Supplementary Materials

Structure−function correlations in mononuclear manganese(III) spin crossover system with big conjugated hexadentate Schiff-base ligands

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Table S1. Hydrogen bond distances and parameters for the complexes of **1-4** (Å,°)

1-SbF_6									
100K					295K				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N3-H19…F5[iv]	0.87(3)	2.20(3)	2.969(3)	145.8(3)	N2-H14…F2[iv]	0.83(5)	2.33(4)	3.03(6)	143.6(4)
2-AsF_6									
100K					**295K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N3-H19…F11[i]	1	2.14	3.01(4)	144.5	N2-H14…F1[iii]	0.75(4)	2.37(4)	3.06(4)	154 (4)
N7-H51…F2 [ii]	0.79(4)	2.35(4)	3.06(4)	150.5(4)					
N11-H83…F14	0.81(4)	2.23(4)	2.90(4)	139.9(4)					
3-PF_6·1/2CH_3OH									
100K					**295K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H14…F6	1(3)	2.26(4)	3.12(3)	143.2(3)	N2-H2…F6viii	0.98(3)	2.30(3)	3.16(3)	145.6(3)
N2-H14…F4	1(3)	2.62(3)	3.31(3)	126.7	N2-H2…F4	0.98(3)	2.64(3)	3.34(3)	128.9(3)
4-ClO_4									
100K					**273K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H2…O2[v]	0.93	2.46	3.067(3)	123	N2-H2…O3[vi]	0.91	2.54	3.170(6)	127

Symmetry codes:(i)-1+x,y,-1+z; (ii) x,y,1+z; (iii)1+x, y, z; (iv)-1+x, y, z; (v)3/2-x,1/2+y,-z; (vi)1/2+x,3/2-y,-z;

Table S2. The variations of octahedral distortion parameters (°) for complexes **1-4**

°	**1-SbF_6** **295 K→ 100 K**	**2-AsF_6** **295 K→ 100 K**	**3-PF_6·1/2CH_3OH** **295 K→ 100 K**	**4-ClO_4** **273 K→ 100 K**
$\Delta\Sigma$[a]	26.64	22.24 27.92 26.61	0.46	7.51
$\Delta\Theta$[a]	38.7	35.7 15.1 38.2	-1.4	15.28

[a] for complex **1,** $\Delta\Sigma = \Sigma_{HS}-\Sigma_{LS}$, $\Delta\Theta = \Theta_{HS}-\Theta_{LS}$

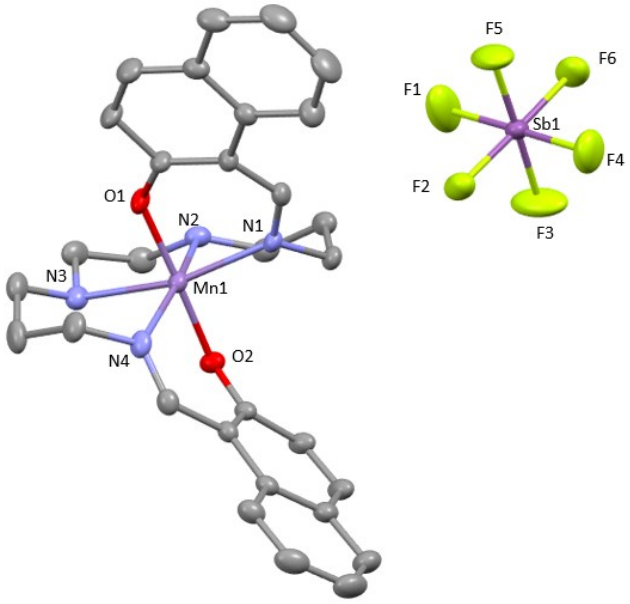

Figure S1. The molecular structure for complex **1** at 100 K, hydrogen atoms have been omitted for clarity.

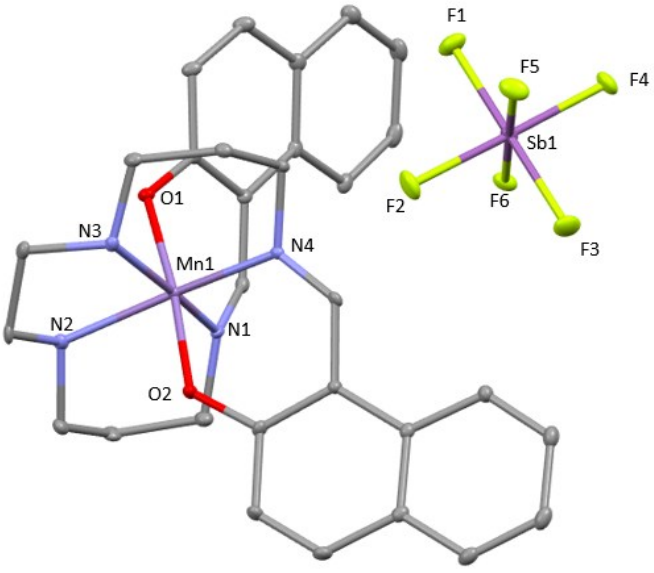

Figure S2. The molecular structure for complex **1** at 295 K, hydrogen atoms have been omitted for clarity.

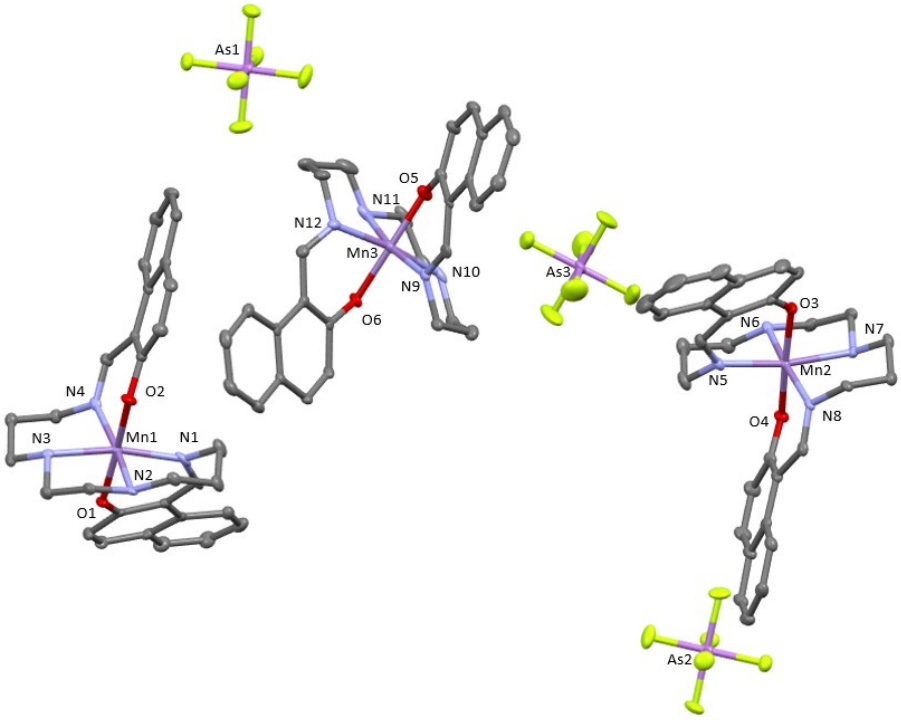

Figure S3. The molecular structure for complex **2** at 100 K, hydrogen atoms have been omitted for clarity.

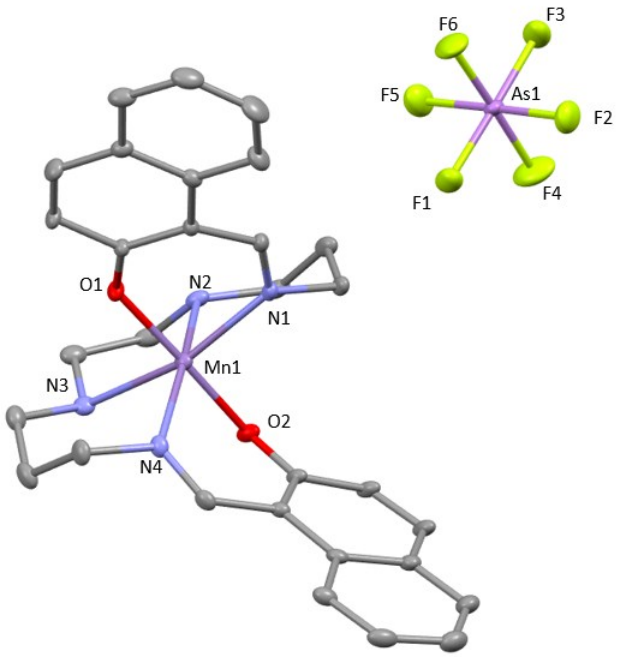

Figure S4. The molecular structure for complex **2** at 295 K, hydrogen atoms have been omitted for clarity.

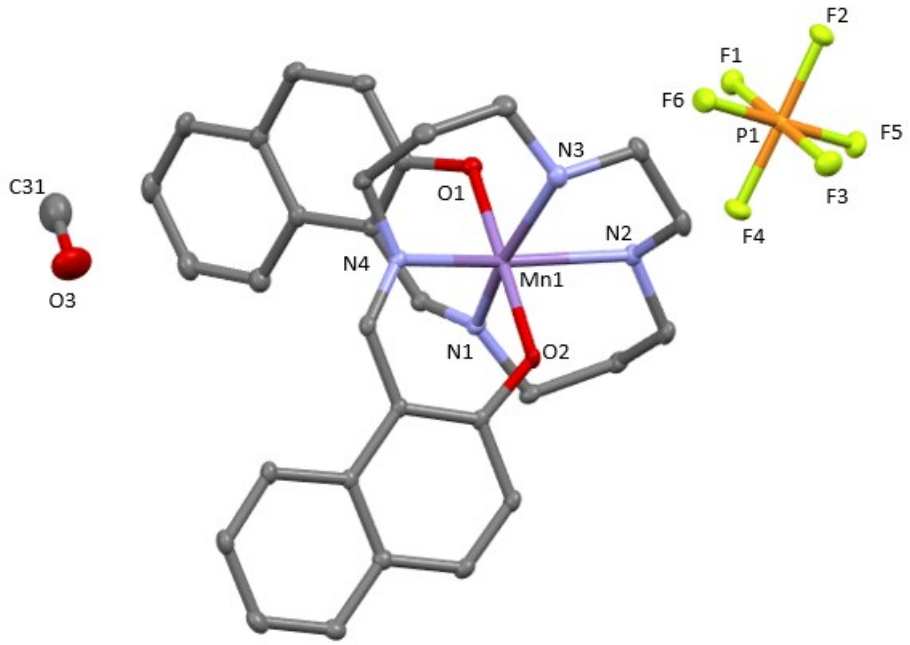

Figure S5. The molecular structure for complex **3** at 100 K, hydrogen atoms have been omitted for clarity.

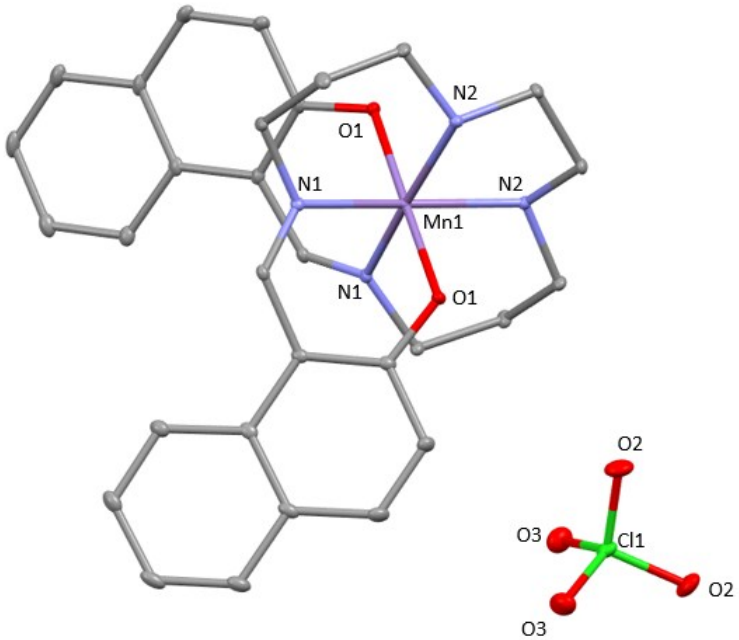

Figure S6. The molecular structure for complex **4** at 100 K, hydrogen atoms have been omitted for clarity.

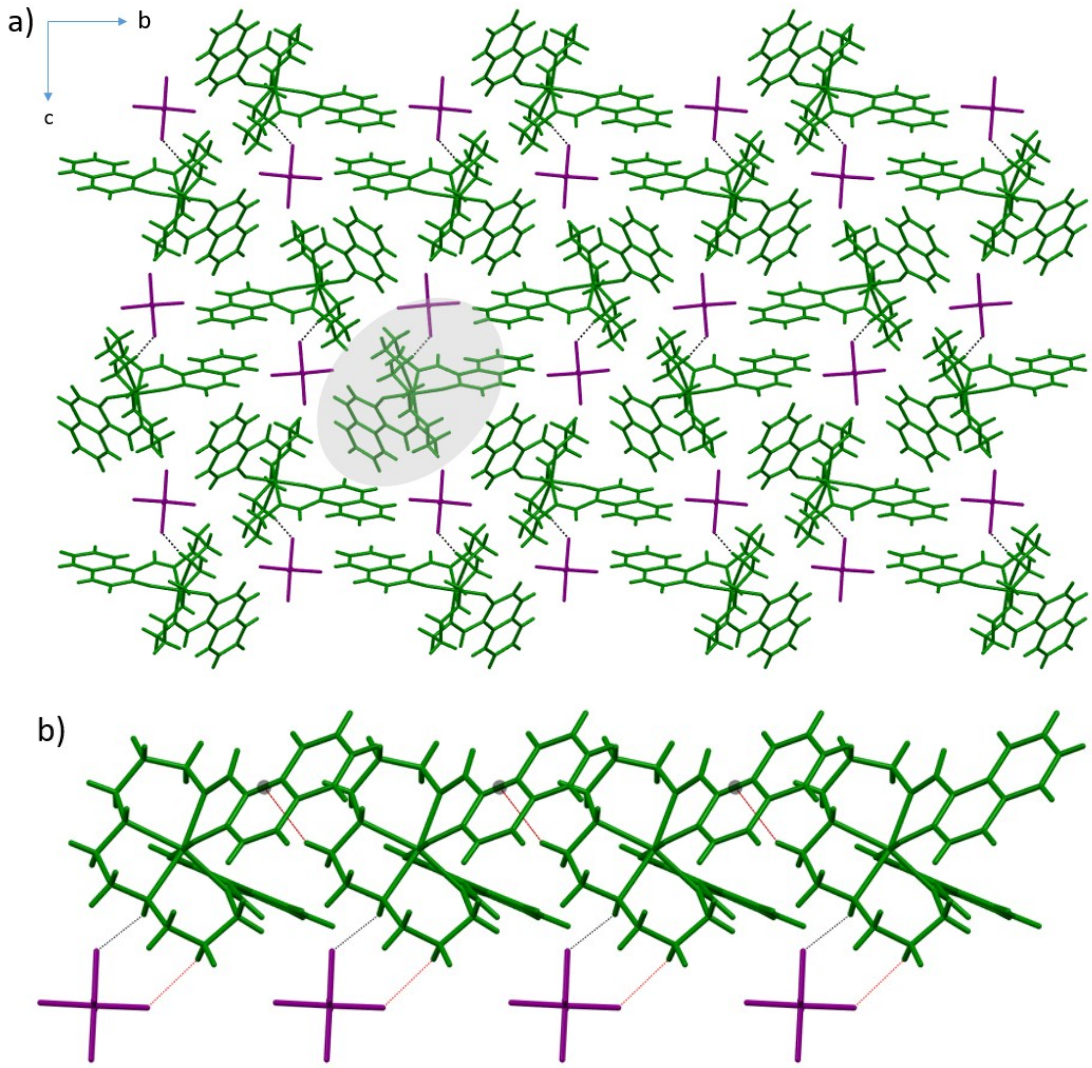

Figure S7. (a) Crystal packing of complex **1** at 295 K, viewed along the *a* axis, showing the N–H···F hydrogen bonds between the $[Mn(naphth\text{-}sal\text{-}N\text{-}1,5,8,12)]^+$ cations and SbF_6^- anions. The chain is shown in the light grey background. (b) The chain viewed along the *c* axis. The N–H···F hydrogen bonds are indicated by black dotted lines. The C–H···π and C–H···F hydrogen bonds are indicated by red dotted lines.

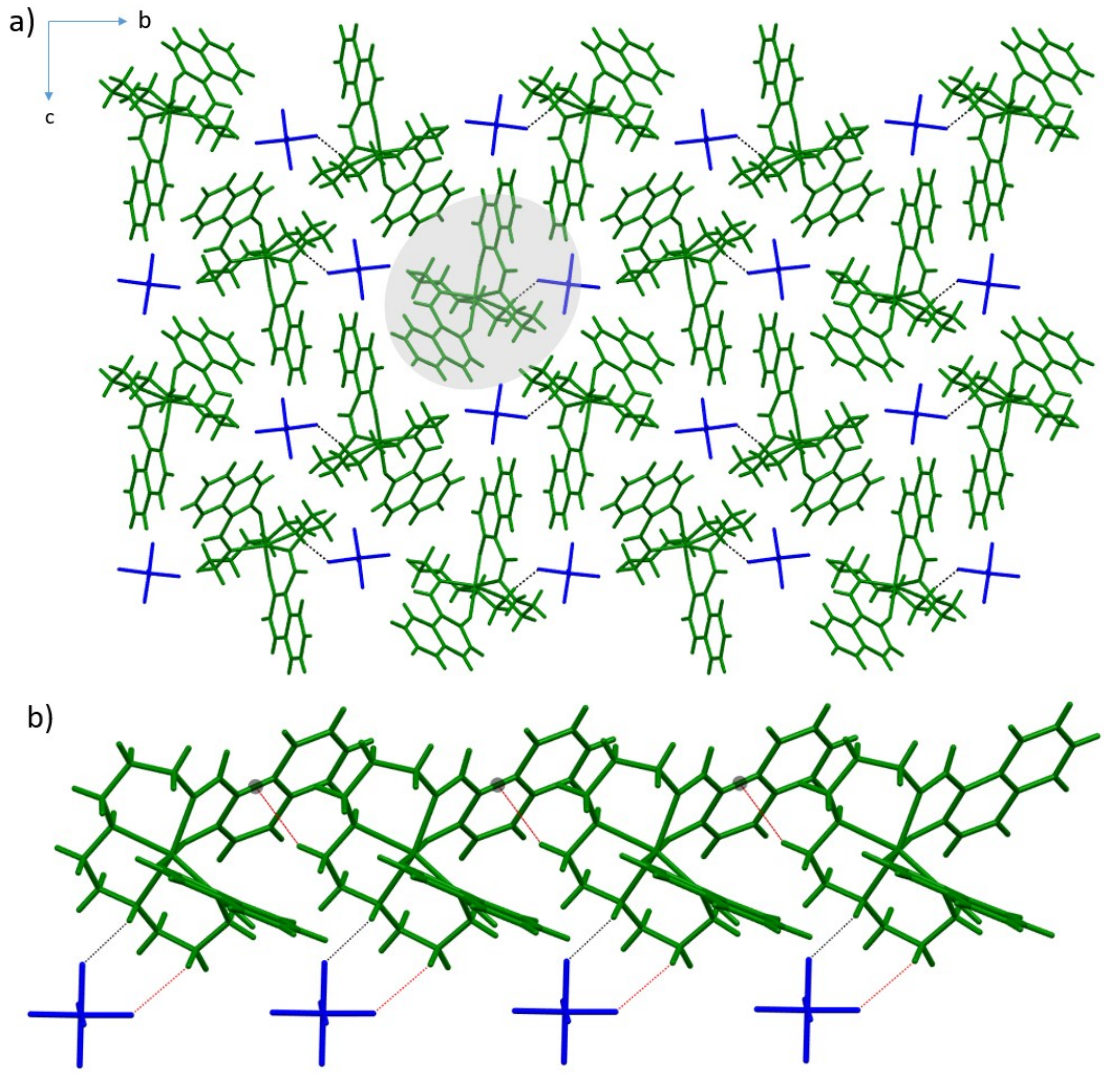

Figure S8. (a) Crystal packing of complex **2** at 295 K, viewed along the *a* axis, showing the N–H···F hydrogen bonds between the $[Mn(naphth\text{-}sal\text{-}N\text{-}1,5,8,12)]^+$ cations and AsF_6^- anions. The chain is shown in the light grey background. (b) The chain viewed along the *c* axis. The N–H···F hydrogen bonds are indicated by black dotted lines. The C–H···π and C–H···F hydrogen bonds are indicated by red dotted lines.

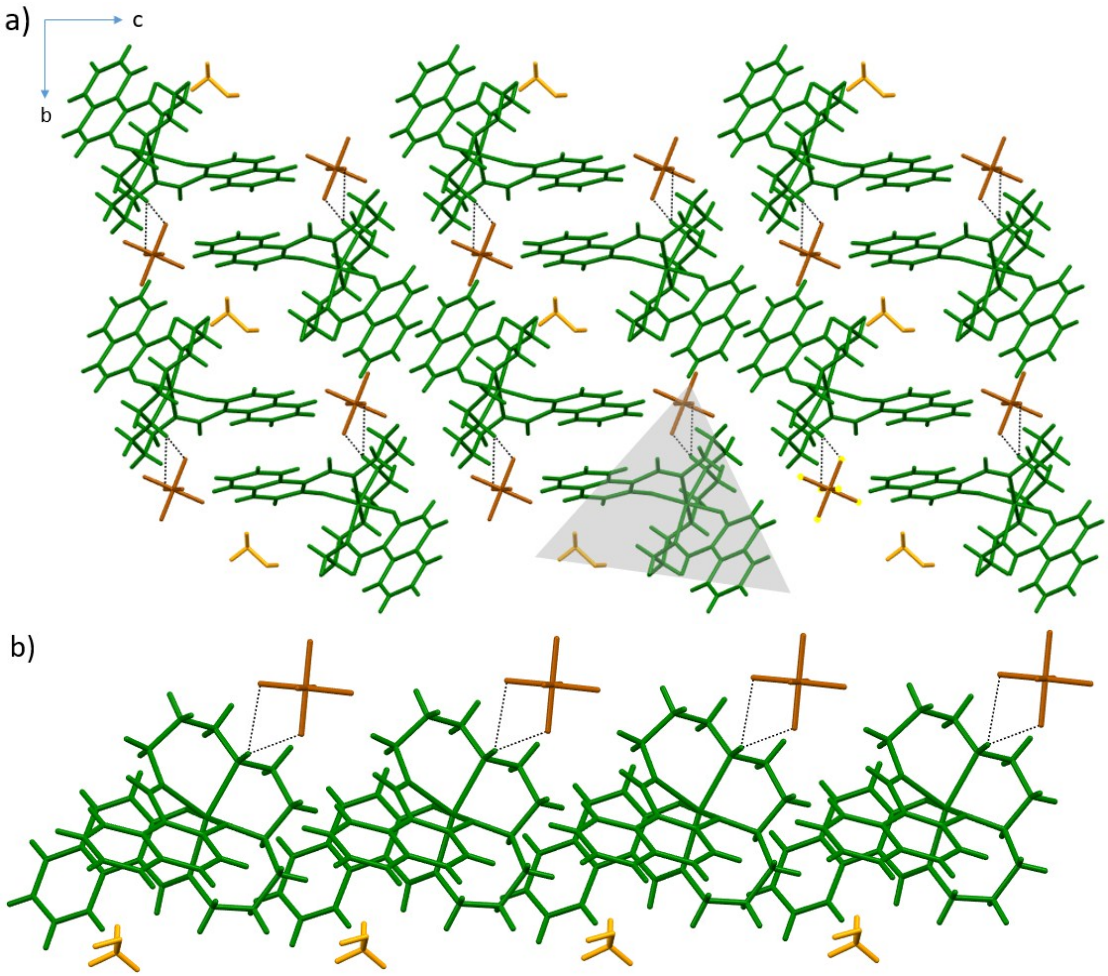

Figure S9. (a) Crystal packing of complex **3** at 295 K, viewed along the *a* axis, showing the N–H···F hydrogen bonds between the $[Mn(naphth\text{-}sal\text{-}N\text{-}1,5,8,12)]^+$ cations and PF_6^- anions. The chain is shown in the light grey triangular background. (b) The chain viewed along the *c* axis.

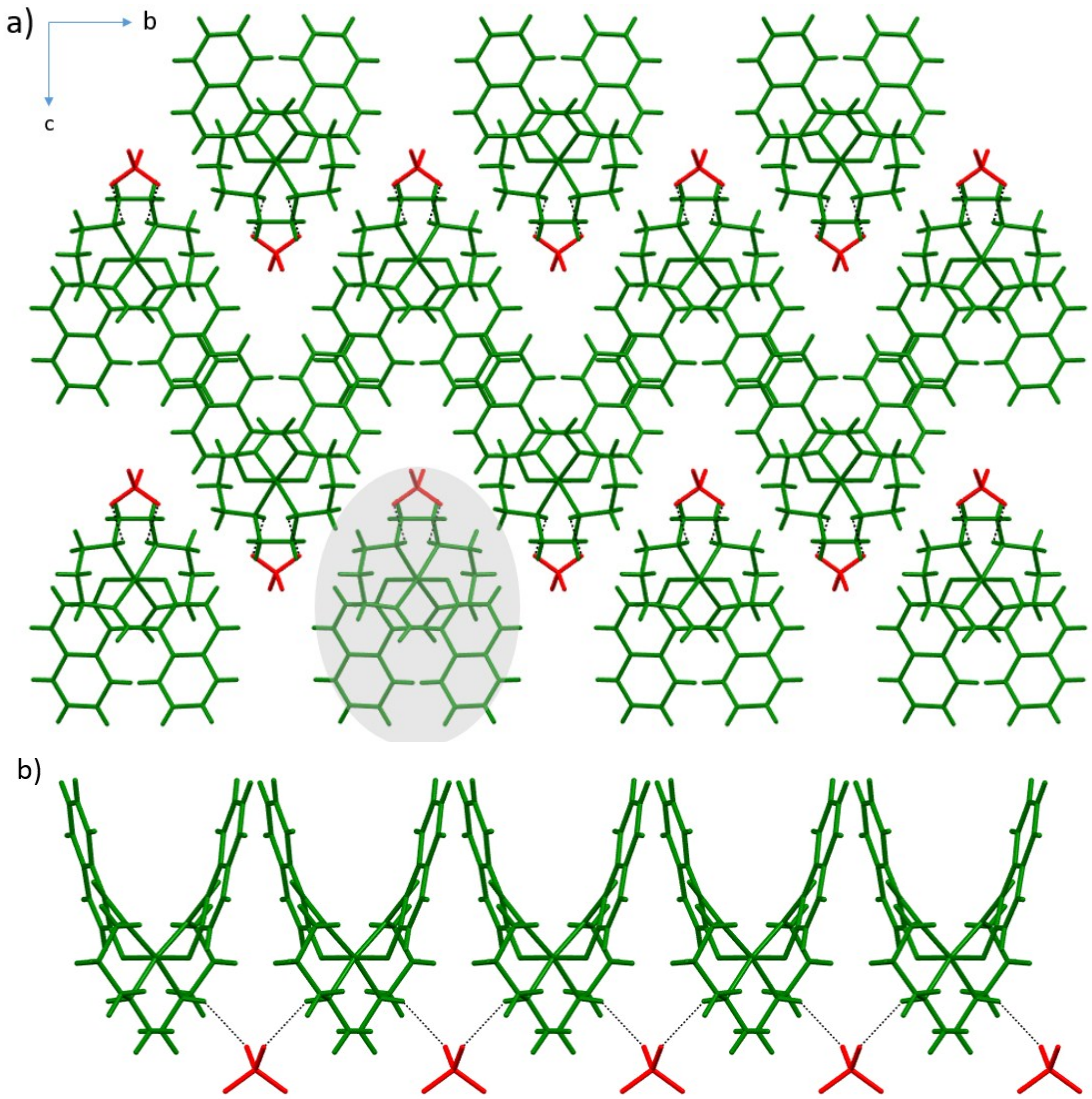

Figure S10. (a) Crystal packing of complex **4** at 273 K, viewed along the *a* axis, showing the N–H···O hydrogen bonds between the $[Mn(naphth\text{-}sal\text{-}N\text{-}1,5,8,12)]^+$ cations and ClO_4^- anions. The chain is shown in the light grey background. (b) The chain viewed along the *c* axis.

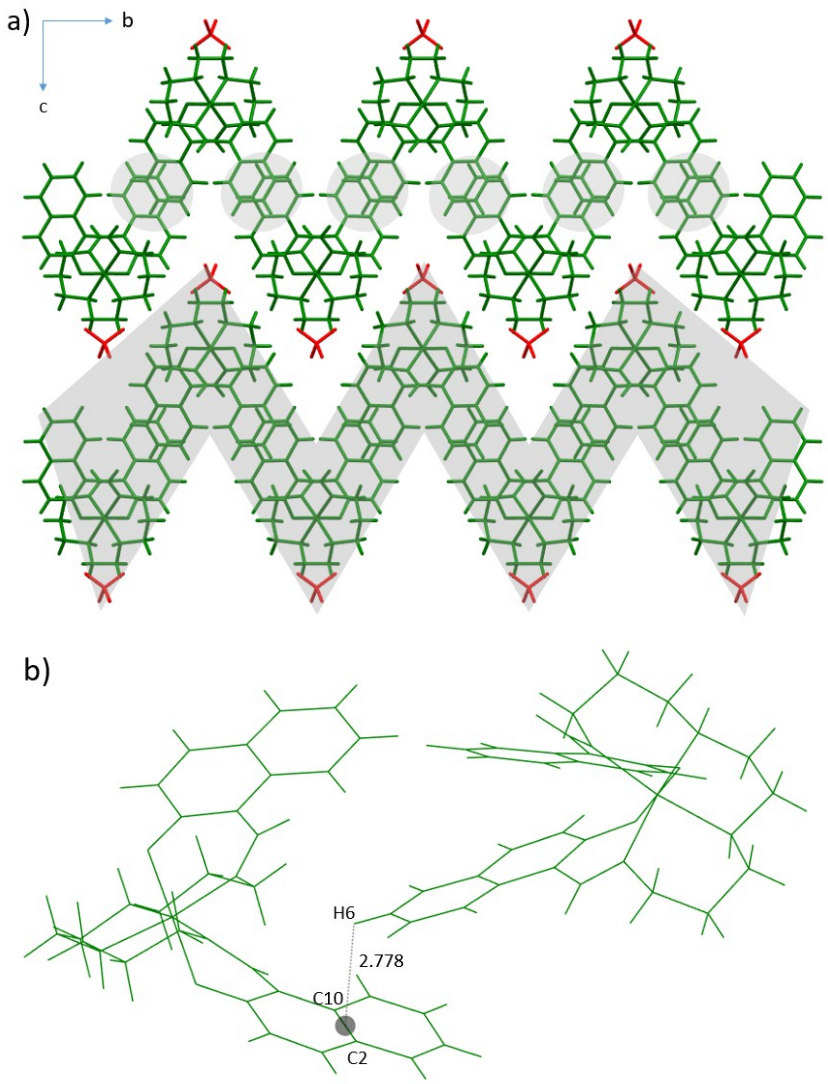

Figure S11. (a) Crystal packing of complex **4** at 100 K. The C-H···π contacts between naphthalene groups from the ligands of the neighboring cation is shown in the light grey elliptical background. (b) The detail of C-H···π contacts between naphthalene groups.

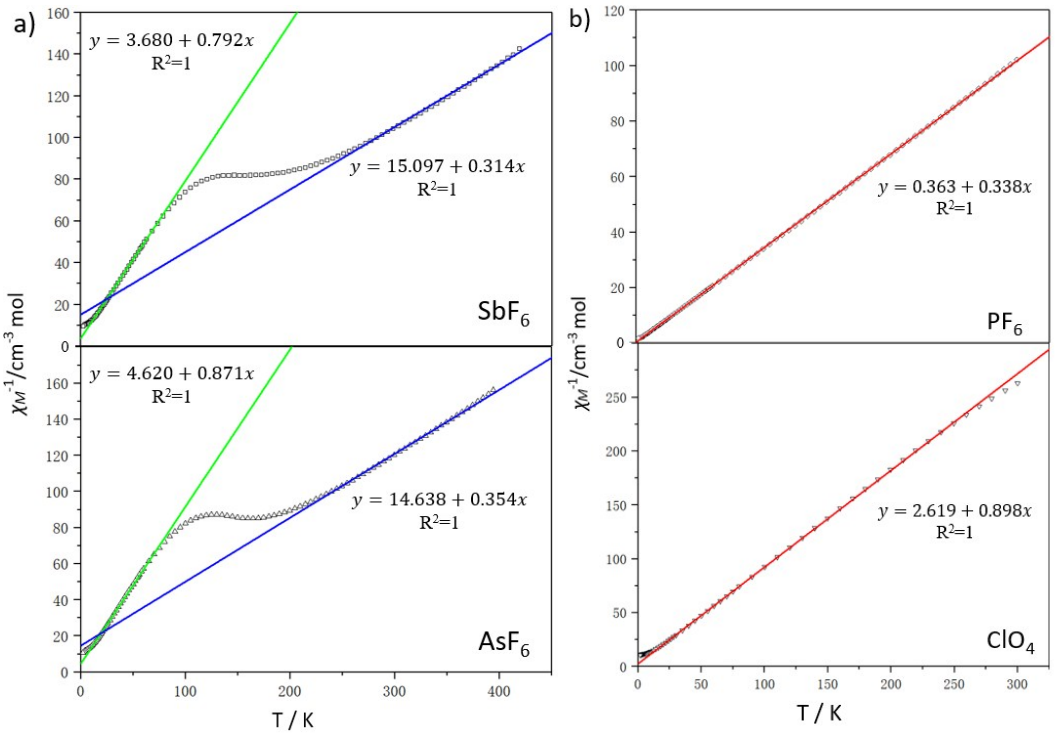

Figure S12. Temperature dependence of the χ_M^{-1} for [Mn(naphth-sal-N-1,5,8,12)]SbF_6 (**1**), [Mn(naphth-sal-N-1,5,8,12)]AsF_6. (**2**), [Mn(naphth-sal-N-1,5,8,12)]PF_6 (**3**) and [Mn(naphth-sal-N-1,5,8,12)]ClO_4 (**4**). (a): The solid line represents the best fit to the Curie–Weiss law from 17 to 80 K and 260 to 400 K for **1** and from 20 to 90 K and 240 to 400 K for **2**. (b): The solid line represents the best fit to the Curie–Weiss law from 20 to 300 K for **3** and from 20 to 250 K for **4**.

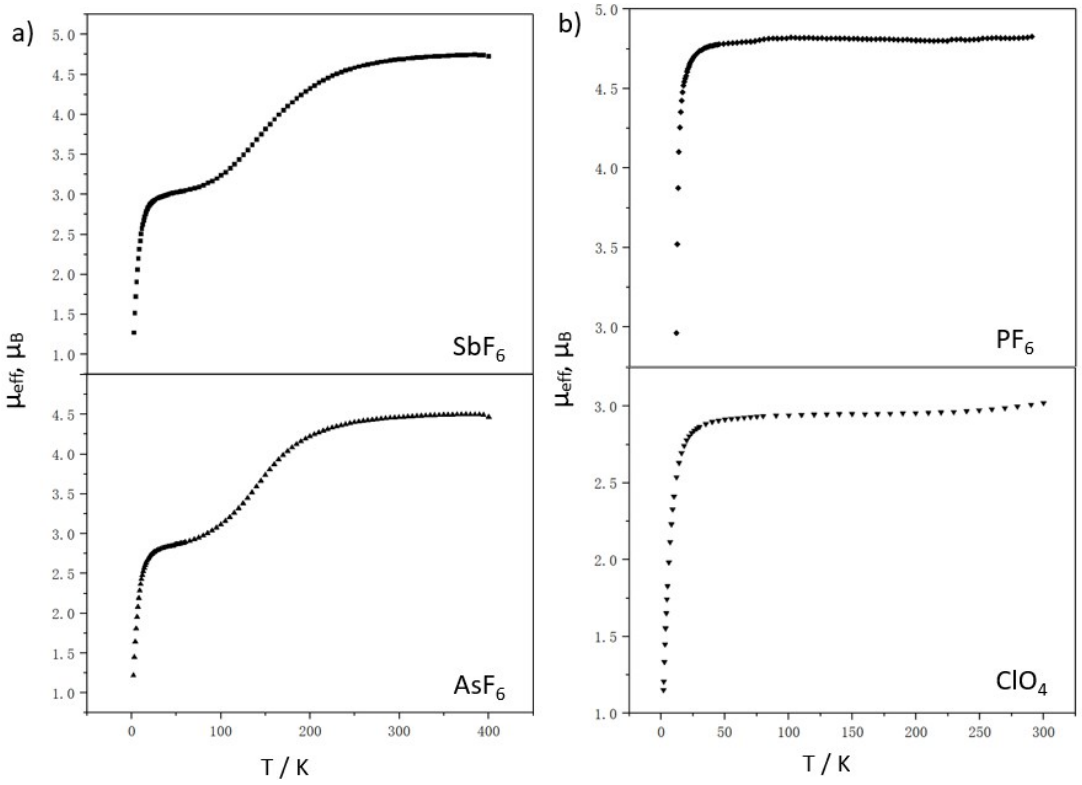

Figure S13. (a) Temperature dependence of the μ_{eff} for [Mn(naphth-sal-N-1,5,8,12)]SbF_6 (**1**) and [Mn(naphth-sal-N-1,5,8,12)]AsF_6 (**2**) between 2–400 K. (b) Temperature dependence of the μ_{eff} for [Mn(naphth-sal-N-1,5,8,12)]PF_6 (**3**) and [Mn(naphth-sal-N-1,5,8,12)]ClO_4 (**4**) between 2–300 K.