Electronic Supplementary Information

A F-Bridged Mn(II) Molecular Square

Seán T. Meally,\textsuperscript{a} Kevin Mason,\textsuperscript{a} Patrick McArdle,\textsuperscript{a} Euan. K. Brechin,\textsuperscript{b} Alan G. Ryder,\textsuperscript{a} and Leigh F. Jones\textsuperscript{a}\textsuperscript{**}

\textbf{Fig. SII} Structures of the {\{Mn\textsubscript{4}F\textsubscript{4}\}} square core in 1. Colour code: Mn (pink), F (green).

\textbf{Table SII}: BVS calculations undertaken for Mn1 in [Mn\textsubscript{4}(\mu\textsubscript{2}-F)\textsubscript{4}(1,10-phen)\textsubscript{8}](NO\textsubscript{3})\textsubscript{4} (1)

<table>
<thead>
<tr>
<th>Calculated as:</th>
<th>Mn1</th>
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<tbody>
<tr>
<td>Mn(II)</td>
<td>2.34</td>
</tr>
<tr>
<td>Mn(III)</td>
<td>2.27</td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>2.20</td>
</tr>
</tbody>
</table>

\textbf{Fig. SII} Infra-Red (black line) and Raman spectra (red line) obtained from crystalline sample of 1.
Fig. SI3 Mass spectrum of 1 from MeCN solution. TOF MS-ES (%) m/z: 181.1 (40, [L+H]+), 227 (70, [55Mn(L)(F)_2]+), 254 (18, [55Mn(L)(F)]^2+), 434 (95, [55Mn_4(L)_8(F)_4]^4+ or [55Mn_2(F)_3(L)_2]^2+), 453 (20, [55Mn(L)(F)_2]+), 477 (85, [55Mn(F)_2(L)_2-Na]^+) 570 (25, [55Mn_2(F)_3(L)_2-(CH_3CN)]^2+), 613 (20, [55Mn_2(F)_3(L)_2-(CH_3CN)_2]^2+).
Fig. SI4 UV/vis spectrum obtained from an CH$_3$CN solution of [Mn$_4$(µ$_2$-F)$_4$(1,10-phen)$_8$](NO$_3$)$_4$ (1).

**X-ray diffraction details on the collection of [Mn$_4$] (1)**

The structure of 1 was collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. The data reduction was carried out on the CrysAlisPro software package. The structure was solved by direct methods (SHELXS-97)\(^1\) and refined by full matrix least squares using SHELXL-97.\(^2\) SHELX operations were automated using the OSCAIL software package.\(^3\) All hydrogen atoms were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the oxygen atoms of the H$_2$O solvent molecules of crystallisation (which were left isotropic).