Supplementary Information

Extended Hybrid Architectures Based on Tetra-Co\textsuperscript{II} Sandwiched Polyoxotungstate

Yu Zhu,\textsuperscript{a} Wei-Hui Fang,\textsuperscript{a} Qi Wei,\textsuperscript{b} and Guo-Yu Yang*\textsuperscript{a,\textsuperscript{b}}

\textsuperscript{a} State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China, E-mail: ygy@fjirsm.ac.cn; Fax: (+86) 591-8371-0051
\textsuperscript{b} MOE Key Laboratory of Cluster Science, School of Chemistry, Beijing Institute of Technology, Beijing 10008, China. E-mail: ygy@bit.edu.cn; Fax: (+86) 10-6891-8572

The first two authors have equal contributions.

Fig. S1. Powder XRD pattern of compound 1.
Fig. S2. Powder XRD pattern of compound 2.
Fig. S3. Powder XRD pattern of compound 3.
Fig. S4. The asymmetric unit of compound 1.
Fig. S5. The coordination environment of the Co1 and Co2 ions in compound 1.
Fig. S6. The asymmetric unit of compound 2.
Fig. S7. The asymmetric unit of compound 3.
Fig. S8. IR spectrum of compound 1.
Fig. S9. IR spectrum of compound 2.
Fig. S10. IR spectrum of compound 3.
Fig. S11. UV-vis diffuse reflectance spectrum of 1.
Fig. S12. UV-vis diffuse reflectance spectrum of 2.
Fig. S13. UV-vis diffuse reflectance spectrum of 3.
Fig. S14. TG curve of compound 1.
Fig. S15. TG curve of compound 2.
Fig. S16. TG curve of compound 3.
Fig. S17. The X-band EPR spectrum of compound 2.
Fig. S18. The X-band EPR spectrum of compound 3.

Table S1. The BVS values of all the W and O atoms from the asymmetrical unit of compound 1-3.
Fig. S1. Powder XRD pattern of compound 1, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.

Fig. S2. Powder XRD pattern of compound 2, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.

Fig. S3. Powder XRD pattern of compound 3, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.
Fig. S4. The asymmetric unit of compound 1.

Fig. S5. The coordination environment of the Co1 and Co2 ions in compound 1.

Fig. S6. The asymmetric unit of compound 2.

Fig. S7. The asymmetric unit of compound 3.
Fig. S8. IR spectrum of compound 1.

Fig. S9. IR spectrum of compound 2.

Fig. S10. IR spectrum of compound 3.
Fig. S11. UV-vis diffuse reflectance spectrum of 1.

Fig. S12. UV-vis diffuse reflectance spectrum of 2.

Fig. S13. UV-vis diffuse reflectance spectrum of 3.
Fig. S14. TG curve of compound 1.

Fig. S15. TG curve of compound 2.

Fig. S16. TG curve of compound 3.
Fig. S17. The X-band EPR spectrum of compound 2.

Fig. S18. The X-band EPR spectrum of compound 3.

Table S1. The BVS values of all the W and O atoms from the asymmetrical unit of compound 1-3.

<table>
<thead>
<tr>
<th>Compound 1:</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W1</td>
<td>6.110</td>
<td>W2</td>
<td>6.167</td>
<td>W3</td>
<td>6.182</td>
<td>W4</td>
<td>6.112</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>6.266</td>
<td>W6</td>
<td>6.209</td>
<td>W7</td>
<td>6.077</td>
<td>W8</td>
<td>6.227</td>
</tr>
<tr>
<td></td>
<td>W9</td>
<td>6.099</td>
<td>Co1</td>
<td>2.160</td>
<td>Co2</td>
<td>2.017</td>
<td>Co3</td>
<td>2.379</td>
</tr>
<tr>
<td></td>
<td>Co4</td>
<td>2.268</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound 2:</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W5</td>
<td>6.261</td>
<td>W6</td>
<td>6.139</td>
<td>W7</td>
<td>6.397</td>
<td>W8</td>
<td>6.185</td>
</tr>
<tr>
<td></td>
<td>W9</td>
<td>6.197</td>
<td>Co1</td>
<td>2.062</td>
<td>Co2</td>
<td>2.056</td>
<td>Co3</td>
<td>1.879</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound 3:</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W1</td>
<td>6.213</td>
<td>W2</td>
<td>6.154</td>
<td>W3</td>
<td>6.218</td>
<td>W4</td>
<td>6.222</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>6.124</td>
<td>W6</td>
<td>6.135</td>
<td>W7</td>
<td>6.133</td>
<td>W8</td>
<td>6.049</td>
</tr>
<tr>
<td></td>
<td>W9</td>
<td>6.183</td>
<td>Co1</td>
<td>1.973</td>
<td>Co2</td>
<td>1.987</td>
<td>Co3</td>
<td>2.035</td>
</tr>
<tr>
<td></td>
<td>Co4</td>
<td>2.454</td>
<td>Co5</td>
<td>2.300</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>