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\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{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.\textsuperscript{1}

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

\[ q = q_{\text{sat}} \frac{bp'}{1 + bp'} \]

with \( T \)-dependent parameter \( b \)

\[ b_\lambda = b_0 \exp \left( \frac{E}{RT} \right) \]

(1)

(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\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4}/CO\textsubscript{2} gas mixture at 296 K in ZJU-60a.

IAST calculations of Adsorption selectivity

Let us first consider the separation of CH\textsubscript{4} from a mixture containing C\textsubscript{2} hydrocarbons and CO\textsubscript{2}. Rather than restrict our investigations to just binary CH\textsubscript{4}/CO\textsubscript{2} mixtures, we consider the selective adsorption of C\textsubscript{2} hydrocarbons and CO\textsubscript{2} from an equimolar 5-component C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4}/CO\textsubscript{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
\[
S_{ads} = \frac{q_1/q_2}{p_1/p_2} 
\]

Here \( p_1 \) and \( p_2 \) are taken to be the partial pressures of \( \text{CO}_2 \) and \( \text{CH}_4 \), respectively. The \( q_1 \) and \( q_2 \) are the molar loadings in the adsorbed phase, \( \text{CO}_2 \) and \( \text{CH}_4 \), 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 \textbf{ZJU-60a}. The methodology used in the breakthrough calculations are provided in our earlier works.\(^\text{2-8}\) Experimental validation of the breakthrough simulation methodology is available in the published literature\(^\text{1,2,9,10}\).

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 \( \text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{CH}_4/\text{CO}_2 \) 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 linker H₄MFDI:** H₄MFDI was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in Scheme S1.

Dimethyl (5-pinacolboryl)isophthalate 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)₂Cl₂ (0.2 g, 0.28 mmol), and dried 1,4-dioxane (50 mL) at 80°C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous MgSO₄ 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%. ¹H NMR (500 MHz, CDCl₃): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1H) ppm.

2, 7-dibromo-9H-fluorene (3.28 g, 10.0 mmol), dimethyl(5-pinacolboryl)isophthalate (9.26 g, 30.0 mmol), and K₂CO₃ (13.82 g, 100.0 mmol) were added to 1,4-dioxane (250 mL), and the mixture deaerated under Ar for 15 min. Pd(PPh₃)₄ (0.47 g, 0.43 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80°C for 3 days under Ar. The resultant mixture was evaporated to dryness and taken up in
CHCl₃ which had been dried over MgSO₄. The CHCl₃ solution was evaporated to dryness and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10 v/v). Yield: 65%. ¹H NMR (500 MHz, CDCl₃), 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 (H₄MFDI-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 pH = 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 (H₄MFDI) (2.87 g, 97% yield). ¹H 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.

**Table 1 S1.** Crystallographic Data Collection and Refinement Results for ZJU-60.

<table>
<thead>
<tr>
<th></th>
<th>ZJU-60</th>
</tr>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C₃₁H₂₂Cu₂O₁₀</td>
</tr>
<tr>
<td>Formula weight</td>
<td>681.57</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.54178</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.4819(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>18.4819(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>34.4495(5)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>10190.8(3)</td>
</tr>
<tr>
<td>Z</td>
<td>6</td>
</tr>
<tr>
<td>Density (calculated g/cm³)</td>
<td>0.666</td>
</tr>
<tr>
<td>Absorbance coefficient (mm⁻¹)</td>
<td>0.988</td>
</tr>
<tr>
<td>F(000)</td>
<td>2076</td>
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<tr>
<td>Crystal size(mm³)</td>
<td>0.43χ0.31χ0.11</td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
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</tr>
<tr>
<td>R₁, wR₂ [I&gt;2σ(I)]</td>
<td>0.0599,0.1569</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0721,0.1636</td>
</tr>
<tr>
<td>Largest difference peak and hole(e/Å³)</td>
<td>0.396,-0.297</td>
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Table S2. Langmuir isotherm parameter fits for ZJU-60a

<table>
<thead>
<tr>
<th></th>
<th>$q_{\text{sat}}$ [mol kg$^{-1}$]</th>
<th>$b_0$ [Pa$^{-v}$]</th>
<th>$E$ [kJ mol$^{-1}$]</th>
<th>dimensionless</th>
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<tr>
<td>C$_2$H$_2$</td>
<td>17</td>
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<td>C$_2$H$_4$</td>
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<td>8.61×10$^{-6}$</td>
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<tr>
<td>C$_2$H$_6$</td>
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<tr>
<td>CH$_4$</td>
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<td>9.56×10$^{-9}$</td>
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<td>1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.8</td>
<td>1.72×10$^{-8}$</td>
<td>14.2</td>
<td>1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>4.5</td>
<td>8.37×10$^{-9}$</td>
<td>11.2</td>
<td>1</td>
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</table>

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* $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{CH}_4/\text{CO}_2$ mixture at total bulk gas phase at 296 K.

**Figure S4** The isosteric heats of adsorption of $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, $\text{CO}_2$ and $\text{CH}_4$ on ZJU-60a.
**Figure S5.** Pulse chromatographic simulations for adsorber packed with **ZJU-60a**. The inlet gas consists of an equimolar 5-component C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$/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, Pa$^{-1}$
- $L$ length of packed bed adsorber, m
- $p_i$ partial pressure of species $i$ in mixture, Pa
\( p_t \) total system pressure, Pa
\( q_{ti} \) 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
\( \varepsilon \) voidage of packed bed, dimensionless
\( \nu \) exponent in Langmuir-Freundlich isotherm, dimensionless
\( \rho \) framework density, kg m\(^{-3}\)
\( \tau \) time, dimensionless

References


