Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

- Synthesis of **5**
- Synthesis of **6** and other Ln analogues
- Table of ligand:metal ion ratios leading to different cluster topologies
- Figure showing the capping behaviour and preservation upon moving from **3** and **4** to **5** and **6** respectively.
- Animations to clearly show the topologies in **5** and **6** (attached in SI as separate files)
- Figures relating to extended structures of **5** and **6**
- Figure of variable-temperature-and-variable-field (VTVB) magnetisation data for **5** and **6**

Synthesis of $[Mn_6^{III}Mn_4^{II}(L1\text{-}8H)_2(\mu_3\text{–}O)_2(\mu_3\text{–}OH)_2(\mu\text{–}CH_3O)_4(H_2O)_4(dmf)_8](dmf)_4$, 5: L_1 (175 mg, 0.135 mmol) and $MnCl_2{\cdot}4H_2O$ (214 mg, 1.08 mmol) were suspended in a 1:1 DMF/MeOH mixture (20 mL) and stirred for 10 minutes. Following this Et_3N (0.2 mL, XS) was added and the resulting purple solution was stirred for additional 2 hours before being filtered. The mother liquor was allowed to slowly evaporate, affording single crystals suitable for *X*-ray diffraction studies. Yield: 140 mg (24 %). Elemental Analysis (%) calculated for **18**, $C_{216}H_{310}Mn_{10}N_{12}O_{40}$: C, 60.84%; H, 7.33%; N, 3.94%. Found: C, 60.68%; H, 7.26%; N, 3.77%.

Synthesis of $[Mn^{III}_6Mn^{II}_2Gd^{III}_2(L_1\text{–}8H)_2(\mu_4\text{–}O)_2(\mu_3\text{–}OH)_2(\mu\text{–}OCH_3)_2(\mu\text{–}OH)_2(MeOH)_4(dmf)_8](NO_3)_2(H_2O)_2$, 6: L_1 (50 mg, 0.039 mmol), $Mn(NO_3)_2{\cdot}6H_2O$ (60 mg, 0.234 mmol), $Gd(NO_3)_3{\cdot}6H_2O$ (35 mg, 0.078 mmol) were suspended in a 1:1 DMF/MeOH mixture (20 mL) and stirred for 10 minutes. Following this Et_3N (0.05 mL, XS) was added and the resulting purple solution stirred for additional 2 hours before being filtered. The mother liquor was exposed to vapour diffusion with diethyl ether in a closed vessel, resulting in the growth of dark purple crystals suitable for *X*-ray diffraction studies. Yield**:** 34 mg (20 %). Elemental Analysis (%) calculated for (**6Gd**), $C_{206}H_{280}Mn_8Gd_2N_{10}O_{44}$: C, 56.82%; H, 6.48%; N, 3.22%. Found: C, 56.59%; H, 6.21%; N, 2.98%. **$Mn^{III}_6Mn^{II}_2Dy^{III}_2$:** BisTBC[4] (50 mg, 0.039 mmol) and $Mn(NO_3)_2{\cdot}xH_2O$ (41.4 mg, 0.234 mmol), $Dy(NO_3)_3{\cdot}5H_2O$ (33.8 mg, 0.078 mmol) were suspended in a 1:1 DMF/MeOH mixture (20 mL) and stirred for 10 minutes. Et_3N (0.05 mL) was added and the resulting purple solution was stirred for additional 2 h and filtered. Yield**:** 23 mg (13 %). Elemental Analysis (%) calculated for **6Dy**, $C_{206}H_{280}Mn_8Dy_2N_{10}O_{44}$: C, 56.68%; H, 6.46%; N, 3.21%. Found: C, 56.41%; H, 6.22%; N, 2.96%. **$Mn^{III}_6Mn^{II}_2Tb^{III}_2$:** BisTBC[4] (50 mg, 0.039 mmol) and $Mn(NO_3)_2{\cdot}$(41.4 mg, 0.234 mmol), $Tb(NO_3)_3{\cdot}6H_2O$ (35 mg, 0.078 mmol) were suspended in a 1:1 DMF/MeOH mixture (20 mL) and stirred for 10 minutes. Et_3N (0.05 mL) was added and the resulting purple solution was stirred for additional 2 h and filtered. Yield: 40 mg (24 %). Elemental Analysis (%) calculated for **6Tb**, $C_{206}H_{280}Mn_8Tb_2N_{10}O_{44}$: C, 56.77%; H, 6.48%; N, 3.21%. Found: C, 56.52%; H, 6.33%; N, 3.01%.

Cluster	Compound	Ligand Ratio	Mn^{2+} ratio	Gd^{3+} ratio	Crystallisation
$[Mn_8]$	**3**	1	2	-	MeCN diffusion
$[Mn_6Gd_2]$	**4**	1	2	1	Et_2O diffusion
$[Mn_{10}]$	**5**	1	8	-	DMF/MeOH
$[Mn_8Gd_2]$	**6**	1	6	2	Et_2O diffusion

Table S1. ligand:metal ion ratios in reactions that result in different cluster topologies

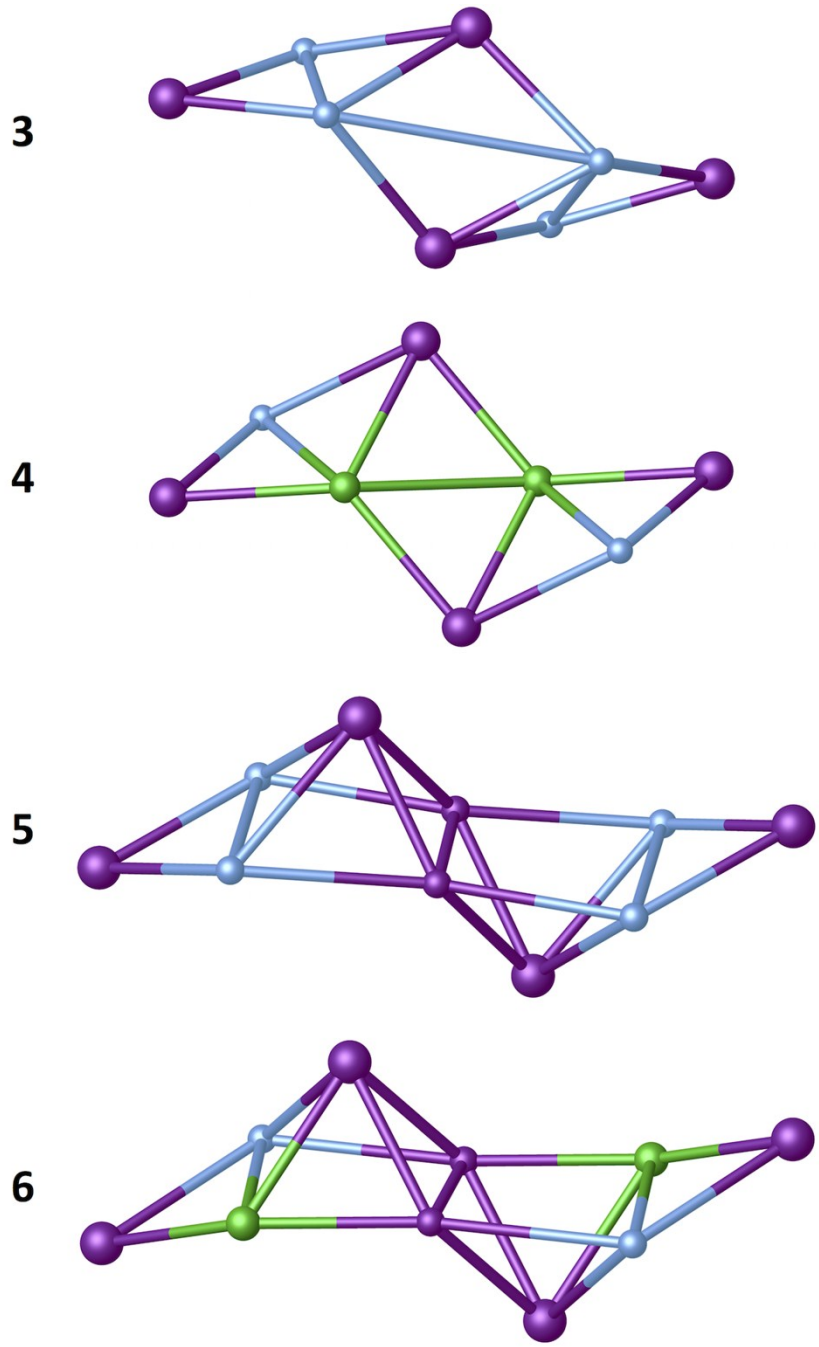

Figure S1. Cluster topologies in **3** – **6** with capping by bis-[C[4]Mn^{III}]$^{-}$ moieties shown as large purple spheres. **5** and **6** represent 'expansion' of **3** and **4** respectively through the introduction of two central Mn^{III} ions in both cases. Colour code Mn^{II} – pale blue, Mn^{III} – purple, Ln^{III} – green. Note: Animations showing the cluster topologies for 5 and 6 are also included in Supporting Information as separate files.

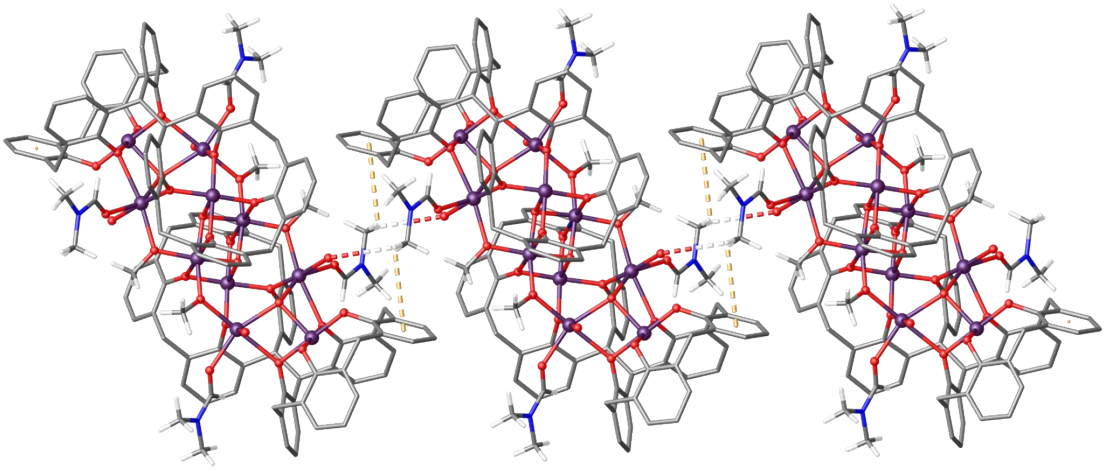

Figure S3. Extended structure of **5** showing complementary H-bonding interactions between neighbouring clusters. The ^{t}Bu groups of L1s, as well as co-crystallised and some ligated solvent are omitted for clarity.

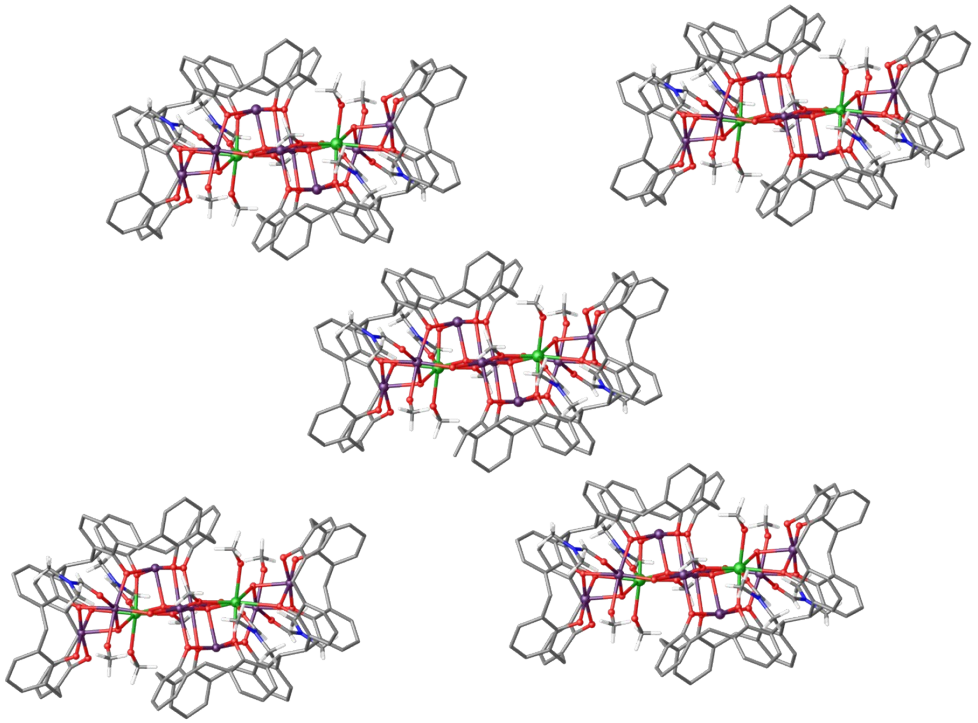

Figure S2. Extended structure of **6** showing large separation between individual clusters. The ^{t}Bu groups of L1s, as well as both ligated and co-crystallised solvent are omitted for clarity.

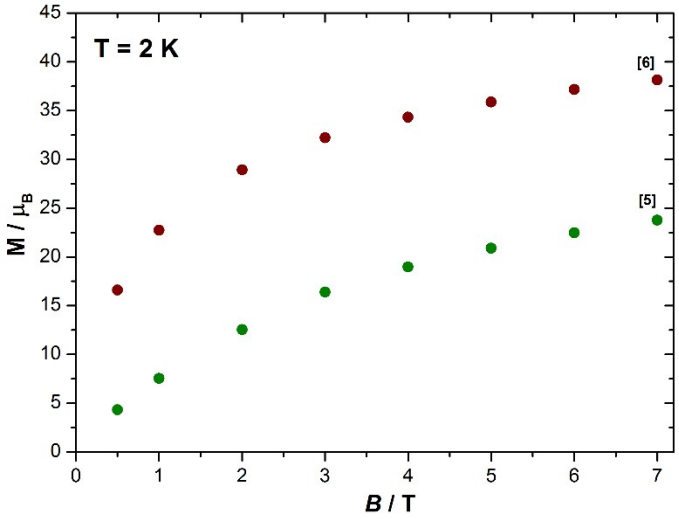

Figure S4. Variable-temperature-and-variable-field (VTVB) magnetisation data of **5** – **6** at T = 2 K and B = 0-7 T.