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A new metal–organic framework with potential for adsorptive separation of methane from carbon dioxide, acetylene, ethylene, and ethane established by simulated breakthrough experiments†

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A new three-dimensional microporous metal–organic framework, Cu_2(MFDI) (**ZJU-60**, H_4MFDI = 5,5′-(9,9-dimethyl-9*H*-fluorene-2,7-diyl)diisophthalic acid), was solvothermally synthesized. **ZJU-60** features a three-dimensional structure with a rare sty-a type topology and has two different types of pore apertures. With open metal sites and suitable pore spaces, **ZJU-60** can readily separate methane in nearly pure form from CO_2 and C_2-hydrocarbon quaternary gas mixtures at room temperature with high separation capacity and moderate selectivity. The separation feasibility has been further established by simulated breakthrough and pulse chromatographic experiments.

1. Introduction

Natural gas often contains impurities such as CO_2, along with C_2-hydrocarbons: C_2H_2, C_2H_4 and C_2H_6. In order to meet pipeline gas specifications, these impurities need to be removed. Methane has been widely utilized as an energy source and raw material. Compared to other conventional automobile fuels such as gasoline (petrol) and diesel, methane can be considered as a cleaner energy alternative due to its clean-burning characteristics, so separation of methane from C_2-hydrocarbons (C_2s) and CO_2 is a very important industrial process.[1] The traditional cryogenic distillation separation technology, which is based on their different vapour pressures and thus boiling points, is very energy-consuming, whereas the alternative oil-absorption method is not efficient.[2] Adsorptive separation is one of the most promising alternative energy- and cost-efficient separation methods, so it is desirable to explore new microporous adsorbents which can selectively separate methane from CO_2 and C_2-hydrocarbons at room temperature.

Among the diverse adsorptive separation materials, metal–organic frameworks (MOFs) have recently shown great promise for such an important application. MOFs can be self-assembled from metal ions or metal-containing clusters with multi-dentate organic linkers through coordination bonding.[3–27] The uniqueness of porous MOFs is that their pore sizes can be systematically tuned with organic linkers of different lengths and geometries while their pore surfaces can be functionalized by the immobilization of different functional sites, such as $-NH_2$ and –OH, and open metal sites for their differential recognition for small molecules and thus for gas separation.[5–15] The first examined MOF (ZIF-8) for C_2s/C_1 separation by ExxonMobil exhibits quite a low separation capacity and selectivity.[28] We significantly enhanced the separation capacity up to about 3.0 mol kg^{-1} and the selectivity up to 35 *via* tuning the pore and cavity sizes in the MOF UTSA-34 for C_2s/C_1 separation.[29] Given the fact that porous MOFs with higher separation capacity and selectivity for the C_2s/C_1 separation can significantly save the energy cost, pursuit of new porous MOF materials for this important application is highly desirable. Herein we report a new copper–organic framework, Cu_2(MFDI) (**ZJU-60**, ZJU = Zhejiang University, H_4MFDI = 5,5′-(9,9-dimethyl-9*H*-fluorene-2,7-diyl)diisophthalic acid), which can separate methane in nearly pure form from CO_2 and C_2-hydrocarbon gas mixtures at room temperature, which has been established exclusively by the sorption isotherms and simulated breakthrough and pulse chromatographic experiments.

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2. Experimental

2.1 Materials and measurements

All the chemicals were commercially available and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Advance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses for C, H, and N were performed on an EA1112 microelement analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 3$–$30°$ range on an X'Pert PRO diffractometer with Cu K_α radiation ($\lambda = 1.542$ Å) at room temperature. Thermogravimetric analyses (TGA) were conducted on a Netszch TGA 209 F3 thermogravimeter with a heating rate of 10 °C min^{-1} in a N_2 atmosphere.

2.2 Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption. To have a guest-free framework, the fresh sample was guest-exchanged with dry acetone at least 10 times, filtered and vacuumed at room temperature for 12 h and then at 383 K until the outgas rate was 5 μmHg min^{-1} prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen and at 273 K with ice-water bath (slush), respectively. As the center-controlled air condition was set up at 23.0 °C, a water bath of 23.0 °C was used for adsorption isotherms at 296.0 K.

2.3 X-ray collection and structure determination

Crystallographic measurements were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Cu K_α radiation ($\lambda = 1.54178$ Å) at 293 K for **ZJU-60**. The measurements of the unit cells and data collections for the crystals of **ZJU-60** were performed with CrysAlisPro. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[30] The structure was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package.[31] All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. H atoms on C atoms were generated geometrically. The solvent molecules in **ZJU-60** are highly disordered. The SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules.[32] Crystallographic data are summarized in Table S1.†

2.4 Synthesis of ZJU-60

A mixture of H_4MDDI (1.04 mg, 0.0020 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.949 mg, 0.0080 mmol) was dissolved in DMF–H_2O (3 mL, 4 : 1, v/v) in a screw-capped vial. After HNO_3 (40 μL) (69%, aq.) was added to the mixture, the vial was capped and placed in an oven at 65 °C for 48 h. The resulting hexagonal flake-shaped single crystals were washed with DMF several times to give **ZJU-60**. Elemental analysis: calcd for $[Cu_2(C_{31}H_{18}O_8)(H_2O)_2](DMF)_8(H_2O)_{12}$: C, 44.56; H, 6.93; N, 7.56; Found: C, 44.56; H, 6.95; N: 7.56%.

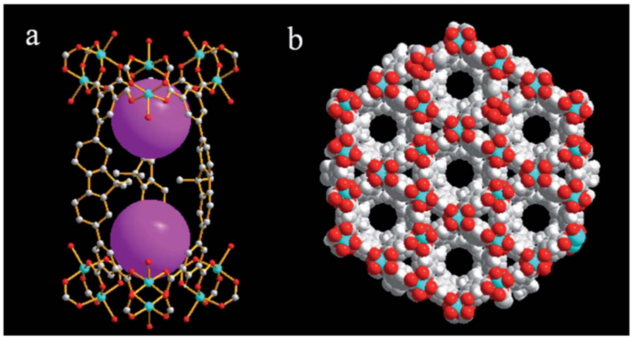

Fig. 1 X-ray single crystal structure of **ZJU-60** indicating (a) a large irregular elongated pore cage of about 4.4 × 8.6 Å^2 in diameter; and (b) the pores along the *c* axis with the size of about 5.4 Å.

3. Results and discussion

ZJU-60 was synthesized from $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_4MFDI in DMF–H_2O with addition of a small amount of nitric acid at 60 °C for 2 days as small blue cuboid block-shaped crystals. The structure of **ZJU-60** was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD, Fig. S1†) and thermogravimetric analysis (TGA, Fig. S2†).

The single-crystal X-ray diffraction analysis reveals that **ZJU-60** crystallizes in a hexagonal space group of $P6_3/mmc$.‡ The framework is composed of paddle wheel dinuclear $Cu_2(COO)_4$ units which are bridged by organic linkers to form a 3D rare stya type structure. The 3D framework of **ZJU-60** has two different types of pores. The large irregular elongated cage of about 4.4 × 8.6 Å^2 runs through the *a* axis (Fig. 1a). Another one along the *c* axis is about 5.4 Å in diameter, taking into account the van der Waals radii (Fig. 1b).

To characterize the permanent porosity, the N_2 sorption isotherm experiments were performed at 77 K. It shows that the suitably activated **ZJU-60a** exhibits reversible Type-I sorption behaviour, characteristic of microporous materials with the saturated sorption amount of N_2 of 561 cm^3 g^{-1} (Fig. 2a). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of **ZJU-60a** are 1627 and 2394 m^2 g^{-1}, respectively. As expected, these values are higher than those of MOF-505 because of the longer linker in **ZJU-60**. **ZJU-60a** has a pore volume of 0.867 cm^3 g^{-1}.

Establishment of the permanent porosity of **ZJU-60a** encourages us to examine its potential application in gas storage and selective gas separation. As shown in Fig. 2b and c, **ZJU-60a** can take up moderate amounts of C_2H_2 of 178.66 and 150.57 cm^3 g^{-1} at 273 and 296 K, respectively, under 1 atm. The

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‡ Crystal data for **ZJU-60**: $C_{31}H_{22}Cu_2O_{10}$, $M = 681.57$, $P6_3/mmc$, $a = b = 18.4819(3)$ Å, $c = 34.4495(5)$ Å, $V = 10\,190.8(3)$ Å^3, $Z = 6$, $D_c = 0.666$ g cm^{-3}, μ(Cu-K_α) = 0.988 mm^{-1}, $F(000) = 2076$, GoF = 1.070, final $R_1 = 0.0599$ for $I > 2\sigma(I)$, and w$R_2 = 0.1636$ for all data. CCDC: 969710.

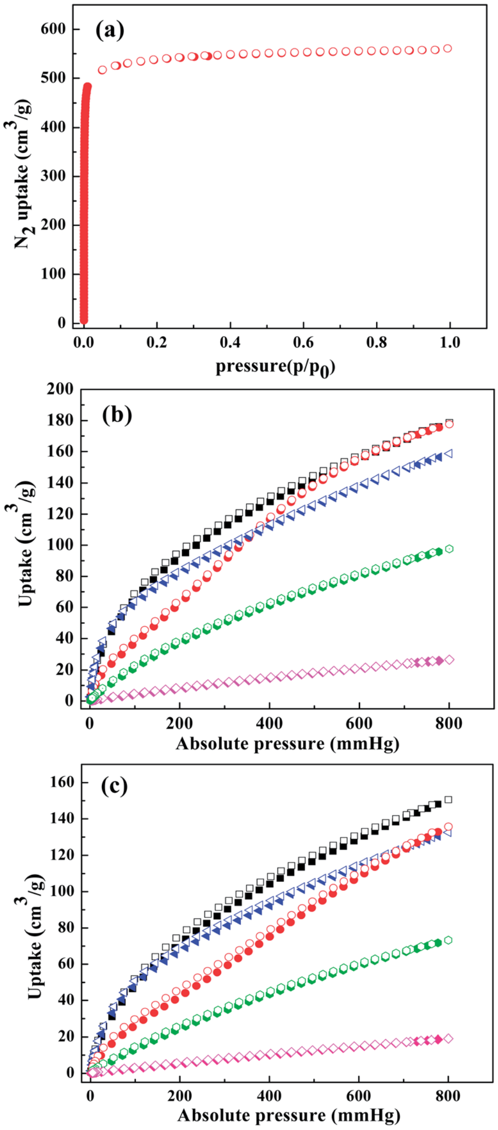

Fig. 2 (a) N_2 sorption isotherm at 77 K and CH_4 (magenta), CO_2 (green), C_2H_6 (red) and C_2H_4 (blue), C_2H_2 (black) sorption isotherms of ZJU-60a at (b) 273 K and (c) 296 K. Solid symbols: adsorption, open symbols: desorption.

amount of adsorbed C_2H_2 in **ZJU-60a** at 296 K is slightly higher than that in MOF-505 (148 cm^3 g^{-1}).[33]

ZJU-60a can take up C_2H_2 (178.67 cm^3 g^{-1}), C_2H_4 (158.71 cm^3 g^{-1}), C_2H_6 (177.59 cm^3 g^{-1}), and CO_2 (97.69 cm^3 g^{-1}) at 1 atm and 273 K, and C_2H_2 (150.57 cm^3 g^{-1}), C_2H_4 (132.55 cm^3 g^{-1}), C_2H_6 (135.66 cm^3 g^{-1}) and CO_2 (73.3 cm^3 g^{-1}) at 1 atm and 296 K, which are much higher than the amount of CH_4 (26.4 cm^3 g^{-1}) at 273 K and that of CH_4 (19.06 cm^3 g^{-1}) at 296 K. Such different sorption enables **ZJU-60a** to be a promising material for highly selective adsorptive separation of C_2-hydrocarbons and CO_2 from CH_4.

In order to establish the feasibility of these gas separations, we performed calculations using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[34] Fig. S3† presents calculations using IAST for the component loading in the adsorbed mixture in equilibrium with an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K in **ZJU-60a.** The IAST calculations indicated that the hierarchy of adsorption strengths is $C_2H_2 > C_2H_4 > C_2H_6 > CO_2 > CH_4$.

The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)q$$

was determined using the pure component isotherm fits. Fig. S4† shows data on the loading dependence of Q_{st} for adsorption of CH_4, CO_2, C_2H_2, C_2H_4 and C_2H_6 on **ZJU-60a**. The isosteric heat of adsorption of CH_4 on **ZJU-60a** is 12.0 kJ mol^{-1}, whereas the isosteric heats of adsorption of C_2H_2, C_2H_4, C_2H_6 and CO_2 are 17.6, 21.4, 19.8 and 15.2 kJ mol^{-1}, respectively. The higher adsorption heats for C_2 hydrocarbons and CO_2 might be due to the comparable pore sizes and open metal sites in **ZJU-60a** with these small C_2 hydrocarbons and CO_2, thereby enforcing their interaction with the host framework, and thus leading to moderately high C_2-hydrocarbons/CH_4 and CO_2/CH_4 selective separation.

To obtain pure CH_4 from natural gas streams, the adsorption selectivity of CO_2 with respect to CH_4 is very important. We used two different metrics to evaluate the performance of **ZJU-60a** for the CO_2/CH_4 separation. The first metric is the adsorption selectivity. Fig. 3 shows the IAST adsorption selectivity, S_{ads}, for equimolar CO_2/CH_4 mixtures at 296 K in **ZJU-60a.** The adsorption selectivities of CO_2 with respect to CH_4 are higher than 5 for **ZJU-60a** for a range of pressures to 100 kPa, indicating that **ZJU-60a** is feasible to separate methane from CO_2 and C_2-hydrocarbons.

Besides the CO_2/CH_4 selectivity, another important metric for pressure swing adsorbers is the uptake capacity for impurities. Fig. 4 presents the IAST calculations for the uptake capacities for the total of four impurities ($C_2H_2 + C_2H_4 + C_2H_6 + CO_2$) in the 5-component mixture. We note that the capacity of **ZJU-60a** for impurity uptake reaches 3 mol L^{-1} at 100 kPa and 296 K, which is higher than that of our recently developed UTSA-34.[29]

In order to properly evaluate the feasibility for the practical separation, the breakthrough experiments were simulated based on the established methodology described in the work of

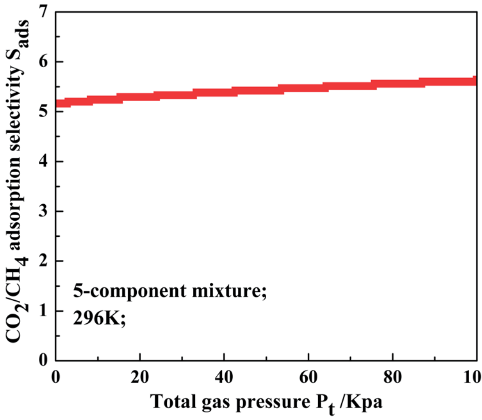

Fig. 3 IAST adsorption selectivities of CO_2/CH_4 for the equimolar $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture in the total bulk gas phase at 296 K.

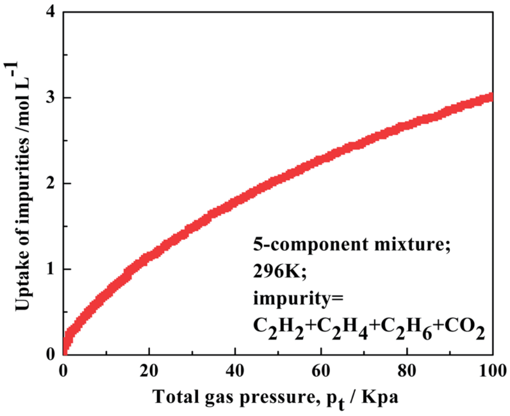

Fig. 4 IAST calculations for the uptake capacities for impurities (C_2H_2 + C_2H_4 + C_2H_6 + CH_4 + CO_2).

Krishna and Long which has been exclusively confirmed by the experimental breakthrough experiments.[35] Fig. 5 presents data on the concentrations at the exit of the adsorber for the chosen MOFs, for illustration purposes. The *x*-axis in Fig. 5 is dimensionless time, τ, defined by dividing the actual time, t, by the characteristic time, $L\varepsilon/u$. We note that the sequence of breakthroughs for the MOFs is CH_4, CO_2, C_2H_6, C_2H_4, and C_2H_2. The adsorbent has the ability to separate CH_4 in pure form from this quaternary mixture.

From the data presented in Fig. 5, we can determine the mol % CH_4 in the exit gas stream. Fig. 6 shows the %CH_4 exiting the adsorber packed with **ZJU-60a**. With the MOFs it is possible to recover pure CH_4 from the gas mixture in a certain interval of time. We arbitrarily set the purity requirement to be 99% CH_4. From a material balance on the adsorber, we can determine the amount of 99% pure CH_4 that can be produced per L of the adsorbent in the fixed bed. The productivity is 0.33 mol L^{-1} for **ZJU-60a**. The separation capability of **ZJU-60a** is also underscored in pulse chromatographic simulations (Fig. S5†). The breakthrough and pulse chromatographic simulations confirm the potency of **ZJU-60** for separation of CH_4 in nearly pure form from gas mixtures containing CO_2, C_2H_2, C_2H_4 and C_2H_6 species at room temperature.

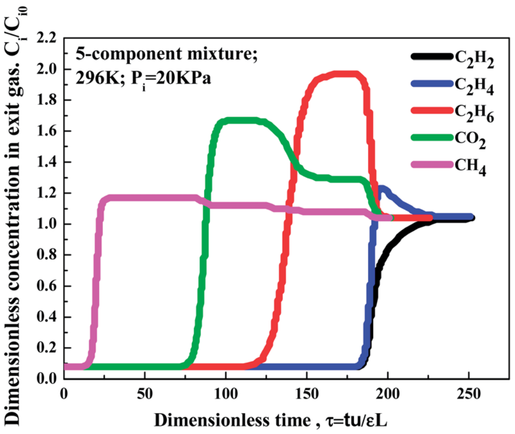

Fig. 5 Breakthrough simulation results for **ZJU-60a** for separation of an equimolar $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture in a fixed bed adsorbent in the total bulk gas phase at 296 K and 100 kPa. The *x*-axis represents the dimensionless time, τ.

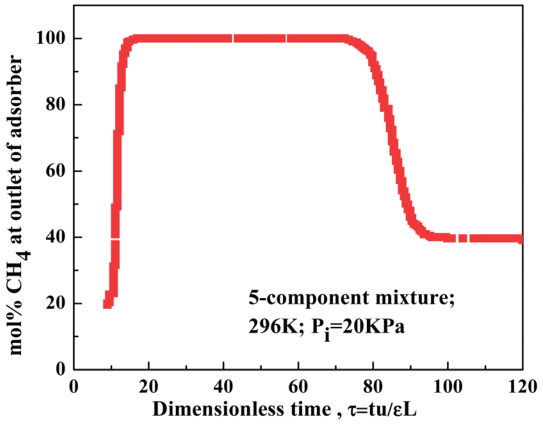

Fig. 6 The %CH_4 exiting the bed adsorber packed with **ZJU-60a**. The inlet gas consists of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K and 100 kPa.

4. Conclusions

In summary, we have synthesized a novel three-dimensional porous metal–organic framework **ZJU-60** for separation of methane in nearly pure form from CO_2 and C_2-hydrocarbon quaternary gas mixtures at room temperature with high separation capacity and moderate selectivity. The high separation capacity is attributed to the suitable pore space and open metal sites within pores of the framework to take up a large amount of hydrocarbons and CO_2. It is expected that this work will initiate more investigations on the emerging MOFs for such industrially important separation.

Acknowledgements

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Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Metal–Organic Frameworks with Potential for Adsorptive Separation of Methane from Carbon Dioxide, Acetylene, Ethylene, and Ethane Established by Simulated Breakthrough Experiments

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Fitting of pure component isotherms

The experimentally measured excess loadings of C_2H_2, C_2H_4, C_2H_6, CH_4, CO_2, and N_2 in **ZJU-60a**, obtained at 273 K and 296 K, were first converted to absolute loadings before data fitting. The procedure for converting excess loadings to absolute loadings is described in detail in the Supporting Information accompanying Wu et al.[1]

The isotherm data at both temperatures were fitted with the Langmuir-Freundlich model

$$q = q_{sat} \frac{bp^{v}}{1 + bp^{v}} \tag{1}$$

with *T*-dependent parameter *b*

$$b_A = b_0 \exp\left(\frac{E}{RT}\right) \tag{2}$$

The Langmuir-Freundlich parameters for **ZJU-60a** are provided in *Tables S2,* Figure S3 presents calculations using IAST for the component loading in the adsorbed mixture in equilibrium with an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K in ZJU-60a.

IAST calculations of Adsorption selectivity

Let us first consider the separation of CH_4 from a mixture containing C_2 hydrocarbons and CO_2. Rather than restrict our investigations to just binary CH_4/CO_2mixtures, we consider the selective adsorption of C_2 hydrocarbons and CO_2 from an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture. The choice of such a mixture is dictated by the fact that such mixture separations are encountered in the process oxidative coupling of methane for producing ethane.

We define the *adsorption selectivity*, defined by

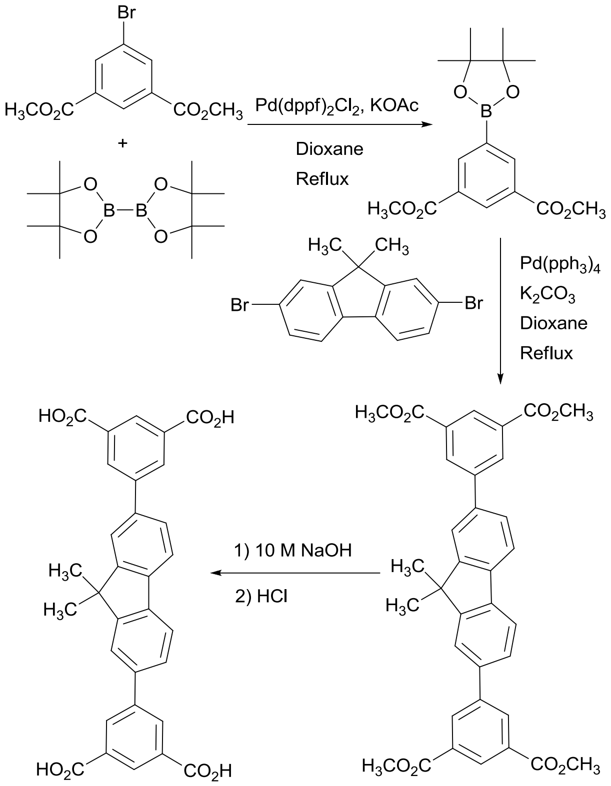
$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad (3)$$

Here p_1 and p_2 are taken to be the partial pressures of CO_2 and CH_4, respectively. The q_1 and q_2 are the molar loadings in the adsorbed phase, CO_2 and CH_4, respectively, expressed in mol per kg of adsorbent material.

Breakthrough in fixed bed adsorber unit

Both selectivities and uptake capacities are important in determining the separation performance in a fixed bed adsorber. For a proper comparison we undertook breakthrough calculations. Figure S5 shows a schematic of packed bed adsorber packed with **ZJU-60a**. The methodology used in the breakthrough calculations are provided in our earlier works.[2-8] Experimental validation of the breakthrough simulation methodology is available in the published literature[1,2,9,10].

The following parameter values were used: length of packed bed, $L = 0.1$ m; fractional voidage of packed bed, $\varepsilon = 0.4$; superficial gas velocity at inlet of adsorber, $u = 0.04$ m/s. The inlet gas consists of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K and 100 kPa.



Scheme S1. Synthetic route to the organic linker used to construct **ZJU-60**.

Synthesis of the organic linekr H_4MFDI: H_4MFDI was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in *Scheme S1*.

Dimethyl (5-pinacolboryl)isopthalate was synthesized by stirring the mixture of dimethyl 5-bromo-benzene-1,3-dicarboxylate (5.4 g, 19.8 mmol), bis(pinacolato)diborane (6.0 g, 23.6 mmol), potassium acetate (5.6 g, 57.2 mmol), Pd(dppf)$_2$Cl$_2$ (0.2 g, 0.28 mmol), and dried 1,4-dioxane (50 mL) at 80^{o}C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, ethylacetate/petroleum ether, 1:8 *v*/*v*). Yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1H) ppm.

2, 7-dibromo-9*H*-fluorene (3.28 g, 10.0 mmol), dimethyl(5-pinacolboryl)isopthalate (9.26 g, 30.0 mmol), and K_2CO_3 (13.82 g, 100.0 mmol) were added to 1,4- dioxane (250 mL), and the mixture deaerated under Ar for 15 min. Pd(PPh$_3$)$_4$ (0.47 g,0.43 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80 ℃ for 3 days under Ar. The resultant mixture was evaporated to dryness and taken up in

$CHCl_3$ which had been dried over $MgSO_4$. The $CHCl_3$ solution was evaporated to dryness and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10 *v*/*v*). Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 4.00 (s, 12 H), 4.08 (s, 2H), 7.73 (d, 2 H), 7.89 (d, 2H), 7.93 (d, 2H) 8.54 (s, 4H), 8.67 (s, 2H) ppm.

Tetramethyl 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalate (H_4MFDI-Me) (3.47g, 6.00mmol) was then suspended in a mixture of 1,4-dioxane (20 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at *p*H = 2. The solid was collected by filtration, washed with water, and dried to give 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalic acid (H_4MFDI) (2.87 g, 97% yield). ^{1}H NMR (500 MHz, DMSO), δ = 1.62 (s, 6 H), 7.77 (d, 2H), 8.01 (s, 2 H), 8.04 (s, 2H), 8.47(s, 6H), 13.48 (s, 4H) ppm.

Table1 S1. Crystallographic Data Collection and Refinement Results for **ZJU-60.**

	ZJU-60
Chemical formula	$C_{31}H_{22}Cu_2O_{10}$
Formula weight	681.57
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a (Å)	18.4819(3)
b (Å)	18.4819(3)
c (Å)	34.4495(5)
V (Å^3)	10190.8(3)
Z	6
Density (calculated g/cm^3)	0.666
Absorbance coefficient (mm^{-1})	0.988
F(000)	2076
Crystal size(mm^3)	0.43χ0.31χ0.11
Goodness of fit on F^2	1.070
R_1, wR_2 $[I>2\sigma(I)]$	0.0599,0.1569
R_1, wR_2 (all data)	0.0721,0.1636
Largestdifference peak and hole(e/Å^3)	0.396,-0.297

Table S2. Langmuir isotherm parameter fits for **ZJU-60a**

	q_{sat} **mol kg^{-1}**	b_0 Pa$^{-\nu}$	E **kJ mol^{-1}**	**dimensionless**
C_2H_2	17	4.13×10^{-6}	8.9	0.66
C_2H_4	15	8.61×10^{-6}	8.5	0.72
C_2H_6	18.7	1.13×10^{-8}	14.7	1
CH_4	7.5	9.56×10^{-9}	12	1
CO_2	8.8	1.72×10^{-8}	14.2	1
N_2	4.5	8.37×10^{-9}	11.2	1

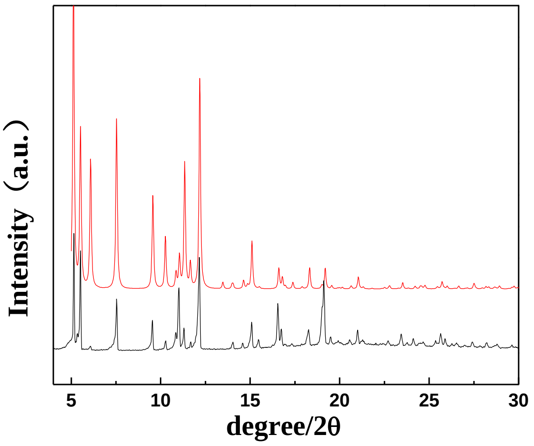


Figure S1. PXRD patterns of as-synthesized **ZJU-60** (black) and the simulated XRD pattern from the single-crystal X-ray structure (red).

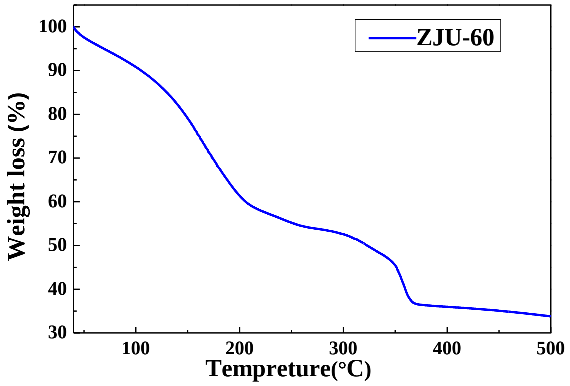


Figure S2. TG of **ZJU-60**

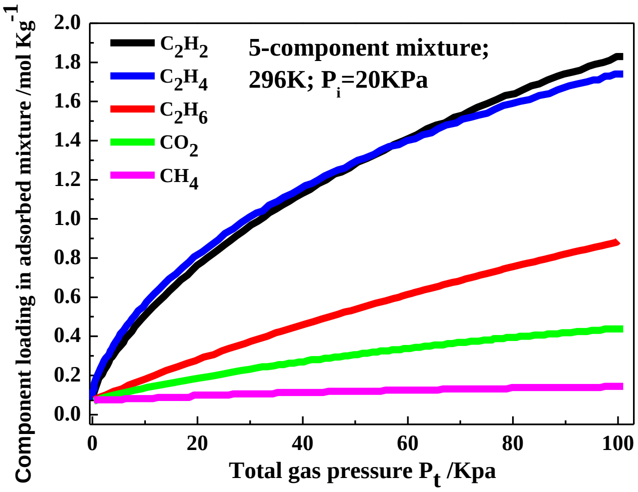


Figure S3. IAST calculations of the component molar loadings in equilibrium with an *equimolar* $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture at total bulk gas phase at 296 K.

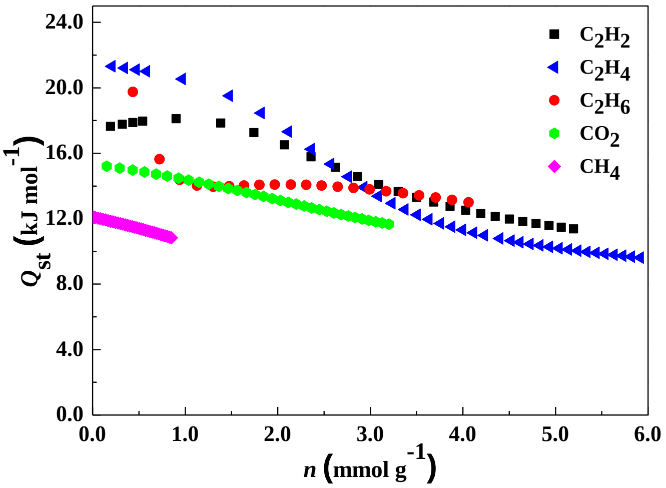


Figure S4 The isosteric heats of adsorption of C_2H_2, C_2H_4, C_2H_6, CO_2 and CH_4 on **ZJU-60a**.

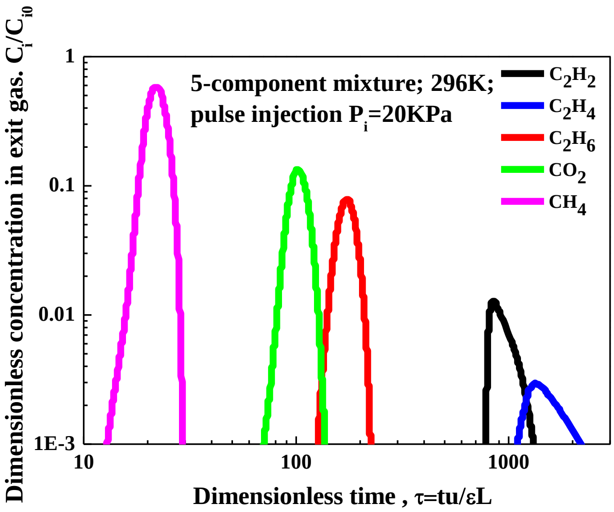


Figure S5. Pulse chromatographic simulations for adsorber packed with **ZJU-60a**. The inlet gas consists of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K and 100 kPa. The pulse duration is 10 s.

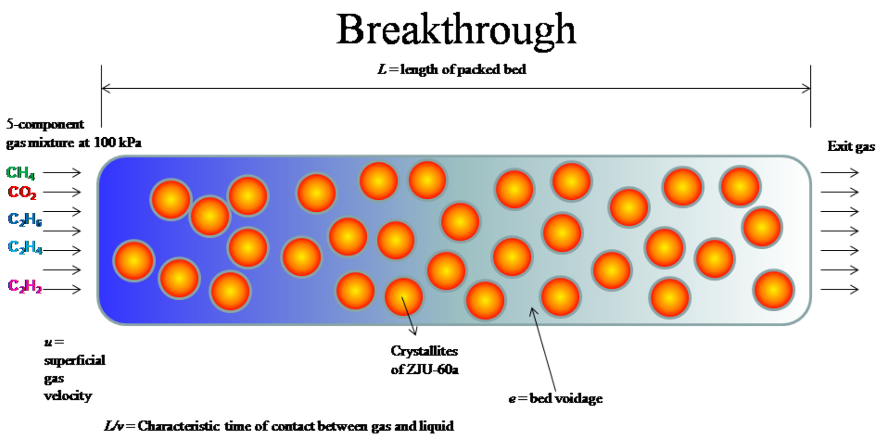


Figure S6. Schematic of packed bed adsorber packed with **ZJU-60a**.

Abbreviations

Notation

b	Langmuir-Freundlich constant, $\mathrm{Pa}^{-\nu}$
L	length of packed bed adsorber, m
p_i	partial pressure of species *i* in mixture, Pa

p_t	total system pressure, Pa
q_i	component molar loading of species *i*, mol kg^{-1}
q_t	total molar loading in mixture, mol kg^{-1}
q_{sat}	saturation loading, mol kg^{-1}
R	gas constant, 8.314 J mol^{-1} K^{-1}
S_{ads}	adsorption selectivity, dimensionless
t	time, s
T	absolute temperature, K
u	superficial gas velocity in packed bed, m s^{-1}
z	distance along the adsorber, m

Greek letters

ε	voidage of packed bed, dimensionless
ν	exponent in Langmuir-Freundlich isotherm, dimension- less
ρ	framework density, kg m^{-3}
τ	time, dimensionless

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