Supplementary Information

Two-Dimensional $^{14}$N HYSCORE Spectroscopy of the Coordination Geometry of Ligands in Dimanganese Di-$\mu$-oxo Mimics of the Oxygen Evolving Complex of Photosystem II $^\dagger$

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One-sentence summary: A Two-Dimensional $^{14}$N HYSCORE Study of Dimanganese Di-$\mu$-oxo Mimics of the Oxygen-Evolving Complex of Photosystem II.

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Key Words: Photosystem II, biomimetic models, mixed-valence coordination complexes, EPR spectroscopy, HYSCORE spectroscopy, \([(\text{bpy})_2\text{Mn}^\text{III}(\mu-\text{O})_2\text{Mn}^\text{IV}(\text{bpy})_2](\text{ClO}_4)_3\) (bpy, 2,2'-bipyridine) and \([\text{H}_2\text{O(terpy)}\text{Mn}^\text{III}(\mu-\text{O})_2\text{Mn}^\text{IV}(\text{terpy})\text{OH}_2](\text{NO}_3)_3\) (terpy = 2,2':6',2''-terpyridine).
Tables

**Table S1.** The experimentally determined $^{14}$N isotropic and anisotropic hyperfine interaction parameters of 2 in aqueous buffer.
Table S1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Nitrogen</th>
<th>Assignment</th>
<th>$A_{iso}$ (MHz)</th>
<th>$T$ (MHz)</th>
<th>$K^{2}(3 + \eta^{2})$ (MHz²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$N_{I}$</td>
<td>Mn(III), axial</td>
<td>13.1 ± 1.0</td>
<td>~ 0.9</td>
<td>1.8 ± 0.5</td>
</tr>
<tr>
<td>(Aqueous buffer)</td>
<td>$N_{II}$</td>
<td>Mn(IV), axial</td>
<td>3.6 ± 0.3</td>
<td>~ 0.2</td>
<td>0.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$N_{III}$</td>
<td>Mn(IV), equatorial</td>
<td>2.3 ± 0.6</td>
<td>~ 0.5</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$N_{IV}$</td>
<td>Mn(III), equatorial</td>
<td>&lt; 2.0</td>
<td>~ 0.6-1.3</td>
<td>~ 1.9</td>
</tr>
</tbody>
</table>
Figure Legends.

Figure S1. The 2D $^{14}$N HYSCORE spectrum of 2 in aqueous buffer at pH 4.3.