Supporting Information

Pyridinium Linkers and Mixing Anions in Cationic Metal-Organic Frameworks

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Experiment Section

Materials and Methods. All commercially available reagents were used as received without further purification. H$_2$ipqPF$_6$ and H$_2$ipqBF$_4$ (H$_2$ipq$^+$ for 1-(3,5-dicarboxyphenyl)-4-(pyridin-4-yl) pyridinium) were prepared according to a reported method.\(^1\) \(^{19}\)F NMR spectra was collected using a Bruker Advance II 400 MHz NMR spectrometer. All materials were dissolved in DCI/DMSO-$d_6$ solvents. TGA was collected using a Netzsch STA 409 PC, using an Al pan at a heating rate of 2°C min$^{-1}$. Elemental analysis was performed using a Perkin Elmer Model 2400 series II. Powder x-ray diffraction patterns were collected using a Rigaku Miniflex II bench top PXRD equipped with a CuK$\alpha$ x-ray source. Gas sorption isotherms were measured on ASAP 2020. Before the measurement, the samples were all activated under a dynamic vacuum up to 10$^{-2}$ Pa in two stages, initially at 25 °C for 6 hrs then to 150 °C at 0.5 °C min$^{-1}$ for 5 hrs until the outgas rate less than 0.2 Pa min$^{-1}$. All compounds were measured with the same equilibrium criterion.

Synthesis of [Cu(ipq)](NO$_3$)$_2$-2DMF-2H$_2$O (CALF-32(NO$_3$)$_2$-g): A mixture of Cu(NO$_3$)$_2$-4H$_2$O (20 mg, 0.1 mmol), H$_2$ipqPF$_6$ (47 mg, 0.1 mmol), N,N-diethylformamide (DMF) (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)](NO$_3$)$_2$-2DMF-H$_2$O in ca. 60% yield. Anal. calcd (%) for C$_{24}$H$_{35}$CuN$_6$O$_{14}$: C, 45.97; H, 4.66; N, 11.17. Found: C, 44.79; H, 4.42; N, 11.12.

Synthesis of [Cu(ipq)]BF$_4$-2DMF-3H$_2$O (CALF-32(BF$_4$)$_2$-g): A mixture of Cu(BF$_4$)$_2$ (24 mg, 0.1 mmol), H$_2$ipqBF$_4$ (41 mg, 0.1 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)]BF$_4$-2DMF-3H$_2$O in ca. 32% yield. \(^{19}\)F NMR (400 MHz, DCI and DMSO-$d_6$; Fig. S1c): $\delta = -148.5, -149.8$ (BF$_4$); Anal. calcd (%) for C$_{24}$H$_{31}$BCuF$_6$N$_6$O$_{12}$: C, 43.03; H, 4.66; N, 8.36. Found: C, 38.94; H, 3.82; N, 8.11.

Synthesis of [Cu(ipq)][(BF$_4$)$_6$]$_{0.8}$PF$_6$-$d_2$-2DMF-3H$_2$O (CALF-32(BF$_4$)$_{0.8}$PF$_6$-$d_2$-g): A mixture of Cu(BF$_4$)$_2$ (24 mg, 0.1 mmol), H$_2$ipqPF$_6$ (47 mg, 0.1 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)][(BF$_4$)$_6$]$_{0.8}$PF$_6$-$d_2$-2DMF-3H$_2$O in ca. 70% yield. \(^{19}\)F NMR (400 MHz, DCI and DMSO-$d_6$; Fig. S1d): $\delta = -71.1, -73.0$ (PF$_6$); -148.7, -150.0 (BF$_4$); Anal. calcd (%) for C$_{24}$H$_{31}$BCuF$_6$N$_6$O$_{12}$PF$_6$-$d_2$: C, 42.30; H, 4.58; N, 8.22. Found: C, 43.96; H, 3.80; N, 7.74.

Synthesis of [Cu(ipq)][(BF$_4$)$_6$]PF$_6$-$d_4$-3DMF-2H$_2$O (CALF-32(BF$_4$)$_{0.6}$PF$_6$-$d_4$-g): A mixture of Cu(BF$_4$)$_2$ (24 mg, 0.1 mmol), H$_2$ipqPF$_6$ (70 mg, 0.15 mmol), DMF (2 mL) and ethanol (0.5 mL) was ultrasonically dissolved and sealed in a 20-mL Pyrex vial and heated at 80 °C for 12 hours, and then cooled by 5 °C/hr to room temperature to give blue crystals of [Cu(ipq)][(BF$_4$)$_6$]PF$_6$-$d_4$-3DMF-2H$_2$O in ca. 28% yield. \(^{19}\)F NMR (400 MHz, DCI and DMSO-$d_6$; Fig. S1e): $\delta = -70.5, -72.4$ (PF$_6$); -147.9, -149.3 (BF$_4$); Anal. calcd (%) for C$_{27}$H$_{38}$B$_2$CuF$_{18}$N$_6$O$_{12}$PF$_6$-$d_4$: C, 43.34; H, 4.85; N, 9.36. Found: C, 43.96; H, 4.03; N, 8.89.

Crystal Structure Determination. Intensity data were collected on a Nonius CCD diffractometer equipped with an Apex II CCD area-detector diffractometer (Mo-K$_\alpha$). The diffraction spots were measured in full, scaled with SCALEPACK, corrected for Lorentz-polarization correction, and integrated using DENZO.\(^2\) The structures were solved with direct method and refined with a full-matrix least-squares technique with the SHELXL program package.\(^3\) Anisotropic thermal parameters were applied to all non-hydrogen atoms except the guest molecules. The organic hydrogen atoms were generated geometrically.


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**Table S1. Crystallographic data.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>CALF-32(NO₃)</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₂₄H₂₉CuN₅O₁₁</td>
</tr>
<tr>
<td>Formula weight</td>
<td>627.06</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>15.6530(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>13.5330(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>13.6150(5)</td>
</tr>
<tr>
<td>β/°</td>
<td>103.918(2)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2799.42(17)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Dc/g cm⁻³</td>
<td>1.488</td>
</tr>
<tr>
<td>μ/μm⁻¹</td>
<td>0.847</td>
</tr>
<tr>
<td>reflns coll.</td>
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<tr>
<td>unique reflns</td>
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<tr>
<td>Rint</td>
<td>0.1194</td>
</tr>
<tr>
<td>R₁ [I &gt; 2σ][a]</td>
<td>0.0928</td>
</tr>
<tr>
<td>wR₂ [I &gt; 2σ][b]</td>
<td>0.2650</td>
</tr>
<tr>
<td>R₁ (all data)</td>
<td>0.1287</td>
</tr>
<tr>
<td>wR₂ (all data)</td>
<td>0.3027</td>
</tr>
<tr>
<td>GOF</td>
<td>1.008</td>
</tr>
</tbody>
</table>

\[ R₁ = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}, \quad wR₂ = \left[ \sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2 \right]^{1/2}. \]

**Table S2. Gas adsorption and selectivity.**

<table>
<thead>
<tr>
<th></th>
<th>CALF-32 (NO₃)</th>
<th>CALF-32 (BF₄)</th>
<th>CALF-32 (BF₄)₀₂₆ (PF₆)₀₂</th>
<th>CALF-32 (BF₄)₀₅₆ (PF₆)₀₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir surface area from N₂ (77 K)/CO₂ (195 K) (m² g⁻¹)</td>
<td>2.5/118</td>
<td>248/430</td>
<td>317/600</td>
<td>955/1186</td>
</tr>
<tr>
<td>Qₐ for CO₂ at low CO₂ loading (kJ mol⁻¹)</td>
<td>32</td>
<td>35</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td>CO₂ uptake at 273 K/298 K at 1 bar (w.t.%)</td>
<td>3.4/2.5</td>
<td>6.6/4.6</td>
<td>8.8/6.1</td>
<td>21/15</td>
</tr>
<tr>
<td>CO₂ uptake at 273 K/298 K at 1 bar (mmol g⁻¹)</td>
<td>0.8/0.6</td>
<td>1.5/1.0</td>
<td>2.0/1.4</td>
<td>4.8/3.4</td>
</tr>
<tr>
<td>N₂ uptake at 273 K at 1 bar (w.t.%)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₄ uptake at 273 K at 1 bar (w.t.%)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>IAST Selectivity at 273 K and 1 bar in CO₂/N₂:13/87 mixture</td>
<td>63</td>
<td>85</td>
<td>157</td>
<td>98</td>
</tr>
<tr>
<td>IAST Selectivity at 273 K and 1 bar in CO₂/CH₄:50/50 mixture</td>
<td>19</td>
<td>18</td>
<td>47</td>
<td>14</td>
</tr>
</tbody>
</table>
Fig. S1 $^{19}$F NMR spectra for compounds (a) H$_2$ipqPF$_6$, (b) CALF-32(NO$_3$), (c) CALF-32(BF$_4$), (d) CALF-32(BF$_4$)$_{0.8}$(PF$_6$)$_{0.2}$ and (e) CALF-32(BF$_4$)$_{0.6}$(PF$_6$)$_{0.4}$
Fig. S2 TGA of synthesized CALF-32(A).

Fig. S3 PXRD patterns of the simulated CALF-32(NO$_3$)$_3$, synthesized and activated CALF-32(A).
Fig. S4 N₂ and CO₂ sorption isotherms of activated CALF-32(A) measured at 77 and 195 K, respectively.
Fig. S5 CO₂, CH₄ and N₂ sorption isotherms of activated CALF-32(A) measured at 273 and 298 K.

Fig. S6 Adsorption enthalpies of CO₂ calculated by isotherms at 273 and 298 K in CALF-32(A).
\[y = \ln(x) + \frac{1}{T}(a_0 + a_1 x + a_2 x^2) + (b_0 + b_1 x)\]

\[R^2 = 0.99974\]

\[a_0 = -3811 \pm 61\]
\[a_1 = 3035 \pm 165\]
\[a_2 = -573 \pm 29\]
\[b_0 = 23.5 \pm 0.2\]
\[b_1 = -6.5 \pm 0.5\]

\[\ln(p / \text{Pa})\]

**CALF-32(NO\textsubscript{3})**
- 273 K
- 298 K

\[y = \ln(x) + \frac{1}{T}(a_0 + a_1 x + a_2 x^2) + (b_0 + b_1 x)\]

\[R^2 = 0.99989\]

\[a_0 = -4156 \pm 41\]
\[a_1 = 1406 \pm 60\]
\[a_2 = -93 \pm 5\]
\[b_0 = 24.3 \pm 0.1\]
\[b_1 = -3.3 \pm 0.2\]

\[\ln(p / \text{Pa})\]

**CALF-32(BF\textsubscript{4})**
- 273 K
- 298 K
Fig. S7 CO$_2$ adsorption isotherms for CALF-32(A) with fitting by virial method.
\[ y = q_m b x^{\frac{1}{n}} \left( 1 + b x^{\frac{1}{n}} \right)^{-1} \]

- **CO\(_2\)**
  - \( R^2 = 0.9992 \)
  - \( q_m = 53 \pm 7 \)
  - \( b = 0.030 \pm 0.003 \)
  - \( n = 1.66 \pm 0.06 \)

- **N\(_2\)**
  - \( R^2 = 0.9991 \)
  - \( q_m = 16 \pm 10 \)
  - \( b = 0.0015 \pm 0.0008 \)
  - \( n = 1.04 \pm 0.06 \)

- **CH\(_4\)**
  - \( R^2 = 0.9998 \)
  - \( q_m = 36 \pm 18 \)
  - \( b = 0.0006 \pm 0.0002 \)
  - \( n = 0.92 \pm 0.03 \)
\[ y = q_m b^* x^{n}(1/n)/(1+b^* x^{n}(1/n)) \]

\[ R^2 = 0.9995 \]

\[
\begin{align*}
q_m &= 82 \pm 6 \\
b &= 0.034 \pm 0.002 \\
n &= 1.52 \pm 0.04
\end{align*}
\]

\[
\begin{align*}
y &= q_m b^* x^{n}(1/n)/(1+b^* x^{n}(1/n)) \\
R^2 &= 0.9989 \\
q_m &= 31 \pm 23 \\
b &= 0.0011 \pm 0.0007 \\
n &= 1.04 \pm 0.05
\end{align*}
\]

\[
\begin{align*}
y &= q_m b^* x^{n}(1/n)/(1+b^* x^{n}(1/n)) \\
R^2 &= 0.9999 \\
q_m &= 61 \pm 10 \\
b &= 0.0019 \pm 0.0002 \\
n &= 1.09 \pm 0.01
\end{align*}
\]
\[
y = \frac{qm \cdot b \cdot x^{(1/n)}}{1 + b \cdot x^{(1/n)}}
\]

*CO\(_2\)*

- \(R^2 = 0.9995\)
- \(qm = 96 \pm 6\)
- \(b = 0.046 \pm 0.002\)
- \(n = 1.56 \pm 0.04\)

*\(N_2\)*

- \(R^2 = 0.9999\)
- \(qm = 39 \pm 11\)
- \(b = 0.0010 \pm 0.0002\)
- \(n = 1.07 \pm 0.01\)

*\(CH_4\)*

- \(R^2 = 0.9996\)
- \(qm = 42 \pm 10\)
- \(b = 0.0027 \pm 0.0005\)
- \(n = 1.09 \pm 0.03\)
Fig. S8 CO₂, N₂ and CH₄ adsorption isotherms for CALF-32(A) with fitting by Langmuir-Freundlich method.