Supporting Information

Cyanide-Bridged Bimetallic 3D Hoffman-Like Coordination Polymers with Tunable Magnetic Behaviour

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Table S1. Selected bond lengths [Å] and angles [°] for 1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>300 K</th>
<th>225 K</th>
<th>150K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N1</td>
<td>2.115(7)</td>
<td>1.946(5)</td>
<td>1.930(5)</td>
</tr>
<tr>
<td>Fe-N2</td>
<td>2.128(8)</td>
<td>1.939(5)</td>
<td>1.928(5)</td>
</tr>
<tr>
<td>Fe-N3</td>
<td>2.198(7)</td>
<td>2.027(5)</td>
<td>2.005(4)</td>
</tr>
<tr>
<td>Ag-C1</td>
<td>2.048(9)</td>
<td>2.066(7)</td>
<td>2.055(6)</td>
</tr>
<tr>
<td>Ag-C2[a]</td>
<td>2.060(10)</td>
<td>2.050(7)</td>
<td>2.040(6)</td>
</tr>
<tr>
<td>N2[b]-Fe-N1</td>
<td>91.4(3)</td>
<td>90.8(2)</td>
<td>90.77(19)</td>
</tr>
<tr>
<td>N2-Fe-N1</td>
<td>88.6(3)</td>
<td>89.2(2)</td>
<td>89.23(19)</td>
</tr>
<tr>
<td>N2[b]-Fe-N3</td>
<td>89.5(3)</td>
<td>89.2(2)</td>
<td>89.38(18)</td>
</tr>
<tr>
<td>N1-Fe-N3[b]</td>
<td>90.0(3)</td>
<td>89.9(2)</td>
<td>89.81(18)</td>
</tr>
<tr>
<td>N2-Fe-N3</td>
<td>90.5(3)</td>
<td>90.8(2)</td>
<td>90.62(18)</td>
</tr>
<tr>
<td>N1-Fe-N3</td>
<td>90.0(3)</td>
<td>90.1(2)</td>
<td>90.19(18)</td>
</tr>
<tr>
<td>C1-Ag-C2[a]</td>
<td>173.9(5)</td>
<td>173.4(3)</td>
<td>173.2(3)</td>
</tr>
<tr>
<td>Fe1-N1-C1</td>
<td>171.1(9)</td>
<td>176.3(6)</td>
<td>176.0(5)</td>
</tr>
<tr>
<td>Fe1-N2-C2</td>
<td>169.1(8)</td>
<td>174.0(6)</td>
<td>175.0(5)</td>
</tr>
<tr>
<td>Ag-C1-N1</td>
<td>176.1(10)</td>
<td>174.4(6)</td>
<td>173.8(5)</td>
</tr>
<tr>
<td>Ag[c].C2-N2</td>
<td>175.4(10)</td>
<td>174.0(7)</td>
<td>171.2(5)</td>
</tr>
</tbody>
</table>

Symmetry codes: a) -x+3/2, y+1/2, -z+1/2; b) -x+3/2, -y+1/2, -z+1; c) -x+3/2, y-1/2, -z+1/2.
Table S2. Selected bond lengths [Å] and angles [°] for 2.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>273 K</th>
<th>100K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N1</td>
<td>2.111(9)</td>
<td>1.940(6)</td>
</tr>
<tr>
<td>Fe-N2[\text{a}]</td>
<td>2.123(9)</td>
<td>1.930(5)</td>
</tr>
<tr>
<td>Fe-N3</td>
<td>2.178(10)</td>
<td>2.005(6)</td>
</tr>
<tr>
<td>Au-C1</td>
<td>1.961(12)</td>
<td>1.972(6)</td>
</tr>
<tr>
<td>Au-C2</td>
<td>1.987(13)</td>
<td>1.971(7)</td>
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<tr>
<td>N2[\text{b}]-Fe-N1</td>
<td>89.9(4)</td>
<td>89.9(2)</td>
</tr>
<tr>
<td>N2[\text{b}]-Fe-N1[\text{c}]</td>
<td>90.1(4)</td>
<td>90.1(2)</td>
</tr>
<tr>
<td>N2[\text{b}]-Fe-N3[\text{c}]</td>
<td>89.4(4)</td>
<td>89.5(2)</td>
</tr>
<tr>
<td>N1-Fe-N3[\text{c}]</td>
<td>90.1(4)</td>
<td>90.7(2)</td>
</tr>
<tr>
<td>N2[\text{b}]-Fe-N1[\text{c}]</td>
<td>89.6(4)</td>
<td>90.5(2)</td>
</tr>
<tr>
<td>N1-Fe-N3</td>
<td>89.9(4)</td>
<td>89.3(2)</td>
</tr>
<tr>
<td>C1-Au-C2</td>
<td>176.7(5)</td>
<td>176.2(3)</td>
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<tr>
<td>Fe1-N1-C1</td>
<td>174.4(12)</td>
<td>178.1(7)</td>
</tr>
<tr>
<td>Fe1[\text{d}]-N2-C2</td>
<td>167.1(10)</td>
<td>174.2(6)</td>
</tr>
<tr>
<td>Au-C1-N1</td>
<td>177.7(15)</td>
<td>175.0(7)</td>
</tr>
<tr>
<td>Au-C2-N2</td>
<td>176.4(11)</td>
<td>174.6(7)</td>
</tr>
</tbody>
</table>

Symmetry codes: a) -x+3/2, y+1/2, -z+3/2; b) x, -y+1, z-1/2; c) -x+3/2, -y+3/2, -z+1; d) -x+3/2, y-1/2, -z+3/2.

Table S3. Selected bond lengths [Å] and angles [°] for 3 at 150 K.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>273 K</th>
<th>Ni-C9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N1</td>
<td>2.217(3)</td>
<td>1.880(4)</td>
</tr>
<tr>
<td>Fe-N3</td>
<td>2.194(3)</td>
<td>1.870(3)</td>
</tr>
<tr>
<td>Fe-N4[\text{a}]</td>
<td>2.144(2)</td>
<td>Ni-C10</td>
</tr>
<tr>
<td>N4[\text{b}]-Fe-N3</td>
<td>90.89(10)</td>
<td>N3[\text{c}]-Fe-N1</td>
</tr>
<tr>
<td>N4[\text{b}]-Fe-N3[\text{c}]</td>
<td>89.11(10)</td>
<td>N3-Fe-N1</td>
</tr>
<tr>
<td>N4[\text{b}]-Fe-N1</td>
<td>90.98(10)</td>
<td>Fe-N3-C9</td>
</tr>
<tr>
<td>N4[\text{b}]-Fe-N1</td>
<td>89.02(10)</td>
<td>Fe[\text{e}]-N4-C10</td>
</tr>
</tbody>
</table>
Symmetry codes: a) -x+2, y-1/2, -z+1/2; b) x, -y+5/2, z+1/2; c) -x+2, -y+2, -z+1; d) x, -y+5/2, z+1/2; e) -x+2, y+1/2, -z+1/2.

Table S4. Selected interatomic distances [Å] at variant temperatures for 1 and 2.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>1</th>
<th></th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
<td>225</td>
<td>150</td>
</tr>
<tr>
<td>&lt;Fe-N&gt;</td>
<td>2.147(8)</td>
<td>1.971(5)</td>
<td>1.954(5)</td>
</tr>
<tr>
<td>Fe-N_{ax}</td>
<td>2.198(7)</td>
<td>2.027(5)</td>
<td>2.005(4)</td>
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<tr>
<td>Fe-N_{eq}</td>
<td>2.122(8)</td>
<td>1.943(5)</td>
<td>1.929(5)</td>
</tr>
<tr>
<td>Fe···Fe</td>
<td>16.622(2)</td>
<td>16.317(9)</td>
<td>16.240(7)</td>
</tr>
</tbody>
</table>

Fig. S1 View of a portion of 3D structure in 1.

Fig. S2 View of a fragment of the 3D interpenetrated framework and the corresponding topological network in 1.
Fig. S3 Thermogravimetric analysis of compounds 1 (left) and 2 (right).

Fig. S4 Temperature dependence of $\chi_M T$ for 3.