

Supporting Information

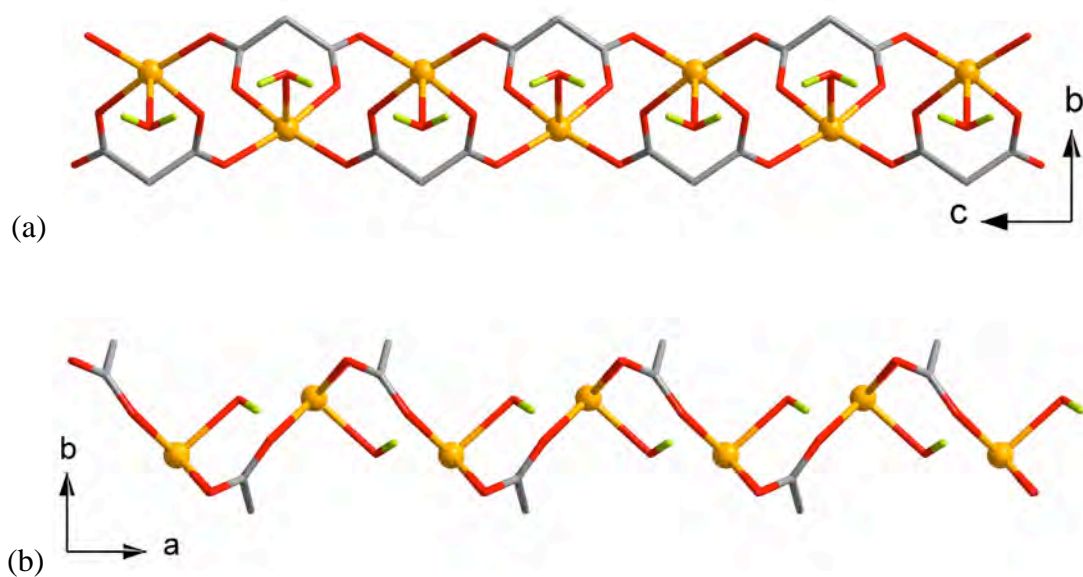


Figure S1. A view of the Rmal-Mn(II) layers in **1-4**, along the crystallographic *a* (a) and *c* axes (b).

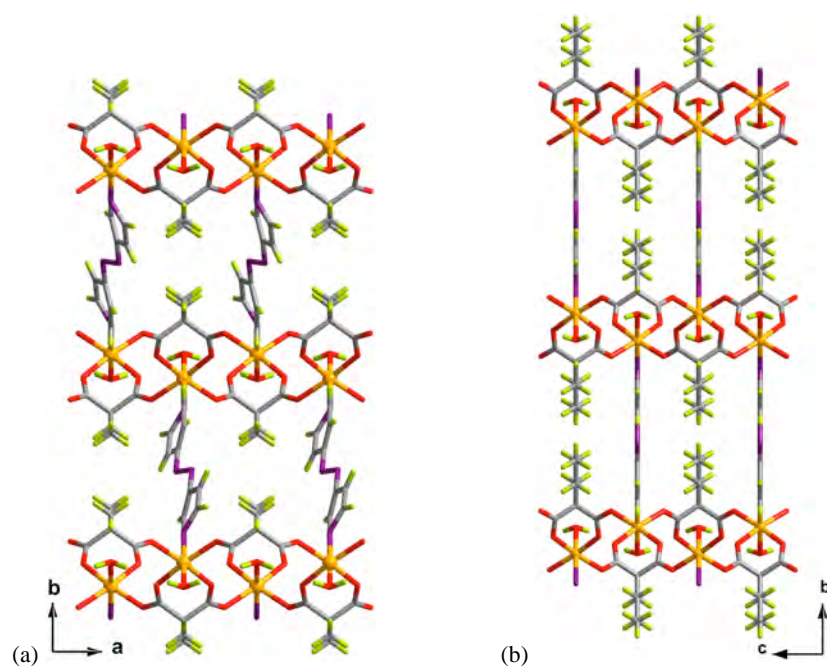


Figure S2. Perspective views of the crystal packing of **2** (a) and **3** (b) along the crystallographic *c* (2) and *a* axes (3).

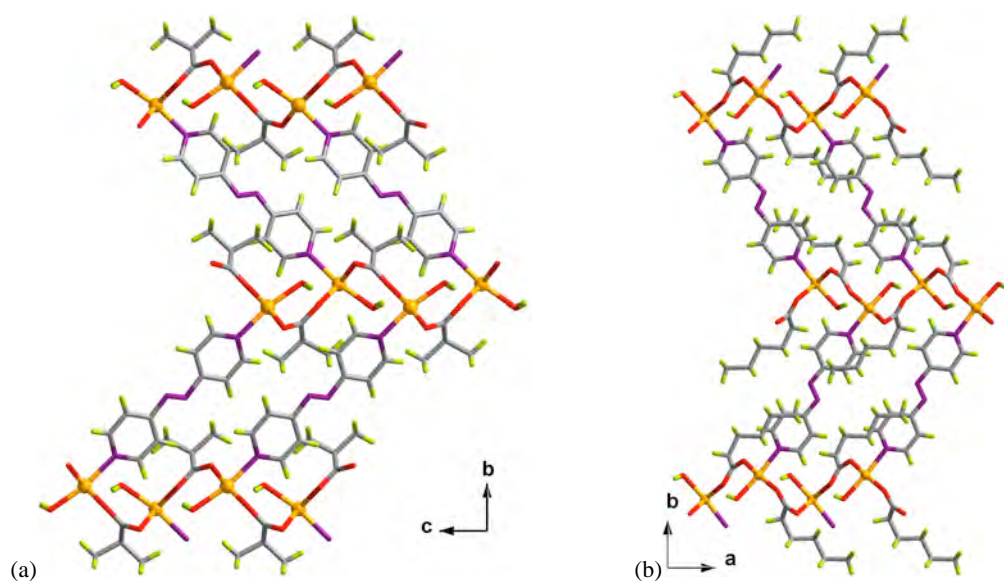


Figure S3. A view of the 3D structure of the compounds **2** (a) and **3** (b) along the crystallographic *a* (**2**) and *c* axes (**3**) showing the corrugated layers of the carboxylate-bridged manganese(II) ions linked through the bis-monodentate azpy ligand.

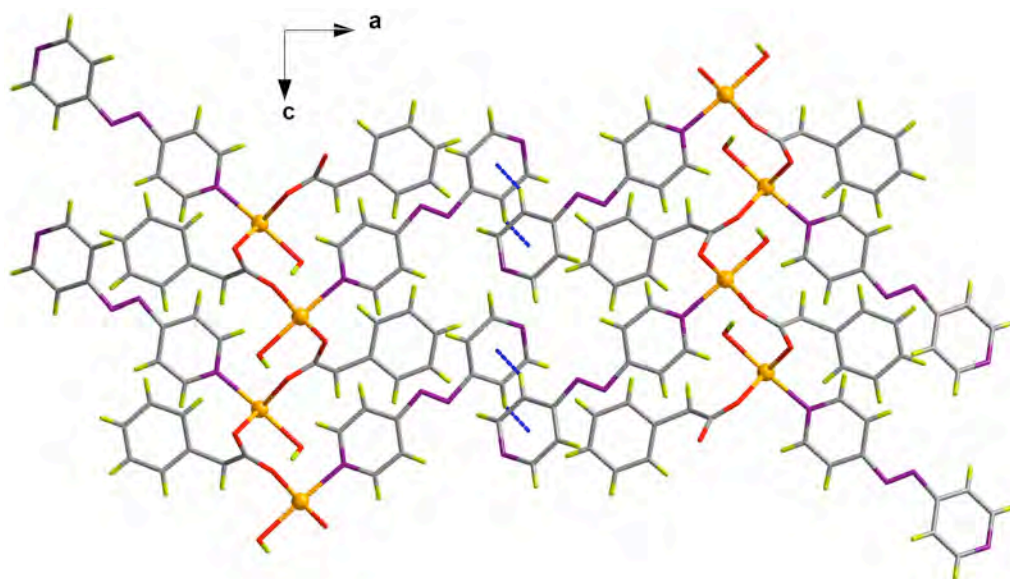


Figure S4. Views of the packing **4** along the crystallographic *b* axis showing the C-H $\cdots \pi$ type interactions (blue dashed lines).

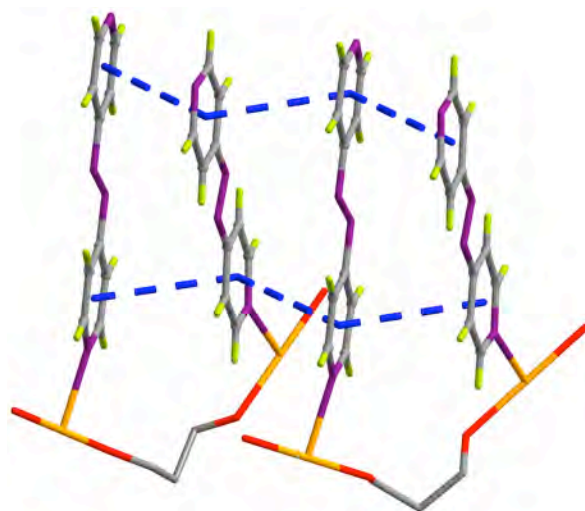


Figure S5. Detail of the π - π type interactions (blue dashed lines) present in **5**.

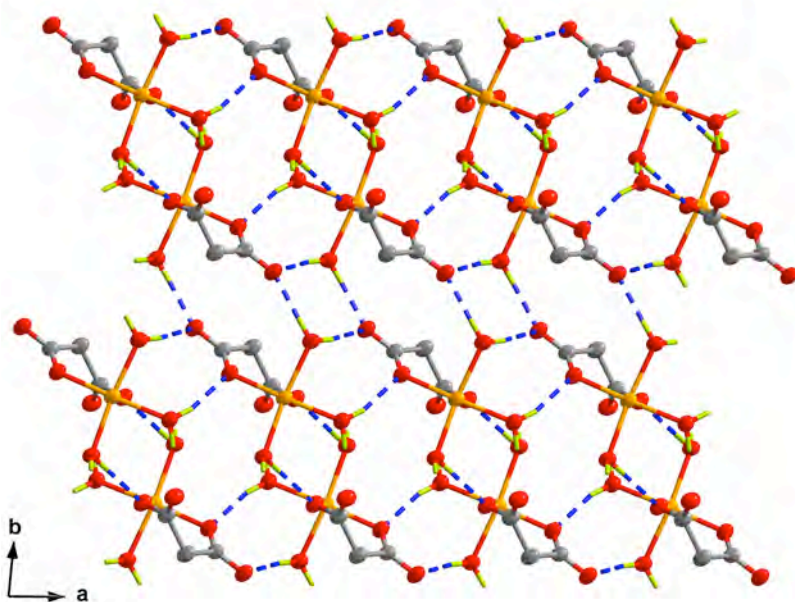


Figure S6. Perspective view of the plane build by the hydrogen bonds (blue and fragmented bonds), along the crystallographic c axis. The azpy and the benzyl groups have been removed for clarity.

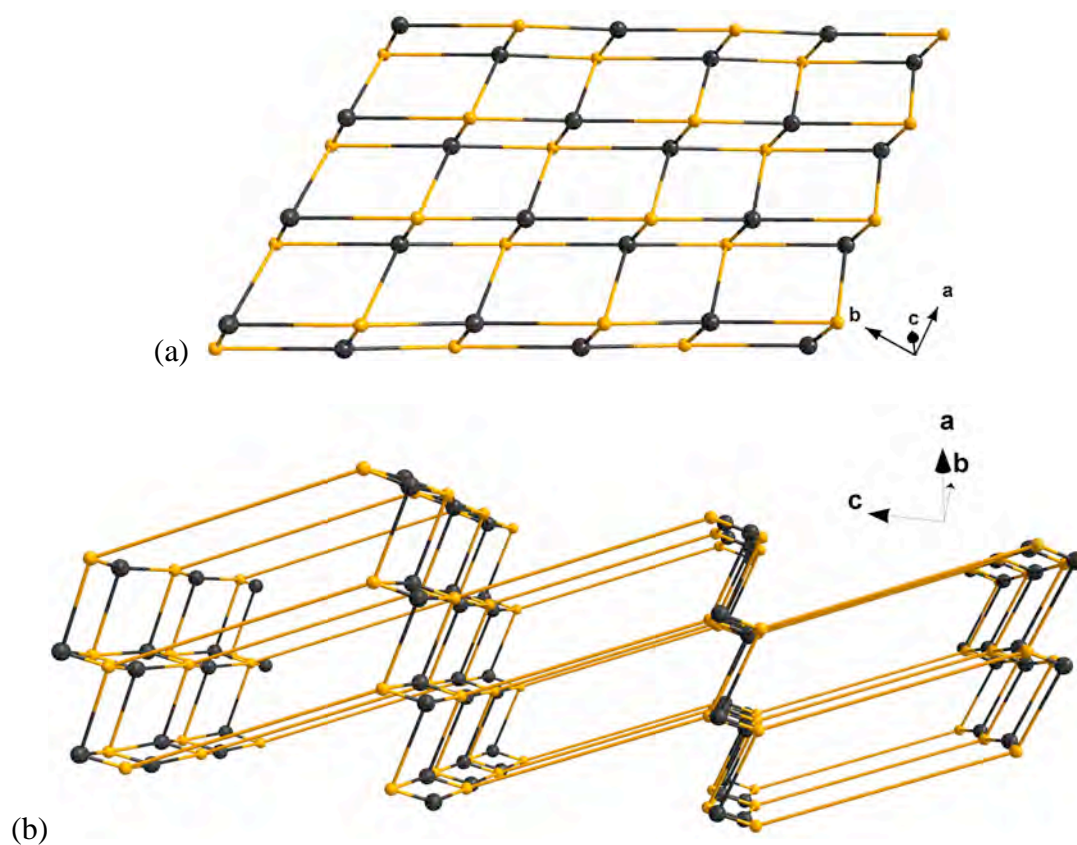


Figure S7. (a) Detail of the $[4^4.6^2]$ layer in **6** built through the hydrogen bonds [the black nodes represent the Rmal ligand and the yellow ones the Mn(II) atoms]. (b) Topological representation of the three-dimensional **tcs**-type topology in **6**. The yellow bonds correspond to the manganese-manganese bridges through the hydrogen bonds involving the azpy ligand, whereas the black and yellow ones correspond to the hydrogen bonds which links the aqua-manganese and the Rmal-Mn(II) units.

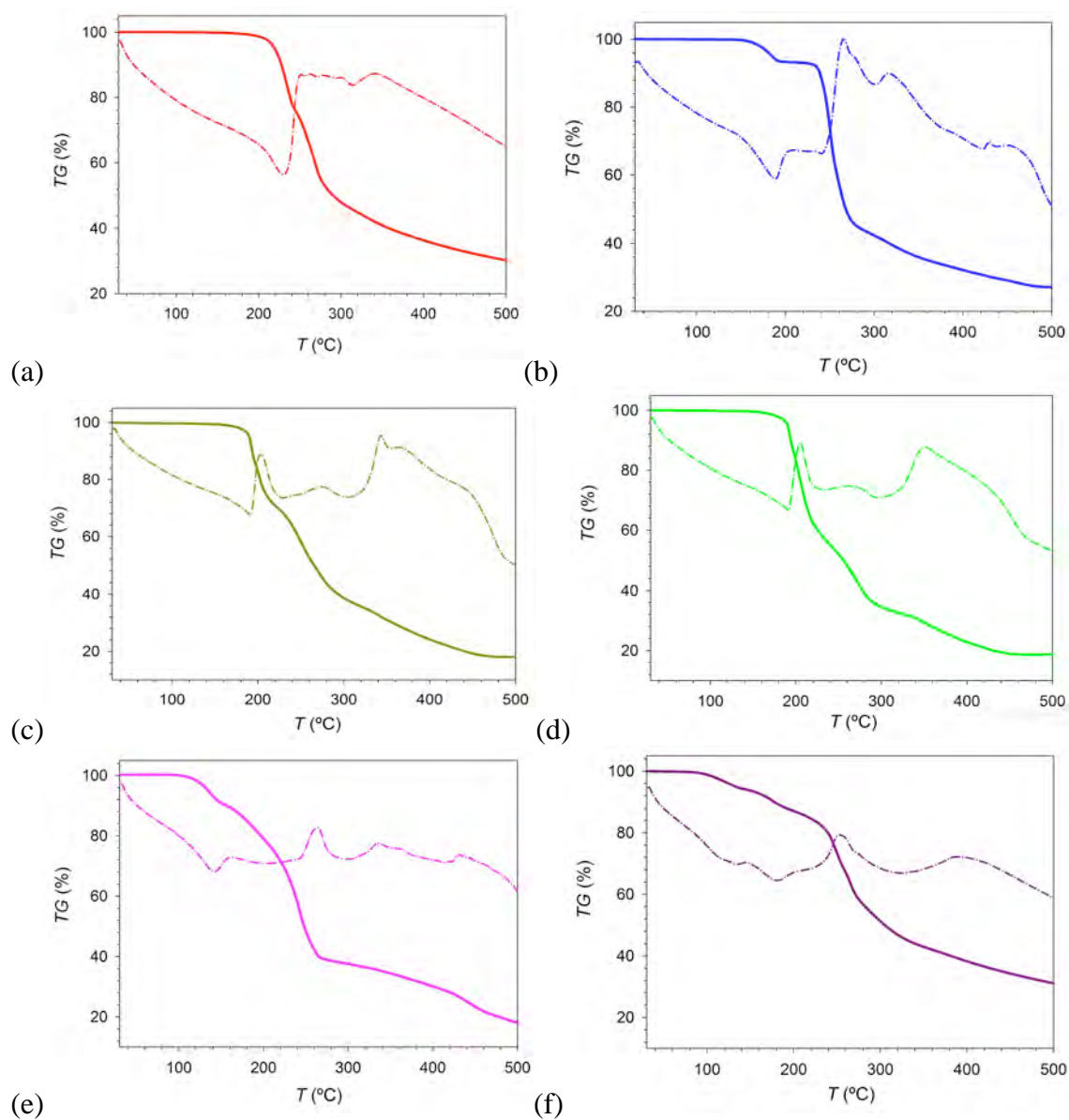


Figure S8. TG/DTG-DTA curves of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f). TG = mass loss (percent) and DTA = ΔT (μV) (\downarrow endo and \uparrow exo).

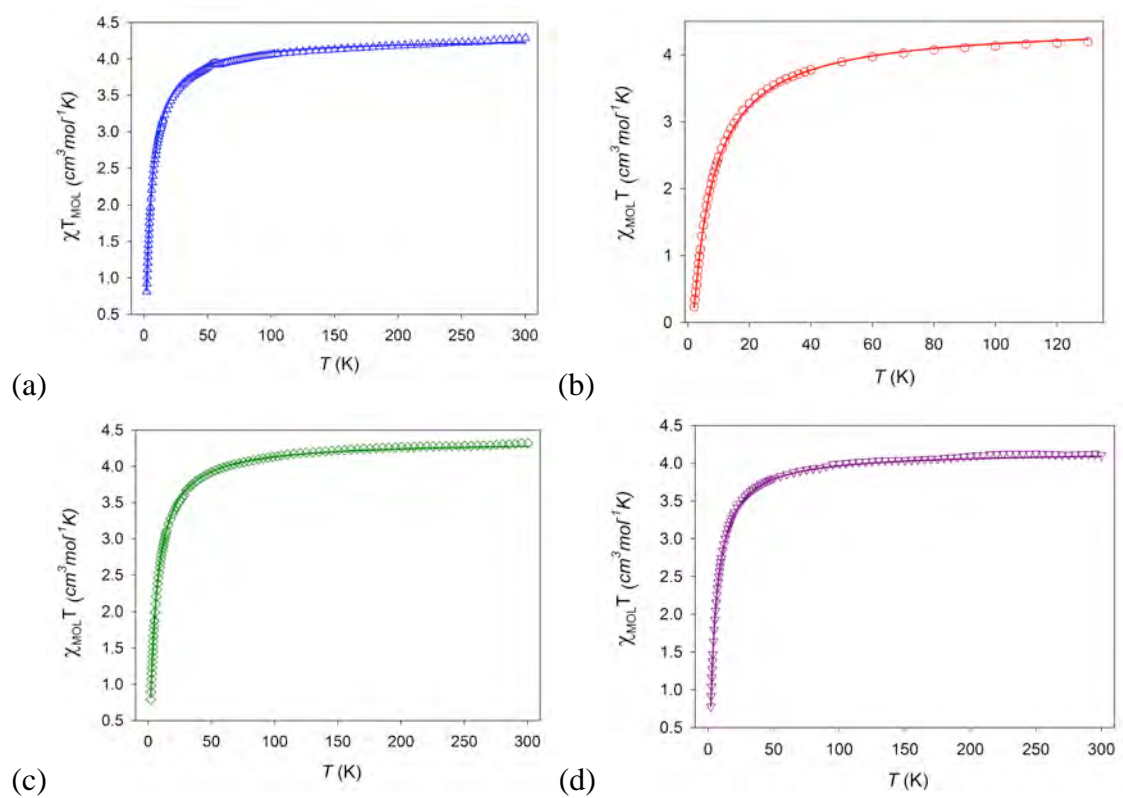


Figure S9. $\chi_M T$ vs. T plots for complexes **1** (a), **2** (b), **3** (c) and **4** (d). The solid line is the best-fit.

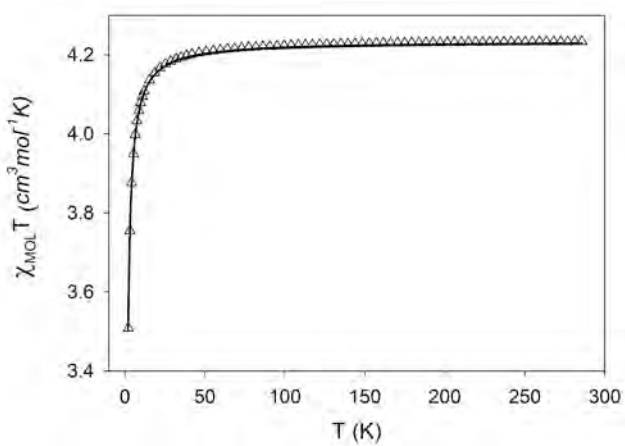


Figure S10. $\chi_M T$ vs. T plot for **5**. The solid line is the best-fit.