

SUPPORTING INFORMATION

Emissive Molecular Nanomagnets: Introducing Optical Properties in Triangular Oximate Mn^{III}_3 SMMs from the Deliberate Replacement of Simple Carboxylate Ligands with their Fluorescent Analogues

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Experimental Section

Syntheses. All experiments were performed under aerobic conditions using materials (reagent grade) and solvents as received. The triangular precursor $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_3(\text{mpko})_3](\text{ClO}_4)$ (**1**) was prepared in yields as high as 95% following the reported procedure.²⁰

$[\text{Mn}_3\text{O}(\text{L1})_3(\text{mpko})_3](\text{ClO}_4)$ (2**).** To a stirred, brown solution of **1** (0.09 g, 0.1 mmol) in CH_2Cl_2 (20 mL) was added solid L1-H (0.10 g, 0.6 mmol). The mixture was stirred for 30 min, and the solvent was then removed *in vacuo*. Toluene (20 mL) was added to the dark brown residue, and the solution was again evaporated to dryness. The addition and removal of toluene was repeated two more times. The resulting dark brown solid was redissolved in THF/MeOH (20 mL, 10:1 v/v) and the solution was layered with Et_2O (40 mL). After 5 days, X-ray quality dark purple single crystals of $2 \cdot x\text{MeOH} \cdot y\text{CH}_2\text{Cl}_2$ were collected by filtration, washed with cold MeOH (2 x 2 mL), and dried under vacuum; the yield was 95%. CCDC deposition number: 955994.

Selected IR data (cm^{-1}) for **2**: 3421 (mb), 3060 (m), 2967 (m), 1596 (s), 1558 (s), 1471 (m), 1396 (m), 1373 (vs), 1355 (s), 1238 (w), 1189 (m), 1089 (vs), 940 (w), 784 (m), 700 (m), 611 (mb), 462(w).

$[\text{Mn}_3\text{O}(\text{L2})_3(\text{mpko})_3](\text{ClO}_4)$ (3**).** To a stirred, brown solution of **1** (0.09 g, 0.1 mmol) in THF/ CH_2Cl_2 (20 mL, 1:1 v/v) was added solid L2-H (0.13 g, 0.6 mmol). The mixture was stirred for 45 min, and the solvent was then removed *in vacuo*. Toluene (20 mL) was added to the dark brown residue, and the solution was again evaporated to dryness. The addition and removal of toluene was repeated two more times. The resulting dark brown solid was redissolved in THF/ CH_2Cl_2 (20 mL, 20:1 v/v) and the solution was layered with $\text{Et}_2\text{O}/\text{MeOH}$ (40 mL, 30:1 v/v). After 6 days, X-ray quality dark brown single crystals of $3 \cdot x\text{MeOH} \cdot y\text{CH}_2\text{Cl}_2$ were collected by filtration, washed with cold MeOH (2 x 2 mL), and dried under vacuum; the yield was 83%. CCDC deposition number: 955993.

Selected IR data (cm^{-1}) for **2**: 3429 (mb), 3051 (m), 1601 (s), 1575 (vs), 1477 (m), 1443 (m), 1419 (m), 1379 (vs), 1315 (vs), 1274 (s), 1180 (m), 1161 (m), 1108 (vs), 1088 (s), 891 (m), 776 (m), 737 (s), 700 (m), 664 (m), 622 (mb), 563 (w), 495 (w), 439 (w).

[Mn₃O(L3)₃(mpko)₃](ClO₄) (4). To a stirred, brown solution of **1** (0.09 g, 0.1 mmol) in THF/CH₂Cl₂ (30 mL, 1:1 v/v) was added solid L3-H (0.15 g, 0.6 mmol). The mixture was stirred for 45 min, and the solvent was then removed *in vacuo*. Toluene (20 mL) was added to the dark brown residue, and the solution was again evaporated to dryness. The addition and removal of toluene was repeated two more times. The resulting dark brown solid was redissolved in THF/CH₂Cl₂ (20 mL, 20:1 v/v) and the solution was layered with Et₂O (40 mL). After 10 days, dark brown, very thin, needle-like crystals of **4**, which were bad X-ray diffractors, were collected by filtration, washed with THF (2 x 2 mL), and dried under vacuum; the yield was 92%. The identity of the product was confirmed by (i) a unit cell determination and comparison with the unit cell of compound of **3**, (ii) IR spectral comparison with complexes **2** and **3**, and (iii) elemental analysis.

Selected IR data (cm⁻¹) for **2**: 3430 (mb), 3051 (m), 1601 (s), 1573 (vs), 1478 (m), 1442 (m), 1419 (m), 1379 (vs), 1315 (vs), 1273 (s), 1181 (m), 1107 (sb), 1086 (s), 892 (m), 776 (m), 738 (s), 700 (m), 664 (m), 622 (mb), 561 (w), 496 (w), 441 (w).

Crystallographic details for both **2** and **3**

All attempts to refine solvent molecules were less than acceptable, leading to large and distorted ellipsoids, poor bond lengths, and significant residual electron density peaks nearby. Various models were examined with different amounts of modelled solvent, and squeeze applied to each one. The best result was achieved from 'Squeezing' all the solvents. This provided a final R-factor at least 1% lower than any other model tried and therefore this was chosen as the best model. As the solvent is not well-resolved crystallographically the exact nature of the solvent (and there may be several types based on the crystallisation method employed) is uncertain. In the CIF files we have included only the chemical formula of the clusters, and none of the solvent. Our opinion is that it makes more sense to do this than to include components that are obviously present, but not crystallographically modelled.

Table S1. Bond Valence Sum^{a,b} Calculations¹ for Manganese and Selected Oxygen Atoms in **2** and **3**

2			
Atom	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	3.21	<u>3.00</u>	3.05
Mn2	3.12	<u>2.92</u>	2.96
Mn3	3.21	<u>3.00</u>	3.05
	BVS	assignment	
O1	1.88	O ²⁻	

3			
Atom	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	3.25	<u>3.04</u>	3.08
	BVS	assignment	
O4	1.94	O ²⁻	

^a The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value.

^b An O BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges is indicative of non-, single- and double-protonation, respectively, but can be altered somewhat by hydrogen bonding.

¹ Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* **1985**, 244.

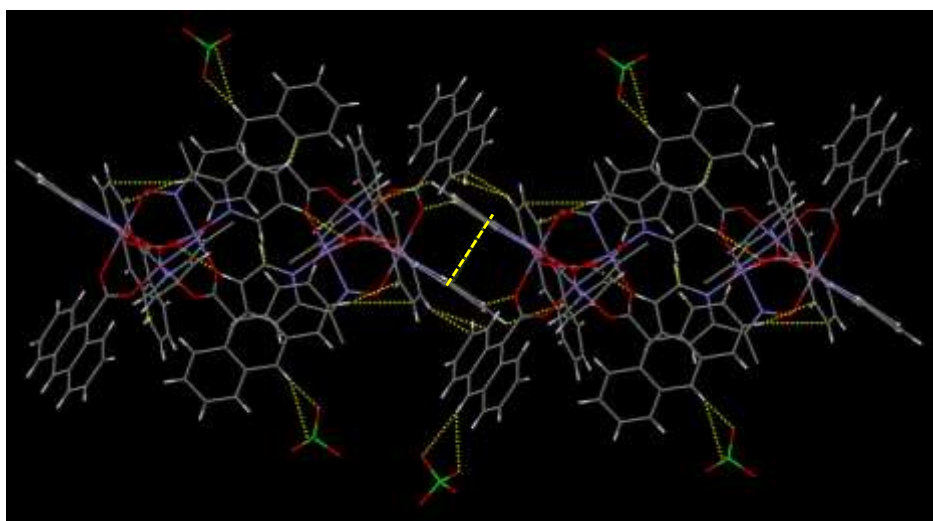
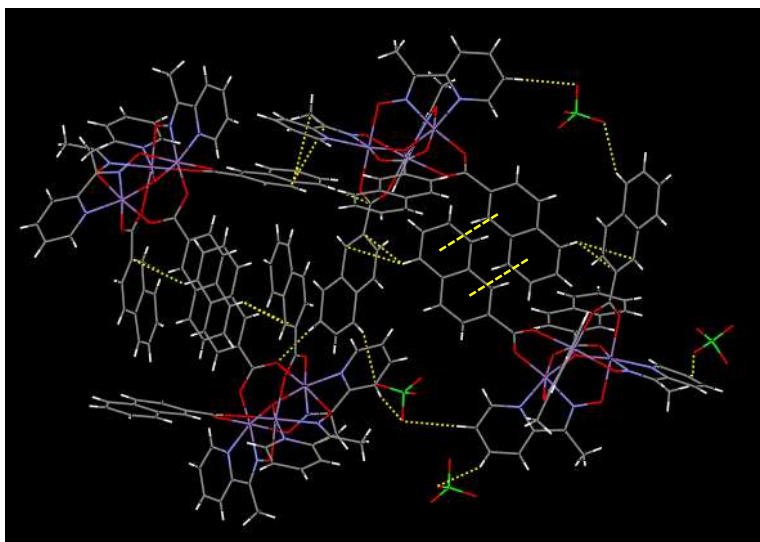


Fig. S1. The supramolecular architectures of complexes **2** (top) and **3** (bottom), emphasizing with yellow dashed lines the intermolecular interactions which serve to link neighboring Mn₃ clusters in the crystal.

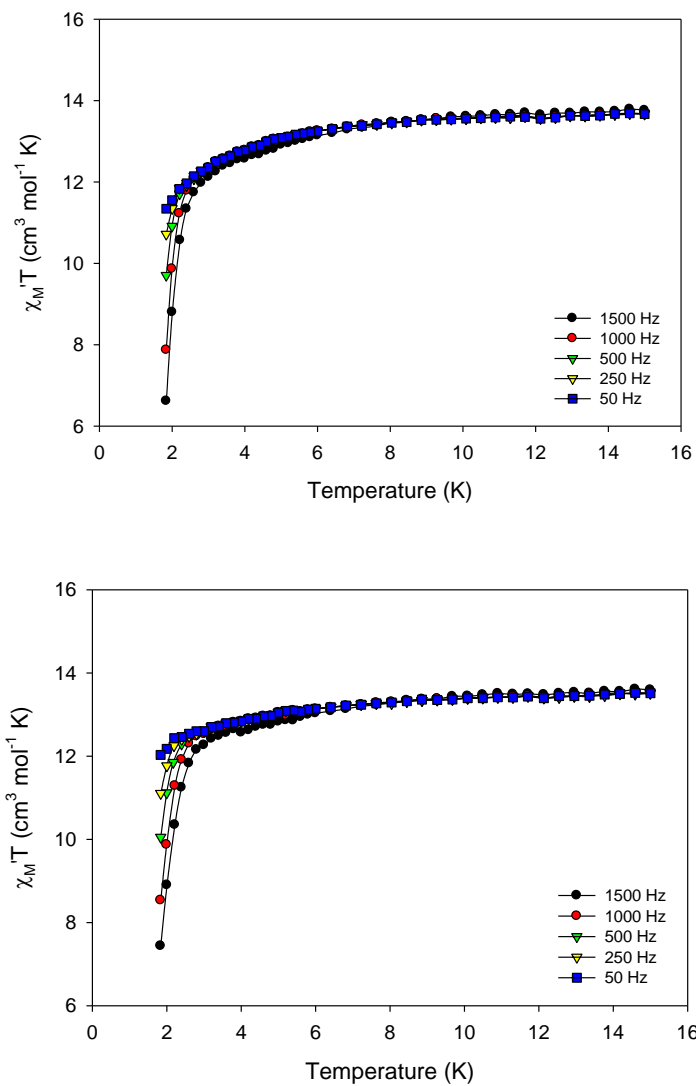


Fig. S2. Plots of the in-phase (χ'_M) (as $\chi'_M T$) ac susceptibility signals of complexes **2** (top) and **3** (bottom) in a 3.5 G field oscillating at the indicated frequencies.

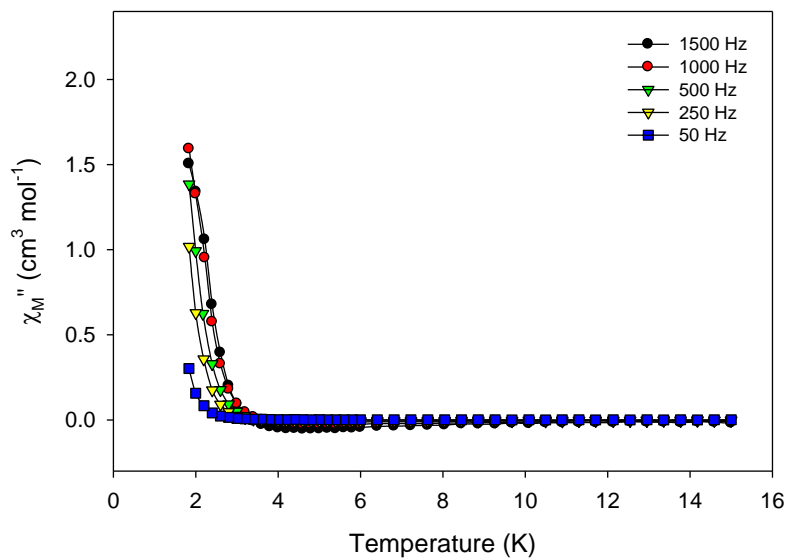


Fig. S3. Plot of the out-of-phase (χ''_M) ac susceptibility signals of complex **3** in a 3.5 G field oscillating at the indicated frequencies.

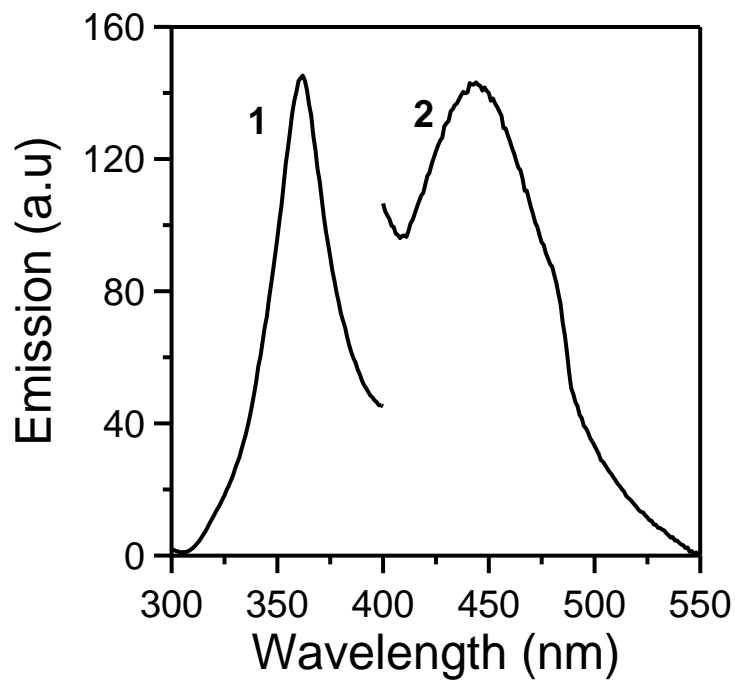


Fig. S4. Excitation (1) and emission (2) spectra of solid mpkoH at room temperature.

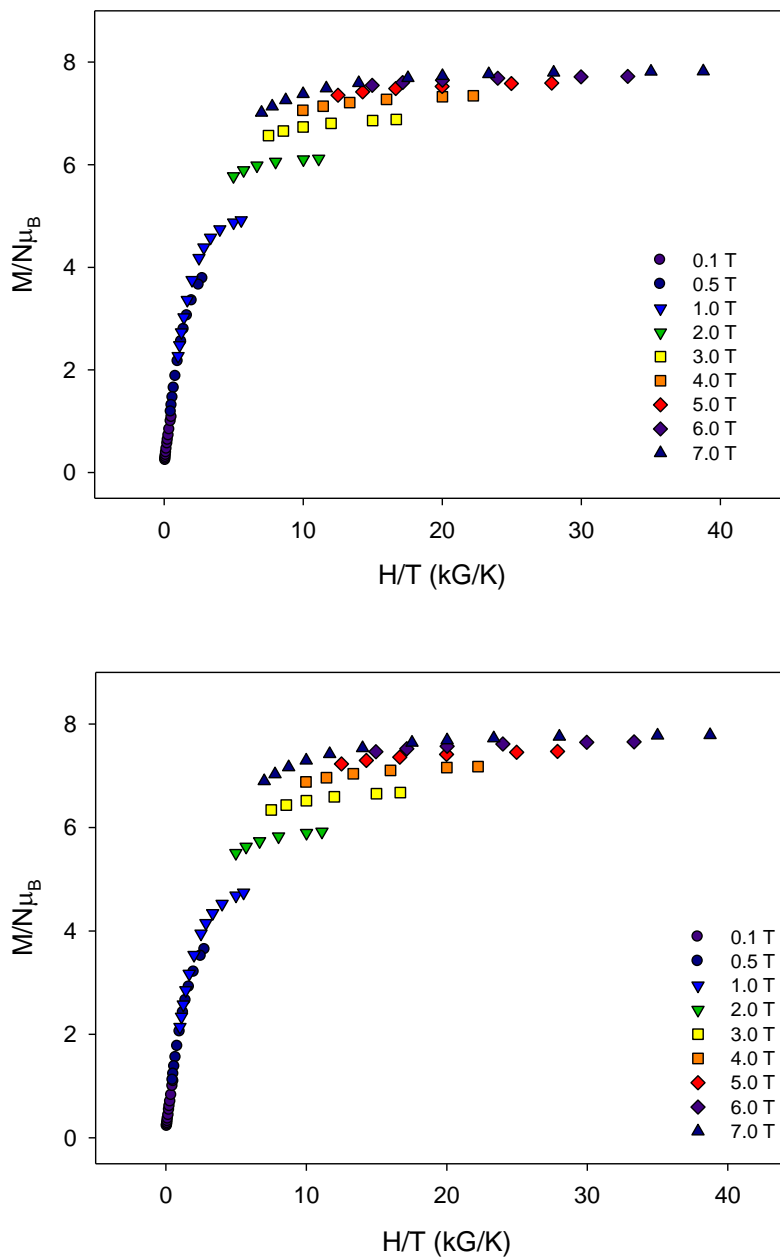


Fig. S5. Plots of reduced magnetization ($M/N\mu_B$) vs H/T for complexes **2** (top) and **3** (bottom) at the indicated fields.