## **SUPPORTING INFORMATION**

## Synthesis, Structure and Magnetic Properties of a Novel Family of Heterometallic Nonanuclear Na<sup>I</sup><sub>2</sub>Mn<sup>III</sup><sub>6</sub>Ln<sup>III</sup> (Ln = Eu, Gd, Tb, Dy) Complexes

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Fig. S1. The molecular packing structure of complex 2 (H atoms and solvent molecules are omitted for clarity).



**Fig. S2**. Molecular structure of the cation  $[Na_2\{Mn_3^{III}(\mu_3-O^{2-})\}_2Eu^{III}(hmmp)_6$  $(O_2CPh)_4(N_3)_2]^+$  in complex **1** (symmetry operation A: -x, -y, -z+1; Hydrogen atoms, counterion and solvent molecules have been omitted for clarity.)

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**Fig. S3**. Molecular structure of the cation  $[Na_2\{Mn_3^{III}(\mu_3-O^{2-})\}_2Tb^{III}(hmmp)_6$  $(O_2CPh)_4(N_3)_2]^+$  in complex **3** (symmetry operation A: -x, -y, -z+1; Hydrogen atoms, counterion and solvent molecules have been omitted for clarity).



**Fig. S4**. Molecular structure of the cation  $[Na_2\{Mn_3^{III}(\mu_3 - O^{2-})\}_2 Dy^{III}(hmmp)_6$  $(O_2CPh)_4(N_3)_2]^+$  in complex **4** (symmetry operation A: -x, -y, -z+1; Hydrogen atoms, counterion and solvent molecules have been omitted for clarity).



**Fig. S5**. Temperature dependence of the in-phase  $(\chi_M')$  and the out-of-phase  $(\chi_M'')$  ac susceptibility components for **2** in a 3.5 G field oscillating at the indicated frequencies.



**Fig. S6**. Temperature dependence of the in-phase  $(\chi_M')$  and the out-of-phase  $(\chi_M'')$  ac susceptibility components for **3** in a 3.5 G field oscillating at the indicated frequencies.



**Fig. S7**. Temperature dependence of the in-phase  $(\chi_M')$  and the out-of-phase  $(\chi_M'')$  ac susceptibility components for **4** in a 3.5 G field oscillating at the indicated frequencies.