Supporting Information

The Dynamic Interplay between Intramolecular and Intermolecular Interactions in Mononuclear Manganese(Ⅲ) SCO Complexes

Chun-Yan Qin[a]• *Sheng-Ze Zhao*[a]• *Hua-Yu Wu*[a]• *Yong-Hua Li*[a]*• *Zi-Kun Wang*[a]• *Zheng Wang*[b]*• *Shi Wang*[a]*

[a] State Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.

[b] College of Chemistry and Chemical Engineering, Key Laboratory of Chemical Additives for China National Light Industry, Shaanxi University of Science and Technology, Xi'an 710021, China

Table S1. Crystallographic Data for **1**−**8**.

	PF_6		AsF_6		SbF_6		BF_4	
CCDC number	2023564	2323563	2023552	2023551	2023566	2023565	2023554	2023553
Empirical formula	$C_{22}H_{26}F_8MnN_4O_2P$	$C_{22}H_{26}F_8MnN_4O_2P$	$C_{22}H_{26}AsF_8MnN_4O_2$	$C_{22}H_{26}AsF_8MnN_4O_2$	$C_{22}H_{26}F_8MnN_4O_2Sb$	$C_{22}H_{26}F_8MnN_4O_2Sb$	$C_{22}H_{26}BF_6MnN_4O_2$	$C_{22}H_{26}BF_6MnN_4O_2$
Formula weight	616.38	616.38	660.33	660.33	707.16	707.17	558.22	558.22
Temperature/K	298(2)	100(2)	298(2)	100(2)	298(2)	100(2)	298.15	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2/n	P2/n	P2/n	P2/n	P2/n	P2/n	$P2_1/c$	$P2_1/c$
a/Å	11.530(4)	11.3518(16)	11.5522(11)	11.3909(12)	11.6715(9)	11.554(6)	9.7586(15)	9.5085(10)
b/Å	8.107(3)	8.0856(11)	8.1697(8)	8.1489(8)	8.2695(6)	8.271(4)	17.613(2)	17.3942(18)
c/Å	13.414(4)	13.2427(18)	13.4202(11)	13.2933(14)	13.5489(10)	13.523(6)	14.820(2)	14.6462(15)
α/°	90	90	90	90	90	90	90	90
β/°	94.156(9)	93.667(3)	94.453(2)	93.862(2)	94.836(2)	94.080(11)	106.582(3)	104.778(2)
γ/°	90	90	90	90	90	90	90	90

Volume/Å^3	1250.6(7)	1213.0(3)	1262.8(2)	1231.1(2)	1303.05(17)	1289.0(11)	2441.2(6)	2342.2(4)
Z	2	2	2	2	2	2	4	4
ρ_{calc}g/cm^3	1.637	1.688	1.737	1.781	1.802	1.822	1.519	1.583
μ/mm^{-1}	0.680	0.702	1.911	1.960	1.606	1.624	0.614	0.640
F(000)	628.0	628.0	664.0	664.0	700.0	700.0	1144.0	1144.0
Crystal size/mm^3	0.11 × 0.08 × 0.07	0.28 × 0.20 × 0.12	0.22 × 0.15 × 0.10	0.11 × 0.1 × 0.07	0.25 × 0.21 × 0.15	0.25 × 0.21 × 0.15	0.11 × 0.1 × 0.07	0.26 × 0.20 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.024 to 56.516	4.884 to 50.05	4.484 to 66.122	4.56 to 75.532	4.812 to 65.442	4.482 to 53.992	4.356 to 50.02	4.43 to 50.05
Index ranges	-10 ≤ h ≤ 15, -10 ≤ k ≤ 10, -17 ≤ l ≤ 16	-13 ≤ h ≤ 11, -9 ≤ k ≤ 9, -15 ≤ l ≤ 15	-16 ≤ h ≤ 17, -12 ≤ k ≤ 7, -18 ≤ l ≤ 20	-19 ≤ h ≤ 17, -13 ≤ k ≤ 13, -22 ≤ l ≤ 18	-17 ≤ h ≤ 17, -8 ≤ k ≤ 12, -20 ≤ l ≤ 19	-14 ≤ h ≤ 14, -5 ≤ k ≤ 10, -16 ≤ l ≤ 17	-11 ≤ h ≤ 10, -16 ≤ k ≤ 20, -17 ≤ l ≤ 16	-7 ≤ h ≤ 11, -20 ≤ k ≤ 20, -17 ≤ l ≤ 17
Reflections collected	8982	7199	15086	16498	14763	7540	15964	15291
Independent reflections	3103 [R_{int} = 0.0401, R_{sigma} = 0.0407]	2151 [R_{int} = 0.0255, R_{sigma} = 0.0255]	4791 [R_{int} = 0.0836, R_{sigma} = 0.0630]	6597 [R_{int} = 0.0285, R_{sigma} = 0.0325]	4803 [R_{int} = 0.0267, R_{sigma} = 0.0305]	2823 [R_{int} = 0.0456, R_{sigma} = 0.0510]	4303 [R_{int} = 0.0248, R_{sigma} = 0.0232]	4136 [R_{int} = 0.0344, R_{sigma} = 0.0332]
Data/restraints/parameters	3103/25/196	2151/0/178	4791/0/178	6597/0/174	4803/0/178	2823/0/178	4303/69/371	4136/0/333
Goodness-of-fit on F^2	1.044	1.064	1.047	1.075	1.053	1.088	1.143	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1269	R_1 = 0.0240, wR_2 = 0.0590	R_1 = 0.0521, wR_2 = 0.1304	R_1 = 0.0293, wR_2 = 0.0718	R_1 = 0.0332, wR_2 = 0.0718	R_1 = 0.0410, wR_2 = 0.1459	R_1 = 0.0370, wR_2 = 0.0977	R_1 = 0.0287, wR_2 = 0.0687
Final R indexes [all data]	R_1 = 0.0607, wR_2 = 0.1342	R_1 = 0.0264, wR_2 = 0.0602	R_1 = 0.0948, wR_2 = 0.1625	R_1 = 0.0365, wR_2 = 0.0754	R_1 = 0.0545, wR_2 = 0.0788	R_1 = 0.0456, wR_2 = 0.1513	R_1 = 0.0476, wR_2 = 0.1153	R_1 = 0.0322, wR_2 = 0.0708
Largest diff. peak/hole / e Å^{-3}	0.92/-0.44	0.31/-0.33	0.65/-1.24	0.57/-0.98	0.54/-0.82	1.44/-1.52	0.28/-0.44	0.33/-0.36
	ClO_4		**Cl**		**Br**		**I**	

CCDC number	2023560	2023559	2023558	2023557	2023556	2023555	2023562	2023561
Empirical formula	$C_{22}H_{26}ClF_2MnN_4O_6$	$C_{22}H_{26}ClF_2MnN_4O_6$	$C_{22}H_{26}ClF_2MnN_4O_2$	$C_{22}H_{26}ClF_2MnN_4O_2$	$C_{22}H_{26}Br_{0.72}Cl_{0.28}F_2MnN_4O_2$	$C_{22}H_{26}Br_{0.71}Cl_{0.29}F_2MnN_4O_2$	$C_{22}H_{26}F_2IMnN_4O_2$	$C_{22}H_{26}F_2IMnN_4O_2$
Formula weight	570.86	570.86	506.86	506.86	538.95	538.46	598.31	598.31
Temperature/K	298(2)	100(2)	298(2)	100(2)	298(2)	100.05	298(2)	100.0
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	Pccn	Pccn	Pccn	Pccn	Pccn	Pccn
a/Å	9.831(4)	9.6711(13)	7.8670(9)	7.665(3)	8.0357(8)	7.6696(13)	8.5204(11)	7.9166(16)
b/Å	17.819(7)	17.599(2)	16.136(2)	16.221(6)	16.0975(15)	16.176(3)	16.1865(19)	16.279(3)
c/Å	14.782(6)	14.657(2)	17.6938(19)	17.762(5)	17.7115(17)	17.944(3)	17.696(2)	18.585(4)
α/°	90	90	90	90	90	90	90	90
β/°	106.738(9)	106.072(3)	90	90	90	90	90	90
γ/°	90	90	90	90	90	90	90	90
Volume/Å^3	2479.8(17)	2397.0(6)	2246.1(4)	2208.5(13)	2291.1(4)	2226.2(7)	2440.5(5)	2395.1(8)
Z	4	4	4	4	4	4	4	4
ρ_{calc}g/cm^3	1.529	1.582	1.499	1.525	1.563	1.606	1.628	1.659
μ/mm^{-1}	0.701	0.725	0.750	0.763	1.911	1.948	1.846	1.881
F(000)	1176.0	1176.0	1048.0	1048.0	1100.0	1099.2	1192.0	1192.0
Crystal size/mm^3	0.28 × 0.23 × 0.20	0.28 × 0.23 × 0.20	0.26 × 0.21 × 0.18	0.26 × 0.21 × 0.18	0.11 × 0.1 × 0.09	0.11 × 0.1 × 0.09	0.26 × 0.20 × 0.14	0.11 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.572 to 56.492	3.704 to 50.038	4.604 to 56.652	5.23 to 50.048	5.25 to 50.05	5.036 to 49.998	4.604 to 52	4.384 to 50.01
Index ranges	-13 ≤ h ≤ 10, -23 ≤ k ≤ 22, -19 ≤ l ≤ 19	-11 ≤ h ≤ 11, -19 ≤ k ≤ 20, -17 ≤ l ≤ 17	-10 ≤ h ≤ 10, -19 ≤ k ≤ 21, -20 ≤ l ≤ 23	-9 ≤ h ≤ 9, -18 ≤ k ≤ 19, -19 ≤ l ≤ 21	-9 ≤ h ≤ 9, -19 ≤ k ≤ 17, -21 ≤ l ≤ 21	-8 ≤ h ≤ 9, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-10 ≤ h ≤ 8, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	-7 ≤ h ≤ 9, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected	21932	15432	17533	12474	13411	12606	14970	9196
Independent reflections	6124	4242	2802	1948	2030	1967	2406	2117

	[R_{int} = 0.0311, R_{sigma} = 0.0281]	[R_{int} = 0.0388, R_{sigma} = 0.0342]	[R_{int} = 0.0601, R_{sigma} = 0.0431]	[R_{int} = 0.0618, R_{sigma} = 0.0396]	[R_{int} = 0.0438, R_{sigma} = 0.0273]	[R_{int} = 0.0433, R_{sigma} = 0.0291]	[R_{int} = 0.0425, R_{sigma} = 0.0268]	[R_{int} = 0.0614, R_{sigma} = 0.0484]
Data/restraints/parameters	6124/0/333	4242/0/333	2802/0/150	1948/0/150	2030/0/147	1967/1/151	2406/0/150	2117/0/146
Goodness-of-fit on F^2	1.031	1.064	1.068	1.052	1.080	1.076	1.045	1.182
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1259	R_1 = 0.0333, wR_2 = 0.0806	R_1 = 0.0463, wR_2 = 0.0892	R_1 = 0.0333, wR_2 = 0.0831	R_1 = 0.0368, wR_2 = 0.0834	R_1 = 0.0272, wR_2 = 0.0660	R_1 = 0.0414, wR_2 = 0.1023	R_1 = 0.0759, wR_2 = 0.1709
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1452	R_1 = 0.0375, wR_2 = 0.0840	R_1 = 0.0952, wR_2 = 0.1102	R_1 = 0.0459, wR_2 = 0.0902	R_1 = 0.0585, wR_2 = 0.0934	R_1 = 0.0362, wR_2 = 0.0701	R_1 = 0.0690, wR_2 = 0.1222	R_1 = 0.1017, wR_2 = 0.1845
Largest diff. peak/hole / e $Å^{-3}$	0.61/-0.50	0.36/-0.45	0.38/-0.45	0.38/-0.28	0.29/-0.30	0.26/-0.43	0.51/-0.84	1.86/-1.72

Table S2. The selected angles (°) for complexes **1-8**.

	PF_6		AsF_6		SbF_6		BF_4	
T/K	298	100	298	100	298	100	100	298
O1-Mn1-O2	176.19(10)	176.13(7)	176.44(13)	176.19(8)	176.39(8)	178.68(9)	176.91(5)	179.22(8)
O1-Mn1-N1	86.90(7)	87.09(5)	86.93(9)	86.97(6)	87.10(5)	86.91(9)	88.57(6)	86.74(9)
O2-Mn1-N1	91.08(7)	90.85(5)	91.17(9)	91.38(7)	90.96(5)	94.18(9)	94.10(6)	93.63(9)
O1-Mn1-N4	91.08(7)	90.85(5)	86.07(10)	91.38(6)	90.96(5)	93.71(10)	93.17(6)	93.92(9)
O2-Mn1-N4	86.90(7)	87.09(5)	86.92(9)	86.97(6)	87.10(5)	86.68(9)	87.85(6)	86.62(8)
N1-Mn1-N4	116.02(11)	115.52(7)	115.56(14)	114.40(10)	114.97(8)	107.40(10)	100.85(6)	107.36(9)
O1-Mn1-N3	85.92(8)	85.91(5)	91.18(9)	86.14(7)	86.02(6)	86.30(10)	85.68(6)	87.82(9)
O2-Mn1-N3	97.05(8)	97.10(5)	96.70(10)	96.22(7)	96.78(6)	92.46(10)	91.43(6)	91.68(9)
N4-Mn1-N3	83.32(9)	83.62(5)	83.58(11)	84.05(7)	83.78(6)	87.21(11)	89.23(6)	84.92(9)
O1-Mn1-N2	97.05(8)	97.10(5)	96.70(10)	86.14(7)	96.78(6)	91.54(11)	91.01(6)	92.83(9)
O2-Mn1-N2	85.92(8)	85.92(5)	86.07(10)	96.22(7)	86.02(6)	87.82(10)	87.62(6)	86.50(9)

N1-Mn1-N2	83.32(9)	83.62(5)	83.58(11)	84.05(8)	83.78(6)	84.74(10)	86.53(6)	87.41(10)
N3-Mn1-N2	78.54(14)	78.38(8)	78.40(17)	78.55(12)	78.56(8)	81.26(11)	83.82(6)	80.93(10)
N1-Mn1-N3	159.49(8)	159.71(5)	159.74(11)	160.13(6)	160.45(8)	160.91(15)	164.26(10)	168.66(6)
N2-Mn1-N4	159.49(8)	159.71(5)	159.74(11)	160.13(6)	160.45(8)	160.91(15)	167.00(10)	171.59(6)
	ClO_4		Cl		Br		I	
T/K	100	298	100	298	100	298	100	298
O1-Mn1-O2	178.49(6)	178.53(9)	177.84(9)	179.31(12)	177.18(16)	178.8(2)	176.1(4)	177.9(2)
O1-Mn1-N1	87.13(6)	87.06(7)	87.73(7)	86.67(9)	88.01(13)	86.29(16)	87.9(3)	86.28(15)
O2-Mn1-N1	94.01(6)	93.82(7)	93.69(7)	93.77(9)	93.87(13)	94.45(18)	94.7(3)	94.95(17)
O1-Mn1-N4	93.31(7)	93.82(7)	93.69(7)	93.77(9)	93.87(13)	94.45(18)	94.7(3)	94.95(17)
O2-Mn1-N4	87.33(6)	87.06(7)	87.73(7)	86.67(9)	88.01(13)	86.29(16)	87.9(3)	86.28(15)
N1-Mn1-N4	105.77(7)	107.22(12)	97.57(10)	102.85(13)	96.82(19)	104.0(2)	97.0(5)	106.7(2)
O1-Mn1-N3	85.96(7)	85.76(7)	86.42(7)	86.77(9)	85.65(13)	86.21(16)	85.2(3)	85.04(16)
O2-Mn1-N3	92.69(7)	93.12(8)	91.99(7)	92.71(9)	92.27(13)	92.88(17)	91.9(3)	93.39(18)
N4-Mn1-N3	87.85(7)	86.01(9)	88.95(8)	87.50(10)	89.43(14)	87.26(18)	89.3(4)	86.60(19)
O1-Mn1-N2	91.22(7)	93.12(8)	91.99(7)	92.71(9)	92.27(13)	92.88(17)	91.9(3)	93.39(18)
O2-Mn1-N2	87.90(7)	85.76(7)	86.42(7)	86.77(9)	85.65(13)	86.21(16)	85.2(3)	85.04(16)
N1-Mn1-N2	84.99(7)	86.01(9)	88.95(8)	87.50(10)	89.43(14)	87.26(18)	89.3(4)	86.60(19)
N3-Mn1-N2	81.94(7)	81.65(13)	85.11(11)	82.87(14)	85.0(2)	82.4(3)	85.2(5)	81.3(3)
N1-Mn1-N3	165.07(7)	166.87(9)	168.07(10)	171.51(7)	171.38(14)	166.89(17)	171.0(4)	164.67(19)
N2-Mn1-N4	168.51(7)	164.06(9)	168.07(10)	171.51(7)	171.38(14)	166.90(17)	171.0(4)	164.67(19)

Table S3. Hydrogen bond distances for complexes **1-8** (Å, °).

1-PF_6	100K					298K				
	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-H11···F1	0.84(2)	2.38(2)	3.2050(19)	169.6(15)	N2-H11···F1	0.78(3)	2.46(3)	3.236(3)	171.6(15)
2-AsF_6	100K					298K				
	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-H11···F1	0.86(2)	2.37(2)	3.220(2)	168(2)	N2-H11···F1	0.84(4)	2.40(4)	3.237(4)	173(3)
3-SbF_6	100K					298K				
	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-H11···F1	0.99(5)	2.32(5)	3.305(6)	174(4)	N2-H11···F1	0.82(3)	2.48(3)	3.3.288(3)	172(2)
4-BF_4	100K					298K				
	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-H11···F4	0.86(2)	2.322(2)	2.982(2)	134.2(18)	N2-H11···F4	0.84(4)	2.42(4)	3.100(5)	139(3)
5-ClO_4	100K					298K				
	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-H11···O5	0.83(3)	2.39(3)	3.092(3)	144(2)	N2-H11···O5	0.80(4)	2.539(4)	3.197(5)	141(3)
6-Cl	100K					298K				
	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-H11···Cl1	0.89	2.54(2)	3.24(3)	136(3)	N2-H11···Cl1	0.879	2.547	3.266(4)	139.59
7-Br	100K					298K				
	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-H13···Br1	0.75(5)	2.69(5)	3.304(4)	142(5)	N2-H13···Br1	0.98	2.59	3.345(5)	134
8-I	100K					298K				
	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-H13···I1	0.930(14)	2.797(10)	3.485(10)	131.7(9)	N2-H13···I1	0.71(7)	2.92(7)	3.555(5)	151(6)

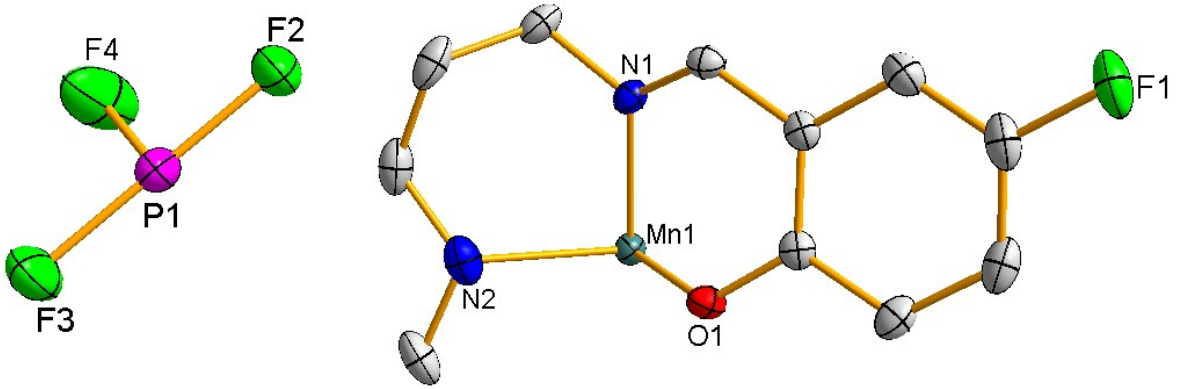


Figure S1. The molecular structure for complex **1** at 100K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

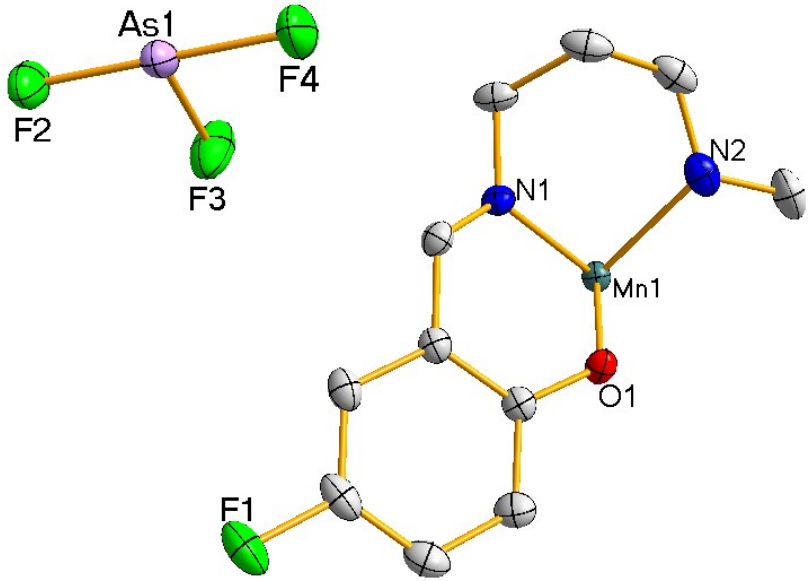


Figure S2. The molecular structure for complex **2** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

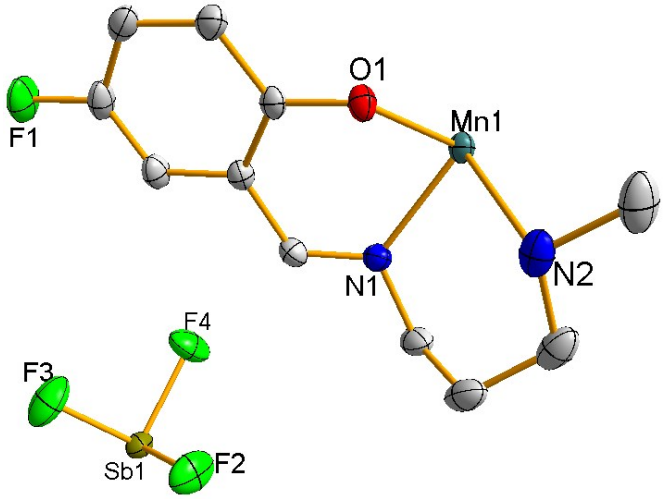


Figure S3. The molecular structure for complex **3** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

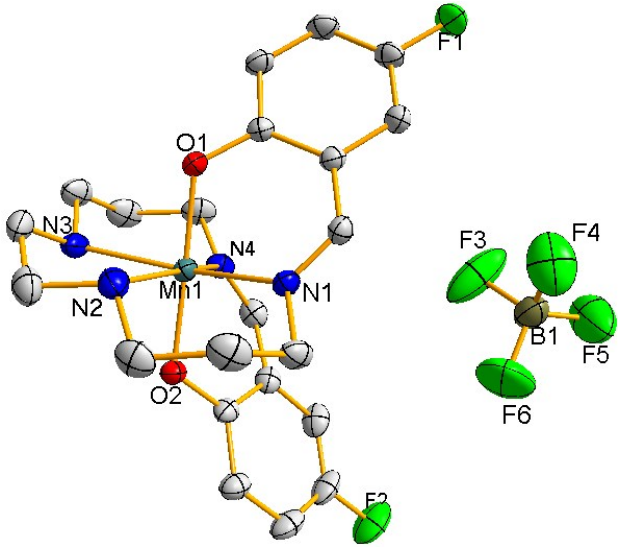


Figure S4. The molecular structure for complex **4** at 100K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

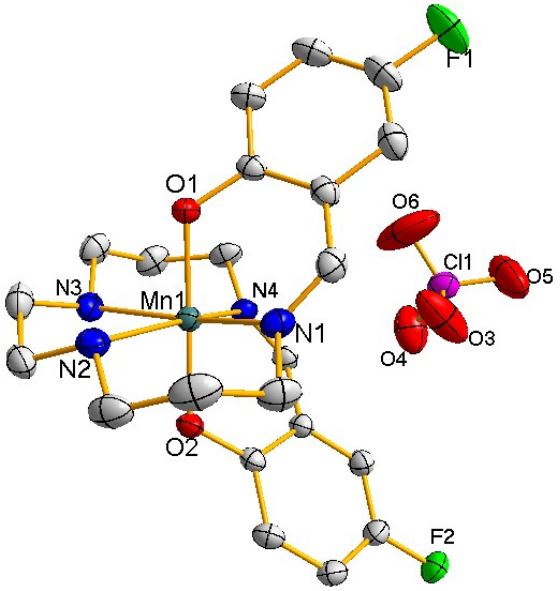


Figure S5. The molecular structure for complex **5** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

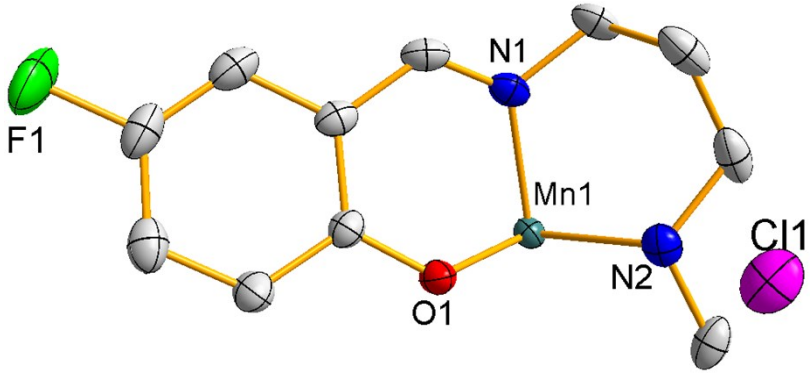


Figure S6. The molecular structure for complex **6** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

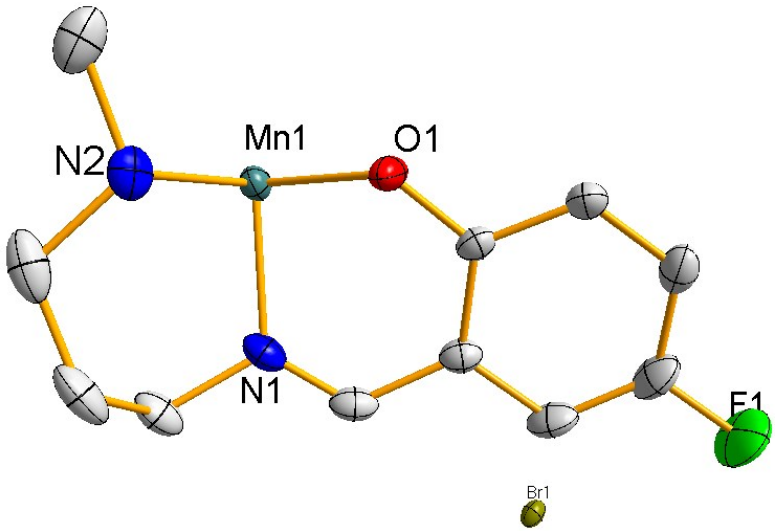


Figure S7. The molecular structure for complex **7** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

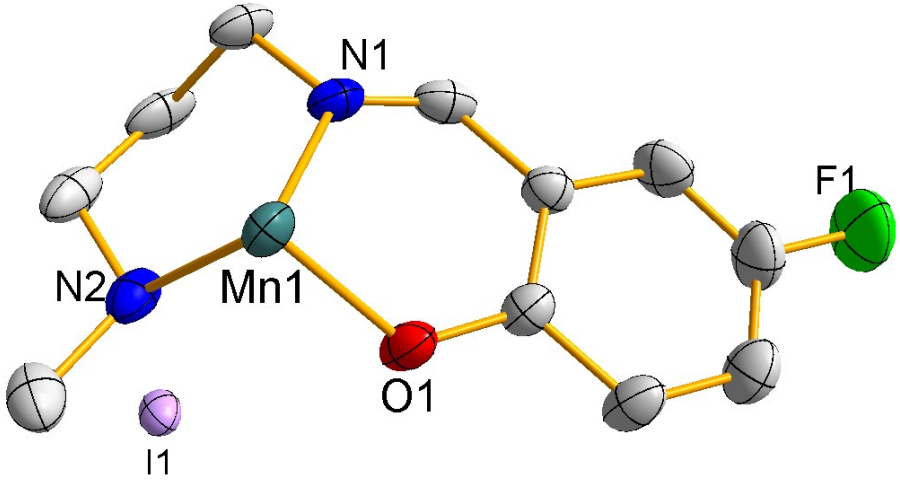


Figure S8. The molecular structure for complex **8** at 100 K, hydrogen atoms have been omitted for clarity. Ellipsoids at 30% probability.

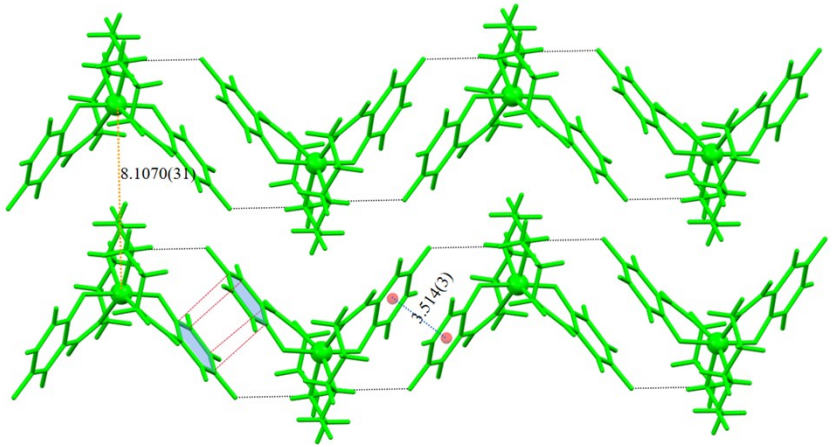


Figure S9. The details of the sublattice formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ chains of complex **1** at 298 K. The interchain Mn···Mn distance is 8.11 Å (orange dotted line). The π-π stacking between the phenolate groups with centroid-centroid distance of 3.514(3) Å and ring-ring distance of 3.367(2) Å (blue).

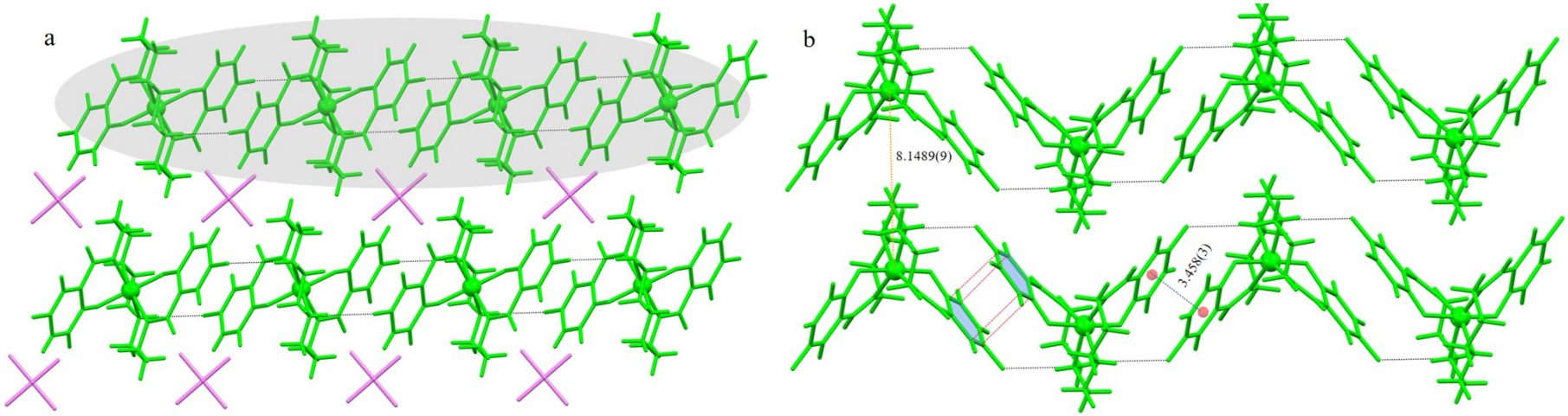


Figure S11. (a) Crystal packing along the *b* axis, showing the N_{am}–H···F_{ph} hydrogen bonds between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations for complex **2** at 100 K. (b) The details of the sublattice formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ chains (gray). The interchain Mn···Mn distance is 8.15 Å (orange dotted line). The π-π stacking between the phenolate groups with centroid-centroid distance of 3.458(3) Å and ring-ring distance of 3.329(1) Å (blue).

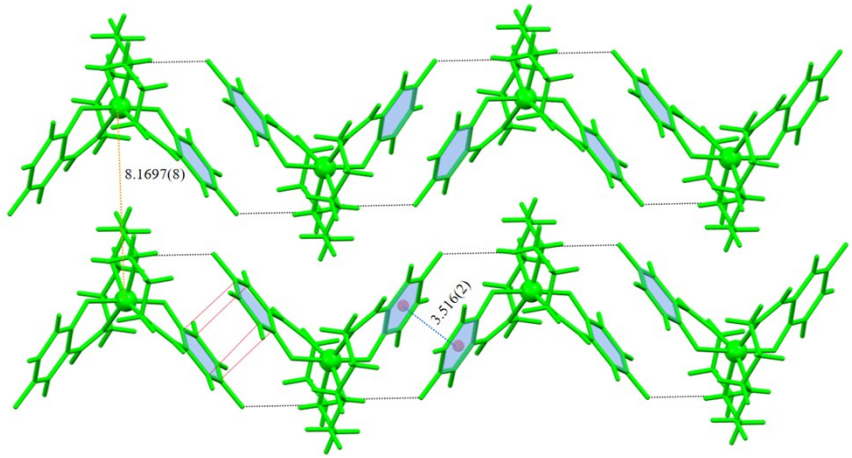


Figure S12. The details of the sublattice formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ chains of **2**. The interchain Mn···Mn distance is 8.17 Å (orange dotted line). The π-π stacking between the phenolate groups with centroid-centroid distance of 3.516(2)Å and ring-ring distance of 3.379(2) Å (blue) at 298 K.

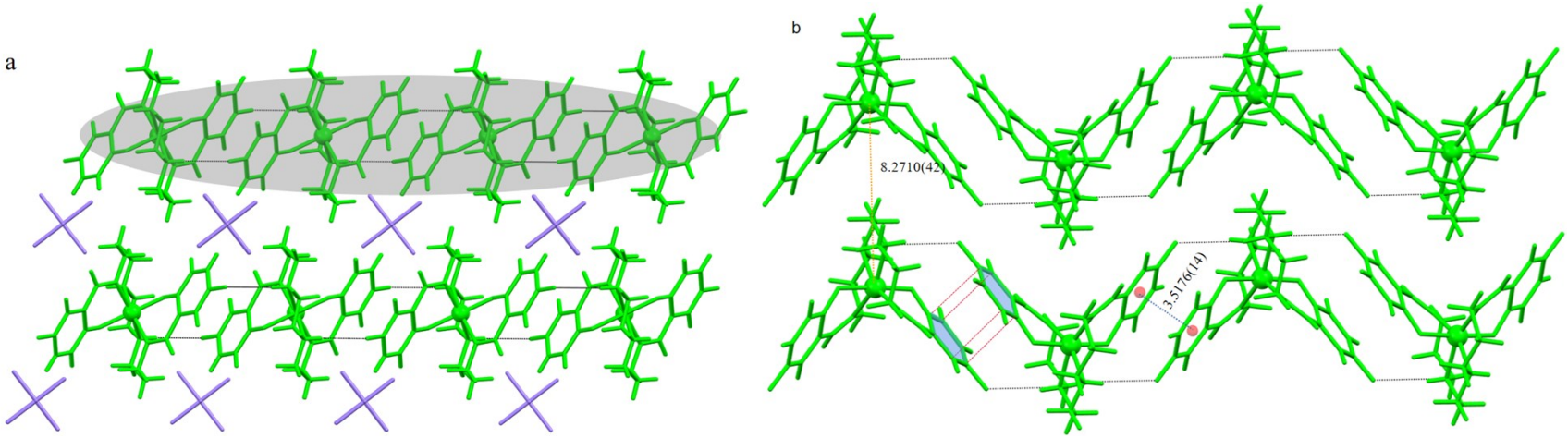


Figure S13. (a) Crystal packing along the *b* axis, showing the N_{am}–H···F_{ph} hydrogen bonds between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations for complex **3** at 100 K. (b) The details of the sublattice formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ chains (gray). The interchain Mn···Mn distance is 8.27 Å (orange dotted line). The π-π stacking between the phenolate groups with centroid-centroid distance of 3.5176(14) Å and ring-ring distance of 3.3991(12) Å (blue).

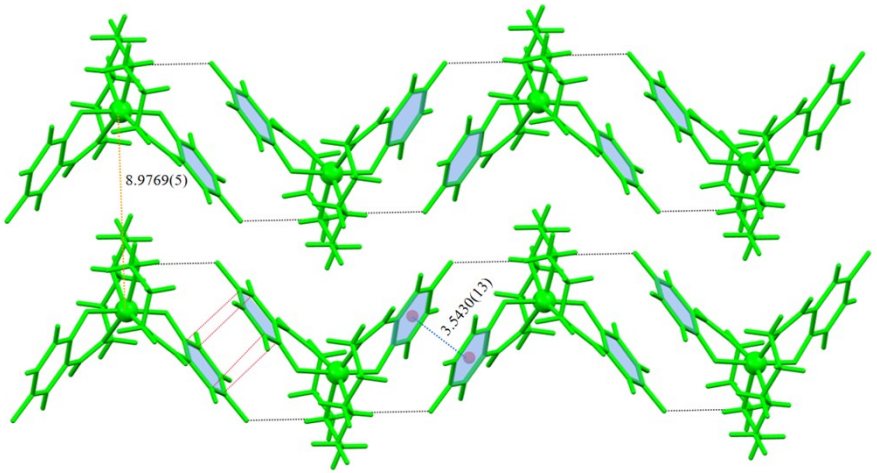
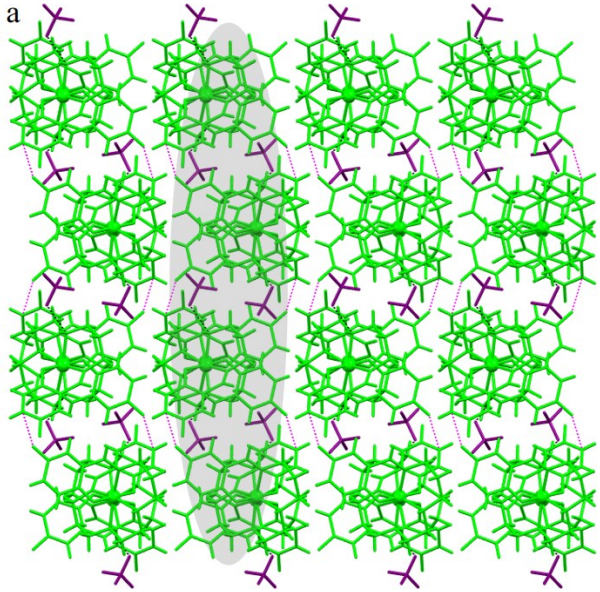


Figure S14. The details of the sublattice formed by the $[Mn(5\text{-}F\text{-}sal\text{-}N\text{-}1,5,8,12)]^{+}$ chains of **3** at 298 K. The interchain Mn···Mn distance is 8.98 Å (orange dotted line). The π-π stackings between the phenolate groups with centroid-centroid distance of 3.5430(13) Å and ring-ring distance of 3.4202(10) Å (blue) .



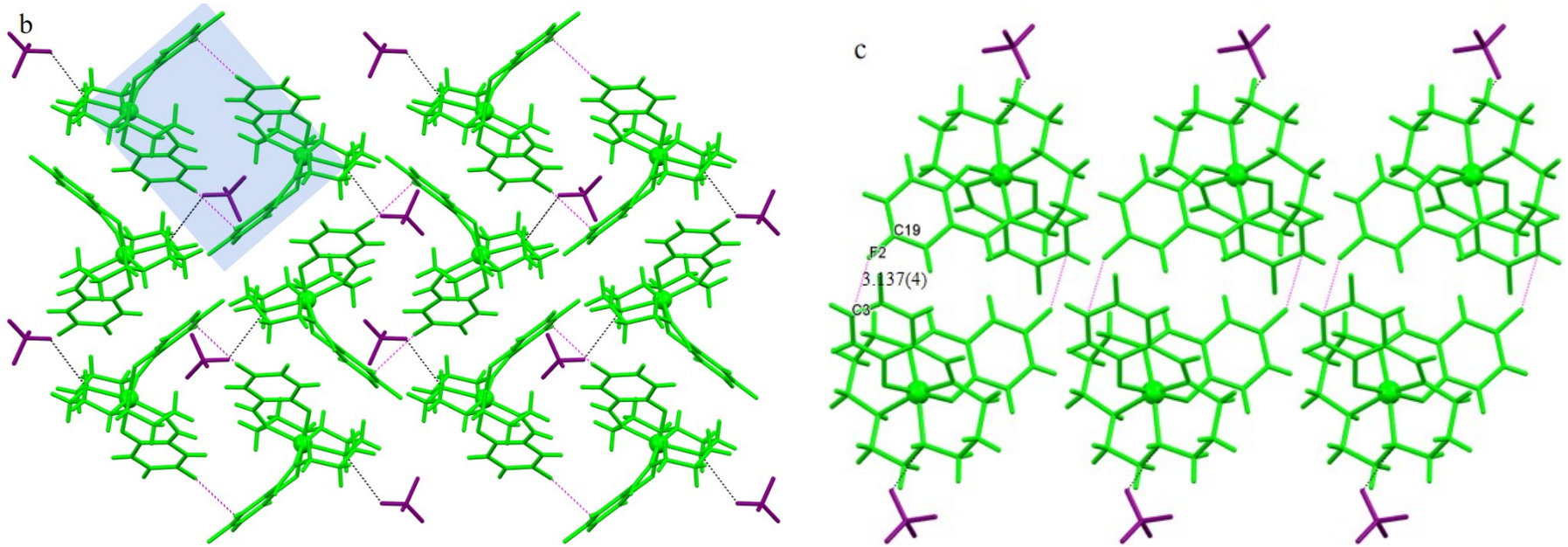


Figure S15. (a) Crystal packing of complex **4** at 295 K, viewed along the *c* axis, showing the N_{am}–H···F_{BF4} hydrogen bonds (black dotted line) between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations and BF_4^- anions and the lone pair···π interactions (magenta dotted line) among the cations. (b) The details of the chain (gray) along the *a* axis. (c) The details of the lone pair···π interactions (blue) between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations characterized by the contact distances C3···F2 = 3.137(4) Å.

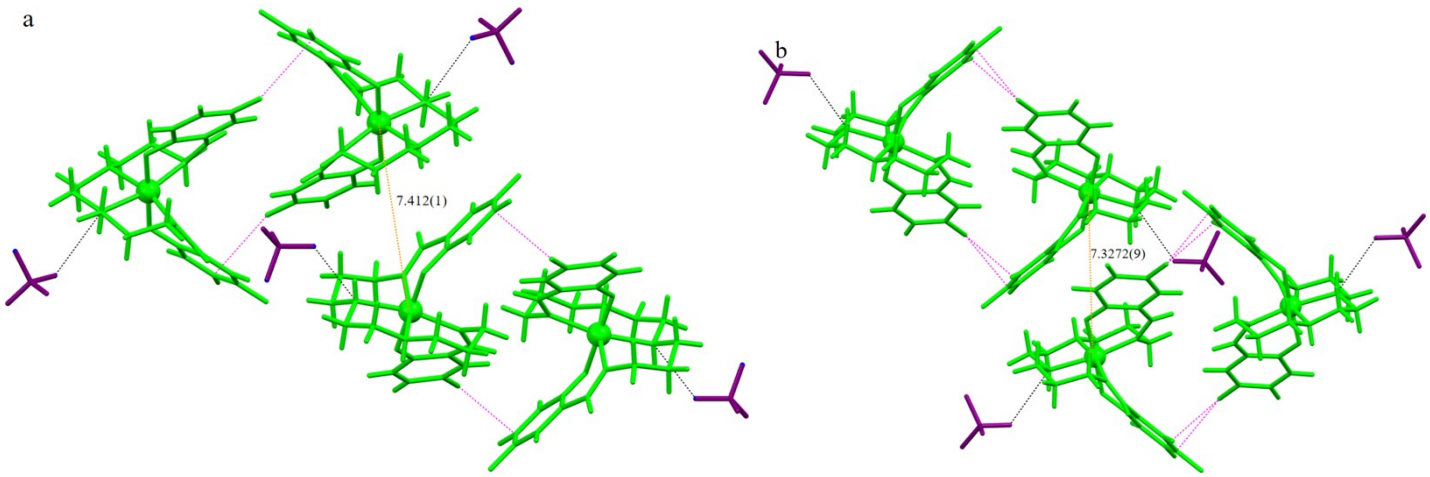


Figure S16. The interchain Mn···Mn distance indicated by a gray dotted line of complex **4.** it is 7.41 Å at 298 K (a) and 7.33 Å at 100 K (b), respectively.

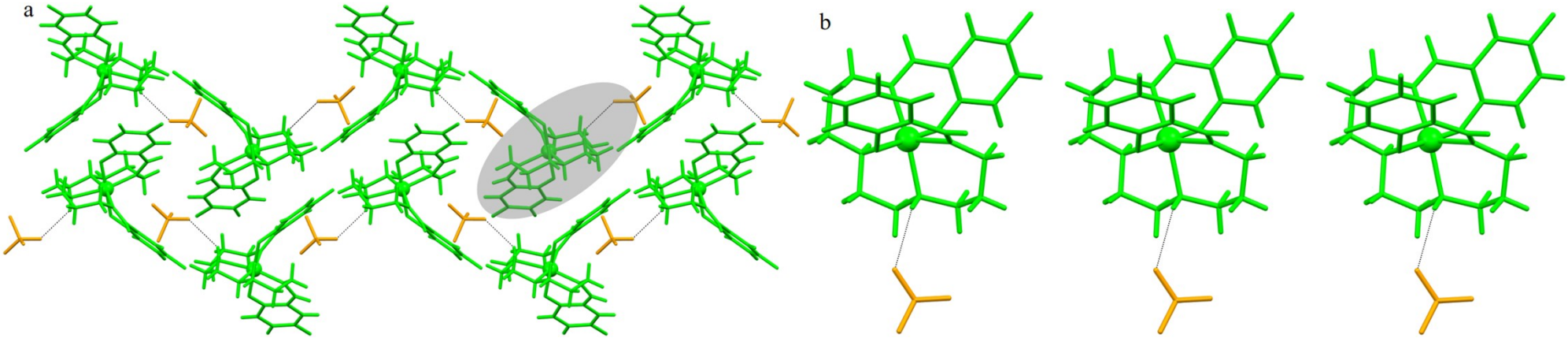


Figure S17. (a) Crystal packing of complex **5** at 295 K, viewed along the *a* axis, showing the N_{am}–H···O_{ClO4} (black) hydrogen bonds between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations and ClO_4^-. (b) The details of the sublattice along the *c* axis (gray).

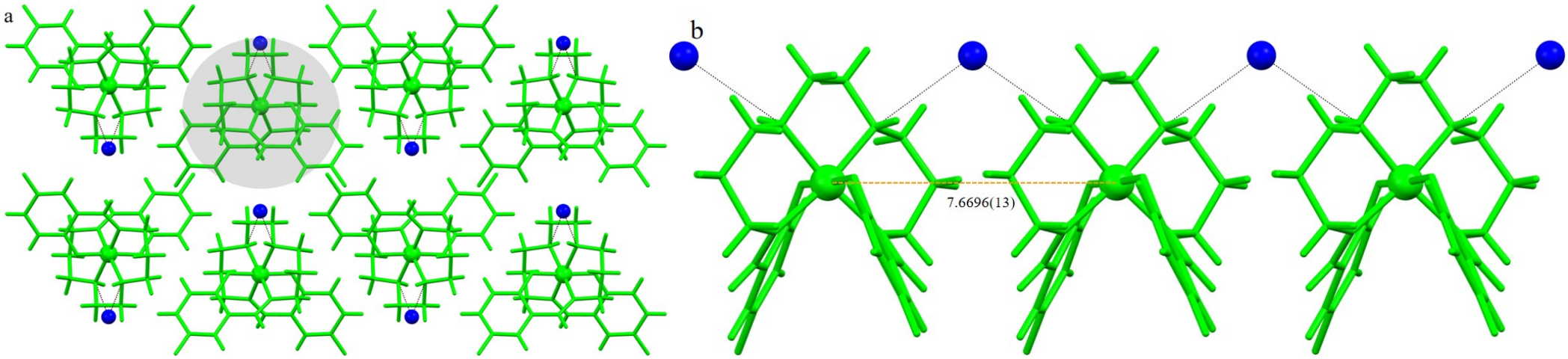


Figure S18. (a) Crystal packing of complex **7** at 100 K, viewed along the *a* axis, showing the N_{am}–H···Br hydrogen bonds between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations and Br^- anions, (b) The details of the sublattice viewed along the *b* axis formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ and Br^-. The intrachain Mn···Mn distance is 7.67 Å at 100 K and 8.04 Å at 298 K.

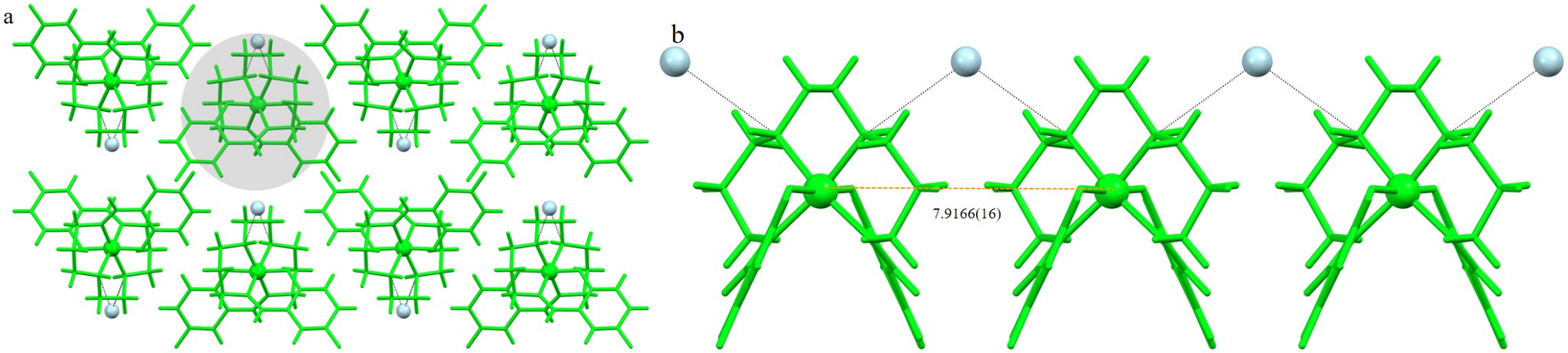


Figure S19. (a) Crystal packing of complex **8** at 100 K, viewed along the *a* axis, showing the N_{am}–H···I hydrogen bonds between the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ cations and I^- anions, (b) The details of the sublattice viewed along the *b* axis formed by the $[Mn(5\text{-F-sal-N-1,5,8,12})]^+$ and I^-. The intrachain Mn···Mn distance is 7.92 Å at 100 K and 8.52 Å at 298 K.

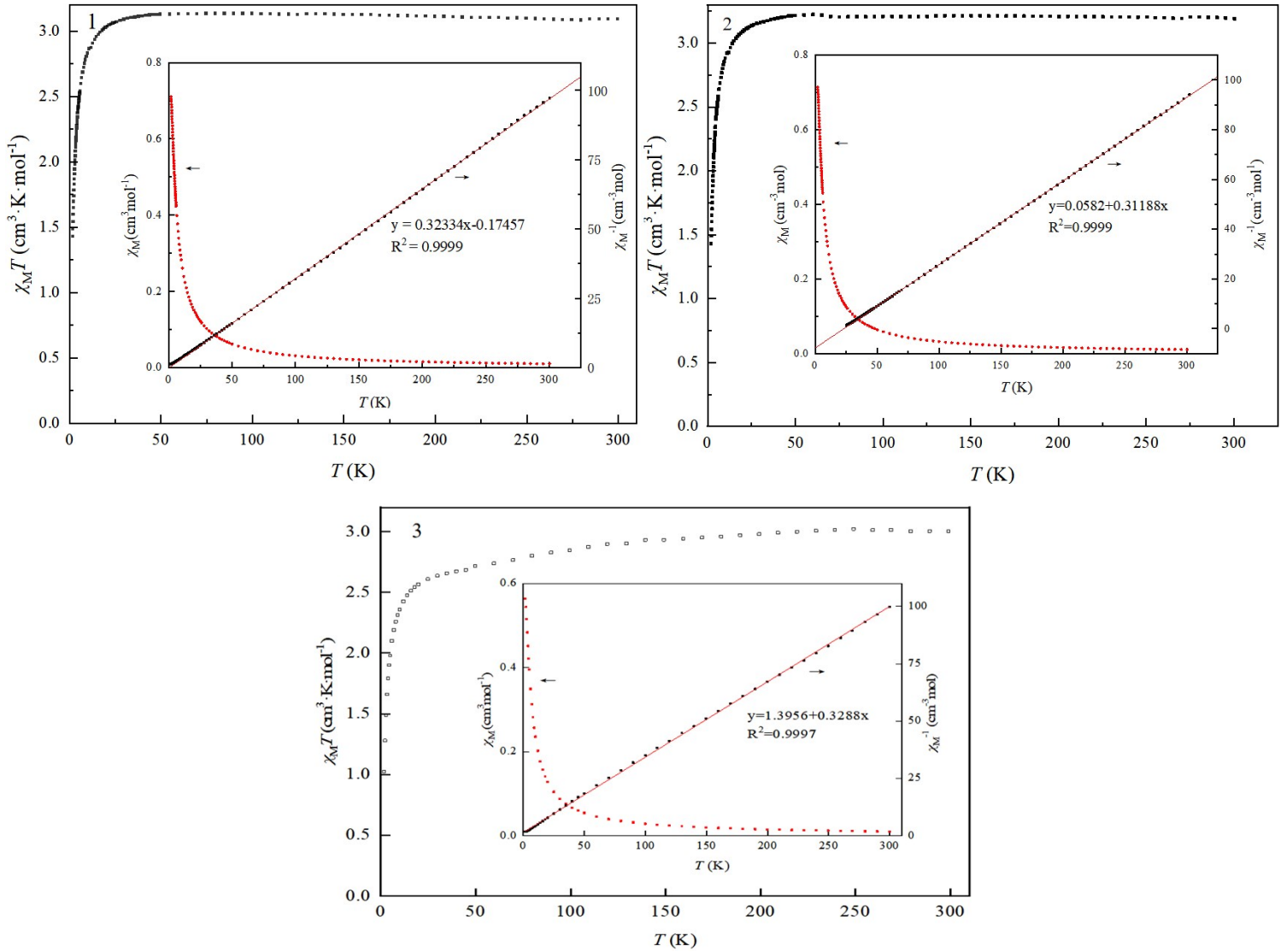


Figure S20. Thermal dependence of the $\chi_M T$ of complexes **1-3**, Insets: thermal dependence of $1/\chi_M$ (red circles) and best fit to the Curie-Weiss expression (solid red line).