High and selective capture of low-concentration CO₂ with an anion-functionalized ultramicroporous metal-organic framework

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ABSTRACT CO₂ capture, especially under low-pressure range, is of significance to maintain long-duration human operation in confined spaces and decrease the CO₂ corrosion and freezing effect for the liquefaction of natural gas. Herein, we for the first time report a novel anion-functionalized ZU-16-Co (TIFSIX-3-Co, TIFSIX=hexafluorotitanate (TiF₆²⁻), 3=pyrazine), which exhibits one-dimensional pore channels decorated by abundant F atoms, for efficient CO₂ capture at a concentration around 400–10,000 ppm. Among its iso-structural MFSIX-3 (M=Si, Ti, Ge) family materials, ZU-16-Co with fine-tuned pore size of 3.62 Å exhibits the highest CO₂ uptake at 0.01 bar (10,000 ppm) and 1 bar (2.63 and 2.87 mmol g⁻¹, respectively). The high CO₂ capture ability of ZU-16-Co originates from the fine-tuned pore dimensions with strong F...C=O host-guest interactions and relatively large pore volumes coming from its longer coordinated Ti–F–Co distance (3.9 Å) in *c* direction. The excellent carbon trapping performance was further verified by dynamic breakthrough tests for CO₂/N₂ (1/99 and 15/85) and CO₂/CH₄ (50/50) mixtures. The adsorption and separation performances, resulting from the fine-tuned pore system with periodic arrays of exposed functionalities, demonstrate that ultramicroporous ZU-16-Co can be a promising adsorbent for low-concentration carbon capture.

Keywords: carbon capture, ultramicroporous metal-organic frameworks, gas adsorption, CO₂/N₂ separation, natural gas purification.

INTRODUCTION

Capture of carbon dioxide (CO₂) is of prime importance and continues to attract intensive research interest. Re-

cently, the global climate change resulting from the emission of greenhouse gas has become increasingly severe [1–4]. Atmospheric CO₂ concentration has surpassed 400 ppm on several occasions since 2013, which represents an increase of over 100 ppm since pre-industrial revolution levels [5–9]. Furthermore, the requirement for long-duration human task performance in confined spaces such as submarines, spacecrafts or under-ground citadels has made the removal of low-concentration CO₂ (< 0.5%) a critical technology [8,10–13]. In particular, the capture of greenhouse gas from dilute emissions has been listed as one of seven chemical separations to change the world [14–16]. Therefore, the removal of low-concentration CO₂ from air, confined spaces, and natural gas has become a growing area of research but with great challenges. Currently, the separation of CO₂ from flue gas (73%–77% N₂, 15%–16% CO₂, as well as water, SO₂ and O₂) [2,17] has been widely investigated and many progresses have been made [18–20]. However, only limited studies have focused on the removal of low-concentration CO₂ around 0.04%–1% (400–10,000 ppm), and it is urgent and highly desirable to design sustainable materials with low cost for carbon capture in long-term confined space applications and natural gas purification.

Compared with the well-developed amine scrubbers, advanced physisorption with physical sorbents has been investigated as promising alternatives and significantly reduced energy footprint for carbon capture [2,17]. A limited number of metal-organic frameworks (MOFs) were investigated for low-concentration CO₂ (0.5%–5%) trapping. For example, Yang *et al.* [21] designed hydroxyl-functionalized MOFs (NOTT-300) to bind with CO₂.

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The CO₂ uptake on NOTT-300 at 0.15 bar and 273 K is 2.64 mmol g⁻¹. However, the CO₂ uptake at low pressure of 0.01 bar and 293 K is less than 0.22 mmol g⁻¹. Long's group [22] synthesized an alkylamine-appended MOF mmen-Mg₂(dobpdc) (mmen: *N,N'*-dimethylethylenediamine; dobpdc⁴⁻: 4,4'-dioxido-3,3'-biphenyldicarboxylate), which shows an exceptional capacity for CO₂ (2.0 mmol g⁻¹) at 0.39 mbar (390 ppm) and 298 K, conditions relevant to removal of CO₂ from air. However, the calculated isosteric heats of adsorption for mmen-Mg₂(dobpdc) is -71 kJ mol⁻¹, which likely corresponds to the chemical adsorption of CO₂ onto the amine sites and makes the adsorbent difficult to regenerate. Therefore, there is still a great challenge to design porous adsorbents with appropriate functional sites combined with suitable pore structures for CO₂ capture at ultra-low concentration. Among the physisorption materials, anion-functionalized MOFs are a new sub-class of porous materials constructed by the metal moiety, organic linkers, and inorganic anions. The reticular design strategy enables the precise control over the pore chemistry of anion-functionalized MOFs by exploitation of molecular blocks [23–32]. Previous study reported by Eddaoudi's group [8] showed that, at a low concentration of 400 ppm and 298 K, NbOFFIVE-1-Ni and SIFSIX-3-Cu adsorbs 1.3 and 1.2 mmol g⁻¹ CO₂, respectively. This study also indicated that reducing the pore size of porous adsorbent is beneficial to enhancing the interactions between CO₂ molecules and the host framework, thus leading to high CO₂ uptake at low pressures. However, the reduction of the pore dimensions often results in the small pore volumes, which in turn leads to low adsorption capacities.

Herein, an anion-functionalized MOF, ZU-16-Co (also termed as TIFSIX-3-Co, TIFSIX=hexafluorotitanate (TiF₆²⁻), 3=pyrazine, ZU=Zhejiang University) with fine-tuned pore chemistry was for the first time reported for the low-concentration CO₂ capture. The highly ordered Lewis basic sites of anions confined in the ultramicropores greatly enhance the binding ability for CO₂. Among MFSIX-3 family materials and NbOFFIVE-1-Ni, ZU-16-Co exhibits the highest pore volume (0.11 cm³ g⁻¹) and CO₂ capture capacity (2.63 mmol g⁻¹) at the concentration of 0.01 bar (10,000 ppm). The excellent trace CO₂ capture ability of ZU-16-Co was verified by static gas adsorption isotherms and dynamic breakthrough tests for CO₂/N₂ (1/99) and CO₂/CH₄ (50/50) mixtures. More importantly, ZU-16-Co obtained in a straightforward way using inexpensive precursors, is robust and easily handled. This comparative study clearly illustrates the structure-function relationships of ZU-16-Co for CO₂

trapping and presents its suitability to remove carbon under low concentrations.

EXPERIMENTAL SECTION

Synthesis of ZU-16-Co (TIFSIX-3-Co)

All reagents were commercially available and used as received without further purification. In a typical process, Co(NO₃)₂·6H₂O (1 mmol), (NH₄)₂TiF₆ (1 mmol) and pyrazine (1.0 g) were mixed in 2 mL water and 2 mL methanol, and stirred for 2 d at room temperature to yield pink color powders. The pink powders were filtrated and washed with 10 mL methanol to remove unreacted reagents. The resultant powders were then heated at 413 K under vacuum conditions for 24 h to obtain the ZU-16-Co material.

Powder X-ray diffraction and structure refinement

Powder X-ray diffraction (PXRD) was carried out at room temperature on a Bruker D8 Advance θ/θ diffractometer using Cu K α radiation ($\lambda=1.5418$ Å). Data treatment and structure solution were initially performed using FullProf software [33]. Then the JANA program was used for Rietveld refinements [34]. CCDC-1979341 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Breakthrough tests

The breakthrough experiments were accomplished by a dynamic gas breakthrough equipment [24]. The experiment was conducted using a stainless-steel column (4.6 mm inner diameter $\times$ 50 mm). The weight of the sample powder packed in the column was 0.70 g for ZU-16-Co. The column was firstly activated at 373 K with He flow (10 mL min⁻¹) for 12 h. After activation, the mixed gas was introduced. Outlet gas from the column was monitored using gas chromatography (GC-490, Agilent) with a thermal conductivity detector (TCD) coupled with an flame ionization detector (FID). After the breakthrough experiment, the sample was regenerated at 373 K with He flow (5 mL min⁻¹).

Other detailed descriptions of experimental techniques and simulations are given in the Supplementary information.

RESULTS AND DISCUSSION

ZU-16-Co was directly constructed by cheap raw materials of TiF₆²⁻ anion, Co²⁺, and pyrazine (Fig. 1a), in which TiF₆²⁻ in the third dimension pillared the two-

Figure 1 Schematic representation of the (a) construction and (b) the pore structure of ZU-16 (TIFSIX-3) materials with pyrazine linker.

dimensional layers formed by Co^{2+} and pyrazine (Fig. 1b). The indexation of the PXRD diagram, carried out using the McMaille software, yielded a primitive orthorhombic cell. The cell parameters, $a=b=7.086(5)$, $c=7.830(5)$, were refined by a whole powder pattern fitting using the Le Bail method, implemented in FULLPROF software. The final Rietveld structure refinement permitted access to satisfactory results: $R_{\text{Bragg}}=0.0316$ and $R_{\text{Factor}}=0.041$ (Table S1). The consistence between the as-synthesized powder patterns with the Rietveld refinement XRD patterns presents the high purity of the as-synthesized ZU-16-Co (Fig. S1). Notably, the cell parameters (a -, b -, and c -axes) of ZU-16-Co are larger than those of isostructural MFSIX-3 materials, signifying ZU-16-Co with larger pore dimensions and pore volume, and the pore volume of ZU-16-Co derived from CO_2 adsorption isotherm at 273 K is $0.11 \text{ cm}^3 \text{ g}^{-1}$ (Fig. S2), which is indeed larger than that of its isostructural materials (Table 1). The Brunauer-

Emmett-Teller (BET) surface area of ZU-16-Co calculated from the CO_2 isotherm at 196 K (Fig. S3) is $260 \text{ m}^2 \text{ g}^{-1}$. The differences in cell parameters present the significant effect of altering the anions and metal ions on systematical tuning the pore dimensions of anion-functionalized MOFs. The reason for the larger cell parameters of ZU-16-Co is that the Ti-F-Co distance ($3.9 \text{ \AA}$) in ZU-16-Co is longer than that in other materials (Table S2). The relatively large pore volume and small pore size of $3.62 \text{ \AA}$ may offer ZU-16-Co high capacity for gas molecules compared with its isostructural materials. The thermal gravimetric analysis (TGA, Fig. S4a) presents that ZU-16-Co is stable until 518 K, and the scanning electron microscopy (SEM) image (Fig. S4b) illustrates that ZU-16-Co exhibits two-dimensional (2D) flake-like morphology with diameter of 1–2 μm .

ZU-16-Co with the moderate surface area and pore volume (Table 1), comprises 1D pore channels with uniform narrow pore size and high density of inorganic anions. These properties are favorable for CO_2 capture. Keeping this in mind, low-pressure CO_2 sorption data were collected on ZU-16-Co and other anion-functionalized MOFs at 298 K (Fig. 2a). Anion-functionalized MOFs provide the expected high affinity for CO_2 at low concentrations as evidenced by the steepness of the CO_2 adsorption isotherms and the attainment of the plateau at relatively low CO_2 pressures. Notably, ZU-16-Co exhibits high CO_2 uptake with a value of 2.87 mmol g^{-1} at 298 K and 1.0 bar. Detailed analysis of the CO_2 adsorption isotherms associated with the isostructural MOFs shows that ZU-16-Co exhibits the highest CO_2 adsorption capacity of 2.63 mmol g^{-1} at 10,000 ppm, among its isostructural materials and the interpenetrated anion-functionalized materials (Fig. 2b), such as SIFSIX-3-Cu (2.34 mmol g^{-1}) [6], NbOFFIVE-1-Ni (1.71 mmol g^{-1})

Table 1 Comparison of the structural information of anion-functionalized ultramicroporous MOFs and CO_2 sorption performances

Material	Pore size ($\text{\AA}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	BET ($\text{m}^2 \text{ g}^{-1}$)	CO_2 uptake at 400 ppm (mmol g^{-1})	CO_2 uptake at 10,000 ppm (mmol g^{-1})	CO_2 uptake at 1 bar (mmol g^{-1})
ZU-16-Co	3.62	0.11	260 ^a	1.05	2.63	2.87
SIFSIX-3-Cu [6]	3.52	0.10	325 ^b	1.24	2.34	2.50
NbOFFIVE-1-Ni [8]	3.21	0.095	280 ^b	1.30	1.71	2.20
SIFSIX-3-Ni [8]	3.71	0.098	368 ^b	0.35	1.9	2.57
TIFSIX-3-Ni	3.4	0.095	295 ^b	0.67	1.75	2.32
SIFSIX-2-Cu-i [37]	4.9	0.31	503 ^c	0.068	0.19	4.71
SIFSIX-14-Cu-i [38]	3.6	0.27	612 ^a	Negligible	1.72	4.70
dptz-CuTiF ₆ [35]	4.5–6.0	0.29	639 ^c	—	2.1	4.51

a) BET surface area calculated from CO_2 isotherms at 196 K; b) Langmuir surface area calculated from CO_2 isotherms at 273 K; c) BET surface area calculated from N_2 isotherms at 77 K.

Figure 2 (a) CO₂ adsorption isotherms on various anion-functionalized ultramicroporous materials at 298 K. (b) Comparison of CO₂ uptakes on various anion-functionalized materials at 10,000 ppm. (c) CO₂, N₂, and CH₄ adsorption isotherms on ZU-16-Co at 298 K.

[8], SIFSIX-3-Ni (1.9 mmol g⁻¹) [8], dpz-CuTiF₆ (2.1 mmol g⁻¹) [35], and UTSA-220 (1.2 mmol g⁻¹) [36]. Such excellent CO₂ sorption behavior at 10,000 ppm might be attributed to the larger pore volume. Within much lower pressure around 400 ppm, ZU-16-Co also exhibits higher CO₂ uptake of 1.05 mmol g⁻¹ than that on SIFSIX-3-Ni (0.42 mmol g⁻¹) and TIFSIX-3-Ni (0.65 mmol g⁻¹).

As shown in Table 1, the pore size-property relationships were investigated. Compared with MFSIX-3 family adsorbents, NbOFFIVE-1-Ni with the smallest pore size of 3.21 Å shows the highest CO₂ uptake (1.3 mmol g⁻¹) at 400 ppm and 298 K. With a relatively large pore size of 3.71 Å, SIFSIX-3-Ni only adsorbs 0.35 mmol g⁻¹ CO₂. ZU-16-Co with moderate pore size of 3.62 Å exhibits compromised CO₂ uptake (1.05 mmol g⁻¹). This presents the significance of the pore size reduction for the increase of CO₂ uptake at low pressures. When the concentration of CO₂ increases to 10,000 ppm, ZU-16-Co with larger pore volume of 0.11 cm³ g⁻¹ shows the highest CO₂ uptake capacity among the MFSIX and NbOFFIVE-1-Ni adsorbents. It can be concluded that the pore size plays the key role in the CO₂ uptake at relatively low pressure, and with the pressure increasing, the pore volume plays increasingly important role in CO₂ capture amount. These results highlight the significant role of crystal engineering towards the design and synthesis of porous materials with improved adsorption performance.

The N₂ uptake on ZU-16-Co at 298 K and 1.0 bar was also collected (Fig. 2c) and found to be only 0.19 mmol g⁻¹, which signifies a high CO₂/N₂ separation selectivity. The high CO₂ uptake at low pressures and low CH₄ and N₂ capture amounts at 1.0 bar present that ZU-16-Co could be used as highly efficient adsorbents for the

separation of CO₂/N₂ and CO₂/CH₄ mixtures. The excellent CO₂ trapping ability at low concentrations and the exclusion of larger molecules on ZU-16-Co may be due to the synergistic effect of high charge density and optimal pore chemistry of ZU-16-Co.

Motivated by the high uptake and preferential binding for CO₂ with larger molecules excluded by ZU-16-Co, the adsorption selectivities of CO₂/N₂ (15/85) and CO₂/CH₄ (50/50) mixtures were calculated based on ideal adsorbed solution theory (IAST) (Fig. S5). The CO₂/N₂ (15/85) separation selectivity on ZU-16-Co is up to 690 at 1.0 bar, much higher than that on r1KCHA (80) [18], NKU-521 (40) [39], UTSA-16 (314) [40], Mg-MOF-74 (150) [40], SIFSIX-2-Cu-i (140) [37] and UTSA-120a (600) [41]. Furthermore, CO₂/CH₄ (50/50) separation selectivity on ZU-16-Co was calculated to be 120, also comparable to the state-of-the-art materials, such as SIFSIX-2-Cu-i (33) [37], SIFSIX-3-Zn (231) [37], 13X (103) [37], Mg-MOF-74 (137) [37], and MOF-505 (27.8) [42].

To obtain deep insights into the thermodynamic adsorption behavior of CO₂ in ZU-16-Co, the host-guest interactions were evaluated by dispersion corrected density functional theory (DFT-D) and Grand Canonical Monte Carlo (GCMC) simulations (Fig. 3a, b). CO₂ molecules occupy high energetically favorable positions in ZU-16-Co, where the electropositive carbon atom of CO₂ is surrounded by four electronegative F atoms from four anions with F...C=O distance of 3.15 Å and the O atoms are further interacting with H atoms from pyrazines (H...O distance of 3.82 Å, Fig. 3a). Such uniform CO₂ interaction distributions in such narrow pore channels are also the prerequisite for adsorbents with high CO₂ uptake at low pressures. Furthermore, the binding configurations of CO₂ obtained by GCMC si-

Figure 3 The calculated CO₂ adsorption binding configuration in ZU-16-Co by (a) DFT-D and (b) GCMC, revealing the close interactions between CO₂ and fluorine atoms of TIFSIX anions (Color code: F, turquoise; Ti, light blue; Co, pink; N, blue; C, Grey; H, white; O, red). Column breakthrough experiments for (c) CO₂/N₂ (1/99, flow rate: 5 mL min⁻¹) and (d) CO₂/CH₄ (50/50, flow rate: 4 mL min⁻¹) conducted on ZU-16-Co. C_A means the real-time concentration, and C₀ means the initial concentration of one gas in mixed mixtures.

mulations (Fig. 3b) are consistent with the DFT-D calculated results.

To evaluate the capture capability of ZU-16-Co for CO₂, the dynamic breakthrough experiments were conducted with CO₂/N₂ (1/99, 15/85) and CO₂/CH₄ (50/50) mixtures at 298 K and atmospheric pressure (Fig. 3c, d and Fig. S6). Remarkably, ZU-16-Co presents excellent CO₂ capture ability, as CO₂ is retained in the column for long times, whereas N₂ and CH₄ break through the ZU-16-Co bed immediately after the gas mixture is fed into the bed. ZU-16-Co could capture CO₂ for ca. 100 min with trapping amount of 0.37 mmol g⁻¹ from 1/99 CO₂/N₂ mixture. In addition, ZU-16-Co also exhibits good separation performance for CO₂/N₂ (15/85) mixture with CO₂ trapping amount of 1.99 mmol g⁻¹ (Fig. S6). For the 50/50 CO₂/CH₄ mixture, CO₂ could be retained in the packed column for over 14 min with CO₂ capture amount of 1.78 mmol g⁻¹ (Fig. 3d). These breakthrough results indicate ZU-16-Co has high selectivity towards CO₂ over CH₄ and N₂, which is in good agreement with the single-gas adsorption data (Fig. 2c). The column of the adsorbent could be regenerated by heating under vacuum or purging He (5 mL min⁻¹ He flow at 373 K for 6 h) with almost no loss in separation performances, indicating ZU-16-Co would be a good candidate for CO₂/N₂ and

CO₂/CH₄ separation.

CONCLUSION

In summary, we for the first time report an anion-functionalized ultramicroporous ZU-16-Co synthesized by cheap raw materials with judiciously fabricated pore dimensions for CO₂ capture at low concentrations. Notably, compared with its isostructural MFSIX-3 materials and NbOFFIVE-1-Ni, ZU-16-Co exhibits the highest CO₂ uptake of 2.63 mmol g⁻¹ at 0.01 bar (10,000 ppm) due to the fine-tuned pore size (3.62 Å) constricted by strong electronegative TiF₆²⁻ anions and the higher pore volume (0.11 cm³ g⁻¹). The single-gas adsorption isotherms combined with the CO₂/N₂ (1/99) breakthrough tests demonstrate the excellent trace carbon capture ability of ZU-16-Co. It could capture CO₂ for 100 min with trapping amount of 0.37 mmol g⁻¹ from 1/99 CO₂/N₂ (CO₂ concentration of 10,000 ppm) mixture. The structural-property relationship between pore dimensions (pore size and pore volume) and carbon capture performance was systematically investigated, and the results manifest that the synergetic effects of the optimized pore chemistry and dimensions endow ZU-16-Co with excellent CO₂ trapping performance at low concentrations. Overall, the low-cost anion-functionalized ZU-16-Co can be an alternative

adsorbent for carbon capture and offers great promise as future suitable physical adsorbents in a confined space system.

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- Adil K, Belmabkhout Y, Pillai RS, *et al.* Gas/vapour separation using ultra-microporous metal-organic frameworks: Insights into the structure/separation relationship. *Chem Soc Rev*, 2017, 46: 3402–3430
- Yu J, Xie LH, Li JR, *et al.* CO₂ capture and separations using MOFs: Computational and experimental studies. *Chem Rev*, 2017, 117: 9674–9754
- Trickett CA, Helal A, Al-Maythaly BA, *et al.* The chemistry of metal-organic frameworks for CO₂ capture, regeneration and conversion. *Nat Rev Mater*, 2017, 2: 1–6
- Li JR, Sculley J, Zhou HC. Metal-organic frameworks for separations. *Chem Rev*, 2012, 112: 869–932
- Belmabkhout Y, Bhatt PM, Adil K, *et al.* Natural gas upgrading using a fluorinated MOF with tuned H₂S and CO₂ adsorption selectivity. *Nat Energy*, 2018, 3: 1059–1066
- Shekhah O, Belmabkhout Y, Chen Z, *et al.* Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture. *Nat Commun*, 2014, 5: 4228
- Madden DG, O’Nolan D, Chen KJ, *et al.* Highly selective CO₂ removal for one-step liquefied natural gas processing by physisorbents. *Chem Commun*, 2019, 55: 3219–3222
- Bhatt PM, Belmabkhout Y, Cadiau A, *et al.* A fine-tuned fluorinated MOF addresses the needs for trace CO₂ removal and air capture using physisorption. *J Am Chem Soc*, 2016, 138: 9301–9307
- Milner PJ, Siegelman RL, Forse AC, *et al.* A diaminopropane-appended metal-organic framework enabling efficient CO₂ capture from coal flue gas *via* a mixed adsorption mechanism. *J Am Chem Soc*, 2017, 139: 13541–13553
- Guo Y, Zhao C, Li C. CO₂ adsorption kinetics of K₂CO₃/activated carbon for low-concentration CO₂ removal from confined spaces. *Chem Eng Technol*, 2015, 38: 891–899
- Belmabkhout Y, Guillerm V, Eddaoudi M. Low concentration CO₂ capture using physical adsorbents: Are metal-organic frameworks becoming the new benchmark materials? *Chem Eng J*, 2016, 296: 386–397
- Keith DW. Why capture CO₂ from the atmosphere? *Science*, 2009, 325: 1654–1655
- Ye Q, Jiang J, Wang C, *et al.* Adsorption of low-concentration carbon dioxide on amine-modified carbon nanotubes at ambient temperature. *Energy Fuels*, 2012, 26: 2497–2504
- Sholl DS, Lively RP. Seven chemical separations to change the world. *Nature*, 2016, 532: 435–437
- Li JR, Yu J, Lu W, *et al.* Porous materials with pre-designed single-molecule traps for CO₂ selective adsorption. *Nat Commun*, 2013, 4: 1538
- Wang Y, Zhao D. Beyond equilibrium: Metal-organic frameworks for molecular sieving and kinetic gas separation. *Cryst Growth Des*, 2017, 17: 2291–2308
- Rozyyev V, Yavuz CT. An all-purpose porous cleaner for acid gas removal and dehydration of natural gas. *Chem*, 2017, 3: 719–721
- Shang J, Li G, Singh R, *et al.* Discriminative separation of gases by a “molecular trapdoor” mechanism in chabazite zeolites. *J Am Chem Soc*, 2012, 134: 19246–19253
- Sanz-Pérez ES, Murdock CR, Didas SA, *et al.* Direct capture of CO₂ from ambient air. *Chem Rev*, 2016, 116: 11840–11876
- Liao PQ, Zhang WX, Zhang JP, *et al.* Efficient purification of ethene by an ethane-trapping metal-organic framework. *Nat Commun*, 2015, 6: 8697
- Yang S, Sun J, Ramirez-Cuesta AJ, *et al.* Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host. *Nat Chem*, 2012, 4: 887–894
- McDonald TM, Lee WR, Mason JA, *et al.* Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg₂(dobpdc). *J Am Chem Soc*, 2012, 134: 7056–7065
- Zhang Z, Ding Q, Peh SB, *et al.* Mechano-assisted synthesis of an ultramicroporous metal-organic framework for trace CO₂ capture. *Chem Commun*, 2020, 56: 7726–7729
- Cui X, Chen K, Xing H, *et al.* Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science*, 2016, 353: 141–144
- Peng YL, Pham T, Li P, *et al.* Robust ultramicroporous metal-organic frameworks with benchmark affinity for acetylene. *Angew Chem Int Ed*, 2018, 57: 10971–10975
- Kumar A, Hua C, Madden DG, *et al.* Hybrid ultramicroporous materials (HUMs) with enhanced stability and trace carbon capture performance. *Chem Commun*, 2017, 53: 5946–5949
- Zhang Z, Yang Q, Cui X, *et al.* Sorting of C₄ olefins with interpenetrated hybrid ultramicroporous materials by combining molecular recognition and size-sieving. *Angew Chem Int Ed*, 2017, 56: 16282–16287
- Belmabkhout Y, Zhang Z, Adil K, *et al.* Hydrocarbon recovery using ultra-microporous fluorinated MOF platform with and without uncoordinated metal sites: I-structure properties relationships for C₂H₂/C₂H₄ and CO₂/C₂H₂ separation. *Chem Eng J*, 2019, 359: 32–36
- Ding Q, Zhang Z, Yu C, *et al.* Exploiting equilibrium-kinetic synergetic effect for separation of ethylene and ethane in a microporous metal-organic framework. *Sci Adv*, 2020, 6: eaaz4322
- Mukherjee S, Sikdar N, O’Nolan D, *et al.* Trace CO₂ capture by an ultramicroporous physisorbent with low water affinity. *Sci Adv*, 2019, 5: eaax9171
- Noro S, Kitagawa S, Kondo M, *et al.* A new, methane adsorbent, porous coordination polymer [{CuSiF₆(4,4’-bipyridine)₂]_n}. *Angew Chem Int Ed*, 2000, 39: 2081–2084
- Zhang Z, Tan B, Wang P, *et al.* Highly efficient separation of linear and branched C₄ isomers with a tailor-made metal-organic framework. *AIChE J*, 2020, 66: e16236
- Matulková I, Holec P, Němec I, *et al.* Temperature-dependent vibrational spectroscopic and X-ray diffraction investigation of nanosized nickel chromite. *J Mol Structure*, 2015, 1090: 70–75
- Sist M, Fischer KFF, Kasai H, *et al.* Low-temperature anharmonicity in cesium chloride (CsCl). *Angew Chem Int Ed*, 2017, 56: 3625–3629
- Liang W, Bhatt PM, Shkurenko A, *et al.* A tailor-made interpenetrated MOF with exceptional carbon-capture performance from flue gas. *Chem*, 2019, 5: 950–963
- Li H, Li L, Lin RB, *et al.* Microporous metal-organic framework with dual functionalities for efficient separation of acetylene from light hydrocarbon mixtures. *ACS Sustain Chem Eng*, 2019, 7: 4897–4902

- 37 Nugent P, Belmabkhout Y, Burd SD, *et al.* Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature*, 2013, 495: 80–84
- 38 Jiang M, Li B, Cui X, *et al.* Controlling pore shape and size of interpenetrated anion-pillared ultramicroporous materials enables molecular sieving of CO₂ combined with ultrahigh uptake capacity. *ACS Appl Mater Interfaces*, 2018, 10: 16628–16635
- 39 Li N, Chang Z, Huang H, *et al.* Specific K⁺ binding sites as CO₂ traps in a porous MOF for enhanced CO₂ selective sorption. *Small*, 2019, 15: 1900426
- 40 Adil K, Bhatt PM, Belmabkhout Y, *et al.* Valuing metal-organic frameworks for postcombustion carbon capture: A benchmark study for evaluating physical adsorbents. *Adv Mater*, 2017, 29: 1702953
- 41 Wen HM, Liao C, Li L, *et al.* A metal-organic framework with suitable pore size and dual functionalities for highly efficient post-combustion CO₂ capture. *J Mater Chem A*, 2019, 7: 3128–3134
- 42 Chen Y, Lv D, Wu J, *et al.* A new MOF-505@GO composite with high selectivity for CO₂/CH₄ and CO₂/N₂ separation. *Chem Eng J*, 2017, 308: 1065–1072

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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阴离子功能化超微孔MOF高效选择性捕获低浓度CO₂

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摘要 CO₂捕获, 尤其低浓度CO₂捕获, 对人类在限域空间中长时间工作、降低天然气液化过程中CO₂腐蚀及冻结效应极为重要. 本文首次报道了一种具有一维孔道的ZU-16-Co (TIFSIX-3-Co)材料, 该材料孔道中含大量电负性F原子, 可实现400–10,000 ppm浓度下CO₂的高效捕获. 相比同构材料, 孔径为3.62 Å的ZU-16-Co在0.01和1.0 bar表现出最高的吸附量, 分别为2.63和2.87 mmol g⁻¹. 模拟研究表明, ZU-16-Co具有优异的CO₂捕获性能是由于其精准调控的孔道与CO₂较强的主客体相互作用(F...C=O)及相对较大的孔容. 此外, 动态混合气(1/99和15/85 CO₂/N₂, 50/50 CO₂/CH₄)固定床穿透实验也表明ZU-16-Co具有优良的CO₂捕获性能. 精准调控的孔化学尺度及周期性排布的电负性功能位点带来的良好的CO₂捕获、分离性能使得超微孔ZU-16-Co成为极具前景的低浓度CO₂吸附剂.