SUPPORTING INFORMATION

Expandable Porous Organic Frameworks
with Built-In Amino and Hydroxyl Functions
for CO₂ and CH₄ Capture

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1. Experimental Part

Synthesis of the monomers and the frameworks

Tris(4-bromophenyl)methanol (1). \( p \)-dibromobenzene (8.7 g, 37.2 mmol) was dissolved in freshly distilled THF (135 ml) in a 2-neck round-bottom flask. The solution was cooled down to \(-78\)°C and a 2.5 M hexane solution of \( n \)-BuLi (13.5 ml, 33.8 mmol) was added dropwise. After 3h, the solution was transferred in a 2-neck round-bottom flask containing diethyl carbonate (1.02 ml, 8.5 mmol) dissolved in THF (3 ml). The solution was subsequently allowed to warm up to room temperature. After 6 h, the reaction was quenched with \( \text{NH}_4\text{Cl} \) saturated aqueous solution (50 ml). The crude product was extracted with EtOAc (3 x 50 ml). The organic fractions were collected, washed with brine and subjected to vacuum. Hexane (60 ml) was added to the crude oil and the solution was heated and sonicated producing a white solid, which was collected by filtration to yield 1 3.38 g (80%). \( ^1\text{H} \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.45 (dd, 6H), 7.12 (dd, 6H), 2.70 (s, 1H).

Tris(4-bromophenyl)methane (2). 1 (1.25 g, 2.52 mmol) was added to a 50 ml round-bottom flask. Formic acid (95% in H\(_2\)O, 25 ml) was added slowly. A condenser was attached and the solution was heated to 100°C for 19 h to give a yellow suspension. The reaction was quenched with saturated Na\(_2\)CO\(_3\) solution (100 ml). The aqueous suspension was washed with Et\(_2\)O (3 x 40 ml) and the combined organic phases were washed with brine and evaporated. The resulting solid was passed through a plug of SiO\(_2\) in pentane, to isolate 2 (0.897 g, 74% yield) as a white crystalline solid. \( ^1\text{H} \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.42 (dd, 6H), 6.93 (dd, 6H), 5.40 (s, 1H).

Tris(4-bromophenyl)methylamine (3). 1 (2 g, 4.03 mmol) and anhydrous CH\(_2\)Cl\(_2\) (20 ml) were added to a 2-neck round-bottom flask. The solution was cooled to 0°C and fresh distilled SOCl\(_2\) (2 ml) was added dropwise. After 5 h, the solvent was evaporated, the resulting solid was diluted in anhydrous toluene (25 ml) and added dropwise to a saturated solution of NH\(_3\)Cl in 25% of aqueous ammonia (25 ml) at 0°C. Then, the reaction was stirred for 24 h at 20°C, and the organic phase was
separated, dried and evaporated. Hexane (20 ml) was added to the crude solid and the solution was sonicated for 30 minutes. The white solid was collected by filtration and dried. Pure 3 (1.046 g, 52.6% yield) was obtained by precipitation of its hydrochloride salt. 1H NMR (300 MHz, CDCl₃): δ 7.42 (dd, 6H), 6.93 (dd, 6H), 4.5 (s, 2H).

**General procedure for framework synthesis.** The catalytic mixture was prepared by adding cis,cis-1,5-cyclooctadiene (1 ml), 2,2′-bpyridyl (1 g) and Ni(COD)₂ (2 g) in freshly distilled DMF (180 ml) and THF (60 ml) and stirred at 0°C for 10 minutes. The porous polymers were obtained by adding dropwise the monomer (0.800 g), dissolved in THF (60 ml), to the catalytic mixture and the resulting mixture was stirred at room temperature for 48 h. The reaction was then quenched by adding concentrated HCl (30 ml), until the solution turned green with a white suspension. The product was filtered and washed with THF (3 x 30 ml), water (3 x 30 ml) and chloroform (3 x 30 ml) and dried in a vacuum at 170°C.

The density of the frameworks, as calculated by He picnometry, corresponds to 1.19, 1.27 and 1.31 g cm⁻³ for TPAF, TPAF-OH and TPAF-NH₂, respectively.

**Post-synthetic lithiation (TAF-OLi).** TAF-OH (100 mg) was dispersed in anhydrous THF (15 ml) under nitrogen at room temperature. Lithium hydride (6.2 mg, 0.778 mmol) was added, and the mixture underwent three freeze-pump-thaw cycles and was stirred overnight. The mixture was filtered through a cannula (endowed with a Teflon filter) under dry nitrogen and subsequently washed twice with anhydrous THF (10 ml). Then, the solvent was removed and the material was activated under vacuum (10⁻¹ mmHg) at 160°C for 12 h to obtain TAF-OLi.

**Adsorption measurements**

N₂ adsorption isotherms at 77 K were collected on a Micromeritics ASAP 2020 instrument, the samples were treated overnight at 180 °C under vacuum. The surface area was calculated from the N₂ adsorption isotherm at 77 K using the data in the pressure range p/p° from 0.015 to 0.1, according to the Brunauer-Emmett-Teller (BET) and Langmuir models. The total pore volume was calculated from the N₂ adsorption isotherms at 77 K by the NLDFT method with the carbon slit pore model up to p/p° 0.98. The microporosity was calculated at p/p° = 0.1.

CO₂, CH₄ and N₂ adsorption isotherms at 298, 283 and 273 K and up to 10 bar were collected on a Micromeritics ASAP 2050 instrument, the temperature was controlled using a Julabo F12-ED refrigerated/heating circulator.

CH₄ adsorption isotherms at high pressure were performed using a Micromeritics High Pressure Volumetric Apparatus (HPVA II), equipped with a pressure-booster compressor. The booster allows the compression of gas from the gas cylinder up to 100 bar. The samples were loaded in a 10 ml steel jar and connected to the instrument by a VCR connection with a 10 um seal-frit gasket to avoid the sample dispersion into the manifold system. After the adsorption experiment, a blank-correction was applied to the isotherm. The blank experiment was performed under the same condition of analysis with the empty jar.

The obtained isotherms are “excess” isotherms. Over 10 bar, the gas density rises above the ideal gas and this was taken into account in the elaboration data. To obtain the total adsorbed amount we considered the total pore volume of the sample and methane density following the relationship: 

\[ n_{\text{tot}}(p) = n_{\text{ex}}(p) + V_p \cdot \rho(p). \]

The density value of methane was taken by the NIST database. The volumetric uptake expressed as the volume of the ideal gas over the volume occupied by the same amount at a certain pressure was measured as follows: 

\[ V/V = (V/g) \cdot \left[ 1/(V_p + 1/d) \right] \]

where d corresponds to the density of the host walls, as measured by He picnometry.
The CO₂ and CH₄ isosteric heats of adsorption were calculated by considering adsorption isotherms at 273 K, 283 K and 298 K and applying van ’t Hoff equation. CO₂/N₂ selectivity was calculated by applying IAST theory. The CO₂, CH₄ isotherms were fitted applying a dual site Langmuir model while the N₂ isotherms were fitted by a single site Langmuir model (MATLAB software).

Single site e dual site Langmuir models:

\[ q(T, P) = q_{sat} \cdot \frac{b \cdot p}{1 + b \cdot p} \]  
\[ q(T, P) = q_{sat,A} \cdot \frac{b_A \cdot p}{1 + b_A \cdot p} + q_{sat,B} \cdot \frac{b_B \cdot p}{1 + b_B \cdot p} \]

Here, \( q(T, P) \) is the adsorbed amount (mol/kg), \( q_{sat} \) is the loading for site A or B (mol/kg), \( b \) is the Langmuir parameter associated with the site A or B (Pa⁻¹) and \( p \) is the pressure (Pa).

The CH₄ isotherms up to 100 bar were fitted by a Langmuir-Freundlich model.

\[ q(T, P) = q_{sat} \cdot \frac{b \cdot p^{\alpha}}{1 + b \cdot p^{\alpha}} \]  
\( \alpha \) is a fitting parameter.

**PXRD**

Powder X-ray diffraction was carried out using a Rigaku Miniflex 600 diffractometer operated with CuKα radiation (\( \lambda = 1.54060 \) Å). The analysis was performed with scanning range between 5° and 40° 2θ, scanning speed of 0.8 deg/min and step width of 0.02°.

**SOLID STATE NMR**

Quantitative solid-state \(^1\)H MAS NMR spectra (single-pulse excitation SPE) were performed with a Bruker Avance III 600 MHz instrument operating at 14.1 T, using a recycle delay of 20 s. A MAS Bruker probe head was used with 2.5 mm ZrO₂ rotors spinning at 30 kHz. The 90° pulse for proton was 2.9 μs. The \(^1\)H chemical shift was referenced to adamantane. Spectral profiles were fit by Lorentzian line shapes.

Solid-state NMR spectra were run at 75.5 MHz for \(^{13}\)C on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with high-power amplifiers (1 kW) and a 4 mm double resonance MAS probe. Quantitative \(^{13}\)C SPE MAS NMR spectra were run using a recycle delay of 60 and 100 s and the spectral profile were fit by Lorentzian line shapes.

\(^{13}\)C\(^{\{^1\}H}\) ramped-amplitude cross polarization (CP) MAS experiments were performed at room temperature at a spinning speed of 12.5 kHz, using contact times of 0.05 and 2 ms. The 90° pulse used for proton was 2.9 μs. Crystalline polyethylene was taken as an external reference at 32.8 ppm from TMS.

A MAS NMR 4mm rotor containing porous TAF-NH₂ has been closed in an home-made apparatus under a controlled atmosphere of \(^{13}\)C enriched CO₂. The CO₂ adsorption has been performed at a constant pressure of 100 torr at 298K for 30’ and at 233 K for 1 h. \(^{13}\)C\(^{\{^1\}H}\) CP MAS NMR and 2D PMLG \(^1\)H - \(^{13}\)C HETCOR spectra of TAF-NH₂-\(^{13}\)CO₂ sample have been collected at 215 K at a
spinning speed of 8 kHz with a contact time of 5 ms. Phase-modulated Lee–Goldburg (PMLG) heteronuclear $^1$H-$^{13}$C correlation (HETCOR) experiments coupled with fast magic angle spinning allowed the recording of the 2D spectra with a high resolution in both hydrogen and carbon dimensions. Narrow hydrogen resonances, with line widths on the order of 1–2 ppm, were obtained with homonuclear decoupling during $t_1$; this resolution permits a sufficiently accurate determination of the proton species in the system. The 2D PMLG $^1$H-$^{13}$C HETCOR spectra were run with an LG period of 18.9 $\mu$s. The efficient transfer of magnetization to the carbon nuclei was performed by applying the RAMP-CP sequence.

Quadrature detection in $t_1$ was achieved by the time proportional phase increments method (TPPI). The carbon signals were acquired during $t_2$ under proton decoupling by applying the two-pulse phase modulation scheme (TPPM).

**DLS**

The particle size distribution was carried out using a Malver Zetasizer equipped with a continuous wave 1 mW He-Ne laser operating at 632.6 nm and an avalanche photodiode detector at 173° with respect to the incident beam.

**SEM**

SEM images was collected using Zeiss Gemini 500 scanning electron microscopy, operating at 5 kV.

**HELIUM PYCNOMETER**

The Helium Pycnometer analysis was performed with a Micromeritics AccuPyC II 1340 Pycnometer with a 1 cm$^3$ sample holder. The samples were previously treated in vacuum at 180 °C for 8 h.

**TGA**

TGA measurements was performed using a Mettler Toledo Star System 1 equipped with a gas controller GC10. The analysis was conducted from 25 to 900°C at 10°C/min in air.

**Swellability**

The TAF framework was degassed at 180°C overnight. 1 cm$^3$ of the sample was immersed in acetone to a final volume of 3.5 cm$^3$. After the addition of acetone, the material swelled to 2.7 cm$^3$. The sample was left 1 h in acetone, then filtered and weighed. The swelling ratio (SR%) was calculated as follows:

$$SR\% = \frac{M_s - M_d}{M_d} \cdot 100$$

$M_s$ and $M_d$ are the powder mass in the swollen and in the dry state, respectively. The same procedure was applied for ethyl acetate and hexane.
2. Elemental analysis

Table S1. Elemental analysis of the frameworks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc</td>
<td>Exp</td>
<td>Calc</td>
<td>Exp</td>
</tr>
<tr>
<td>TPAF</td>
<td>94.57%</td>
<td>91.63%</td>
<td>5.43%</td>
<td>5.52%</td>
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<td>0%</td>
<td>0.38%</td>
<td>0%</td>
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<tr>
<td>TPAFOH</td>
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<td>5.09%</td>
<td>5.31%</td>
</tr>
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<td>0%</td>
<td>0.48%</td>
<td>6.22%</td>
<td>6.00%</td>
</tr>
<tr>
<td>TPAFNH2</td>
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<td>85.71%</td>
<td>5.51%</td>
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</tr>
<tr>
<td></td>
<td>5.46%</td>
<td>5.09%</td>
<td>0%</td>
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</table>

3. Thermogravimetric analysis (TGA)

Figure S1. TGA runs of TPAF (blue line), TPAF-OH (red line) and TPAF-NH$_2$ (green line) compounds in air.

4. Powder x-ray diffraction

Figure S2. PXRD patterns of the frameworks.
5. $^1$H and $^{13}$C solid state NMR

**Figure S3.** $^1$H solid state NMR with deconvolution. A) TAF-OH, B) TAF-NH2 and C) TAF.
Figure S4. $^{13}$C CP MAS of TAF at contact time of 2 ms (black) and 50 μs (blue).

Table S2. $^{13}$C chemical shifts of TAF.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ (ppm)</th>
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<td>2</td>
<td>129.30</td>
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<tr>
<td>3</td>
<td>126.82</td>
</tr>
<tr>
<td>C-H</td>
<td>56.16</td>
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</table>
Figure S5. $^{13}$C CP MAS of TAFOH at contact time of 2 ms (black) and 50 μs (blue).

Table S3. $^{13}$C chemical shifts of TAFOH.

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<td>2</td>
<td>128.12</td>
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<tr>
<td>3</td>
<td>126.31</td>
</tr>
<tr>
<td>C-OH</td>
<td>81.32</td>
</tr>
</tbody>
</table>
**Figure S6.** $^{13}$C CP MAS of TAF-NH$_2$ at contact time of 2 ms (black) and 50 μs (blue).

**Table S4.** $^{13}$C chemical shifts of TAF-NH$_2$.

<table>
<thead>
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<th>Assignment</th>
<th>δ (ppm)</th>
</tr>
</thead>
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<td>1</td>
<td>148.00</td>
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<tr>
<td>4</td>
<td>139.82</td>
</tr>
<tr>
<td>2</td>
<td>128.39</td>
</tr>
<tr>
<td>3</td>
<td>126.31</td>
</tr>
<tr>
<td>C-NH$_2$</td>
<td>65.70</td>
</tr>
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</table>
6. Infrared spectroscopy

![Infrared spectra of TPAFH (blue), TPAF-OH (red) and TPAF-NH$_2$ (green).](image)

**Figure S7.** Infrared spectra of TPAFH (blue), TPAF-OH (red) and TPAF-NH$_2$ (green).

FT-IR spectroscopy allows us to determine some structural features and confirms the retention of chemical functionalities upon the synthesis of the framework. Distinctive bands related to the functionality on the ternary carbon appear in the regions 1000-1600 cm$^{-1}$ and 3000-3600 cm$^{-1}$. In TAF-OH the C-O stretching gives rise to a sharp peak at 1158 cm$^{-1}$ observed for tertiary alcohols. In the region above 3000 cm$^{-1}$ a broad band at 3580 cm$^{-1}$ is associated to the presence of O-H groups. No such stretching bands are present in the TAF. TAF-NH$_2$ shows peculiar absorption bands at 3320 and 3380 cm$^{-1}$ due to symmetric and asymmetric stretching of N-H bond of the primary amine.
7. Pore size distribution from CO$_2$ adsorption isotherm

![Graph showing pore size distribution from CO$_2$ adsorption isotherms at 273K.](image)

**Figure S8.** Pore size distribution from CO$_2$ adsorption isotherms at 273K.

8. Swellability measurements

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Weight of dry TAF (g)</th>
<th>Weight of swollen TAF (g)</th>
<th>Weight of solvent adsorbed (g)</th>
<th>Volume of solvent adsorbed (ml)</th>
<th>SR%</th>
<th>Q (ml/g)</th>
</tr>
</thead>
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<tr>
<td>Acetone</td>
<td>0.1085</td>
<td>0.5055</td>
<td>0.3970</td>
<td>0.5</td>
<td>366%</td>
<td>4.6</td>
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<tr>
<td>Ethyl acetate</td>
<td>0.1080</td>
<td>0.8964</td>
<td>0.7884</td>
<td>0.87</td>
<td>730%</td>
<td>8.05</td>
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<tr>
<td>Hexane</td>
<td>0.1010</td>
<td>0.5697</td>
<td>0.4687</td>
<td>0.71</td>
<td>460%</td>
<td>7.03</td>
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**Table S5.** Data analysis of swellability in TAF.
Figure S9. Swellability process in acetone (above) and hexane (below).

9. Scanning electron microscope (SEM)

Figure S10. SEM imagines of TAF-OH
10. CO$_2$ adsorption isotherms

**Figure S11.** CO$_2$ adsorption isotherms at 195 K of TAF (blue circles), TAF-NH$_2$ (green circles), TAF-OH (red circles).

**Figure S12.** CO$_2$ adsorption isotherms TAF at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).
Figure S13. CO$_2$ adsorption isotherms of TAF-OH at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).

Figure S14. CO$_2$ adsorption isotherms of TAF-NH$_2$ at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).
Table S6. Amount of CO₂ adsorbed in the TAF compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET m²/g</th>
<th>CO₂ 1 bar 273 K mmol/g mg/g</th>
<th>CO₂ 1 bar 283 K mmol/g mg/g</th>
<th>CO₂ 1 bar 298 K mmol/g mg/g</th>
<th>CO₂ 0.15 bar 298 K mmol/g mg/g</th>
<th>CO₂/N₂ Selectivity at 1 bar and 298K</th>
<th>ΔH CO₂ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAF</td>
<td>1383</td>
<td>2.8</td>
<td>2.2</td>
<td>1.5</td>
<td>0.26</td>
<td>14</td>
<td>25.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>123.2</td>
<td>96.8</td>
<td>66.0</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAF-OH</td>
<td>984</td>
<td>3.0</td>
<td>2.4</td>
<td>1.7</td>
<td>0.32</td>
<td>17</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>132.0</td>
<td>105.6</td>
<td>74.8</td>
<td>14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAF-NH₂</td>
<td>1190</td>
<td>3.2</td>
<td>2.6</td>
<td>1.9</td>
<td>0.34</td>
<td>19</td>
<td>53.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140.8</td>
<td>114.4</td>
<td>83.6</td>
<td>15.0</td>
<td></td>
<td></td>
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</table>

Table S7. The adsorbed amount $q_{sat}$ for site A or B (mol/kg) and the Langmuir parameter $b$ associated with the site A or B (Pa⁻¹).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_{sat,A}$ (mol/kg)</th>
<th>$b_{0,A}$ (Pa⁻¹)</th>
<th>$q_{sat,B}$ (mol/kg)</th>
<th>$b_{0,B}$ (Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAF</td>
<td>2.0</td>
<td>4.4x10⁻¹₀</td>
<td>13.7</td>
<td>2.4x10⁻¹₀</td>
</tr>
<tr>
<td>TAF-OH</td>
<td>1.9</td>
<td>6.5x10⁻¹₀</td>
<td>9.6</td>
<td>8.0x10⁻¹₁</td>
</tr>
<tr>
<td>TAF-NH₂</td>
<td>6.8</td>
<td>1.4x10⁻¹¹</td>
<td>6.8</td>
<td>4.7x10⁻¹₀</td>
</tr>
</tbody>
</table>
11. CH₄ adsorption isotherms

![CH₄ adsorption isotherms](image)

**Figure S15.** CH₄ adsorption isotherms at 195 K of TAF (blue circles), TAF-NH₂ (green circles), TAF-OH (red circles).

![CH₄ adsorption isotherms](image)

**Figure S16.** CH₄ adsorption isotherms TAF at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).
**Figure S17.** CH$_4$ adsorption isotherms of TAF-OH at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).

**Figure S18.** CH$_4$ adsorption isotherms of TAF-NH$_2$ at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).
12. N$_2$ adsorption isotherms

**Figure S19.** N$_2$ adsorption isotherms of TAF at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).

**Figure S20.** N$_2$ adsorption isotherms of TAF-OH at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).
Figure S21. \( \text{N}_2 \) adsorption isotherms of TAF-NH2 at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).

13. Adsorption isotherms of TAF-OLi

Figure S22. \( \text{N}_2 \) isotherm of TAF-OLi at 77 K.
<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Langmuir surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropores/Total pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAF-OLi</td>
<td>870</td>
<td>972</td>
<td>0.35</td>
<td>90</td>
</tr>
</tbody>
</table>

**Table S8.** Adsorption data of TAF-OLi

**Figure S23.** CO₂ isotherm of TAF-OLi at 195 K.
Figure S24. CO₂ isotherms of TAF-OLi at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).

Figure S25. CH₄ isotherm of TAF-OLi at 195 K
Figure S26. CH$_4$ isotherms of TAF-OLi at 273 (light blue circles), 283 (dark blue circles), 298 K (grey circles).