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SI-1. $^1$H NMR spectra of 1, 2, 3, 5, H$_2$L1, H$_2$L2, H$_2$L3 and H$_4$L4.

Figure S1: $^1$H NMR spectra of (1) in CDCl$_3$

Figure S2: $^1$H NMR spectra of H$_2$L1 in [D6]DMSO
Figure S3: $^1$H NMR spectra of (2) in CDCl$_3$

Figure S4: $^1$H NMR spectra of H$_2$L$_2$ in [D6]DMSO
Figure S5: $^1$H NMR spectra of (3) in CDCl$_3$

Figure S6: $^1$H NMR spectra of H$_2$L3 in [D6]DMSO
Figure S7: $^1$H NMR spectra of (5) in CDCl$_3$

Figure S8: $^1$H NMR spectra of H$_4$L$_4$ in [D6]DMSO
SI-2. $^{13}$C NMR spectra of 1, 2, 3, 5, H$_2$L1, H$_2$L2, H$_2$L3 and H$_4$L4.

**Figure S9:** $^{13}$C NMR spectra of (1) in CDCl$_3$

**Figure S10:** $^{13}$C NMR spectra of H$_2$L1 in [D6] DMSO
Figure S11: $^{13}$C NMR spectra of (2) in CDCl$_3$

Figure S12: $^{13}$C NMR spectra of H$_2$L$_2$ in [D6] DMSO
**Figure S13:** $^{13}$C NMR spectra of (3) in CDCl$_3$

**Figure S14:** $^{13}$C NMR spectra of H$_2$L3 in [D6] DMSO
**Figure S15:** $^{13}$C NMR spectra of (5) in CDCl$_3$

**Figure S16:** $^{13}$C NMR spectra of H$_4$L$_4$ in [D$_6$]DMSO
SI-3. IR transmission spectra of (1), (1) after cyanation reaction, H$_2$L1, (2), H$_2$L2, (3), H$_2$L3 and H$_4$L4.

**Figure S17:** IR transmission spectra of (1)

**Figure S18:** IR transmission spectra of (1) after cyanation reaction
Figure S19: IR transmission spectra of $\text{H}_2\text{L}1$

Figure S20: IR transmission spectra of (2)
Figure S21: IR transmission spectra of H$_2$L2

Figure S22: IR transmission spectra of (3)
Figure S23: IR transmission spectra of H₂L₃

Figure S24: IR transmission spectra of H₄L₄
SI-4 Selected distances and angles within the crystal structure of (6), (7), (8) and (9).

**Table S1:** Selected distances (Å) within the crystal structure of (6).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1- O14</td>
<td>1.911(8)</td>
</tr>
<tr>
<td>Cu1- O4</td>
<td>1.960(8)</td>
</tr>
<tr>
<td>Cu1- O6</td>
<td>1.975(9)</td>
</tr>
<tr>
<td>Cu1- O15</td>
<td>1.977(8)</td>
</tr>
<tr>
<td>Cu1- O5</td>
<td>2.165(8)</td>
</tr>
<tr>
<td>Cu1- Cu4</td>
<td>2.5871(11)</td>
</tr>
<tr>
<td>Cu2- O10</td>
<td>1.950(9)</td>
</tr>
<tr>
<td>Cu2- O13</td>
<td>1.952(8)</td>
</tr>
<tr>
<td>Cu2- O3(^1)</td>
<td>1.961(8)</td>
</tr>
<tr>
<td>Cu2- O7</td>
<td>1.965(8)</td>
</tr>
<tr>
<td>Cu2- O20</td>
<td>2.176(9)</td>
</tr>
<tr>
<td>Cu2- Cu3</td>
<td>2.6215(11)</td>
</tr>
<tr>
<td>Cu3- O8</td>
<td>1.957(8)</td>
</tr>
<tr>
<td>Cu3- O2</td>
<td>1.962(9)</td>
</tr>
<tr>
<td>Cu3- O9(^1)</td>
<td>1.962(9)</td>
</tr>
<tr>
<td>Cu3- O22</td>
<td>1.965(9)</td>
</tr>
<tr>
<td>Cu3- O1</td>
<td>2.188(9)</td>
</tr>
<tr>
<td>Cu4- O16</td>
<td>1.946(8)</td>
</tr>
<tr>
<td>Cu4- O17</td>
<td>1.948(9)</td>
</tr>
<tr>
<td>Cu4- O11</td>
<td>1.967(8)</td>
</tr>
<tr>
<td>Cu4- O12</td>
<td>1.993(8)</td>
</tr>
<tr>
<td>Cu4- O21</td>
<td>2.193(8)</td>
</tr>
</tbody>
</table>

Symmetry code: (1) x-1, y+1, z.

In MOF (6) the deviation of Cu1 from the plane made of O4, O6, O14 and O15 is 0.207(5) Å. The deviation of Cu2 from the plane made of O3, O7, O10 and O13 is 0.207(6) Å. The deviation of Cu3 from the plane made of O2, O8, O9 and O22 is 0.167(6) Å. The deviation of Cu4 from the plane made of O11, O12, O16 and O17 is 0.171(5) Å.
Table S2: Selected distances (Å) within the crystal structure of (7).

Cu1- O11 1.909(13)
Cu1- O8  1.917(16)
Cu1- O3  1.932(12)
Cu1- O12 1.973(13)
Cu1- O20 2.128(17)
Cu1- Cu2 2.610(3)
Cu2- O4  1.927(13)
Cu2- O7  1.982(14)
Cu2- O6  1.977(16)
Cu2- O1  1.996(13)
Cu2- O21 2.19(2)
Cu3- O17 1.939(16)
Cu3- O2  1.941(15)
Cu3- O13 1.981(16)
Cu3- O9  2.056(15)
Cu3- O18 2.12(2)
Cu3- Cu4 2.583(4)
Cu4- O10 1.919(17)
Cu4- O16 1.959(15)
Cu4- O14 1.984(11)
Cu4- O5  1.999(12)
Cu4- O15 2.189(13)

In MOF (7) the deviation of Cu1 from the plane made of O3, O8, O11 and O12 is 0.156(8) Å. The deviation of Cu2 from the plane made of O1, O4, O6 and O7 is 0.236(8) Å. The deviation of Cu3 from the plane made of O2, O9, O13 and O17 is 0.193(9) Å. The deviation of Cu4 from the plane made of O5, O10, O14 and O16 is 0.201(9) Å.
Table S3: Selected distances (Å) within the crystal structure of (8).

Cu1- O4$^1$ 1.942(8)
Cu1- O1$^1$ 1.964(7)
Cu1- O2 1.979(7)
Cu1- O5 2.003(8)
Cu1- O3 2.131(5)
Cu1- Cu1$^1$ 2.6191(14)

Symmetry codes: (1) –x+1, y, -z+1.

The deviation of Cu1 from the plane created by O1, O2, O4 and O5 is 0.190(2) Å.

Table S4: Selected distances (Å) within the crystal structure of (9).

Cu1- O15 1.899(7)
Cu1- O16 1.932(7)
Cu1- O12 1.961(6)
Cu1- O14$^1$ 1.992(6)
Cu1- O19 2.149(7)
Cu1- Cu4 2.6451(16)
Cu2- O17 1.947(7)
Cu2- O20 1.952(7)
Cu2- O3 2.009(7)
Cu2- O6$^2$ 2.022(7)
Cu2- O11 2.135(7)
Cu2- Cu3 2.6493(16)
Cu3- O4$^2$ 1.913(6)
Cu3- O9 1.924(6)
Cu3- O13 1.954(7)
Cu3- O10 1.976(6)
Cu3- O22 2.122(7)
Cu4- O5$^1$ 1.952(7)
Cu4- O21 1.955(7)
Cu4- O2 2.002(7)
Cu4- O1 2.009(7)

Symmetry codes: (1) -x+3/2, -y+1, z-1/2; (2) x+1/2, -y+1/2, -z+1

In MOF(9) the deviation of Cu1 from the plane created by O12, O14, O15 and O16 is 0.461(4) Å. The deviation of Cu2 from the plane created by O3, O6, O17 and O20 is 0.197(5) Å. The deviation of Cu3 from the plane created by O4, O9, O10 and O13 is 0.290(4) Å. The deviation of Cu4 from the plane created by O1, O2, O5 and O21 is 0.018(4) Å.

SI-5. Comparison between the X-ray powder diffraction (XRPD) patterns collected at room temperature of the bulk products of (6), (7), (9) and the simulated patterns from their respective crystal structures.
Figure S25: Comparison between the XRPD pattern recorded at 293 K of (6) (black) and the simulated pattern from the single-crystal structure determined at 150 K (red). ($\lambda = 1.5406$ Å).

Figure S26: Comparison between the XRPD pattern recorded at 293 K of (7) (black) and the simulated pattern from the single-crystal structure determined at 100 K (red). ($\lambda = 1.5406$ Å).
Figure S27: Comparison between the XRPD pattern recorded at 293 K of (9) (black) and the simulated pattern from single crystal structure determined at 150 K (red). ($\lambda = 1.5406$ Å).
SI-6. Pattern-matching (Le Bail fit) of the X-ray powder diffraction pattern of (9) collected at room temperature.

**Figure S28:** Pattern-matching (Le Bail fit) of the diffraction pattern of (9). ($\lambda = 1.5406 \text{ Å}; R_p = 4.79, R_{wp} = 6.79$).
SI-7. TGA of (6), (7), (8), (9) and TDXD of (6) and (8).

**Figure S29:** TGA under dynamic air of as-synthesized (6) with a heating rate of 2 °C.min⁻¹ until 500 °C. The sharp form of the curve at ~300°C is due to a strong endothermic effect during ligand decomposition.

**Figure S30:** TGA curves under dynamic air of as synthesized (7) (black line) and activated (7) (red line) with a heating rate of 0.2 °C.min⁻¹ until 500 °C. The sharp form of the curve at ~250°C is due to a strong endothermic effect during ligand decomposition.
Figure S31: TGA under dynamic air of as-synthesized (8) with a heating rate of 0.2 °C.min⁻¹ until 450 °C. The sharp form of the curve at ~275°C is due to a strong endothermic effect during ligand decomposition.

Figure S32: TGA curves in air of as-synthesized (9) (black line) and activated (9) (red line) with a heating rate of 0.2 °C.min⁻¹ until 450 °C.
Figure S33: TDXD of (6) in air with a heating rate of 0.2 °C.min⁻¹ and a step of 10°C per pattern ($\lambda = 1.5406$ Å).

Figure S34: TDXD of (8) in air with a heating rate of 0.2 °C.min⁻¹ ($\lambda = 1.5406$ Å).
SI-8. Gas sorption properties of (9).

**Figure S35:** N₂ adsorption isotherm of (9) at 77 K.

**Figure S36:** CO₂ sorption isotherm of (9) at 303 K. Black and red curves represent adsorption and desorption, respectively.
Figure S37: \( \text{CH}_4 \) sorption isotherm of (9) at 303 K. Black and red curves represent adsorption and desorption, respectively.