Electronic Supporting Information

A Highly Stable Indium Phosphonocarboxylate Framework as a Multifunctional Sensor for Cu$^{2+}$ and Methylviologen Ions

Wenyan Dan, Xiaofeng Liu, Mingli Deng, Yun Ling, Zhenxia Chen*, Yaming Zhou*

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China

Tel: + 86 21 65643925, Fax:+86 21 65642261, e-mail:zhxchen@fudan.edu.cn; ymzhou@fudan.edu.cn
Table S1 Selected bond lengths (Å) and angles (°) for InPCF-1.

Table S2 Hydrogen bonds for InPCF-1\textsuperscript{a}.

Table S3 Comparison of some MOFs for sensing Cu\textsuperscript{2+} ion at room temperature.

Figure S1 Packing view of InPCF-1 (Water and hydrogen atoms is omitted for clarity yellow columns are added to highlight the 1-D channels).

Figure S2 TGA curve of as-synthesized InPCF-1.

Figure S3 The PXRD patterns for InPCF-1 in boiling water for up to 7 days.

Figure S4 The PXRD patterns for InPCF-1 measured during chemical stability tests. (a) In refluxing EtOH at 80 °C for up to 7 days. (b) In refluxing toluene at 110 °C for up to 7 days.

Figure S5 The CO\textsubscript{2} isotherms at 273 K and 298 K for InPCF-1.

Figure S6 The CO\textsubscript{2} isotherms at 273 K and 298 K (symbols) and the Virial equation fits (lines) for InPCF-1.

Figure S7 Isosteric heats of CO\textsubscript{2} adsorption for InPCF-1.

Figure S8 The CH\textsubscript{3}OH isotherm at 298 K for InPCF-1.

Figure S9 The H\textsubscript{2}O isotherm at 298 K for InPCF-1.

Figure S10 The C\textsubscript{2}H\textsubscript{5}OH isotherm at 298 K for InPCF-1.

Figure S11 Solid state luminescence spectra of ligand and InPCF-1\textsubscript{a} upon excitation at 290 nm at room temperature.

Figure S12 Luminescence spectra of ligand and InPCF-1\textsubscript{a} in DMF solution upon excitation at 290 nm.

Figure S13 Multiple cycles for the quenching by Cu(NO\textsubscript{3})\textsubscript{2} and the recovery after filtration and ultrasonic washing by DMF for three times. The red bars show the pristine intensity and
regenerated ones after washing; while the blue bars show the intensities after addition of Cu(NO$_3$)$_2$@DMF solutions..........................................................................................................................16

Figure S14 PXRD of InPCF-1a and sample after immersing M(NO$_3$)$_2$(M = Cu$^{2+}$ Zn$^{2+}$ Ni$^{2+}$ Co$^{2+}$) DMF solution.......................................................................................................................................18

Figure S15 Photographs of InPCF-1a soaked in DMF solution containing M(NO$_3$)$_2$ with 10$^{-2}$ M, a) Cu$^{2+}$, b) Co$^{2+}$, c) Ni$^{2+}$, d) Zn$^{2+}$ for 24 h.................................................................19

Figure S16 The EDS of the solid samples of InPCF-1a-Cu$^{2+}$ obtained by centrifugal separation of InPCF-1a soaked in DMF solution containing M(NO$_3$)$_2$ with 10$^{-2}$ M, washing with DMF, and drying in 60 °C oven.................................................................20

Figure S17 X-ray photoelectron spectroscopy (XPS) spectra of Cu$^{2+}$-incorporated InPCF-1a.....21

Figure S18 (a) and (b) Concentration-dependent luminescence intensities of InPCF-1a by the addition of different contents of MV$^{2+}$ DMF solution (Ex at 290 nm)..................................................22

Figure S19 Luminescence spectra of InPCF-1a, InPCF-1a with 29 mM diphenyl, and InPCF-1a with 29 mM methylviologen..........................................................................................................................23
Table S1 Selected bond lengths (Å) and angles (°) for InPCF-1.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>In(1)-O(2)</td>
<td>2.072(6)</td>
</tr>
<tr>
<td>In(1)-O(3)</td>
<td>2.119(7)</td>
</tr>
<tr>
<td>In(1)-O(1)#1</td>
<td>2.141(5)</td>
</tr>
<tr>
<td>In(1)-O(1)#2</td>
<td>2.141(5)</td>
</tr>
<tr>
<td>In(1)-O(5)</td>
<td>2.254(7)</td>
</tr>
<tr>
<td>In(1)-O(6)</td>
<td>2.302(7)</td>
</tr>
<tr>
<td>In(1)-O(1)#1</td>
<td>2.141(5)</td>
</tr>
<tr>
<td>In(1)-O(1)#2</td>
<td>2.141(5)</td>
</tr>
<tr>
<td>P(1)-O(1)</td>
<td>1.527(7)</td>
</tr>
<tr>
<td>P(1)-O(1)#3</td>
<td>1.528(5)</td>
</tr>
<tr>
<td>O(3)-C(14)</td>
<td>1.259(14)</td>
</tr>
<tr>
<td>O(5)-C(13)</td>
<td>1.261(12)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(1)#1</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(1)#2</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(3)-In(1)-O(1)#1</td>
<td>160.5(2)</td>
</tr>
<tr>
<td>O(3)-In(1)-O(1)#2</td>
<td>160.5(2)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(3)</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(3)-In(1)-O(5)</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(3)-In(1)-O(6)</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(3)-In(1)-O(6)</td>
<td>99.27(12)</td>
</tr>
<tr>
<td>O(1)-In(1)-O(1)#1</td>
<td>160.5(2)</td>
</tr>
<tr>
<td>O(1)-In(1)-O(1)#2</td>
<td>160.5(2)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(5)</td>
<td>129.2(3)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(1)#1</td>
<td>129.2(3)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(1)#2</td>
<td>129.2(3)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(5)</td>
<td>173.7(3)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(6)</td>
<td>173.7(3)</td>
</tr>
<tr>
<td>O(2)-In(1)-O(6)</td>
<td>173.7(3)</td>
</tr>
<tr>
<td>O(1)-In(1)-O(1)#1</td>
<td>93.13(12)</td>
</tr>
<tr>
<td>O(1)-In(1)-O(1)#2</td>
<td>93.13(12)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 -y+1/2, -x+1/2, -z+3/2; #2 -y+1/2, -x+1/2, z+1/2; #3 x, y, -z+2; #4 -y+1, x, z; #5 y, -x, -z+2; #6 -y, x, z; #7 y, -x+1, -z+2; #8 -y+1/2, -x+1/2, z-1/2
**Table S2 Hydrogen bonds for InPCF-1.**

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>d(D–H) / Å</th>
<th>d(H···A) / Å</th>
<th>d(D···A) / Å</th>
<th>&lt;DHA / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(8)-H(8B)...O(1)</td>
<td>0.85</td>
<td>2.16</td>
<td>2.991(18)</td>
<td>165.4</td>
</tr>
<tr>
<td>O(9)-H(9A)...O(4)#8</td>
<td>0.85</td>
<td>1.93</td>
<td>2.78(3)</td>
<td>179.0</td>
</tr>
</tbody>
</table>

*Symmetry code: #8 -y+1/2, -x+1/2, z-1/2*
Table S3 Comparison of some MOFs for sensing Cu^{2+} ion at room temperature

<table>
<thead>
<tr>
<th>MOFs</th>
<th>$K_{sv}$/M$^{-1}$</th>
<th>Active sites</th>
<th>The charge of frameworks</th>
<th>Pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>InPCF-1</td>
<td>1840.1</td>
<td>Uncoordinated carbonyl oxygen sites</td>
<td>anion</td>
<td>7.19 × 7.19 Å²</td>
</tr>
<tr>
<td>[Eu(pdc)]$_n$$^1$</td>
<td>89.4</td>
<td>Uncoordinated pyridyl nitrogen sites</td>
<td>neutral</td>
<td>6.3 × 8.5 Å²</td>
</tr>
<tr>
<td>[Mg(DHT)]$_n$$^2$</td>
<td>170.2</td>
<td>Uncoordinated hydroxyl oxygen sites</td>
<td>neutral</td>
<td>5.3 × 5.5 Å²</td>
</tr>
<tr>
<td>{[Tb$_d$(µ$_3$-OH)$_4$(BPDC)$_3$(BPDC)$_3$(H$_2$O)$_8$]-ClO$_4$}$_n$$^3$</td>
<td>344.7</td>
<td>Uncoordinated pyridyl nitrogen sites</td>
<td>cationic</td>
<td>4.5 × 5.5 Å²</td>
</tr>
<tr>
<td>[Eu$_2$(FMA)$_2$(OX)(H$_2$O)$_4$]$_n$$^4$</td>
<td>528.7</td>
<td>Carboxylate oxygen sites</td>
<td>neutral</td>
<td>4.0 × 5.0 Å², 3.8 × 3.8 Å²</td>
</tr>
<tr>
<td>[Eu$_3$(L)$_2$(HCOO)$_2$(DMF)$_2$(H$_2$O)] [H$_2$N(Me)$_2$]$^5$</td>
<td>2350</td>
<td>Uncoordinated pyridyl nitrogen sites</td>
<td>anion</td>
<td>4.5 × 5.5 Å²(window)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11 Å (cage)</td>
</tr>
</tbody>
</table>

References

Figure S1 Packing view of InPCF-1 (Water and hydrogen atoms is omitted for clarity yellow columns are added to highlight the 1-D channels).
Figure S2 TGA curve of as-synthesized InPCF-1.
Figure S3 The PXRD patterns for InPCF-1 in boiling water for up to 7 days.
Figure S4 The PXRD patterns for InPCF-1 measured during chemical stability tests. (a) In refluxing EtOH at 80 °C for up to 7 days. (b) In refluxing toluene at 110 °C for up to 7 days.
Figure S5 The CO$_2$ isotherms at 273 K and 298 K for **InPCF-1**.
Figure S6 The CO$_2$ isotherms at 273 K and 298 K (symbols) and the Virial equation fits (lines) for InPCF-1.

\[ R^2 = 0.99992 \]
\[ a_0 = -4028.044 \]
\[ a_1 = 542.570 \]
\[ a_2 = -137.963 \]
\[ a_3 = 64.576 \]
\[ b_0 = 18.932 \]
Figure S7 Isosteric heats of CO$_2$ adsorption for InPCF-1
Figure S8 The CH$_3$OH isotherm at 298 K for InPCF-1.
Figure S9 The H$_2$O isotherm at 298 K for InPCF-1.
Figure S10 The C\textsubscript{3}H\textsubscript{5}OH isotherm at 298 K for InPCF-1.
Figure S11 Solid state luminescence spectra of ligand and InPCF-1a upon excitation at 290 nm at room temperature.
**Figure S12** Luminescence spectra of ligand and InPCF-1a in DMF solution upon excitation at 290 nm.
Figure S13 Multiple cycles for the quenching by Cu(NO$_3$)$_2$ and the recovery after filtration and ultrasonic washing by DMF for three times. The red bars show the pristine intensity and regenerated ones after washing; while the blue bars show the intensities after addition of Cu(NO$_3$)$_2$@DMF solutions.
Figure S14 PXRD of InPCF-1a and sample after immersing $\text{M(NO}_3\text{)}_2 (\text{M = Cu}^{2+} \text{ Zn}^{2+} \text{ Ni}^{2+} \text{ Co}^{2+})$ DMF solution
Figure S15 Photographs of InPCF-1a soaked in DMF solution containing M(NO$_3$)$_2$ with $10^{-2}$ M, a) Cu$^{2+}$, b) Co$^{2+}$, c) Ni$^{2+}$, d) Zn$^{2+}$ for 24 h.
Figure S16 The EDS of the solid samples of InPCF-1a-Cu$^{2+}$ obtained by centrifugal separation of InPCF-1a soaked in DMF solution containing M(NO$_3$)$_2$ with 10$^{-2}$ M, washing with DMF, and drying in 60 °C oven.
Figure S17 X-ray photoelectron spectroscopy (XPS) spectra of Cu$^{2+}$-incorporated InPCF-1a.
Figure S18 (a) and (b) Concentration-dependent luminescence intensities of InPCF-1a by the addition of different contents of MV$^{2+}$ DMF solution (Ex at 290 nm)
Figure S19 Luminescence spectra of InPCF-1a, InPCF-1a with 29 mM diphenyl, and InPCF-1a with 29 mM methylviologen.