

Controlling Pore Shape and Size of Interpenetrated Anion-Pillared Ultramicroporous Materials Enables Molecular Sieving of CO₂ Combined with Ultrahigh Uptake Capacity

Mengdie Jiang,[†] Bin Li,^{*,‡,§} Xili Cui,[†] Qiwei Yang,[†] Zongbi Bao,[†] Yiwen Yang,[†] Hui Wu,[§] Wei Zhou,[§] Banglin Chen,[‡] and Huabin Xing^{*,†}

[†]Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, and

[‡]State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

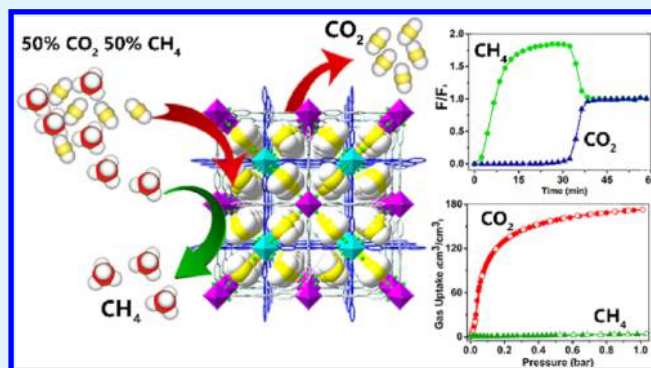
[§]Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, United States

[§]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States

Supporting Information

ABSTRACT: The separation of carbon dioxide (CO₂) from hydrocarbons is a critical process for the production of clean energy and high-purity chemicals. Adsorption based on molecular sieving is an energy-saving separation process; however, most of molecular sieves with narrow and straight pore channels exhibit low CO₂ uptake capacity. Here, we report that a twofold interpenetrated copper coordination network with a consecutive pocket-like pore structure, namely, SIFSIX-14-Cu-i (SIFSIX = hexafluorosilicate, 14 = 4,4'-azopyridine, i = interpenetrated) is a remarkable CO₂/CH₄ molecular sieving adsorbent which completely blocks the larger CH₄ molecule with unprecedented selectivity, whereas it has excellent CO₂ uptake (172.7 cm³/cm³) under the ambient condition. The exceptional separation performance of SIFSIX-14-Cu-i is attributed to its unique pore shape and functional pore surface, which combine a contracted pore window (3.4 Å) and a relatively large pore cavity decorated with high density of inorganic anions. Dispersion-corrected density functional theory calculation and neutron powder diffraction were performed to understand the CO₂ binding sites. The practical feasibility of SIFSIX-14-Cu-i for CO₂/CH₄ mixtures separation was validated by experimental breakthrough tests. This study not only demonstrates the great potential of SIFSIX-14-Cu-i for CO₂ separation but also provides important clues for other gas separations.

KEYWORDS: metal–organic frameworks, molecular sieving, gas adsorption, carbon dioxide, methane, separation



INTRODUCTION

The separation of carbon dioxide (CO₂) from methane and relevant hydrocarbons is a critical process for the production of clean energy and high-purity chemicals.^{1–3} For example, natural gas including shale gas contains methane, ethane, propane, and other impurities like CO₂, sulfur dioxide, and so on.^{4,5} The existence of CO₂ in natural gas will lower the calorific value and corrode the pipelines, which necessitate a CO₂ removal process.^{6–9} Hydrocarbons like ethane, ethylene, and propylene produced from steam cracking also inevitably mixed with a small amount of CO₂, which must be removed for purification.^{10–14} Physisorption using porous materials as adsorbents is regarded as a promising method for CO₂ separation and capture owing to its low-energy consumption and mild operation condition.^{15–17} Up to date, a great variety of porous materials such as porous polymers,^{18–21} zeolites,^{22,23}

carbon materials,^{24–26} metal–organic frameworks (MOFs) and/or porous coordination polymers (PCPs),^{15,27–36} and covalent-organic frameworks (COFs)^{37–41} have been investigated for CO₂ capture and separation. Among these porous materials, MOFs and/or PCPs are prominent because of their diversiform variety, high porosity, and tailorable pore size and pore functionality.^{42–48} Optimal porous materials for CO₂ separation through physisorption should exhibit both high uptake capacity and high selectivity toward CO₂ over other gases. However, the trade-off between uptake capacity and selectivity of porous materials has been identified as a major obstacle for efficient gas adsorptive separation.⁴⁹

Received: February 27, 2018

Accepted: April 19, 2018

Published: April 19, 2018

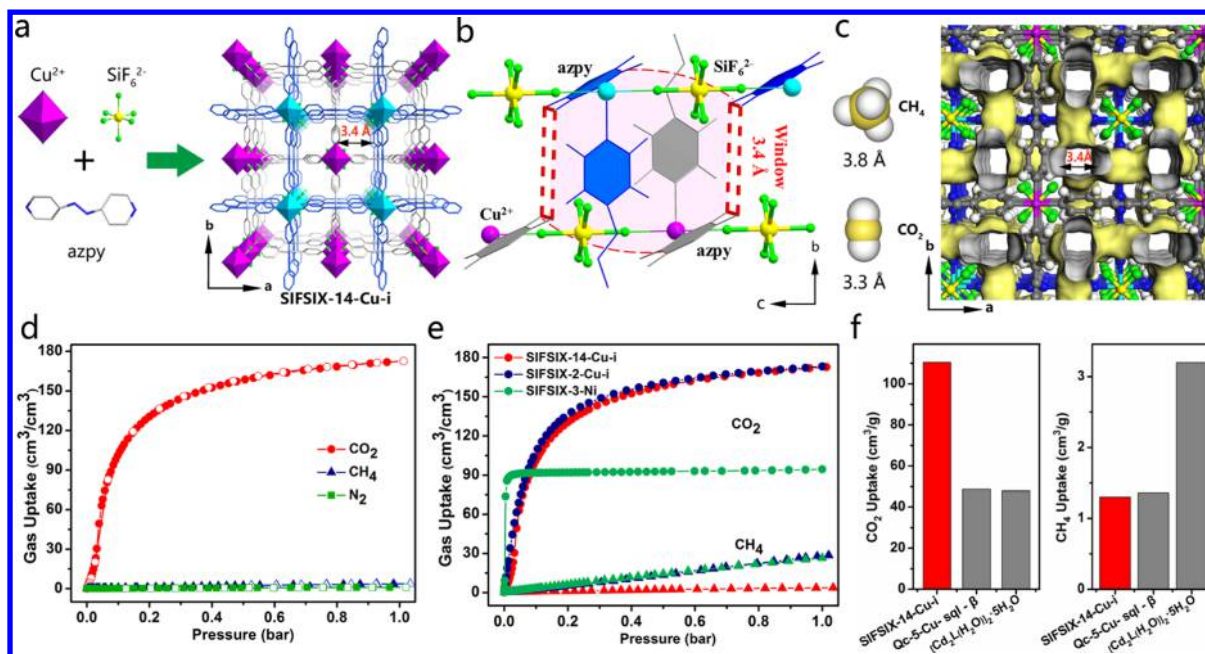


Figure 1. Gas adsorption isotherms and structure description of SIFSIX-14-Cu-i. (a) Sketch of the metal node, inorganic pillar, organic linker, and the skeleton structure of SIFSIX-14-Cu-i viewed along the *c*-axis. (b) Diagrammatic sketch presents a pore of the pocket structure. (c) Packing diagram along the *c*-axis, showing the pore surfaces of 3D channels highlighted as yellow/gray (inner/outer) curved planes with pore size of 3.4 Å. (The different nets are highlighted in royal blue and gray color for clarity in (a–c); guest molecules are omitted in c for clarity. Color code: Si, yellow; F, green; Cu, blue/purple in different nets.) (d,e) Adsorption isotherms of CO₂ (circle), CH₄ (triangle) and N₂ (square) on SIFSIX-14-Cu-i (d), SIFSIX-2-Cu-i and SIFSIX-3-Ni (e) at 273 K. (f) Comparison of CO₂ and CH₄ adsorption capacity in different molecular sieving materials including SIFSIX-14-Cu-i, Qc-5-Cu-sql-β and [Cd₂L(H₂O)]₂·5H₂O at 293 K.

Molecular sieving can reach extremely high selectivity because molecules with kinetic diameters larger than the pore will be completely excluded, whereas smaller ones can pass through. However, molecular sieving is very hard to achieve.^{50–52} It requires exquisite control on the structure of materials with intermediate pore apertures, whose size shall be just between the kinetic diameters of the separated molecules. In the system of CO₂ and CH₄ separation, the kinetic diameters of CH₄ and CO₂ are 3.8 and 3.3 Å, respectively, which are extremely close to each other. To our knowledge, only a few of porous materials can sieve CO₂ over CH₄ at near ambient conditions.^{53–58} For instance, Qc-5-Cu-sql-β⁵⁰ that has the square lattice network and narrow pore size (3.3 Å) adsorbs CO₂ (72.2 cm³/cm³), whereas it excludes CH₄ at 293 K and 1 bar. By precisely controlling the pore dimension, [Cd₂L(H₂O)]₂·5H₂O⁵⁹ and [Cu(bc ppm)H₂O]⁶⁰ with narrow straight pores also exhibit an obvious size-sieving effect for CO₂ and CH₄/N₂ with moderate CO₂ capacity of 101.2 and 47.4 cm³/cm³, respectively. These materials have extremely high selectivity because they adsorb CO₂, whereas they block CH₄. However, the CO₂ uptake capacity of these materials is moderate owing to their narrow, consecutive, and straight pore channels that don't have enough space to hold plentiful CO₂. In other words, these porous materials enable the molecular sieving at the cost of reducing the uptake capacity.

Herein, we report that anion-pillared interpenetrated copper coordination network, SIFSIX-14-Cu-i (SIFSIX = hexafluoro-silicate, 14 = 4,4'-azopyridine, i = interpenetrated, also called UTSA-200) is a remarkable CO₂/CH₄ molecular sieving adsorbent which completely blocks the larger CH₄ molecules, whereas it has excellent CO₂ uptake (172.7 cm³/cm³ or 121.9 cm³/g) under the ambient condition. The exceptional molecular sieving effect of the interpenetrated porous material

is attributed to its unique consecutive pocket-like channel, which has a small pore window and a relatively large pore cavity. Its pore window size of 3.4 Å is between the kinetic diameters of CO₂ and CH₄, so it can sieve CO₂ from the CH₄ with unprecedented selectivity. At the same time, SIFSIX-14-Cu-i contains high density of electronegative F group in the pore cavity that provides sufficient sites and space for gas storage and enables exceptional CO₂ capacity. The single-component adsorption isotherms of CO₂ and CH₄ on SIFSIX-14-Cu-i were measured at different temperatures. The binding sites of CO₂ within the material were investigated by simulation studies and experimental diffraction measurements. The excellent performance of SIFSIX-14-Cu-i for CO₂/CH₄ separation was validated by column breakthrough experiments.

RESULTS AND DISCUSSION

Structure Descriptions. An anion-pillared copper coordination network with a doubly interpenetrated structure, SIFSIX-14-Cu-i,^{61,62} was synthesized (Figure 1a). SIFSIX-14-Cu-i is a variant of the well-known SIFSIX-2-Cu-i¹⁵ with a smaller aperture size (3.4 Å vs 4.4 Å). We use the shorter linker 4,4'-azopyridine (azpy, 9.0 Å) to replace the 4,4'-dipyridylacetylene (9.6 Å) with the purpose of shrinking the pore. The organic linkers and metal nodes form the two-dimensional interpenetrated nets, which were pillared by SiF₆²⁻ to generate the three-dimensional pcu frameworks. Because of the tiny pore space, the pyridine ring in the organic linker interacts with the fluorine atom in the SiF₆²⁻ pillar through C–H···F hydrogen bonding which induces the tilting of pyridine ring (Figures 1b and S1). The tilting of zigzag linker generates a contracted pore window with a size of 3.4 Å (H–H distance) (Figure 1b,c), which has the potential to sieve the molecules of CO₂ and CH₄. On the other hand, the pore volume of SIFSIX-14-Cu-i is 0.27

Table 1. Gas Adsorption and Selectivity Results and Comparisons

MOFs	S_{BET}^a (m ² /g)	pore size (Å)	adsorption uptake		uptake ratio ^b	CO ₂ Q_{st} (kJ/mol) ^c	refs
			CO ₂ (cm ³ /cm ³)	CH ₄ (cm ³ /cm ³)			
“SIFSIX” Series ^g (273 K)							
SIFSIX-14-Cu-i	612 ^d	3.6 × 3.6 ^f	172.7	3.8	46.7	37.7	this work
SIFSIX-2-Cu-i	503	4.9 × 4.9	173.1	28.6	6.2	31.9	15
SIFSIX-3-Ni	368	4.2 × 4.2	94.4	26.5	3.6	51.0	63
Molecular Sieving (298 K)							
SIFSIX-14-Cu-i	612 ^d	3.6 × 3.6 ^f	149.6/156.6 ^e	1.3/1.8 ^e	116.1/84.9 ^e	37.7	this work
Qc-5-Cu-sql-β	222 ^d	3.3	72.2 ^e	1.9 ^e	37.2	36.0	50
[Cd ₂ L(H ₂ O)] ₂ ·5H ₂ O	147	5.2	101.2 ^e	2.4 ^e	42.9	36.9	59
[Cu(bc ppm)H ₂ O]	155 ^d	3.6	47.4 ^e			29.0	60

^aBET surface area calculated from N₂ isotherms at 77 K. ^bSelectivity calculated by uptake ratio of CO₂/CH₄ at 1 bar. ^c Q_{st} values of CO₂ at low surface coverage. ^dBET surface area calculated from CO₂ isotherms at 196 K. ^eAt a temperature of 293 K. ^fThe average pore size of the pocket-like pore. ^gMeasured in this work.

cm³/g, which is slight lower than SIFSIX-2-Cu-i (0.31 cm³/g).⁶² In brief, SIFSIX-14-Cu-i has a consecutive pocket-like pore structure that is composed of small pore windows and relative large pore cavities (Figure 1b,c). The Brunauer–Emmett–Teller (BET) surface area and framework density of the activated SIFSIX-14-Cu-i structure are 612 m²/g and 1.4175 g/cm³, respectively. The structure and stability of SIFSIX-14-Cu-i were characterized by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Figures S2 and S3). The PXRD patterns were verified to match those calculated from single-crystal data, and the framework maintains stability to about 200 °C.

Gas Adsorption and Separation Behaviors. The adsorption isotherms of CO₂, CH₄, and N₂ on SIFSIX-14-Cu-i were measured at 273–333 K (Figures 1d, 4d, and S4–S6) and found to be completely reversible without hysteresis. As shown in Figure 1d, although CO₂ and CH₄ have similar kinetic diameters, they exhibit very different adsorption isotherms on SIFSIX-14-Cu-i. At 273 K and 1 bar, only very limited CH₄ (3.8 cm³/cm³) sorption is noticed but significant CO₂ uptake (172.7 cm³/cm³) is observed. At 298 K and 1 bar, SIFSIX-14-Cu-i still holds high CO₂ uptake capacity (149.6 cm³/cm³) that is a remarkable value for CO₂ adsorption in porous materials (Figure S9). The combination molecular sieving effect and high adsorption capacity is attributed to the unique consecutive pocket-like pore channels of SIFSIX-14-Cu-i as depicted in Figure 1b,c. The narrow pore window (3.4 Å, H–H distance) of SIFSIX-14-Cu-i is smaller than the kinetic diameter of CH₄ but little larger than that of CO₂, so it allows the CO₂ molecules to get through but blocks the CH₄. On the other hand, SIFSIX-14-Cu-i has relatively large pore cavity and high density of SIF₆^{2−} anions for gas adsorption which enable outstanding CO₂ capacity. Interestingly, the CO₂ adsorption isotherms are stepwise which imply the existence of guest-induced transition in the flexible framework. As shown in Figure S7, the transition is triggered by a certain amount (about 1 mmol/g) of the CO₂ adsorption. After transition, the framework becomes more obedient to absorb CO₂, so the CO₂ uptake increases rapidly than before which leading to a stepwise adsorption isotherm.

For comparing the separation performance of "SIFSIX" series materials, we selected two benchmark SIFSIX materials including SIFSIX-2-Cu-i¹⁵ and SIFSIX-3-Ni.^{30,63} The CO₂ and CH₄ adsorption and selectivity data are collected in Table 1 and Figures 1e and S10. As shown in Figure 1e, at 273 K and 1 bar, the CO₂ loadings on SIFSIX-14-Cu-i and SIFSIX-

2-Cu-i are comparable (172.7 and 173.1 cm³/cm³, respectively), but the CH₄ uptake on SIFSIX-14-Cu-i (3.8 cm³/cm³) is significantly lower than that on SIFSIX-2-Cu-i (28.6 cm³/cm³). We also can see that the CH₄ uptake on SIFSIX-14-Cu-i is much lower than that on SIFSIX-3-Ni (26.5 cm³/cm³), whereas the CO₂ capacity of SIFSIX-14-Cu-i is nearly twice than that of SIFSIX-3-Ni (94.4 cm³/cm³). This can be explained by the pore structures of SIFSIX materials. SIFSIX-14-Cu-i and SIFSIX-2-Cu-i have similar pore volumes, which lead to comparable CO₂ uptakes. The pore window size of SIFSIX-14-Cu-i is much smaller than that of SIFSIX-2-Cu-i (3.4 vs 5.2 Å) and even smaller than SIFSIX-3-Ni (4.2 Å). It is small enough to block CH₄ molecules, so the CH₄ loading on SIFSIX-14-Cu-i reduces obviously. Because of the limited of pore volume (0.157 cm³/g), SIFSIX-3-Ni has only about half CO₂ capacity of SIFSIX-14-Cu-i. In general, among three "SIFSIX" materials, SIFSIX-14-Cu-i exhibits the best performance with both high CO₂ uptake and high CO₂/CH₄ selectivity. Actually, CO₂ uptake of SIFSIX-14-Cu-i is among the top level of reported MOFs, including Mg-MOF-74⁶⁴ and UTSA-16⁶⁵ (details in Figure S6).

More importantly, comparing with other benchmark materials with the molecular sieving effect, SIFSIX-14-Cu-i is optimal both on the selectivity and capacity (detail data see Table 1). These materials all have very low CH₄ loading, whereas CO₂ loading is different. SIFSIX-14-Cu-i has a capacity of 156.6 cm³/cm³ at 293 K and 1 bar (Figure S11), which is much higher than that of Qc-5-Cu-sql-β (72.2 cm³/cm³, 293 K), [Cd₂L(H₂O)]₂·5H₂O (101.2 cm³/cm³, 293 K), and [Cu(bc ppm)H₂O] (47.4 cm³/cm³, 293 K). Furthermore, comparing the amount of CO₂ adsorption per gram, the advantage of SIFSIX-14-Cu-i (110.5 cm³/g) is more obvious among the molecular sieving materials (such as Qc-5-Cu-sql-β (48.8 cm³/g) and [Cd₂L(H₂O)]₂·5H₂O (47.9 cm³/g)) depicted as in Figure 1f. It is really remarkable that SIFSIX-14-Cu-i does not lose the CO₂ adsorbing capacity while achieving the molecular sieving. It attributes to its consecutive pocket-like pore structure and plenty of anions in the pore surface.

On the basis of previous single-component adsorption data, the CO₂/CH₄ selectivity was evaluated by calculating the gas uptake ratio at 1 bar. As shown in Figure 2a and Table 1, the uptake ratio of CO₂/CH₄ on SIFSIX-14-Cu-i at 273 and 298 K is up to 46.7 and 116.1, respectively. To the best of our knowledge, it is the highest value ever reported in porous materials and much higher than SIFSIX-3-Ni (4.3), Zeolite 13X

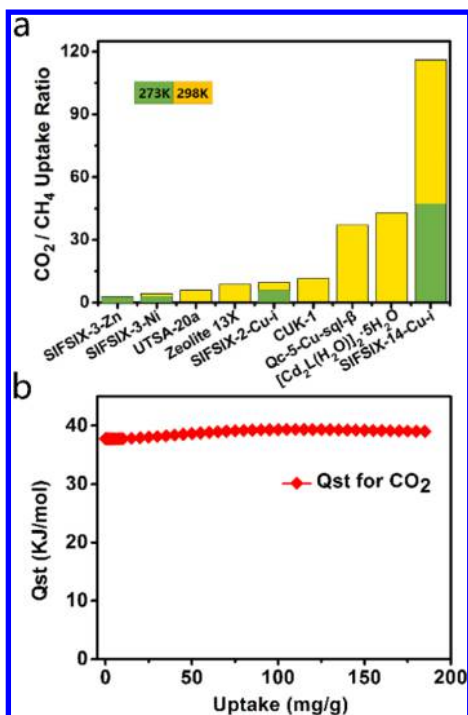


Figure 2. Uptake Ratio and Q_{st} calculations of SIFSIX-14-Cu-i. (a) Comparison of the uptake ratio of “SIFSIX” materials and other reported materials. (b) Isosteric heat of CO₂ adsorption, Q_{st} , in SIFSIX-14-Cu-i.

(8.7), Qc-5-Cu-sql-β (37.2), and [Cd₂L(H₂O)]₂·5H₂O (42.9) under similar conditions. The isosteric heat of adsorption (Q_{st}) of SIFSIX-14-Cu-i was derived from the isotherm data at 273 and 298 K based on the virial model (Figures 2b and S12).⁶⁶ The Q_{st} is 37.7 kJ/mol at zero loading and remains relatively constant with the increasing uptake, which indicates the homogeneous adsorption sites for CO₂ molecules. Comparing with SIFSIX-2-Cu-i (31.9 kJ/mol), the Q_{st} value of SIFSIX-14-Cu-i has enhanced, possibly attributable to its relatively narrower pores.

Simulation Studies. To gain a deep understanding of the adsorption properties of gas within SIFSIX-14-Cu-i, molecular simulations of CO₂ adsorption were performed using the dispersion-corrected density functional theory (DFT-D) method. Figure 3a,b shows the optimized structure of CO₂ adsorption in SIFSIX-14-Cu-i as viewed along the *b*-axis and *c*-axis of the framework. The simulations reveal that the small window size of 3.4 Å would allow two CO₂ molecules to access and get adsorbed in each pore cavity. The electropositive carbon atoms in CO₂ molecules are attracted to the SiF₆²⁻ pillaring anions, the calculated distance of O=C⋯F interaction is 2.57 Å. The DFT-D calculated binding energy (ΔE) of CO₂ molecules on SIFSIX-14-Cu-i is 37.28 kJ/mol. Additionally, the adsorbed CO₂ are oriented with the torsion angle of 29.52°, which can be partially attributed to the interaction between the electronegative oxygen atom of CO₂ and electropositive hydrogen atom of the linkers. The shortest C=O⋯H hydrogen bond distance is 2.61 Å (Figure S1). In contrast, the CH₄ molecule (3.8 Å) is larger than the pore window (3.4 Å), so it cannot enter the modeled cavities and thereby be excluded. In view of our simulation results, the molecular sieving effect of CO₂ over CH₄ in SIFSIX-14-Cu-i is strongly supported. Furthermore, we performed experimental neutron

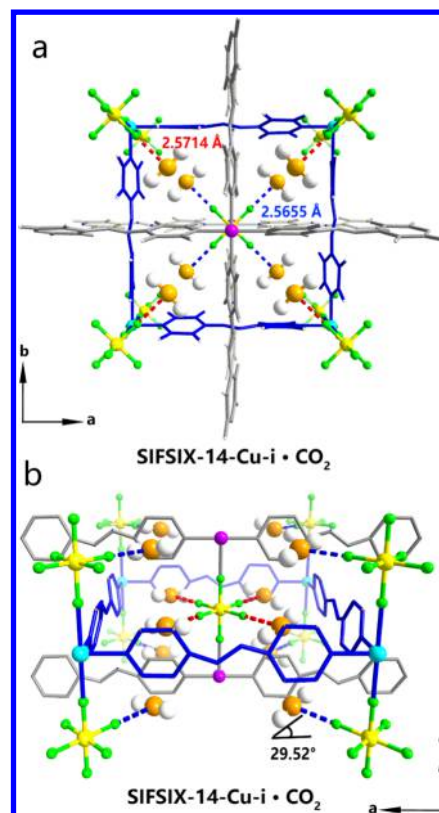


Figure 3. Simulation study of SIFSIX-14-Cu-i. (a,b) DFT-D calculated CO₂ adsorption binding sites in SIFSIX-14-Cu-i, as viewed along the *c*- and *b*-axes, respectively. Different nets are highlighted in gray and royal blue for clarity. Color code: O, white; C (in CO₂), orange; Si, yellow; F, green; Cu, blue/purple in different nets.

powder diffraction measurements to confirm the DFT-D findings. The data of a CO₂-loaded sample were collected at 200 K. The CO₂ adsorption sites obtained from Rietveld refinement of the neutron powder diffraction data (Figures S13 and S14) are fully consistent with the results of DFT-D calculation. Each CO₂ binds at one SiF₆²⁻ anion site and the experimental distance of the O=C⋯F bond is ~2.50 Å.

Breakthrough Curve Measurements. To evaluate the feasibility of SIFSIX-14-Cu-i for the CO₂/CH₄ separation, real-time dynamic breakthrough tests were conducted using CO₂/CH₄ (50/50, v/v) mixtures as feed. The breakthrough curves for CO₂/CH₄ (50/50) separation at 273 K is depicted in Figure 4a (for details, see Tables S3 and S4). The curve of SIFSIX-14-Cu-i shows that CH₄ breaks through the column immediately, indicating the block-off effect of this material. Nevertheless, CO₂ breakthrough on SIFSIX-14-Cu-i occurs at 34.6 min later with the calculated adsorption capacity of 154.6 cm³/cm³ (equivalent to 6901 mmol/L) during 0– τ_{break} , correlating well with the CO₂ uptake capacity (158.4 cm³/cm³, 273 K, and 0.5 bar) from the single-component adsorption isotherm. These experimental data indicate that SIFSIX-14-Cu-i is a promising material for CO₂/CH₄ separation.

Excellent cycle performance and easy regeneration of adsorbents are essential to reduce the cost of a practical process. Considering this aspect, we performed multiple column breakthrough tests with CO₂/CH₄ (50/50) mixtures as feed to verify the stable separation ability of SIFSIX-14-Cu-i. As shown in Figures 4b and S15, almost no significant decline is observed on both CO₂ capture capacity and breakthrough time

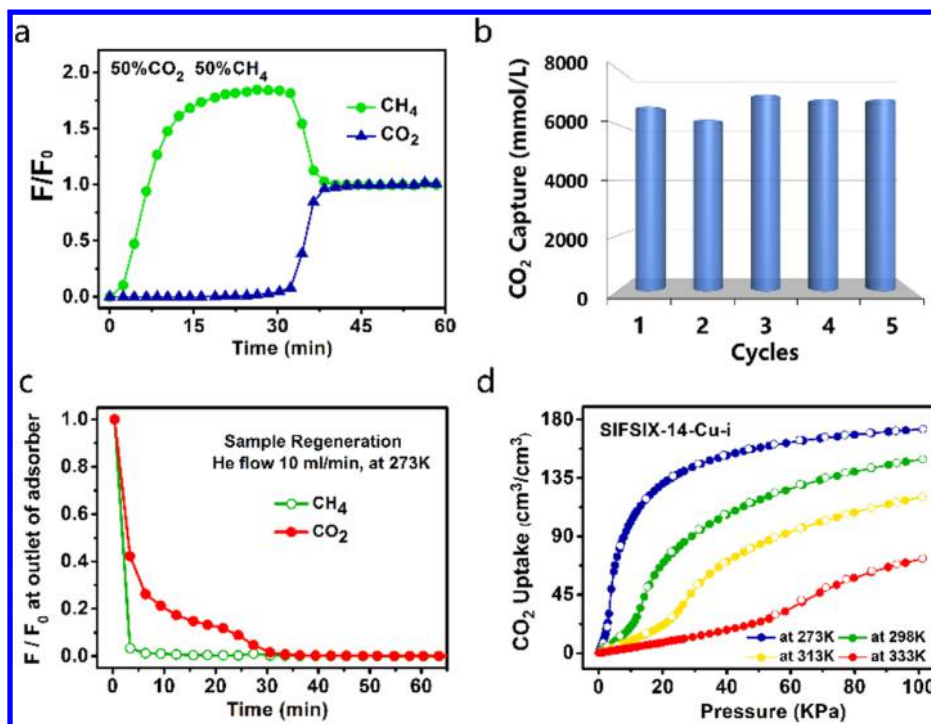


Figure 4. Experimental column breakthrough and regeneration results. (a) Experimental column breakthrough curves for equimolar CO_2/CH_4 mixtures with SIFSIX-14-Cu-i at 273 K and 1 bar. (b) Recyclability of CO_2 captured amount on SIFSIX-14-Cu-i after multiple mixed-gas column breakthrough tests. (c) Experimental desorption curves for CO_2 and CH_4 on SIFSIX-14-Cu-i at 273 K and 10 mL/min He flow. (d) Adsorption and desorption isotherms of CO_2 at different temperatures from 273 to 333 K.

during 5 cycles, indicating excellent cycle performance of SIFSIX-14-Cu-i. The PXRD also verifies that SIFSIX-14-Cu-i retains its stability after breakthrough experiments (Figure S2). The adsorbent was regenerated by purging the He flow at 10 mL/min through the column after the breakthrough test with the CO_2/CH_4 (50/50) mixed gas at 273 K and 1 bar. The regeneration curves depicted on Figure 4c indicate that almost all of the CH_4 and CO_2 are removed after 40 min. CH_4 is immediately eluted by helium because it's excluded by SIFSIX-14-Cu-i. CO_2 takes a little longer to elute because of the interaction with adsorbent, but 40 min is still a short time for MOF material regeneration at 273 K. Furthermore, from Figure 4d, we can see that the CO_2 adsorption isotherms of SIFSIX-14-Cu-i have strong response to the temperature increase. This is because the interactions between the framework and guests at low temperature are more stable than at high temperature, so the CO_2 uptake increases more rapidly and reaches the triggering amount more easily. As shown in Figure S8, we can see that under the same CO_2 triggering amount, the higher the temperature, the greater the transition pressure is. Therefore, under the same pressure, the CO_2 capacity at low temperature is higher than that of at high temperature. As a result, when the temperature increases from 273 to 313 K, it resulted in 54% decrease in CO_2 uptake at 0.5 bar. The decreased value even reaches to 87% when the temperature changes from 273 to 333 K. It indicates that CO_2 desorption can occur under mild temperature conditions and SIFSIX-14-Cu-i is very easy to be regenerated.

CONCLUSIONS

In summary, this work reports that an anion-pillared interpenetrated ultramicroporous material, SIFSIX-14-Cu-i, is a remarkable molecular sieve for CO_2/CH_4 separation with

unprecedented selectivity (uptake ratio: 111.6) and excellent CO_2 uptake capacity ($172.7 \text{ cm}^3/\text{cm}^3$, at 273 K and 1 bar). This work also shows that precisely controlling the pore shape and size of the MOF structure to form consecutive pocket-like pore channels is an effective strategy to simultaneously achieve the size-sieving effect and high gas uptake capacity. In SIFSIX-14-Cu-i, the narrow pore window of 3.4 Å blocks off the CH_4 , whereas it allows CO_2 to pass through the pore channels. Simultaneously, the abundant inorganic anions in relatively large pore cavity enable exceptional CO_2 uptake capacity. Therefore, SIFSIX-14-Cu-i exhibits unprecedented selectivity and capacity for CO_2/CH_4 separation. The isosteric heat of CO_2 (37.7 kJ/mol) on SIFSIX-14-Cu-i is relatively low, which enables facile regeneration conditions. The excellent separation performance of SIFSIX-14-Cu-i establishes it as a benchmark for CO_2/CH_4 separation and indicates that SIFSIX-14-Cu-i is a promising candidate for CO_2 separation. Additionally, this study provides useful clues to simultaneously achieve molecular sieving and high uptake capacity in porous materials for other important gas separations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b03358.

Experimental sections including the descriptions of materials needed and experimental methods such as the synthesis of SIFSIX-14-Cu-i, characterization techniques, gas adsorption measurements, calculations of isosteric heat of adsorption, density functional theory calculations, neutron diffraction experiments, and column breakthrough experiments for CO_2/CH_4 gas mixture (PDF)

Langmuir–Freundlich parameters fit for CO₂ and CH₄ in SIFSIX-14-Cu-i at 273 and 298 K; breakthrough calculations for the separation of CO₂/CH₄ mixture containing 50% CO₂ at 273 K; schematic picture showing the DFT-D optimized CO₂ adsorption configuration in SIFSIX-14-Cu-i; comparisons of PXRD patterns; TGA curves of SIFSIX-14-Cu-i; adsorption isotherms of CO₂ and CH₄ on “SIFSIX” materials; comparison of CO₂ uptake for various MOF materials at 298 K and 1 bar; virial fit of CO₂ isotherms of SIFSIX-14-Cu-i; cycling column breakthrough curves of SIFSIX-14-Cu-i for CO₂/CH₄ separations (50/50, v/v) at 273 K and 1 bar; and schematic illustration of the apparatus for the breakthrough experiments; neutron diffraction structure of CO₂/SIFSIX-14-Cu-i (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: bin.li@zju.edu.cn (B.L.).

*E-mail: xinghb@zju.edu.cn (H.X.).

ORCID

Bin Li: 0000-0002-7774-5452

Qiwei Yang: 0000-0002-6469-5126

Zongbi Bao: 0000-0003-4327-3028

Hui Wu: 0000-0003-0296-5204

Wei Zhou: 0000-0002-5461-3617

Banglin Chen: 0000-0001-8707-8115

Huabin Xing: 0000-0002-7418-0046

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (grant LZ18B060001), National Natural Science Foundation of China (no. 2172560321436010), National Program for Support of Top-notch Young Professionals (to H.X.), and Welch Foundation (grant AX-1730 to B.C.).

REFERENCES

- (1) Yu, J.; Xie, L.-H.; Li, J.-R.; Ma, Y.; Seminario, J. M.; Balbuena, P. B. CO₂ Capture and Separations Using MOFs: Computational and Experimental Studies. *Chem. Rev.* **2017**, *117*, 9674–9754.
- (2) Adil, K.; Belmabkhout, Y.; Pillai, R. S.; Cadiau, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Gas/Vapour Separation Using Ultra-Microporous Metal–organic Frameworks: Insights into the Structure/Separation Relationship. *Chem. Soc. Rev.* **2017**, *46*, 3402–3430.
- (3) Chaemchuen, S.; Kabir, N. A.; Zhou, K.; Verpoort, F. Metal–organic Frameworks for Upgrading Biogas via CO₂ Adsorption to Biogas Green Energy. *Chem. Soc. Rev.* **2013**, *42*, 9304–9332.
- (4) Cui, X.; Yang, Q.; Yang, L.; Krishna, R.; Zhang, Z.; Bao, Z.; Wu, H.; Ren, Q.; Zhou, W.; Chen, B.; Xing, H. Ultrahigh and Selective SO₂ Uptake in Inorganic Anion-Pillared Hybrid Porous Materials. *Adv. Mater.* **2017**, *29*, 1606929.
- (5) Yang, S.; Liu, L.; Sun, J.; Thomas, K. M.; Davies, A. J.; George, M. W.; Blake, A. J.; Hill, A. H.; Fitch, A. N.; Tang, C. C.; Schröder, M. Irreversible Network Transformation in a Dynamic Porous Host Catalyzed by Sulfur Dioxide. *J. Am. Chem. Soc.* **2013**, *135*, 4954–4957.
- (6) Xuan, Z.-H.; Zhang, D.-S.; Chang, Z.; Hu, T.-L.; Bu, X.-H. Targeted Structure Modulation of “Pillar-Layered” Metal–Organic Frameworks for CO₂ Capture. *Inorg. Chem.* **2014**, *53*, 8985–8990.
- (7) Zheng, S.-T.; Bu, J. T.; Li, Y.; Wu, T.; Zuo, F.; Feng, P.; Bu, X. Pore Space Partition and Charge Separation in Cage-within-Cage Indium–Organic Frameworks with High CO₂ Uptake. *J. Am. Chem. Soc.* **2010**, *132*, 17062–17064.
- (8) Bae, Y.-S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punnnathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q. Separation of CO₂ from CH₄ Using Mixed-Ligand Metal–Organic Frameworks. *Langmuir* **2008**, *24*, 8592–8598.
- (9) Hu, Z.; Zhang, K.; Zhang, M.; Guo, Z.; Jiang, J.; Zhao, D. A Combinatorial Approach towards Water-Stable Metal–Organic Frameworks for Highly Efficient Carbon Dioxide Separation. *ChemSusChem* **2014**, *7*, 2791–2795.
- (10) Horike, S.; Kishida, K.; Watanabe, Y.; Inubushi, Y.; Umeyama, D.; Sugimoto, M.; Fukushima, T.; Inukai, M.; Kitagawa, S. Dense Coordination Network Capable of Selective CO₂ Capture from C1 and C2 Hydrocarbons. *J. Am. Chem. Soc.* **2012**, *134*, 9852–9855.
- (11) Zhang, J.-P.; Chen, X.-M. Optimized Acetylene/Carbon Dioxide Sorption in a Dynamic Porous Crystal. *J. Am. Chem. Soc.* **2009**, *131*, 5516–5521.
- (12) Chen, K.-J.; Scott, H. S.; Madden, D. G.; Pham, T.; Kumar, A.; Bajpai, A.; Lusi, M.; Forrest, K. A.; Space, B.; Perry, J. J.; Zaworotko, M. J. Benchmark C₂H₂/CO₂ and CO₂/C₂H₂ Separation by Two Closely Related Hybrid Ultramicroporous Materials. *Chem* **2016**, *1*, 753–765.
- (13) Zhang, J.-W.; Hu, M.-C.; Li, S.-N.; Jiang, Y.-C.; Zhai, Q.-G. Design of Highly Connected Cd-Tetrazolate-Dicarboxylate Frameworks with Enhanced CO₂/CH₄ and C2 Hydrocarbons/CH₄ Separation Performance. *Cryst. Growth Des.* **2016**, *16*, 6430–6435.
- (14) Duan, J.; Higuchi, M.; Foo, M. L.; Horike, S.; Rao, K. P.; Kitagawa, S. A Family of Rare Earth Porous Coordination Polymers with Different Flexibility for CO₂/C₂H₄ and CO₂/C₂H₆ Separation. *Inorg. Chem.* **2013**, *52*, 8244–8249.
- (15) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous Materials with Optimal Adsorption Thermodynamics and Kinetics for CO₂ Separation. *Nature* **2013**, *495*, 80–84.
- (16) Huck, J. M.; Lin, L.-C.; Berger, A. H.; Shahrak, M. N.; Martin, R. L.; Bhowan, A. S.; Haranczyk, M.; Reuter, K.; Smit, B. Evaluating Different Classes of Porous Materials for Carbon Capture. *Energy Environ. Sci.* **2014**, *7*, 4132–4146.
- (17) Lyndon, R.; Konstant, K.; Ladewig, B. P.; Southon, P. D.; Kepert, P. C. J.; Hill, M. R. Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release. *Angew. Chem., Int. Ed.* **2013**, *52*, 3695–3698.
- (18) Shi, Y.-Q.; Zhu, J.; Liu, X.-Q.; Geng, J.-C.; Sun, L.-B. Molecular Template-Directed Synthesis of Microporous Polymer Networks for Highly Selective CO₂ Capture. *ACS Appl. Mater. Interfaces* **2014**, *6*, 20340–20349.
- (19) Saleh, M.; Lee, H. M.; Kemp, K. C.; Kim, K. S. Highly Stable CO₂/N₂ and CO₂/CH₄ Selectivity in Hyper-Cross-Linked Heterocyclic Porous Polymers. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7325–7333.
- (20) Wang, Y.; Yang, Q.; Zhong, C.; Li, J. Graphene-like Poly(Triazine Imide) as N₂-Selective Ultrathin Membrane for Postcombustion CO₂ Capture. *J. Phys. Chem. C* **2016**, *120*, 28782–28788.
- (21) Suo, X.; Xia, L.; Yang, Q.; Zhang, Z.; Bao, Z.; Ren, Q.; Yang, Y.; Xing, H. Synthesis of Anion-Functionalized Mesoporous Poly(Ionic Liquid)s via a Microphase Separation-Hypercrosslinking Strategy: Highly Efficient Adsorbents for Bioactive Molecules. *J. Mater. Chem. A* **2017**, *5*, 14114–14123.
- (22) Bae, T.-H.; Hudson, M. R.; Mason, J. A.; Queen, W. L.; Dutton, J. J.; Sumida, K.; Micklash, K. J.; Kaye, S. S.; Brown, C. M.; Long, J. R. Evaluation of Cation-Exchanged Zeolite Adsorbents for Post-

Combustion Carbon Dioxide Capture. *Energy Environ. Sci.* **2013**, *6*, 128–138.

(23) Song, Z.; Dong, Q.; Xu, W. L.; Zhou, F.; Liang, X.; Yu, M. Molecular Layer Deposition-Modified 5A Zeolite for Highly Efficient CO₂ Capture. *ACS Appl. Mater. Interfaces* **2018**, *10*, 769–775.

(24) Hao, G.-P.; Li, W.-C.; Qian, D.; Lu, A.-H. Rapid Synthesis of Nitrogen-Doped Porous Carbon Monolith for CO₂ Capture. *Adv. Mater.* **2010**, *22*, 853–857.

(25) Fu, N.; Wei, H.-M.; Lin, H.-L.; Li, L.; Ji, C.-H.; Yu, N.-B.; Chen, H.-J.; Han, S.; Xiao, G.-Y. Iron Nanoclusters as Template/Activator for the Synthesis of Nitrogen Doped Porous Carbon and Its CO₂ Adsorption Application. *ACS Appl. Mater. Interfaces* **2017**, *9*, 9955–9963.

(26) Huang, K.; Chai, S.-H.; Mayes, R. T.; Veith, G. M.; Browning, K. L.; Sakwa-Novak, M. A.; Potter, M. E.; Jones, C. W.; Wu, Y.-T.; Dai, S. An Efficient Low-Temperature Route to Nitrogen-Doping and Activation of Mesoporous Carbons for CO₂ Capture. *Chem. Commun.* **2015**, *51*, 17261–17264.

(27) He, H.; Sun, F.; Aguila, B.; Perman, J. A.; Ma, S.; Zhu, G. A Bifunctional Metal–organic Framework Featuring the Combination of Open Metal Sites and Lewis Basic Sites for Selective Gas Adsorption and Heterogeneous Cascade Catalysis. *J. Mater. Chem. A* **2016**, *4*, 15240–15246.

(28) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. Porous Materials with Pre-Designed Single-Molecule Traps for CO₂ Selective Adsorption. *Nat. Commun.* **2013**, *4*, 1538.

(29) Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. Crystal Engineering of an Nbo Topology Metal–Organic Framework for Chemical Fixation of CO₂ under Ambient Conditions. *Angew. Chem., Int. Ed.* **2014**, *53*, 2615–2619.

(30) Bhatt, P. M.; Belmabkhout, Y.; Cadiau, A.; Adil, K.; Shekhah, O.; Shkurenko, A.; Barbour, L. J.; Eddaoudi, M. 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.

(31) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. An Isoreticular Series of Metal–Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake Capacity. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357–5361.

(32) Zhang, L.; Jiang, K.; Jiang, M.; Yue, D.; Wan, Y.; Xing, H.; Yang, Y.; Cui, Y.; Chen, B.; Qian, G. A Highly Stable Amino-Coordinated MOF for Unprecedented Block off N₂ Adsorption and Extraordinary CO₂/N₂ Separation. *Chem. Commun.* **2016**, *52*, 13568–13571.

(33) Zhao, J.; Wang, Q.; Sun, C.; Zheng, T.; Yan, L.; Li, M.; Shao, K.; Wang, X.; Su, Z. A Hexanuclear Cobalt Metal–organic Framework for Efficient CO₂ Reduction under Visible Light. *J. Mater. Chem. A* **2017**, *5*, 12498–12505.

(34) Li, B.; Zhang, Z.; Li, Y.; Yao, K.; Zhu, Y.; Deng, Z.; Yang, F.; Zhou, X.; Li, G.; Wu, H.; Nijem, N.; Chabal, Y. J.; Lai, Z.; Han, Y.; Shi, Z.; Feng, S.; Li, J. Enhanced Binding Affinity, Remarkable Selectivity, and High Capacity of CO₂ by Dual Functionalization of a Rht-Type Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2012**, *51*, 1412–1415.

(35) Lau, C. H.; Babarao, R.; Hill, M. R. A Route to Drastic Increase of CO₂ Uptake in Zr Metal Organic Framework UiO-66. *Chem. Commun.* **2013**, *49*, 3634–3636.

(36) Li, L.; Bell, J. G.; Tang, S.; Lv, X.; Wang, C.; Xing, Y.; Zhao, X.; Thomas, K. M. Gas Storage and Diffusion through Nanocages and Windows in Porous Metal–Organic Framework Cu₂(2,3,5,6-Tetramethylbenzene-1,4-Diisophthalate)(H₂O)₂. *Chem. Mater.* **2014**, *26*, 4679–4695.

(37) Huang, N.; Chen, X.; Krishna, R.; Jiang, D. Two-Dimensional Covalent Organic Frameworks for Carbon Dioxide Capture through Channel-Wall Functionalization. *Angew. Chem.* **2015**, *127*, 3029–3033.

(38) Zeng, Y.; Zou, R.; Zhao, Y. Covalent Organic Frameworks for CO₂ Capture. *Adv. Mater.* **2016**, *28*, 2855–2873.

(39) Zou, C.; Li, Q.; Hua, Y.; Zhou, B.; Duan, J.; Jin, W. Mechanical Synthesis of COF Nanosheet Cluster and Its Mixed Matrix Membrane

for Efficient CO₂ Removal. *ACS Appl. Mater. Interfaces* **2017**, *9*, 29093–29100.

(40) Furukawa, H.; Yaghi, O. M. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009**, *131*, 8875–8883.

(41) Lan, J.; Cao, D.; Wang, W.; Smit, B. Doping of Alkali, Alkaline-Earth, and Transition Metals in Covalent-Organic Frameworks for Enhancing CO₂ Capture by First-Principles Calculations and Molecular Simulations. *ACS Nano* **2010**, *4*, 4225–4237.

(42) Cadiau, A.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Pillai, R. S.; Shkurenko, A.; Martineau-Corcus, C.; Maurin, G.; Eddaoudi, M. Hydrolytically Stable Fluorinated Metal–Organic Frameworks for Energy-Efficient Dehydration. *Science* **2017**, *356*, 731–735.

(43) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal–Organic Frameworks. *Science* **2013**, *341*, 1230444.

(44) Li, L.; Lin, R.-B.; Krishna, R.; Wang, X.; Li, B.; Wu, H.; Li, J.; Zhou, W.; Chen, B. Flexible–Robust Metal–Organic Framework for Efficient Removal of Propyne from Propylene. *J. Am. Chem. Soc.* **2017**, *139*, 7733–7736.

(45) Herm, Z. R.; Wiers, B. M.; Mason, J. A.; van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. Separation of Hexane Isomers in a Metal–Organic Framework with Triangular Channels. *Science* **2013**, *340*, 960–964.

(46) Noro, S.-i.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. Framework Engineering by Anions and Porous Functionalities of Cu(II)/4,4'-Bpy Coordination Polymers. *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.

(47) Zhang, Z.; Yang, Q.; Cui, X.; Yang, L.; Bao, Z.; Ren, Q.; Xing, H. Sorting of C₄ Olefins with Interpenetrated Hybrid Ultramicroporous Materials by Combining Molecular Recognition and Size-Sieving. *Angew. Chem., Int. Ed.* **2017**, *56*, 16282–16287.

(48) Wang, Y.; Li, L.; Dai, P.; Yan, L.; Cao, L.; Gu, X.; Zhao, X. Missing-Node Directed Synthesis of Hierarchical Pores on a Zirconium Metal–organic Framework with Tunable Porosity and Enhanced Surface Acidity via a Microdroplet Flow Reaction. *J. Mater. Chem. A* **2017**, *5*, 22372–22379.

(49) Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M. J.; Chen, B. Pore Chemistry and Size Control in Hybrid Porous Materials for Acetylene Capture from Ethylene. *Science* **2016**, *353*, 141–144.

(50) Chen, K.-J.; Madden, D. G.; Pham, T.; Forrest, K. A.; Kumar, A.; Yang, Q.-Y.; Xue, W.; Space, B.; Perry, J. J.; Zhang, J.-P.; Chen, X. M.; Zaworotko, M. J. Tuning Pore Size in Square-Lattice Coordination Networks for Size-Selective Sieving of CO₂. *Angew. Chem., Int. Ed.* **2016**, *55*, 10268–10272.

(51) Peng, Y.; Li, Y.; Ban, Y.; Jin, H.; Jiao, W.; Liu, X.; Yang, W. Metal–Organic Framework Nanosheets as Building Blocks for Molecular Sieving Membranes. *Science* **2014**, *346*, 1356–1359.

(52) Dinca, M.; Long, J. R. Strong H₂ Binding and Selective Gas Adsorption within the Microporous Coordination Solid Mg₃(O₂C-C₁₀H₆-CO₂)₃. *J. Am. Chem. Soc.* **2005**, *127*, 9376–9377.

(53) Yoon, J. W.; Jhung, S. H.; Hwang, Y. K.; Humphrey, S. M.; Wood, P. T.; Chang, J.-S. Gas-Sorption Selectivity of CUK-1: A Porous Coordination Solid Made of Cobalt(II) and Pyridine-2,4-Dicarboxylic Acid. *Adv. Mater.* **2007**, *19*, 1830–1834.

(54) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. Microporous Manganese Formate: A Simple Metal–Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties. *J. Am. Chem. Soc.* **2004**, *126*, 32–33.

(55) Du, L.; Lu, Z.; Zheng, K.; Wang, J.; Zheng, X.; Pan, Y.; You, X.; Bai, J. Fine-Tuning Pore Size by Shifting Coordination Sites of Ligands and Surface Polarization of Metal–Organic Frameworks To Sharply Enhance the Selectivity for CO₂. *J. Am. Chem. Soc.* **2013**, *135*, 562–565.

(56) Morishige, K. Adsorption and Separation of CO₂/CH₄ on Amorphous Silica Molecular Sieve. *J. Phys. Chem. C* **2011**, *115*, 9713–9718.

- (57) Anson, A.; Lin, C. C. H.; Kuznicki, S. M.; Sawada, J. A. Adsorption of Carbon Dioxide, Ethane, and Methane on Titanosilicate Type Molecular Sieves. *Chem. Eng. Sci.* **2009**, *64*, 3683–3687.
- (58) Zhao, X.; Bell, J. G.; Tang, S.-F.; Li, L.; Mark Thomas, K. Kinetic Molecular Sieving, Thermodynamic and Structural Aspects of Gas/Vapor Sorption on Metal Organic Framework $[\text{Ni}_{1.5}(\text{4,4'}$ -Bipyridine) $_{1.5}(\text{H}_3\text{L})(\text{H}_2\text{O})_3][\text{H}_2\text{O}]_7$ Where $\text{H}_6\text{L} = 2,4,6$ -Trimethylbenzene-1,3,5-Triyl Tris(Methylene)Triphosphonic Acid. *J. Mater. Chem. A* **2016**, *4*, 1353–1365.
- (59) Hou, L.; Shi, W.-J.; Wang, Y.-Y.; Guo, Y.; Jin, C.; Shi, Q.-Z. A Rod Packing Microporous Metal–organic Framework: Unprecedented Ukv Topology, High Sorption Selectivity and Affinity for CO_2 . *Chem. Commun.* **2011**, *47*, 5464–5466.
- (60) Bloch, W. M.; Babarao, R.; Hill, M. R.; Doonan, C. J.; Sumby, C. J. Post-Synthetic Structural Processing in a Metal–Organic Framework Material as a Mechanism for Exceptional CO_2/N_2 Selectivity. *J. Am. Chem. Soc.* **2013**, *135*, 10441–10448.
- (61) O’Nolan, D.; Kumar, A.; Zaworotko, M. J. Water Vapor Sorption in Hybrid Pillared Square Grid Materials. *J. Am. Chem. Soc.* **2017**, *139*, 8508–8513.
- (62) Li, B.; Cui, X.; O’Nolan, D.; Wen, H.-M.; Jiang, M.; Krishna, R.; Wu, H.; Lin, R.-B.; Chen, Y.-S.; Yuan, D.; Xing, H.; Zhou, W.; Ren, Q.; Qian, G.; Zaworotko, M. J.; Chen, B. An Ideal Molecular Sieve for Acetylene Removal from Ethylene with Record Selectivity and Productivity. *Adv. Mater.* **2017**, *29*, 1704210.
- (63) Elsaidi, S. K.; Mohamed, M. H.; Schaefer, H. T.; Kumar, A.; Lusi, M.; Pham, T.; Forrest, K. A.; Space, B.; Xu, W.; Halder, G. J.; Liu, J.; Zaworotko, M. J.; Thallapally, P. K. Hydrophobic Pillared Square Grids for Selective Removal of CO_2 from Simulated Flue Gas. *Chem. Commun.* **2015**, *51*, 15530–15533.
- (64) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.
- (65) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. Microporous Metal–Organic Framework with Potential for Carbon Dioxide Capture at Ambient Conditions. *Nat. Commun.* **2012**, *3*, 954.
- (66) Czepirski, L.; JagieŁŁo, J. Virial-Type Thermal Equation of Gas–solid Adsorption. *Chem. Eng. Sci.* **1989**, *44*, 797–801.