Supporting Information for

A flexible metal azolate framework with drastic luminescence response toward solvent vapors and carbon dioxide

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Fig. S1. TGA curve of the as synthesized 1·g

Fig. S2. Variable-temperature PXRD patterns of 1·g

Fig. S3. PXRD patterns of 1·g, 1', 1'-BEN, 1'-NBEN, 1'-H2O, 1·EtOH, and 1·MeOH.
Fig. S4. TGA curve of \(1'\cdot\text{NBEN}, 1'\cdot\text{BEN}, 1\cdot\text{MeOH}, 1\cdot\text{EtOH}, \) and \(1'\cdot\text{H}_2\text{O}\)

Table S1 Summary of guest sorption amounts of \(1'\)

<table>
<thead>
<tr>
<th></th>
<th>MeOH</th>
<th>EtOH</th>
<th>H(_2)O</th>
<th>Ben</th>
<th>Nben</th>
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<tbody>
<tr>
<td>Weight loss</td>
<td>25%</td>
<td>24%</td>
<td>15.5%</td>
<td>15%</td>
<td>13.5%</td>
</tr>
<tr>
<td>Formula</td>
<td>(1\cdot32.5)MeOH (1\cdot21.4)EtOH (1\cdot31.8)H(_2)O (1'\cdot7.0)Ben (1'\cdot4.0)Nben</td>
<td></td>
<td></td>
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</tbody>
</table>

[a] \(1\) and \(1'\) refers to \(\text{Zn}_7(\text{ip})_{12}(\text{OH})_2\)

Fig. S5 \(\text{CO}_2\) sorption isotherms of \(1'\) at 273 K
Fig. S6 Adsorption enthalpies of CO₂ fitted by the virial equation from adsorption isotherms measured at 273 and 298 K and calculated by the Clausius-Clapeyron equation.

Fig. S7. Photoluminescence excitation spectra of 1·g, 1', 1'·BEN, 1·MeOH, 1·EtOH, 1'·H₂O, and methanol solution of Hip (10⁻⁶ M).
**Fig. S8.** Photoluminescence emission profiles of 1·MeOH under dynamic vacuum (at the beginning, pressure above 1000 mTorr cannot be read by the low-pressure sensor). Loading MeOH increases the emission intensity of both the crystalline and quasi-amorphous phases. The phase transition from crystalline to quasi-amorphous also increases the emission intensity, which surpass the effect of MeOH desorption.

**Fig. S9** PXRD patterns of film of 1·g thin film grown on a zinc plate.
Fig. S10 Luminescence decay profiles of 1, 1', 1·EtOH, 1·MeOH, 1·BEN, 1·H2O and methanol solution of Hip (10⁻⁶ M).

Table S2 Fitted lifetimes corresponding to Fig. S11.

<table>
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<tr>
<th></th>
<th>τ₁(ns)</th>
<th>Rel%</th>
<th>τ₂</th>
<th>Rel%</th>
<th>τ₃</th>
<th>Rel%</th>
<th>χ² weighted-average lifetime (ns)</th>
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<tr>
<td>1·g</td>
<td>0.84(1)</td>
<td>64.06(1)</td>
<td>2.91(4)</td>
<td>35.94(1)</td>
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<td>1.006</td>
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<tr>
<td>1'</td>
<td>0.39(1)</td>
<td>69.51(5)</td>
<td>2.1(2)</td>
<td>25.66(1)</td>
<td>5.2(5)</td>
<td>14.83(2)</td>
<td>0.996</td>
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<tr>
<td>1·BEN</td>
<td>0.24(3)</td>
<td>9.6(5)</td>
<td>2.47(6)</td>
<td>36.94(3)</td>
<td>10.47(10)</td>
<td>53.44(1)</td>
<td>1.000</td>
</tr>
<tr>
<td>1·H₂O</td>
<td>0.12(2)</td>
<td>14.1(1)</td>
<td>2.14(4)</td>
<td>35.52(2)</td>
<td>8.12(6)</td>
<td>50.64(1)</td>
<td>1.004</td>
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<tr>
<td>1·MeOH</td>
<td>0.69(2)</td>
<td>37.53(2)</td>
<td>2.52(2)</td>
<td>62.47(2)</td>
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<td>0.998</td>
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<tr>
<td>1·EtOH</td>
<td>0.54(1)</td>
<td>45.46(3)</td>
<td>1.90(2)</td>
<td>54.54(2)</td>
<td></td>
<td></td>
<td>1.006</td>
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<tr>
<td>1·CO₂</td>
<td>0.37(1)</td>
<td>22.1(1)</td>
<td>2.62(6)</td>
<td>36.45(2)</td>
<td>9.1(1)</td>
<td>40.86(1)</td>
<td>0.996</td>
</tr>
</tbody>
</table>
**Fig. S11** Perspective view of the contact of adjacent ip⁻ ligands in 1·g.