Electronic Supplementary Information (ESI)

A Microporous Cu$^{2+}$ MOF based on a Pyridyl – Isophthalic Acid Schiff Base Ligand with High CO$_2$ Uptake

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Low pressure CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} sorption isotherms, determination of heat of adsorption and selectivity (CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4}) calculations using IAST.

**Heat of adsorption.** To calculate heats of adsorptions, the corresponding adsorption isotherms at different temperatures were simultaneously fitted using the virial type\textsuperscript{1} Equation 1:

\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]  

(1)

The heat of adsorption at zero coverage was calculated from Equation 2, where as a function of surface coverage, from Equation 3:

\[
Q_{st} = -Ra_o
\]  

(2)

\[
Q_{st} (N) = -R \sum_{i=0}^{m} a_i N^i
\]  

(3)

For the determination of the isosteric heat of adsorption using the Clausious Clapeyron equation a commercially available software, ASiQwin (version 3.01) purchased from Quantachrome, was used.

**Gas selectivity using IAST.** The corresponding calculations were performed according to an established procedure.\textsuperscript{2} Specifically, the single-component adsorption isotherms were described by fitting the data with the following virial-type equation:

\[
p = \frac{n}{K} \exp\left( c_1 n + c_2 n^2 + c_3 n^3 + c_4 n^4 \right)
\]  

(4)

where \( p \) is the pressure in Torr, \( n \) is the adsorbed amount in mmol g\textsuperscript{-1}, \( K \) is the Henry constant in mmol g\textsuperscript{-1} Torr\textsuperscript{-1} and \( c_i \) are the constants of the virial equation.
The free energy of desorption at a given temperature and pressure of the gas is obtained from the analytical integration of eq. (4):

\[ G(T,p) = RT \int_{0}^{p} \frac{n}{p} dp = RT \left( n + \frac{1}{2}c_1n^2 + \frac{2}{3}c_2n^3 + \frac{3}{4}c_3n^4 + \frac{4}{5}c_4n^5 \right) \]  

(5)

The free energy of desorption is a function of temperature and pressure \( G(T,p) \) and describes the minimum work (Gibbs free energy) that required to completely degas the adsorbent surface.

For a binary mixture of component \( i \) and \( j \) eq. (5) yields the individual pure loadings \( n_0^i \) and \( n_0^j \) at the same free energy of desorption:

\[ G_0^i(n_0^i) = G_0^j(n_0^j) \]  

(6)

The partial pressure of component \( i \) and \( j \) in an ideal adsorption mixture is given by the following equations:

\[ py_i = p_i^0(n_0^i)x_i \]  

(7)

\[ py_j = p_j^0(n_0^j)x_j \]  

(8)

where \( y_i (=1-y_j) \) and \( x_i (=1-x_j) \) is the molar fraction of component \( i \) in the gas phase and the adsorbed phase respectively and \( p_i^0, p_j^0 \) is the pure component pressure of \( i \) and \( j \) respectively. From eq. (6)-(8) and (3), the selectivity for the adsorbates \( i \) and \( j \) (\( S_{ij} \)) and the total pressure (\( p \)) of the gas mixture were calculated from eq. (9) and eq. (10), respectively.

\[ S_{ij} = \frac{x_i/y_i}{x_j/y_j} = \frac{p_j^0}{p_i^0} \]  

(9)
\[ p = \sum_{i} (p_i^0 x_i) \] (10)

**Figure S12.** Virial type fitting of CO\(_2\) adsorption isotherms of Cu-PEIP at 273 K and 298 K according to equation 1.

\[ \ln(P), \text{ torr} \]

\[ \text{CO}_2 \text{ uptake, mg g}^{-1} \]

\[ \text{Chi}^2/\text{DoF} = 6.7197 \times 10^{-6} \]

\[ R^2 = 0.99999 \]

\[ a_0 = -4.1145 \pm 0.00001 \]
\[ a_1 = 22.66276 \pm 0.000075 \]
\[ a_2 = -0.00761 \pm 0.000069 \]
\[ a_3 = 0.0001 \pm 0.000001 \]
\[ a_4 = -7.33398 \pm 1.5483E-8 \]
\[ a_5 = 14.3555 \pm 0.000016 \]
\[ b_0 = -0.00565 \pm 0.000016 \]
\[ b_1 = 0.00021 \pm 0.000001 \]

\[ \text{Chi}^2/\text{DoF} = 6.5803 \times 10^{-6} \]

\[ R^2 = 0.99999 \]

\[ a_0 = -2.55227 \pm 8.3413 \]
\[ a_1 = 8.78916 \pm 2.6476 \]
\[ a_2 = 0.0483 \pm 0.00007 \]
\[ a_3 = -0.00931 \pm 0.000036 \]
\[ a_4 = 0.00014 \pm 0.000007 \]
\[ b_0 = 12.473 \pm 0.002643 \]
\[ b_1 = -0.01687 \pm 0.000875 \]
\[ b_2 = 0.00004 \pm 0.00005 \]
**Figure S13.** Virial type fitting of CH$_4$ adsorption isotherms of Cu-PEIP at 273 K and 298 K according to equation 1.

![Virial Type Fitting of CH$_4$ Adsorption Isotherms](image.png)

**Figure S14.** CH$_4$ isosteric heat of adsorption ($Q_{st}$) of Cu-PEIP as a function of surface coverage, calculated from a virial-type analysis. The corresponding Clausius-Clapeyron calculation is shown with the solid line.

![CH$_4$ Isosteric Heat of Adsorption](image.png)

**Table S1.** Comparison of Cu-PEIP with selected MOFs in terms of BET surface area, crystallographic density and total CH$_4$ uptake at 65 bar, working capacity (5-65 bar) at 298 K and isosteric heat of adsorption.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET area m$^2$ g$^{-1}$</th>
<th>Crystal density g cm$^{-3}$</th>
<th>Total gravimetric uptake g g$^{-1}$</th>
<th>Total volumetric uptake cm$^3$ cm$^{-3}$</th>
<th>Gravimetric working capacity g g$^{-1}$</th>
<th>Volumetric working capacity cm$^3$ cm$^{-3}$</th>
<th>$Q_{st0}$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-PEIP</td>
<td>1785</td>
<td>0.645</td>
<td>0.166</td>
<td>176</td>
<td>0.119</td>
<td>125</td>
<td>21.2</td>
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<tr>
<td>MAF-38</td>
<td>2022</td>
<td>0.761</td>
<td>0.247</td>
<td>263</td>
<td>0.176</td>
<td>187</td>
<td>21.6</td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>1350</td>
<td>1.195</td>
<td>0.148</td>
<td>251</td>
<td>0.077</td>
<td>129</td>
<td>21.4</td>
</tr>
</tbody>
</table>
Table S2. Comparison of Cu-PEIP with selected MOFs in terms of total CH4 uptake, and working capacity between 5-35 bar and 5-80 bar at 298 K.7

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area, m² g⁻¹</th>
<th>Density, g cm⁻³</th>
<th>Total uptake at 35 bar, cm³ g⁻¹</th>
<th>Total uptake at 80 bar, cm³ g⁻¹</th>
<th>Workin g capacity at 35 bar, cm³ cm⁻³ g⁻¹</th>
<th>Workin g capacity at 80 bar, cm³ cm⁻³ g⁻¹</th>
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</thead>
<tbody>
<tr>
<td>UTSA-76⁴</td>
<td>2820</td>
<td>0.699</td>
<td>0.263</td>
<td>257</td>
<td>0.201</td>
<td>197</td>
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<tr>
<td>NU-111⁵</td>
<td>4930</td>
<td>0.409</td>
<td>0.360</td>
<td>205</td>
<td>0.313</td>
<td>177</td>
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<td>0.216</td>
<td>267</td>
<td>0.154</td>
<td>190</td>
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<tr>
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<td>0.197</td>
<td>230</td>
<td>0.136</td>
<td>157</td>
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<td>NU-1100⁶</td>
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<td>160</td>
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<tr>
<td>Cu-PEIP</td>
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<td>1814</td>
<td>0.762</td>
<td>150</td>
<td>0.176</td>
<td>99</td>
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<tr>
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<td>2229</td>
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<td>226</td>
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<tr>
<td>MOF-520</td>
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<td>3930</td>
<td>0.586</td>
<td>162</td>
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<tr>
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</table>
Figure S15. Hydrogen sorption isotherms of Cu-PEIP recorded at 77 K and 87 K.

Figure S16. Virial type fitting of H₂ adsorption isotherms of Cu-PEIP at 77 K and 87 K according to equation 1.
**Figure S17.** Hydrogen isosteric heat of adsorption (\(Q_{st}\)) of Cu-PEIP as a function of surface coverage, calculated from a virial-type analysis. The corresponding Clausius-Clapeyron calculation is show with the solid line.

**Figure S18.** High pressure \(\text{H}_2\) adsorption isotherm (up to 100 bar) of Cu-PEIP recorded at 77 K.
References


