

Electronic Supplementary Information

Facile adaptation of 1D Mn(II) chain motifs to form 3D azo-pyridine-based coordination polymers

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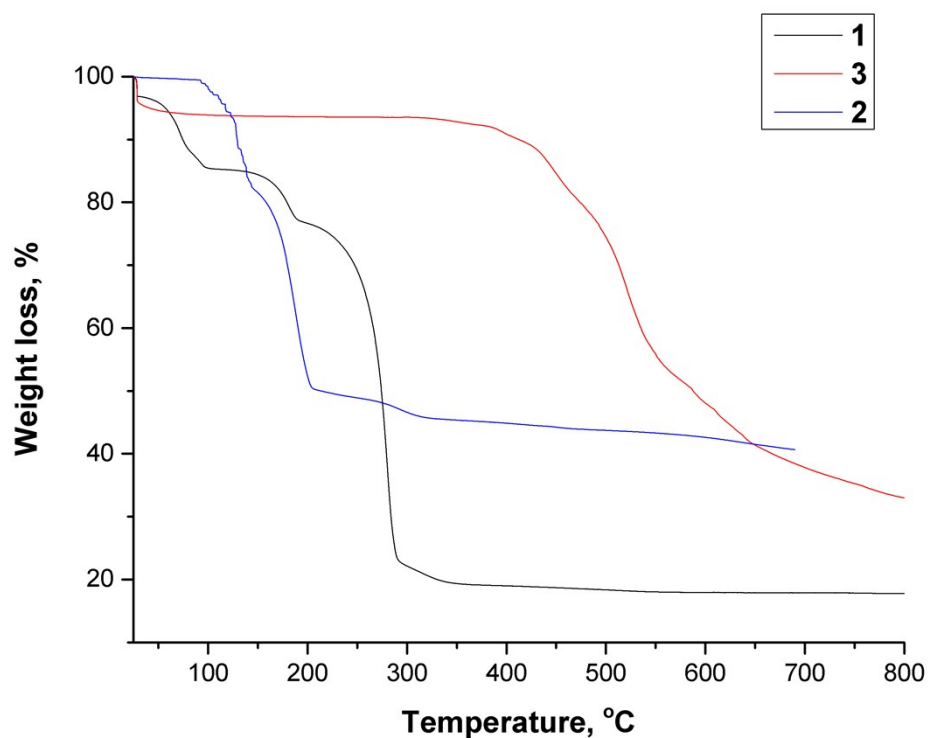


Fig. S1 TGA plot of compounds **1-3** measured under a nitrogen atmosphere (heating rate 2 °C min⁻¹); Comment: Compound **3** was dried and stored at room temperature and the constitutional CH₃CN molecules were lost prior to the measurement.

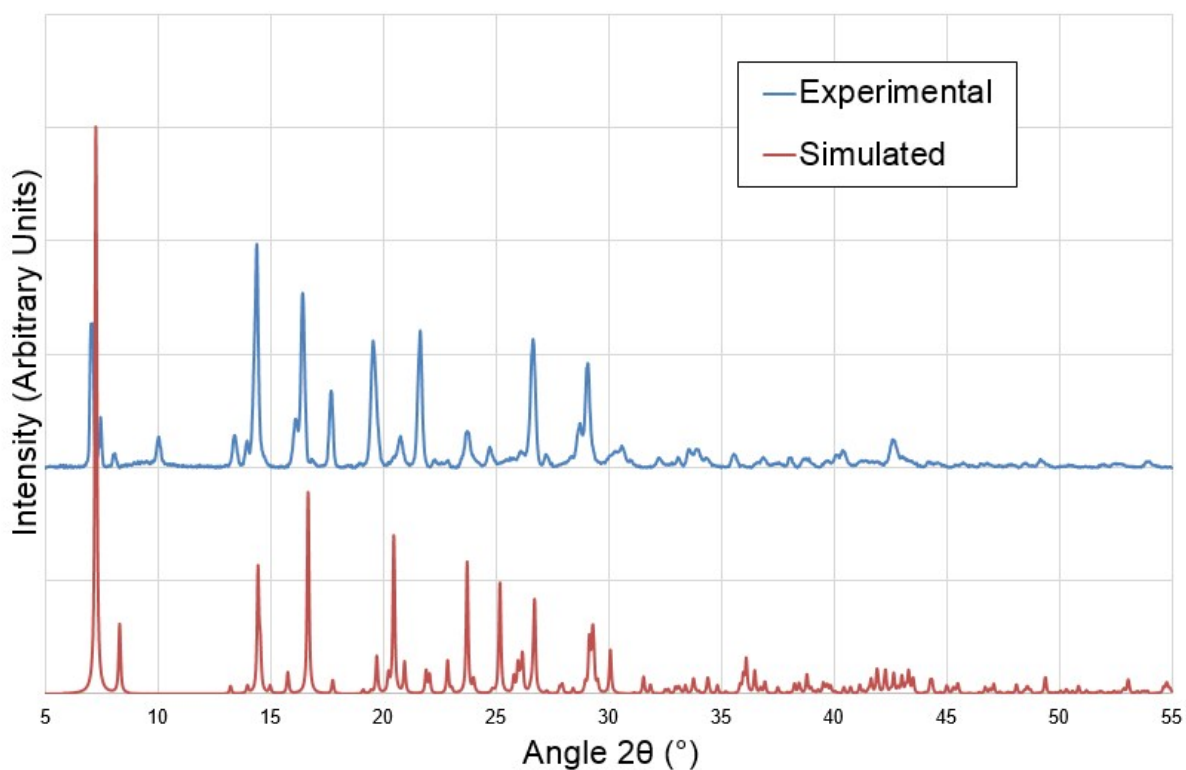


Fig. S2 X-ray powder diffraction pattern for complex **1**, measured at room temperature (blue) compared with the calculated pattern from the single crystal data at 100K (red). The signal at ca. 10° results most likely from a small quantity of an impurity that derive from the reactants.

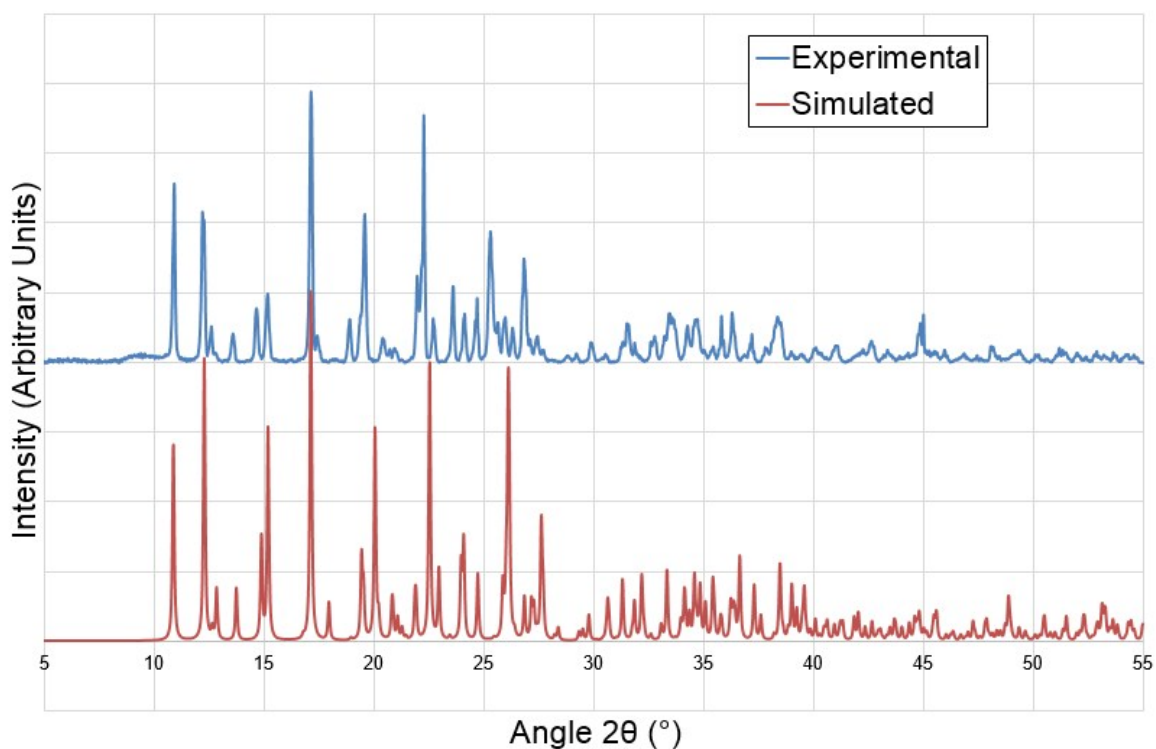


Fig.S3 X-ray powder diffraction pattern for complex **2**, measured at room temperature (blue) compared with the calculated pattern from the single crystal data at 100K (red).

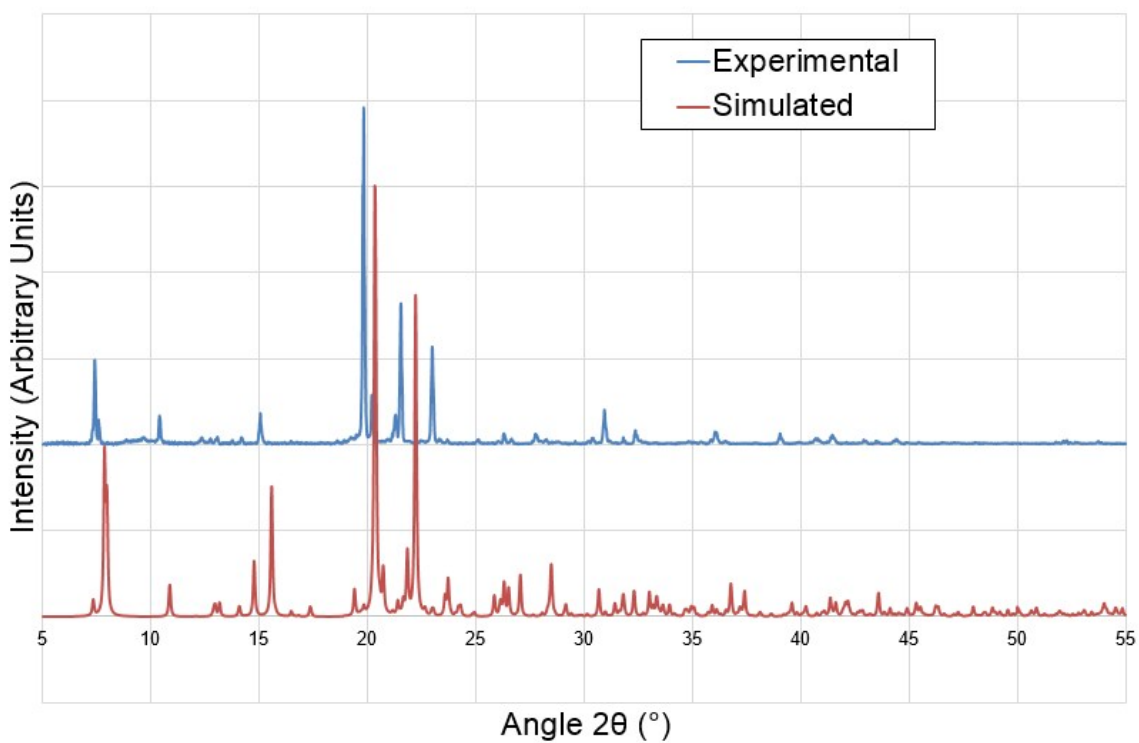


Fig. S4 X-ray powder diffraction pattern for complex **3**, measured at room temperature (blue) compared with the calculated pattern from the single crystal data at 100K (red).

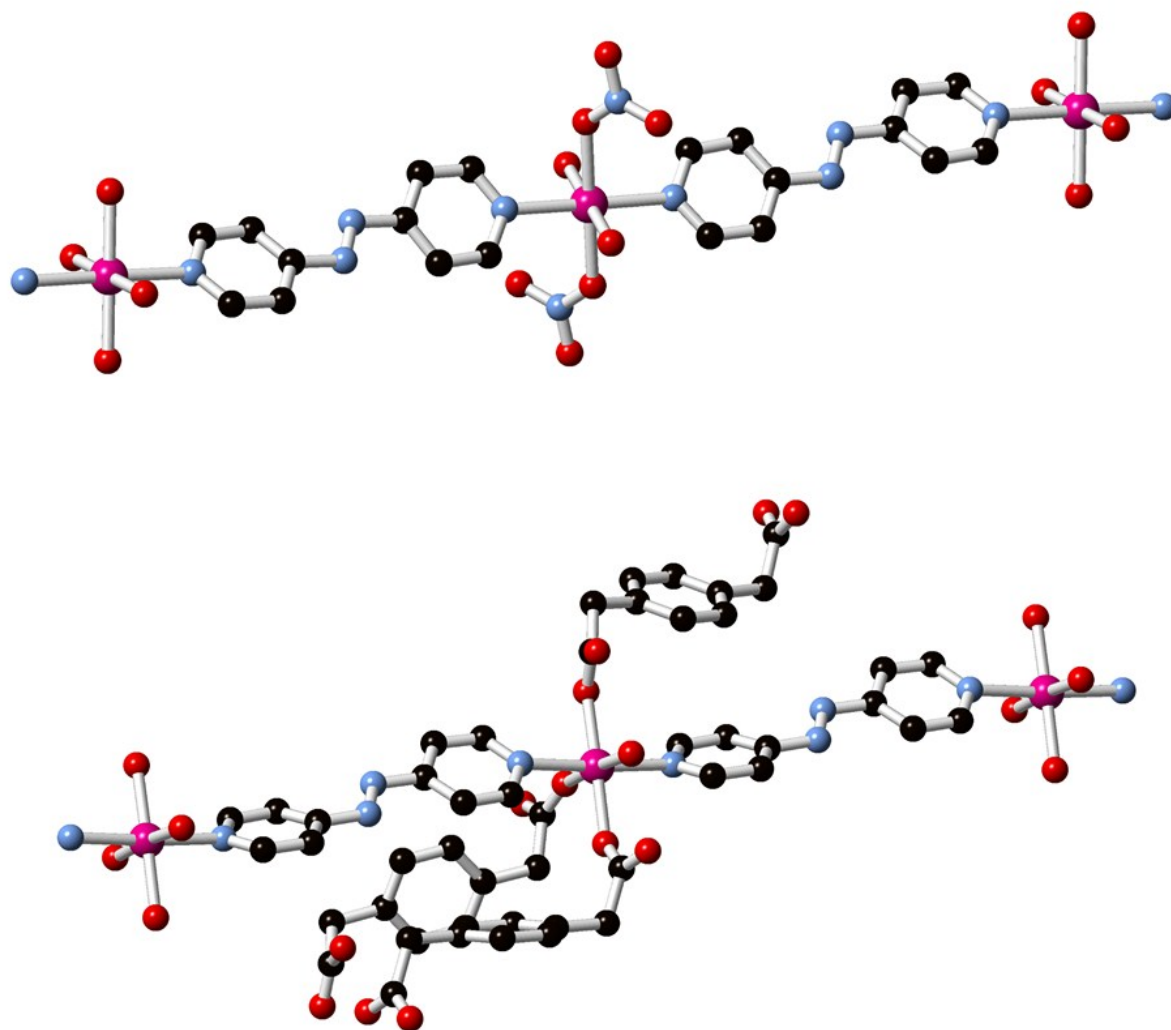


Fig. S5 Comparison of the *poly*-[Mn(azopy)] linear repeating unit in the structures of **1** (top) and **3** (bottom). Hydrogen atoms are omitted for clarity.

Table S1 Hydrogen bonding parameters for complexes **1** and **3**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|------------------|----------|-----------------|-----------------|-----------------|-----------------|----------------|
| Complex 1 | | | | | | |
| O1 | H1A | O5 ¹ | 0.897(14) | 1.855(16) | 2.749(4) | 174(6) |
| O1 | H1A | N2 ¹ | 0.897(14) | 2.61(2) | 3.447(4) | 155(4) |
| O1 | H1B | O5 ² | 0.896(14) | 1.872(17) | 2.763(4) | 172(4) |
| O2 | H2A | O8 ³ | 0.898(14) | 1.88(2) | 2.757(4) | 165(4) |
| O2 | H2B | O8 ⁴ | 0.895(14) | 1.862(16) | 2.749(4) | 171(5) |
| O2 | H2B | N3 ⁴ | 0.895(14) | 2.63(3) | 3.456(4) | 155(4) |
| | | | | | | |
| | | | | | | |
| Complex 3 | | | | | | |
| O4 | H4 | O6 ⁶ | 0.863(9) | 1.762(11) | 2.5997(11) | 163.0(19) |
| O7 | H7A | O6 | 0.859(19) | 1.906(19) | 2.7077(10) | 154.8(18) |
| O7 | H7B | O1 ⁵ | 0.84(2) | 1.88(2) | 2.7125(9) | 175.4(18) |
| O4B | H4B | O6 ⁶ | 1.09 | 1.75 | 2.542(8) | 125 |

¹1/2+X,5/2-Y,+Z; ²1+X,+Y,+Z; ³-1+X,+Y,+Z; ⁴-1/2+X,3/2-Y,+Z; ⁵3/2-X,-1/2+Y,1/2-Z; ⁶1/2+X,1/2-Y,-1/2+Z