Jiang, K.; Yang, L.; Li, L.; Hu, E.; Yang, L.; Shao, K.; Xing, H.; Cui, Y.; Yang, Y. Benchmark C2H2/CO2 separation in an ultra-microporous metal–organic framework via copper (I)-Alkynyl chemistry. *Angew. Chem. Int. Ed.* **2021**, *133*, 16131-16138.

[22]Gao, J.; Qian, X.; Lin, R. B.; Krishna, R.; Wu, H.; Zhou, W.; Chen, B. Mixed metal–organic framework with multiple binding sites for efficient C2H2/CO2 separation. *Angew. Chem. Int. Ed.* **2020**, *59*, 4396-4400.

[23]Peng, Y. L.; Pham, T.; Li, P.; Wang, T.; Chen, Y.; Chen, K. J.; Forrest, K. A.; Space, B.; Cheng, P.; Zaworotko, M. J. Robust ultramicroporous metal–organic frameworks with benchmark affinity for acetylene. *Angew. Chem. Int. Ed.* **2018**, *57*, 10971-10975.

[24] Sharma, S.; Mukherjee, S.; Desai, A. V.; Vandichel, M.; Dam, G. K.; Jadhav, A.; Kociok-Köhn, G.; Zaworotko, M. J.; Ghosh, S. K. Efficient Capture of Trace Acetylene by an Ultramicroporous Metal–Organic Framework with Purine Binding Sites. *Chem. Mater.* **2021**, *33*, 5800-5808.

[25]Zhang, L.; Jiang, K.; Zhang, J.; Pei, J.; Shao, K.; Cui, Y.; Yang, Y.; Li, B.; Chen, B.; Qian, G. Low-Cost and High-Performance Microporous Metal–Organic Framework for Separation of Acetylene from Carbon Dioxide. *ACS Sustainable Chem. Eng.* **2019**, *7*, 1667-1672.

[26]Li, Y.-Z.; Wang, G.-D.; Ma, L.-N.; Hou, L.; Wang, Y.-Y.; Zhu, Z. Multiple Functions of Gas Separation and Vapor Adsorption in a New MOF with Open Tubular Channels. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4102-4109.

[27]Niu, Z.; Cui, X.; Pham, T.; Verma, G.; Lan, P. C.; Shan, C.; Xing, H.; Forrest, K. A.; Suepaul, S.; Space, B. A MOF-based ultra-strong acetylene nano-trap for highly efficient C2H2/CO2 separation. *Angew. Chem. Int. Ed.* **2021**, *133*, 5343-5348.

[28]Xu, N.; Jiang, Y.; Sun, W.; Li, J.; Wang, L.; Jin, Y.; Zhang, Y.; Wang, D.; Duttwyler, S. Gram-Scale Synthesis of an Ultrastable Microporous Metal-Organic Framework for Efficient Adsorptive Separation of C2H2/CO2 and C2H2/CH4. *Molecules* **2021**, *26*, 5121.

[29] Sanii, R.; Hua, C.; Patyk-Kazmierczak, E.; Zaworotko, M. J. Solvent-directed control over the topology of entanglement in square lattice (sql) coordination networks. *Chem. Commun.* **2019**, *55*, 1454-1457.

[30]Chen, K.-J.; Scott, Hayley S.; Madden, David G.; Pham, T.; Kumar, A.; Bajpai, A.; Lusi, M.; Forrest, Katherine A.; Space, B.; Perry, John J.; Zaworotko, Michael J. Benchmark C2H2/CO2 and CO2/C2H2 Separation by Two Closely Related Hybrid Ultramicroporous Materials. *Chem* **2016**, *1*, 753-765.

[31] Chen, K.-J.; Madden, D. G.; Mukherjee, S.; Pham, T.; Forrest, K. A.; Kumar, A.; Space, B.; Kong, J.; Zhang, Q.-Y.; Zaworotko, M. J. Synergistic sorbent separation for one-step ethylene purification from a four-component mixture. *Science* **2019**, *366*, 241–246.

[32] Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. Direct Observation and Quantification of CO2 Binding Within an Amine-Functionalized Nanoporous Solid. *Science* **2010**, *330*, 650-653.