

Supporting Information

Gradual Spin Crossover Behaviour in a Linear Trinuclear Fe^{II} Complex.

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Equation S1

$$a = \frac{J_1}{kT}$$

$$b = \frac{J_2}{kT}$$

$$\chi T = \frac{Ng^2\mu_B^2}{3k} \left[\frac{84\exp(6a + 6b) + 30\exp(6b) + 6\exp(-4a + 6b) + 30\exp(4a + 2b) + 6\exp(2b) + 6\exp(2b)}{7\exp(6a + 6b) + 5\exp(6b) + 3\exp(-4a + 6b) + 5\exp(4a + 2b) + 3\exp(2b) + 1\exp(-2a + 2b) + 3\exp(2b)} \right]$$

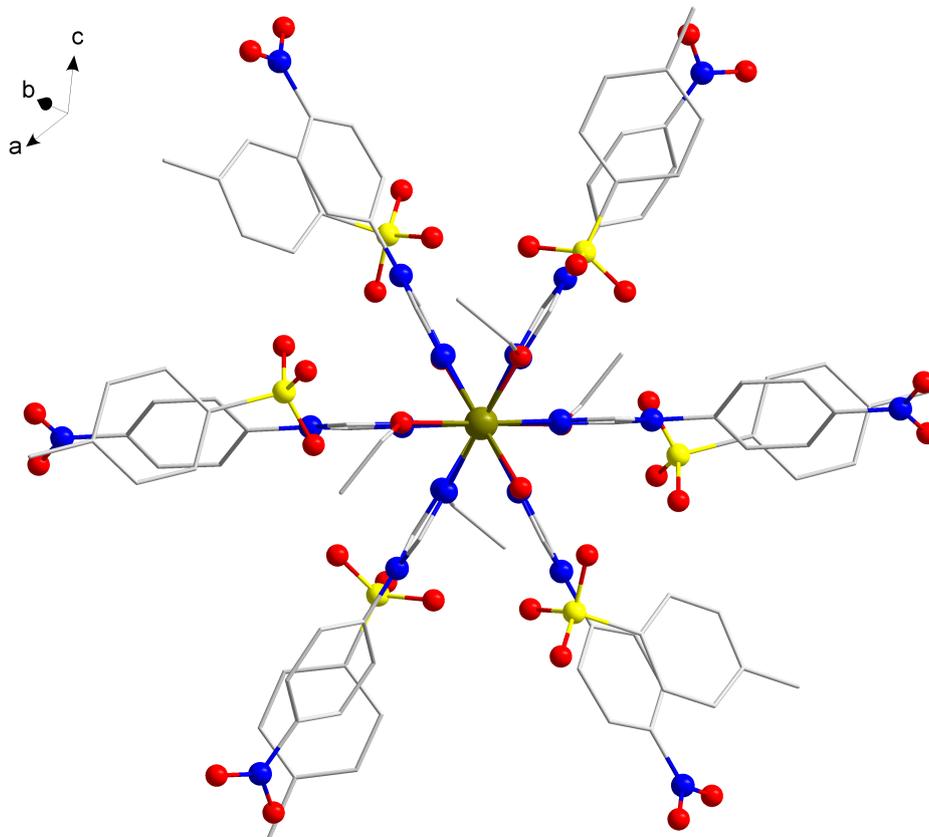


Fig. S1 The molecular structure of **1** viewed along the axial axis of the linear trimer showing the emplacement of the *p*-tolylsulfonate counter anions. The hydrogen atoms are omitted for clarity. Colour code: Dark Yellow (Fe), Red (O), Blue (N), Grey (C), Yellow (S).

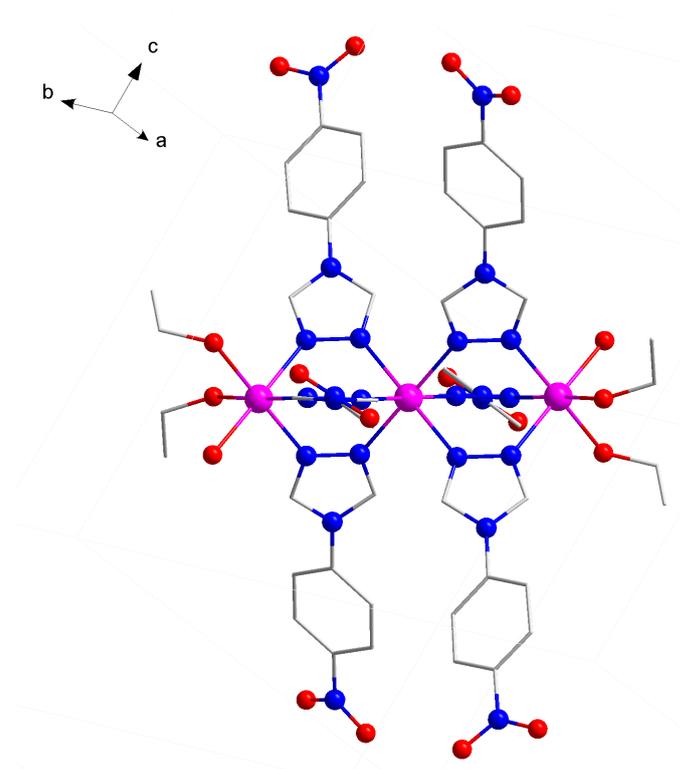


Fig. S2 The molecular structure of **2**. The hydrogen atoms and counter anions are omitted for clarity.
Colour code: Pink (Co), Red (O), Blue (N), Grey (C).

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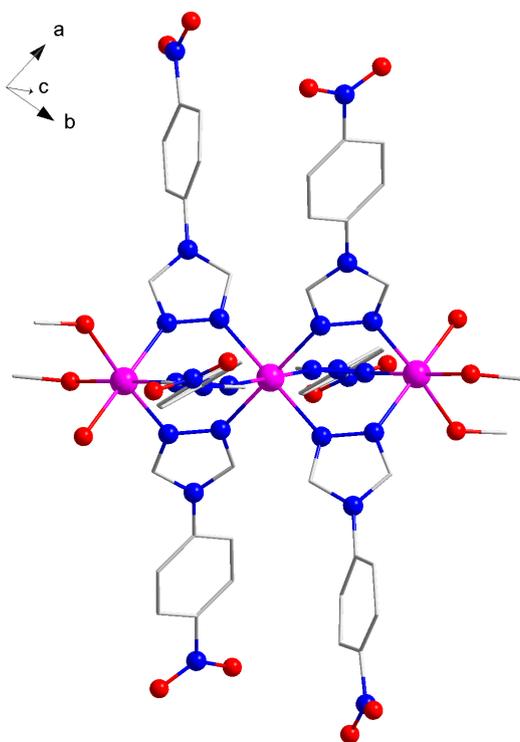


Fig. S3 The molecular structure of **3**. The hydrogen atoms and counter anions are omitted for clarity.
Colour code: Pink (Co), Red (O), Blue (N), Grey (C).

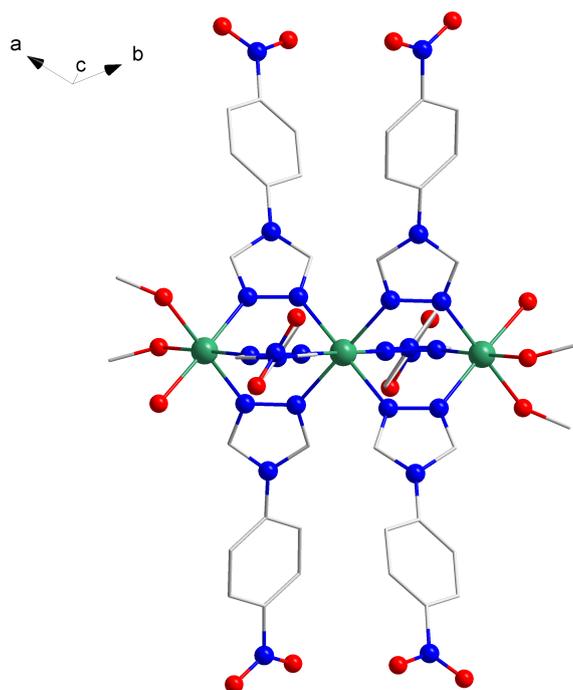
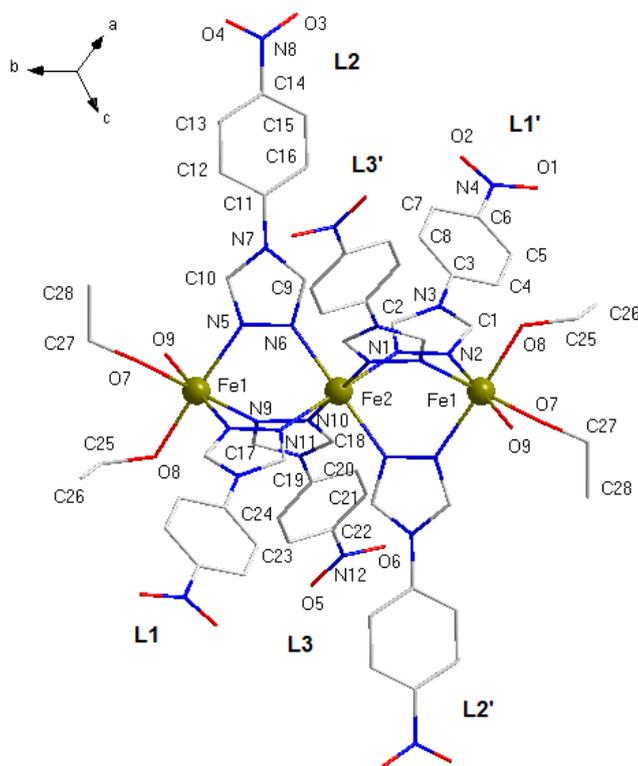


Fig. S4 The molecular structure of **4**. The hydrogen atoms and counter anions are omitted for clarity.
Colour code: Green (Ni), Red (O), Blue (N), Grey (C).



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Fig. S5 Labelled structure of **1**. Ligand labels are equivalent by pair (L1-L1', L2-L2' and L3-L3'). Equivalent labels are used for compounds **2**, **3** and **4**. The *p*-tolylsulfonate counter anions, the solvents of crystallization and the hydrogen atoms are omitted for clarity.
Colour code: Dark Yellow (metal, Fe for **1**), Red (O), Blue (N), Grey (C).

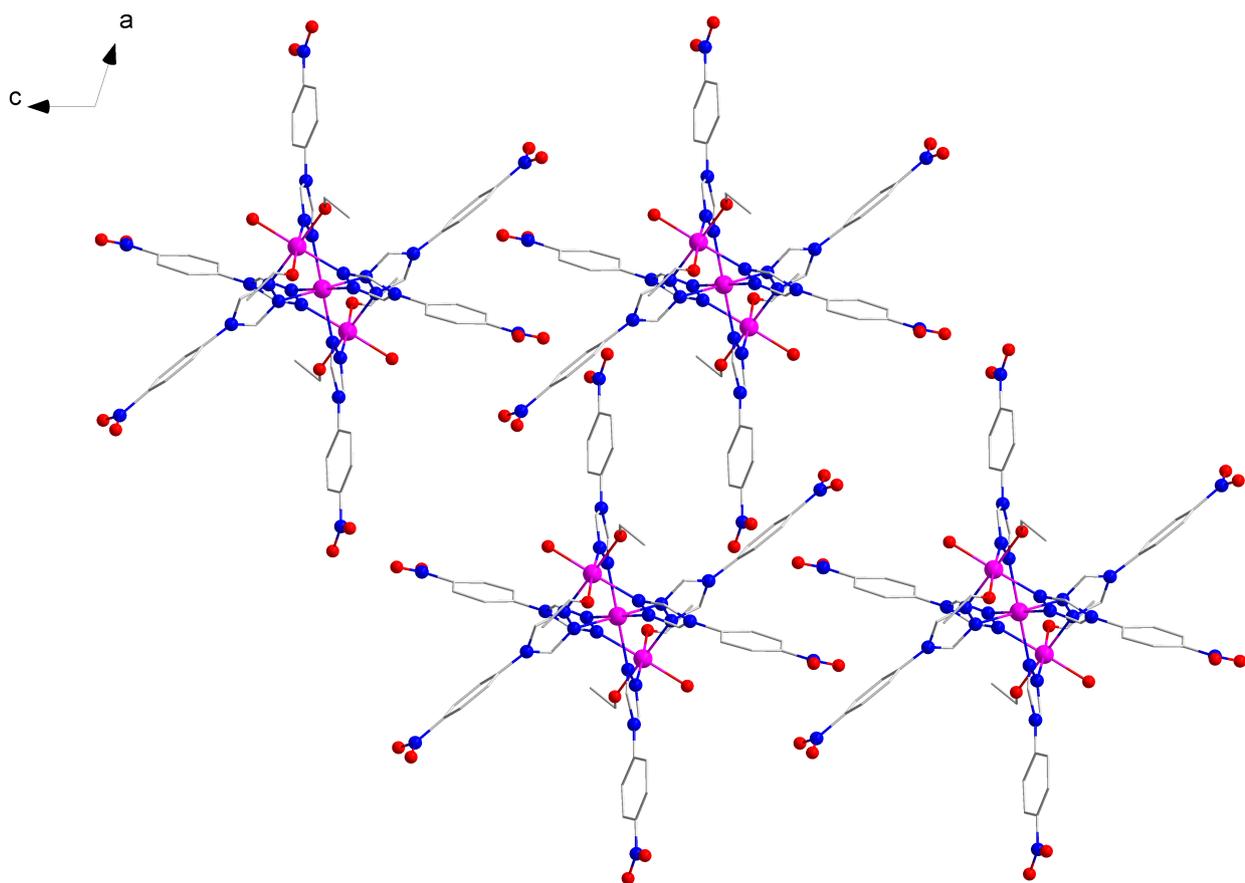


Fig. S6 The packing arrangement of **2** viewed along the *b*-axis. The *p*-tolylsulfonate counter anions, the solvents of crystallization and the hydrogen atoms are omitted for clarity. Colour code: Pink (Co), Red (O), Blue (N), Grey (C).

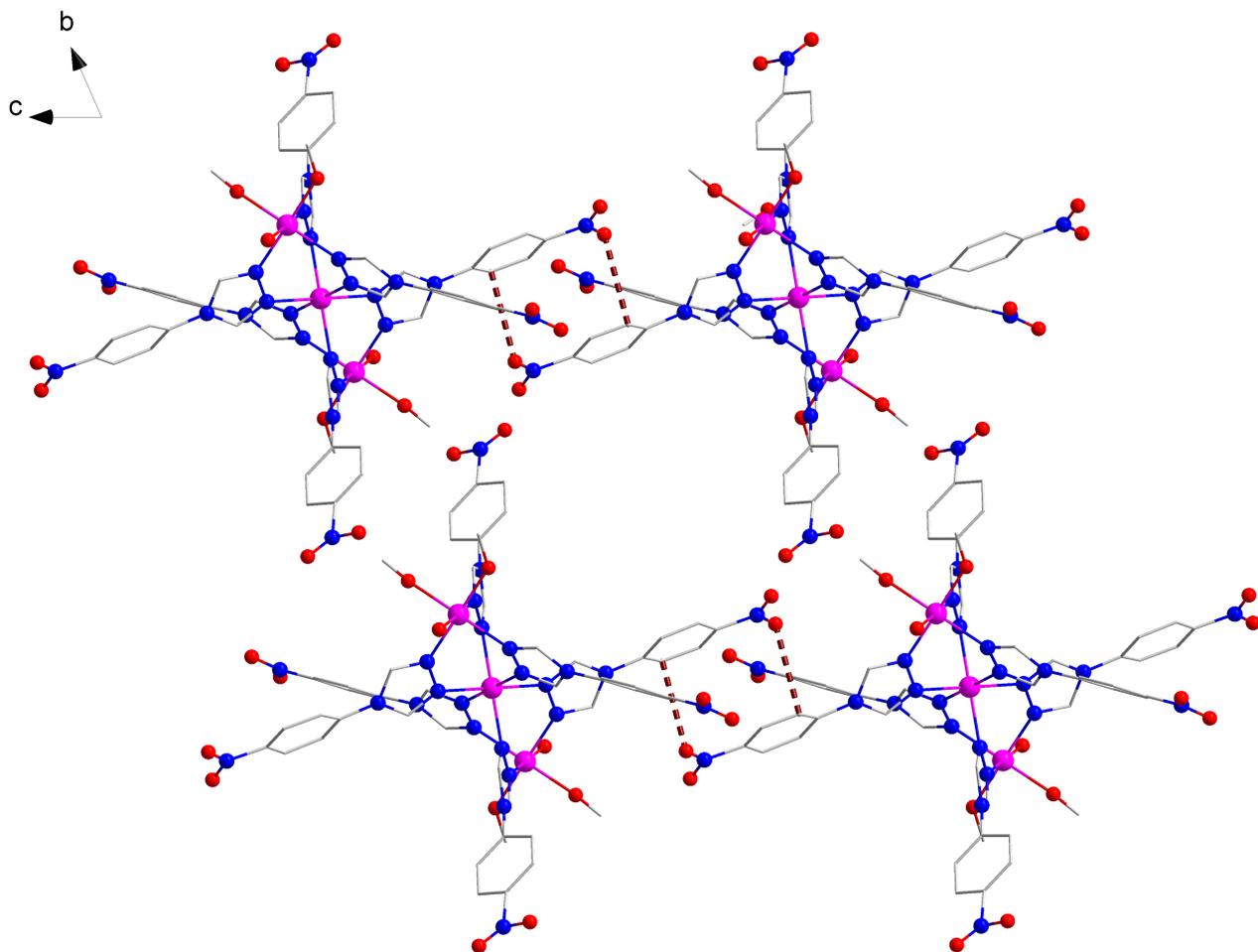


Fig. S7 The packing arrangement of **3**. Electrostatic interactions between the ligands are represented by the dark red fragmented lines. The *p*-tolylsulfonate counter anions, the solvents of crystallization and the hydrogen atoms are omitted for clarity.
Colour code: Pink (Co), Red (O), Blue (N), Grey (C).

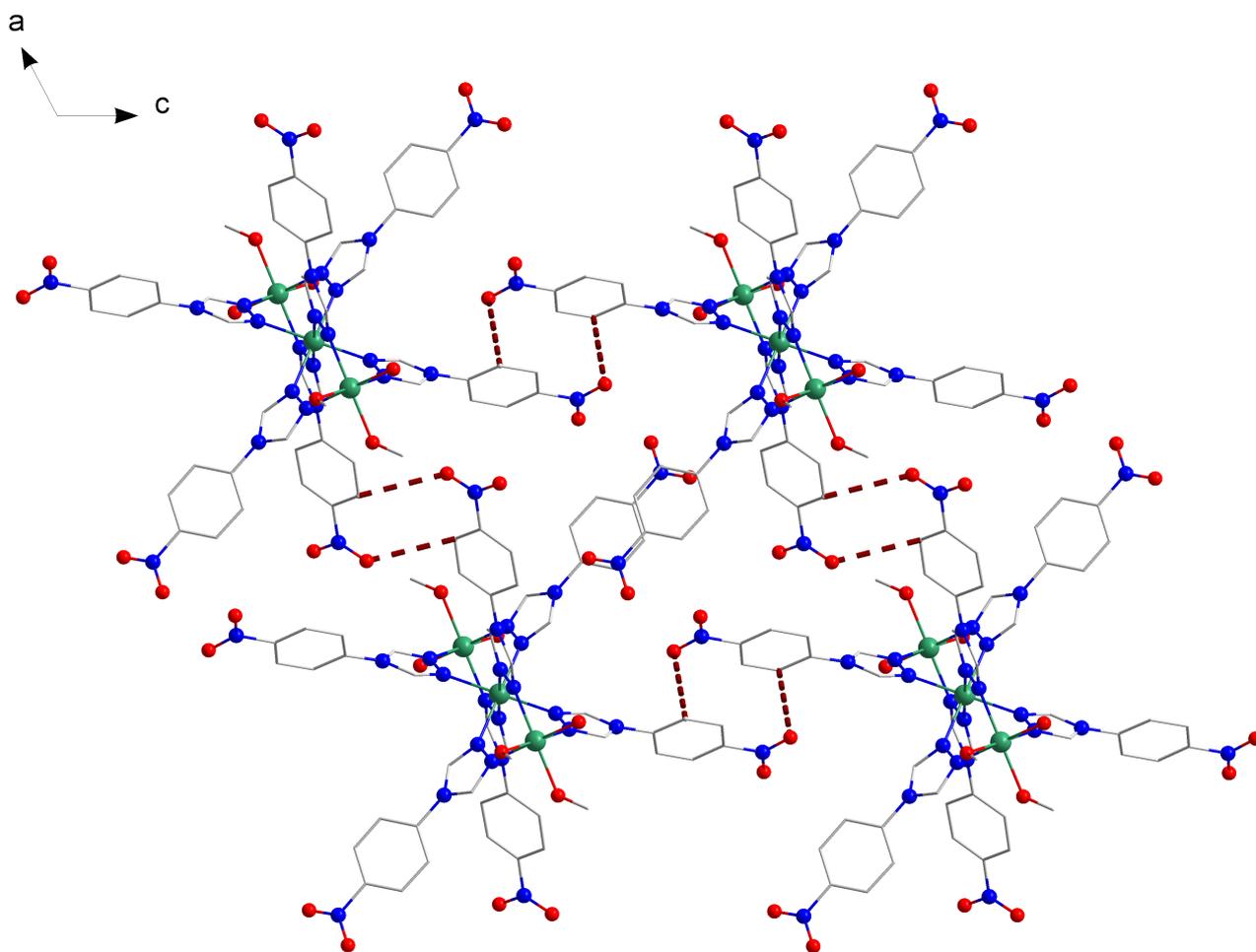


Fig. S8 The packing arrangement of **4**. Electrostatic interactions between the ligands are represented by the dark red fragmented lines. The *p*-tolylsulfonate counter anions, the solvents of crystallization and the hydrogen atoms are omitted for clarity.
Colour code: Green (Ni), Red (O), Blue (N), Grey (C).

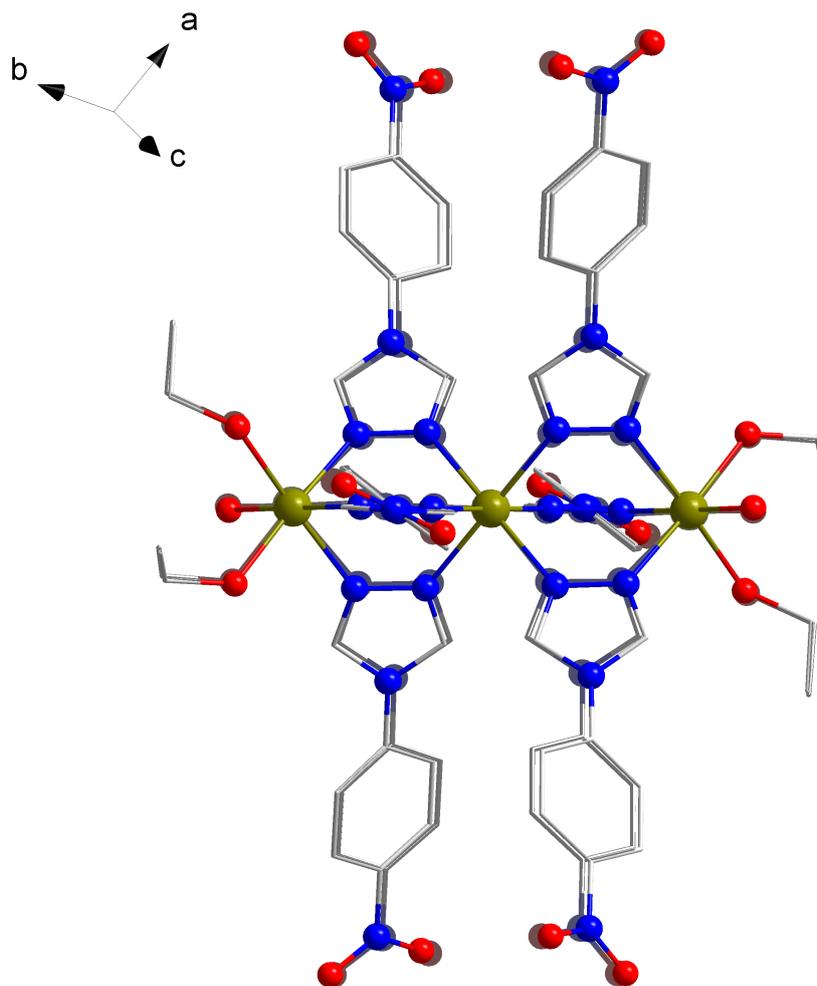


Fig. S9 Shadow superposition of the molecular structures of **1** measured at 100 (shadow) and 181 K (clear). The hydrogen atoms and counter anions are omitted for clarity. Colour code: Dark Yellow (Fe), Red (O), Blue (N), Grey (C).

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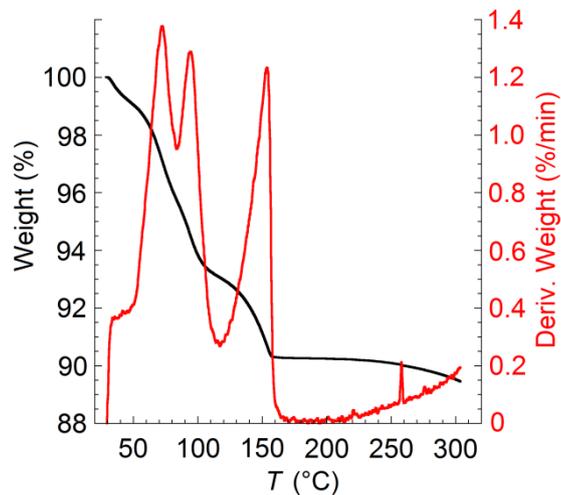


Fig. S10 Thermogravimetric analysis (TGA) of **1** between 25 and 300 °C.

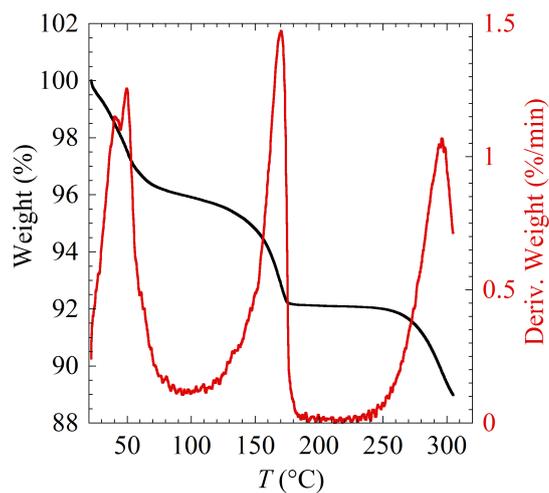


Fig. S11 Thermogravimetric analysis (TGA) of **2** between 25 and 300 °C.

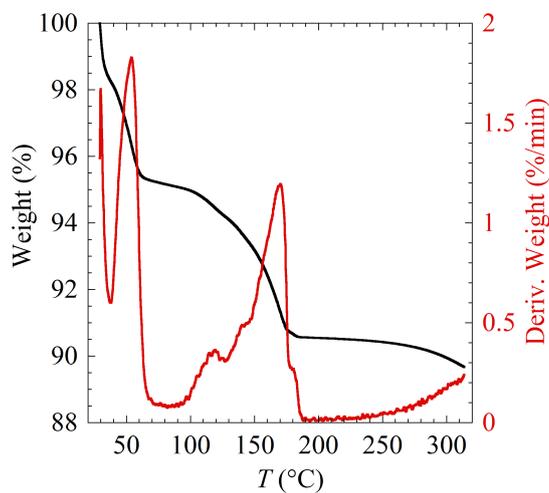


Fig. S12 Thermogravimetric analysis (TGA) of **3** between 25 and 300 °C.

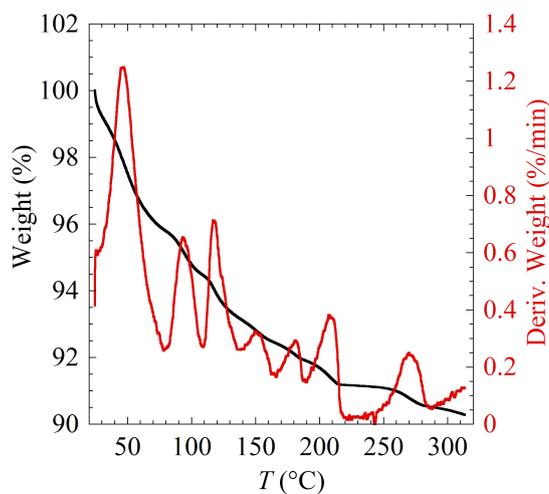


Fig. S13 Thermogravimetric analysis (TGA) of **4** between 25 and 300 °C.

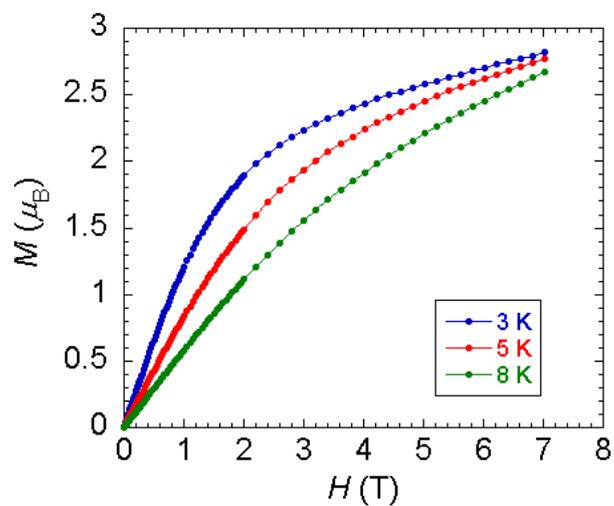


Fig. S14 Field dependence of the magnetization of 2 at 3, 5 and 8 K from 0 to 7 T.

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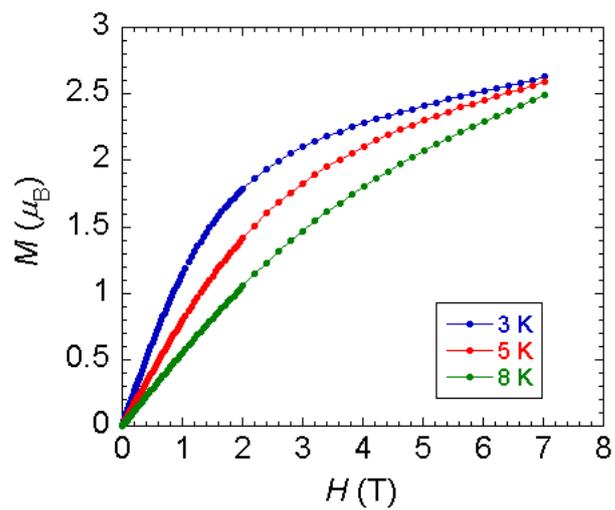


Fig. S15 Field dependence of the magnetization of 3 at 3, 5 and 8 K from 0 to 7 T.

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