Effect of pendant isophthalic acid moieties on the adsorption properties of light hydrocarbons in HKUST-1-like tbo-MOFs: Application to methane purification and storage

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tbo-MOF-2 and tbo-MOF-3

**Fig. S1**

a) L1: The ligand in tbo-MOF-2 is constructed from tetra-isophthalate termini (red) connected through alkoxy (i.e., methoxy) links (black) to a 4-connected benzene core (blue). b) Representative section from the crystal structure of 3-periodic tbo-MOF-2, showing polyhedral cages. c) Each type of polyhedral cage in tbo-MOF-2; truncated tetrahedron (red), truncated cube (yellow), and truncated cuboctahedron (green). d) L2: Functionalized version of L1, with pendant isophthalate moieties at the 3- and 6- positions. e) Representation of the largest cage from the 3-periodic tbo-MOF-3; the open space is reduced due to pendant groups, as indicated by the relatively small vDW sphere.
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N\textsubscript{2} adsorption at 77 K

For sorption measurements, each compound, tbo-MOF-2 and tbo-MOF-3, were loaded into a sample cell wet, excess solvent was decanted using a syringe and then any remaining solvent was evaporated by allowing a continuous flow of N\textsubscript{2} to pass through the sample cell. Then, the sample was loaded onto the degasser.

Gas sorption measurements were conducted on the fully-evacuated tbo-MOFs after exchanging the guest molecules in tbo-MOF-2 and tbo-MOF-3 with CH\textsubscript{3}CN and chloroform, respectively for 5 days. The argon sorption isotherms for both materials revealed reversible type I isotherms, which are characteristic of microporous materials (Fig. S2).

The pore size distribution, calculated from the Ar isotherms, revealed the presence of three distinct pore sizes, which correspond to the truncated tetrahedron, truncated cube, and truncated cuboctahedron. Accordingly, the estimated diameter of the cages is 7.7, 11.2 and 14.5 Å in tbo-MOF-2 and 7.2, 9.6 and 10.8 Å in tbo-MOF-3.

Fig. S2 Adsorption-desorption isotherms of Ar on the parent, tbo-MOF-2 (1), and tbo-MOF-3 (2).
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Adsorption isotherms of CO₂, CH₄, C₂H₆, C₂H₄, C₃H₈, and C₃H₆

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme S1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flow meters, and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere, and is able to perform adsorption measurements across a wide pressure range (i.e., from 0 to 20 MPa). The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount (Ω). Correction for the buoyancy effect is required to determine the excess and absolute adsorbed amount using equations 1 and 2, where \( V_{\text{adsorbent}} \) and \( V_{\text{ss}} \) and \( V_{\text{adsorbed phase}} \) refer to the volume of the adsorbent, the volume of the suspension system, and the volume of the adsorbed phase, respectively.

\[
\Omega = m_{\text{absolute}} - \rho_{\text{gas}} \left( V_{\text{adsorbent}} + V_{\text{ss}} + V_{\text{adsorbed phase}} \right) \quad (1)
\]

\[
\Omega = m_{\text{excess}} - \rho_{\text{gas}} \left( V_{\text{adsorbent}} + V_{\text{ss}} \right) \quad (2)
\]

The buoyancy effect resulting from the adsorbed phase may be taken into account via correlation with the pore volume or with the theoretical density of the sample.
These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined using the Refprop equation of state (EOS) database and checked experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas-phase density as a function of pressure and temperature is therefore possible.

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 200 mg of sample is outgassed at 473 K at a residual pressure of $10^{-6}$ mbar. The temperature during adsorption measurements is held constant by using a thermostat-controlled circulating fluid.
Toth Model for single gas adsorption fitting

In the current work, the Toth model was used to fit the pure gas isotherms because of its suitable behavior at both low and high pressure and its simple formulation as expressed by equation 3 (Toth, 2002)\(^1\)

\[
    n = n_s \frac{KP}{(1 + (KP)^m)^{1/m}}
\]

(3)

where \(n\) is the amount adsorbed, \(n_s\) is the amount adsorbed at saturation, \(P\) is the equilibrium pressure, \(K\) is the equilibrium constant, and \(m\) is a parameter indicating the heterogeneity of the adsorbent.

Fig. S3 Density of CH\(_4\) (adsorbed phase) as a function of pressure in our tbo-MOFs compared to the corresponding data for the best (methane storage) MOFs reported so far (UTSA-20,\(^2\) PCN-14,\(^3\) Ni-MOF-74,\(^4\) and tbo-MOF-1 (HKUST-1)\(^5\)).
Table S1 Volumetric CH$_4$ working capacity using adsorption and desorption at 5 bar and 35 bar, respectively, for tbo-MOF-2, tbo-MOF-3, UTSA-20, PCN-14, Ni-MOF-74, gea-MOF-1 and tbo-MOF-1 (HKUST-1).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Estimated CH$_4$ adsorption uptake at 5 bar cm$^3$ (STP)/cm$^3$</th>
<th>Estimated CH$_4$ adsorption uptake at 35 bar cm$^3$ (STP)/cm$^3$</th>
<th>Working storage uptake cm$^3$ (STP)/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tbo-MOF-2</td>
<td>40</td>
<td>160</td>
<td>120</td>
</tr>
<tr>
<td>tbo-MOF-3</td>
<td>50</td>
<td>125</td>
<td>75</td>
</tr>
<tr>
<td>UTSA-20</td>
<td>100</td>
<td>180</td>
<td>80</td>
</tr>
<tr>
<td>PCN-14</td>
<td>75</td>
<td>190</td>
<td>115</td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>105</td>
<td>225</td>
<td>120</td>
</tr>
<tr>
<td>gea-MOF-1</td>
<td>40</td>
<td>140</td>
<td>100</td>
</tr>
<tr>
<td>HKUST-1 (tbo-MOF-1)</td>
<td>75</td>
<td>225</td>
<td>150</td>
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</table>
Fig. S4 High pressure hydrogen adsorption at 77 K of the parent tbo-MOF-2.
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Physical-chemical properties of probe molecules and adsorption equilibrium data

**Table S2** Physical-chemical properties of sorbates molecules (Li et al. 2009).^6^

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Kinetic diameter/ Å</th>
<th>Polarizability × 10^{25}/cm^3</th>
<th>Dipole moment × 10^{18}/ esu cm</th>
<th>Quadrupole moment × 10^{26}/ esu cm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3.76</td>
<td>25.93</td>
<td>0</td>
<td>0</td>
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<tr>
<td>CO₂</td>
<td>3.3</td>
<td>29.11</td>
<td>0</td>
<td>4.3</td>
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<tr>
<td>C₂H₆</td>
<td>4.44</td>
<td>44.3-44.7</td>
<td>0</td>
<td>0.65</td>
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<tr>
<td>C₂H₄</td>
<td>4.16</td>
<td>42.52</td>
<td>0</td>
<td>1.5</td>
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<tr>
<td>C₃H₈</td>
<td>5.12</td>
<td>62.9-93.7</td>
<td>0.084</td>
<td>0</td>
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<td>C₃H₆</td>
<td>4.67</td>
<td>62.6</td>
<td>0.366</td>
<td>0</td>
</tr>
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</table>

**Table S3** Toth parameters for adsorption on tbo-MOFs.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₂H₄</th>
<th>C₃H₈</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.0869</td>
<td>0.51441</td>
<td>1.0258</td>
<td>12.8020</td>
<td>6.9220</td>
<td>0.1410</td>
</tr>
<tr>
<td>m</td>
<td>0.5113</td>
<td>1.6757</td>
<td>0.5358</td>
<td>0.71738</td>
<td>1.2296</td>
<td>1.2973</td>
</tr>
<tr>
<td>ns</td>
<td>5.4277</td>
<td>5.4256</td>
<td>6.3450</td>
<td>5.9300</td>
<td>5.2637</td>
<td>9.1795</td>
</tr>
<tr>
<td>K</td>
<td>0.1275</td>
<td>2.3898</td>
<td>2.0544</td>
<td>56.8600</td>
<td>65.2091</td>
<td>0.5205</td>
</tr>
<tr>
<td>m</td>
<td>0.9822</td>
<td>0.7827</td>
<td>0.6599</td>
<td>0.4500</td>
<td>0.9161</td>
<td>0.8091</td>
</tr>
</tbody>
</table>
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**Prediction of multicomponent gas adsorption Ideal Adsorption Solution Theory (IAST)**

The Ideal Adsorption Solution Theory (IAST) proposed by Mayer and Prausnitz (1965) uses pure gas adsorption isotherms to predict the mixture adsorption equilibrium at the temperature of interest. For IAST application, the main condition to be fulfilled is the availability of (i) good quality single component adsorption data of different gases, and (ii) an excellent curve fitting model for such data (Chen and Sholl, 2007; Bae et al., 2008). In the current work, MSL and DSL models were used to fit the pure gas isotherms, as mentioned earlier.

The most important equations used in the IAST calculation are listed hereafter:

\[ f_i = x_i f_i^0 (\pi) \]  \hspace{1cm} (3)

\[ \frac{\pi A}{RT} = \int_0^{f_i^0} n_i d \ln f_i \]  \hspace{1cm} (4)

\[ \frac{1}{n_i} = \sum \frac{x_i}{n_i^0} \]  \hspace{1cm} (5)

\[ S_{CO_2-i} = \frac{x_{CO_2}/x_i}{y_{CO_2}/y_i} \]  \hspace{1cm} (6)

where \( f_i \) is the fugacity of component \( i \) in the gas phase; \( f_i^0 \) is the standard-state fugacity (i.e., the fugacity of pure component \( i \) at the equilibrium spreading pressure of the mixture, \( \pi \)); \( x_i \) and \( y_i \) are the mole fractions of component \( i \) in the adsorbed and gas phase, respectively; \( A \) is the surface area of the adsorbent; \( n_i \) is the number of moles adsorbed of pure component \( i \) (i.e.,
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the pure-component isotherm); and $n_i^0$ is the number of moles adsorbed of pure component $i$ at the standard-state pressure.

Equation 3 is the central equation of IAST, specifying the equality of the chemical potential of component $i$ in the gas and the adsorbed phase (which is assumed to be ideal in the sense of Raoult’s law). Equation 4 allows the calculation of the spreading pressure from the pure-component adsorption isotherm. The total amount adsorbed of the mixture, $n_t$, and the selectivity of CO$_2$ with respect to $i$, $S_{CO_2,i}$, are given by equations 5 and 6, respectively. The selectivity, $S_{CO_2,i}$, reflects the efficiency of CO$_2$ separation.
Binary gas mixture adsorption prediction using Ideal Adsorption Solution Theory (IAST)

Fig. S5 CO₂ selectivity over CH₄ for CO₂/CH₄: 05/95 mixture on tbo-MOF-2 and tbo-MOF-3.
Fig. S6 CO₂ selectivity over N₂ for CO₂/N₂: 10/90 mixture on tbo-MOF-2 and tbo-MOF-3.
Fig. S7 C\textsubscript{3}H\textsubscript{8} selectivity over CH\textsubscript{4} for C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4}: 05/95 mixture on tbo-MOF-2 and tbo-MOF-3.
Fig. S8 C$_2$H$_4$ selectivity over CH$_4$ for C$_2$H$_4$/CH$_4$: 05/95 mixture on tbo-MOF-2 and tbo-MOF-3.
Fig. S9 C$_3$H$_6$ selectivity over CO$_2$ for C$_3$H$_6$/CO$_2$: 50/50 mixture on tbo-MOF-2 and tbo-MOF-3.
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References


