Supplementary Materials

Structural Insights into the Counterion Effects on the Manganese(III) Spin Crossover System with Hexadentate Schiff-Base Ligands

Shi Wang[a]*•Wu-Tan Xu[a]•Wen-Rui He[a]•Shinya Takaishi[b]•Yong-Hua Li[a]*•Masahiro Yamashita[b]•Wei Huang[ac]

[a] *Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China.*

E-mail: iamswang@njupt.edu.cn

http://smse.njupt.edu.cn/

[b] *Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan*

[c] *Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China.*

Table S1. Hydrogen Bond Distances and Parameters for the complex of **1**−**4** (Å, °)

Compound	D–H···A	D–H	H···A	D···A	D–H···A	Symmetry Code
1 100 K	N(2)--H(31)···O(7)	0.90(6)	2.10(6)	2.948(8)	156(7)	x,-1+y,z
	C(3)--H(7)···O(8)	0.93	2.59	3.515(9)	175	x,1-y,1/2+z
	C(8)--H(9)···O(8)	0.93	2.41	3.283(9)	157	
	C(15)--H(10)···O(8)	0.93	2.57	3.351(11)	142	1-x,1-y,1-z
	C(20)--H(13)···O(5)	0.93	2.47	3.338(9)	155	
	C(13)--H(5)···O(5)	0.96	2.59	3.524(16)	164	1-x,2-y,1-z
	C(23)--H(26)···O(5)	0.97	2.58	3.189(10)	121	x,-1+y,z
	C(23)--H(26)···O(7)	0.97	2.56	3.379(10)	143	x,-1+y,z
1 293 K	N(2) --H(16)···O(7)	0.80(3)	2.25(3)	2.991(5)	154(3)	2-x,-1+y,1/2-z
	C(8) --H(7)···O(8)	0.93	2.43	3.319(6)	159	
	C(20)--H(23)···O(5)	0.93	2.51	3.382(6)	156	
2 100 K	N(2)--H(14)···F(2)	0.88(3)	2.20(3)	2.951(3)	144(3)	-1+x,1/2-y,-1/2+z
	N(3)--H(19)···O(3)	0.89(3)	2.47(3)	3.320(3)	160(3)	-1+x,y,z
	C(17)--H(26)···F(4)	0.95	2.30	3.210(3)	162	
	C(17)--H(26)···F(3)	0.95	2.49	3.274(3)	140	
	C(1)--H(2)···F(2)	0.98	2.37	3.282(4)	155	2-x,1/2+y,1/2-z
	C(9)--H(9)···F(4)	0.99	2.50	3.321(3)	140	x,1/2-y,-1/2+z
	C(16)--H(25)···F(4)	0.99	2.44	3.351(3)	153	
2 293 K	N(3)--H(31)···F(2)	0.77(6)	2.37(7)	3.014(8)	142(6)	-1+x,y,z
	C(21)--H(5)···F(2)	0.98	2.49	3.404(12)	156	2-x,1-y,-z
	C(8)--H(10)···F(1)	0.95	2.53	3.298(8)	138	x,1/2-y,1/2+z
	C(8)--H(10)···F(3)	0.95	2.35	3.288(9)	168	x,1/2-y,1/2+z
3 100 K	N(3) --H(19)···O(3)	0.79(3)	2.49(3)	3.245(3))	161(3)	-1+x,y,z
	C(1) --H(2)···O(6)	0.98	2.49	3.346(6)	146	3/2-x,1/2+y,1/2-z
	C(9) --H(8)···O(6)	0.99	2.43	3.407(4)	170	1/2+x,1/2-y,1/2+z
	C(15)--H(22)···O(7)	0.99	2.51	3.297(4)	136	-1+x,y,z
	C(22)--H(31)···O(7)	0.95	2.49	3.429(4)	168	3/2-x,-1/2+y,1/2-z
3 293 K	N(3)--H(19)···O(3)	0.83(4)	2.53(4)	3.306(4)	157(4)	-1+x,y,z
	C(22)--H(31)···O(5)	0.95	2.53	3.466(6)	168	5/2-x,1/2+y,1/2-z
	C(5) --H(4)···O(6)	0.98	2.52	3.379(8)	146	5/2-x,-1/2+y,1/2-z
	C(9) --H(9)···O(6)	0.99	2.46	3.443(6)	170	1/2+x,1/2-y,1/2+z
	C(15)--H(23)···O(5)	0.99	2.55	3.339(6)	137	-1+x,y,z
4 100 K	N(3) --H(31)···O(5)	0.72(3)	2.34(3)	2.968(3)	146(3)	
	C(3) --H(1)···O(6)	0.95	2.50	3.304(4)	143	1/2-x,1+y,-1/2+z
	C(8) --H(4)···O(7)	0.95	2.37	3.231(3)	151	-1/2+x,2-y,z
	C(13)--H(23)···O(5)	0.99	2.59	3.085(4)	111	2−x, y, 3/2−z
	C(1) --H(10)···F(3)	0.98	2.47	3.382(4)	155	1/2-x,1+y,-1/2+z
	C(14) --H(25)···F(3)	0.99	2.48	3.305(4)	141	1/2-x,y,-1/2+z
	C(15) --	0.99	2.52	3.390(3)	146	

	H(28)···F(1)					
	C(17) --H(5)···O(5)	0.95	2.51	3.384(3)	152	x,1+y,z
4 293 K	N(3) --H(19)···O(6)	0.93	2.30	3.042(14)	136	
	C(8) --H(7)···O(5)	0.95	2.46	3.32717)	152	-1/2+x,1-y,z
	C(13)--H(18)···O(6)	0.99	2.59	3.134(18)	114	
	C(1) --H(3)···F(3)	0.98	2.51	3.452(18)	161	1/2-x,1+y,1/2+z

Table S2. The average trigonal distortion angle Φ and octahedral distortion parameter Σ (°) for complexes **1**-**4**

	1 ClO_4				**2 BF_4**		**3 NO_3**		**4 CF_3SO_3**	
	Mn1		Mn2		100 K	293 K	100 K	293 K	100 K	293 K
	100 K	293 K	100 K	293 K						
Σ	31.96	45.06	64.6	64.22	76.62	74.3	69.63	71.36	71.59	72.2
Φ	54.61	73.82	103.46	103.51	112.31	115.16	112.8	113.97	112.6	111.27

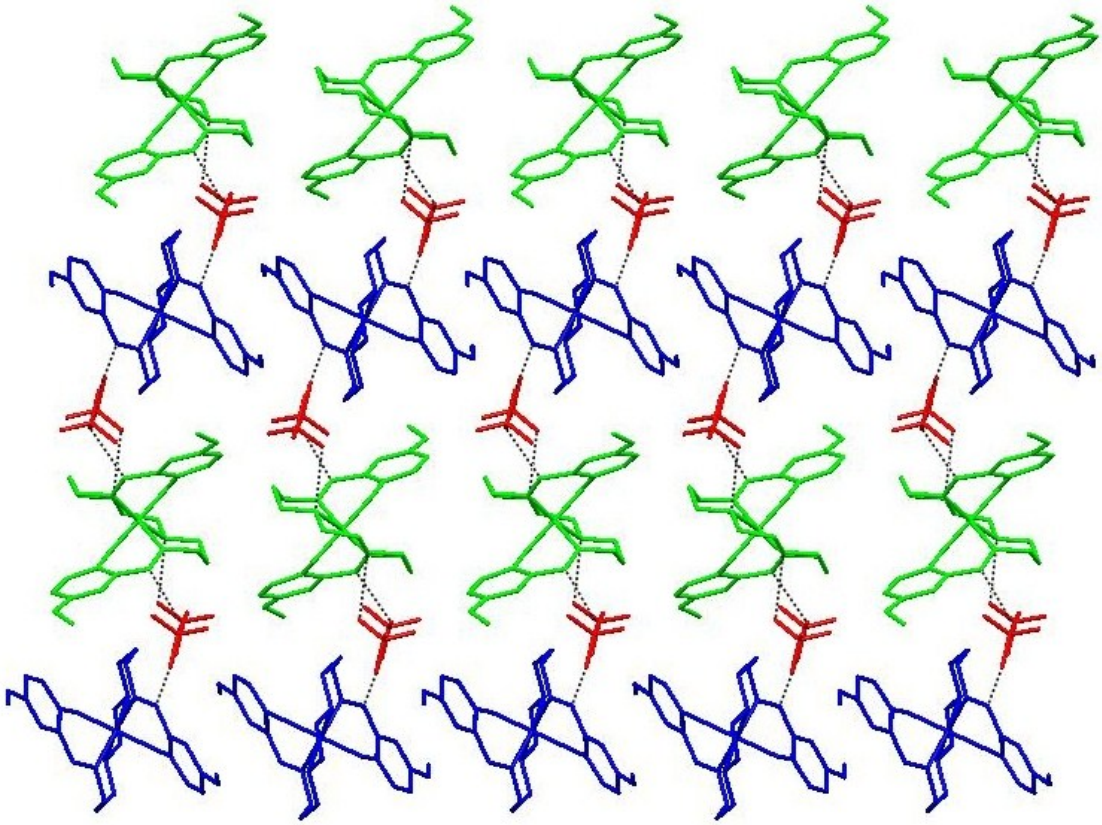

Figure S1. Crystal packing of compound **1** at 293 K, viewed along the *b* axis, showing the N–H···O and C–H···O hydrogen bonds between the cation and the anion. The Mn1 and Mn2 units are shown in green and blue, respectively.

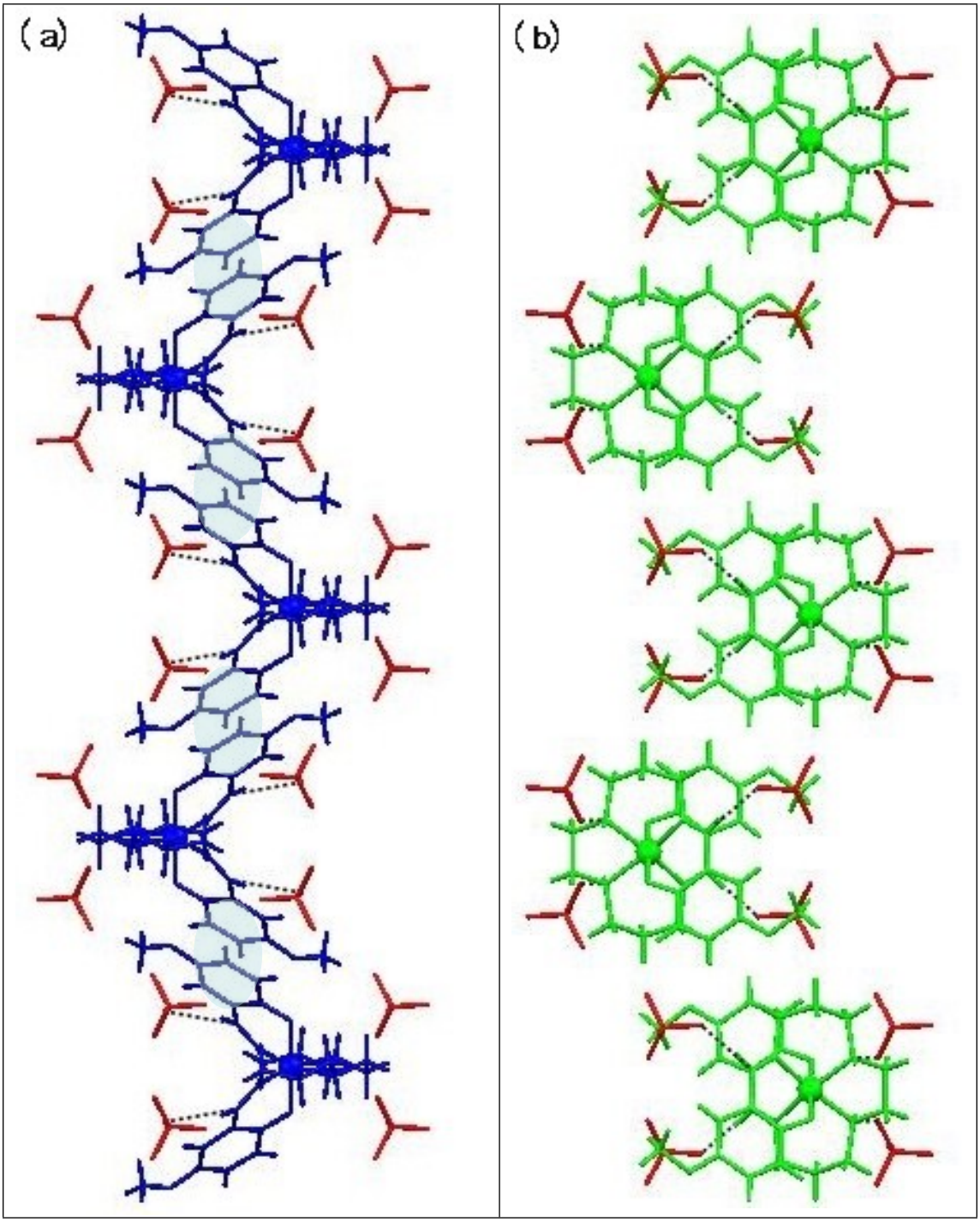

Figure S2. Crystal packing of the Mn2 (a) and Mn1 (b) units of compound **1** at 293 K, viewed along the *a* axis, showing the network of links mediated by perchlorate anions. The stacking effects between ligands of the neighboring Mn2 units is shown in the light blue background.

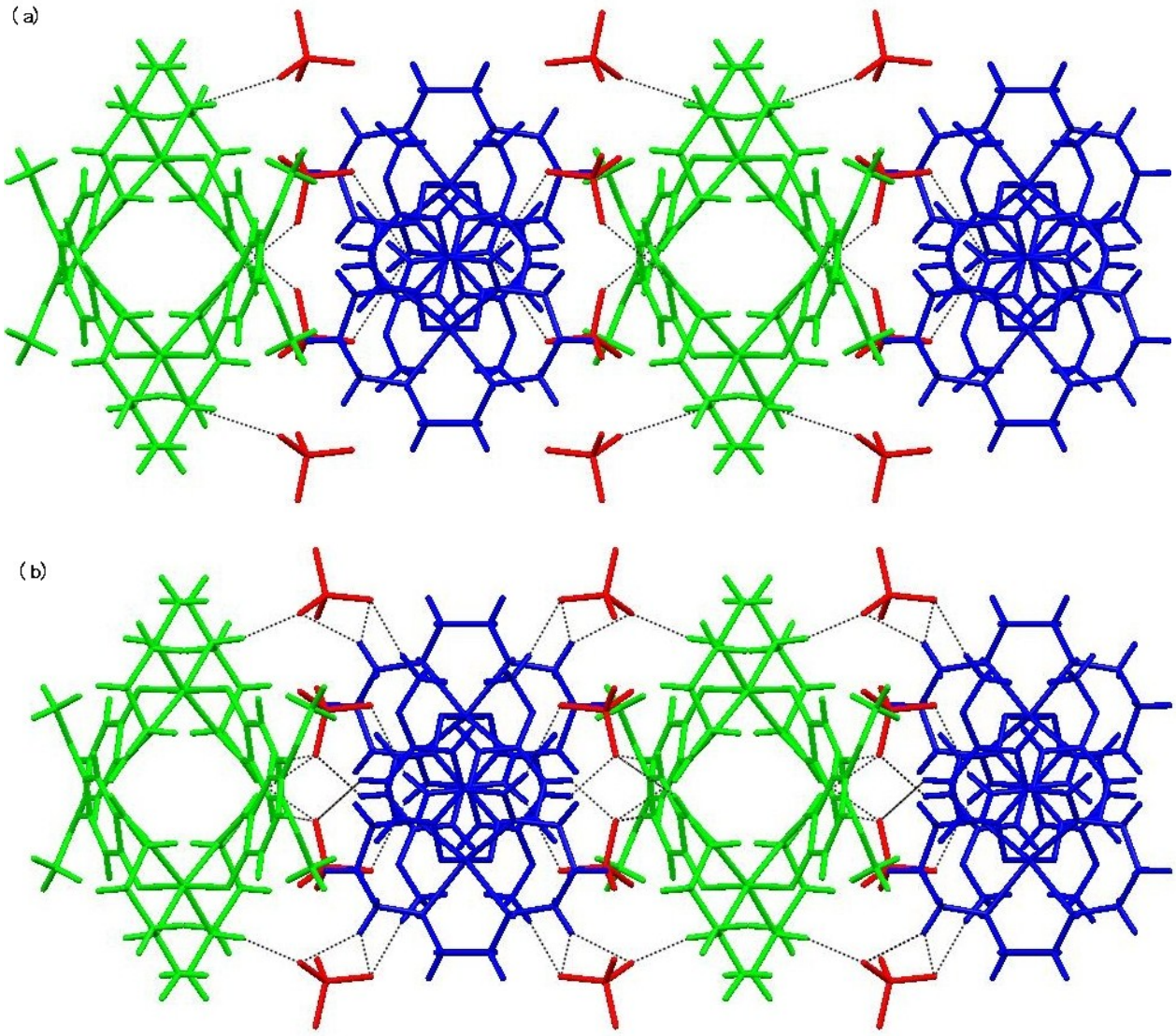

Figure S3. Crystal packing of compound **1** at (a) 293 and (b) 100 K, viewed along the *c* axis, showing the N–H···O and C–H···O hydrogen bonds between the cation and the anion. The Mn1 and Mn2 units are shown in green and blue, respectively.

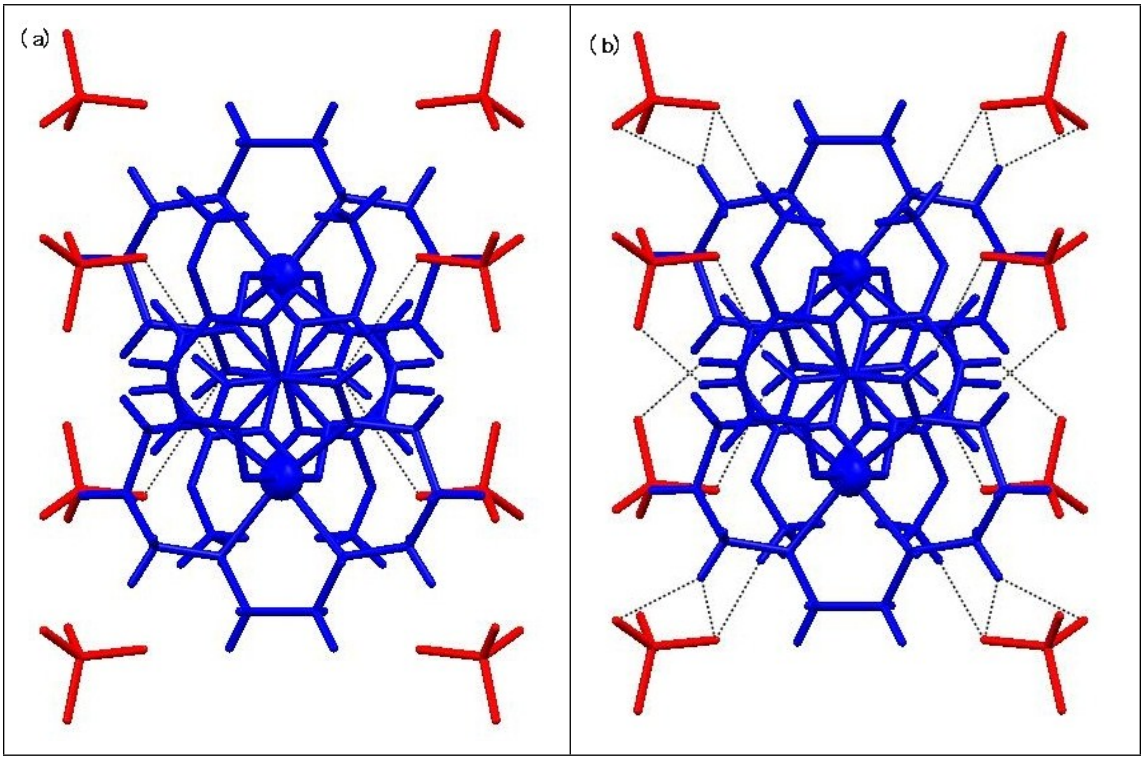

Figure S4. Crystal packing of the Mn2 units of compound **1** at (a) 293 and (b) 100 K, viewed along the *c* axis. The Mn2 units (having no spin-conversion effect, here in HS state) are blue, showing the network of links mediated by perchlorate anions.

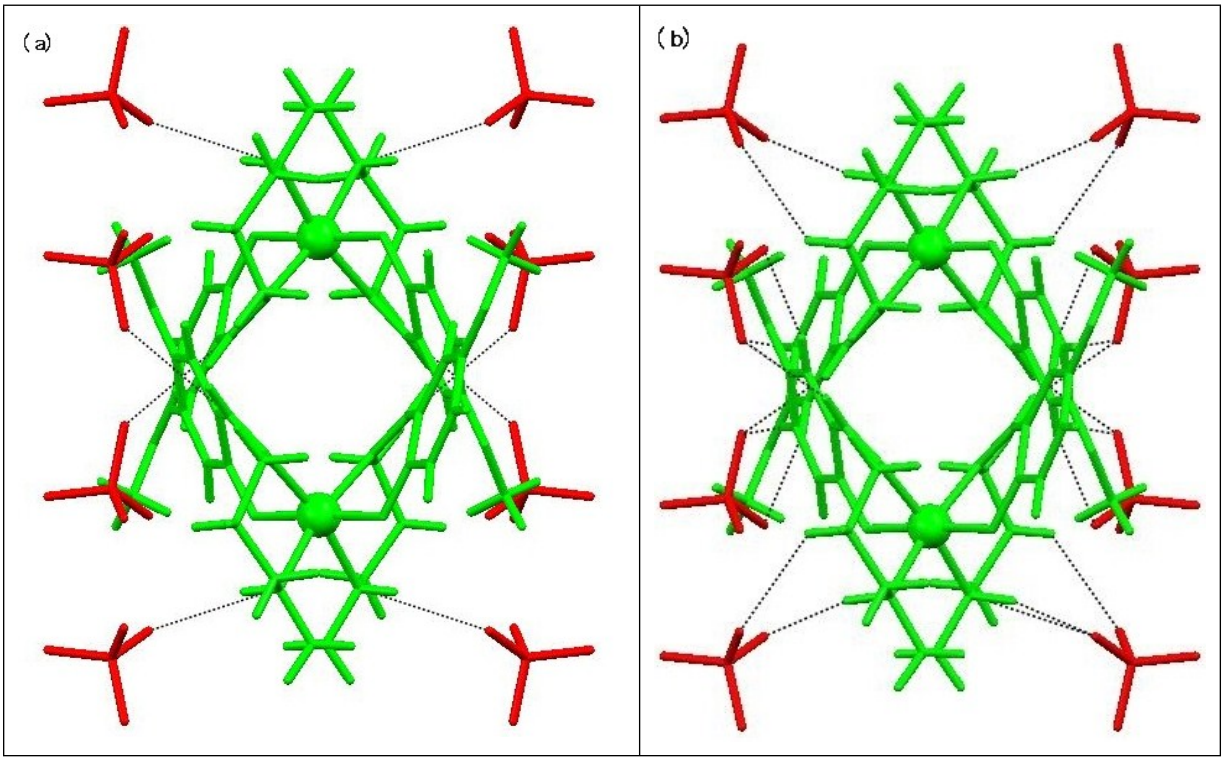

Figure S5. Crystal packing of the Mn1 units of compound **1** at (a) 293 and (b) 100 K, viewed along the *c* axis. The Mn1 units (showing the spin-conversion effect) are green, showing the network of links mediated by perchlorate anions.

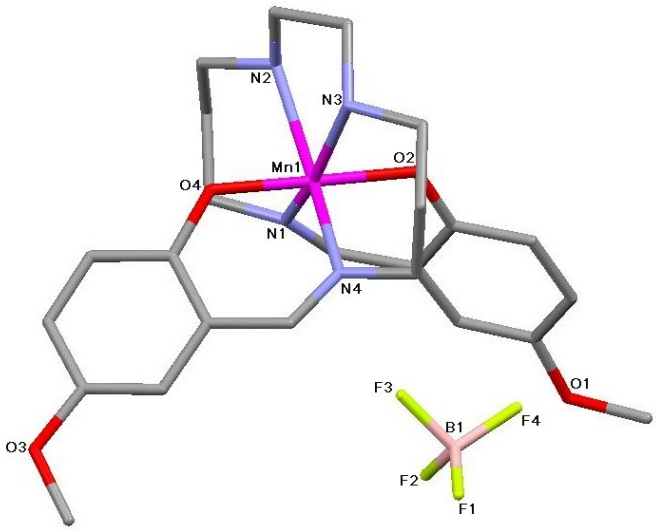

Figure S6. The molecular structure for compound **2** at 293 K, hydrogen atoms have been omitted for clarity.

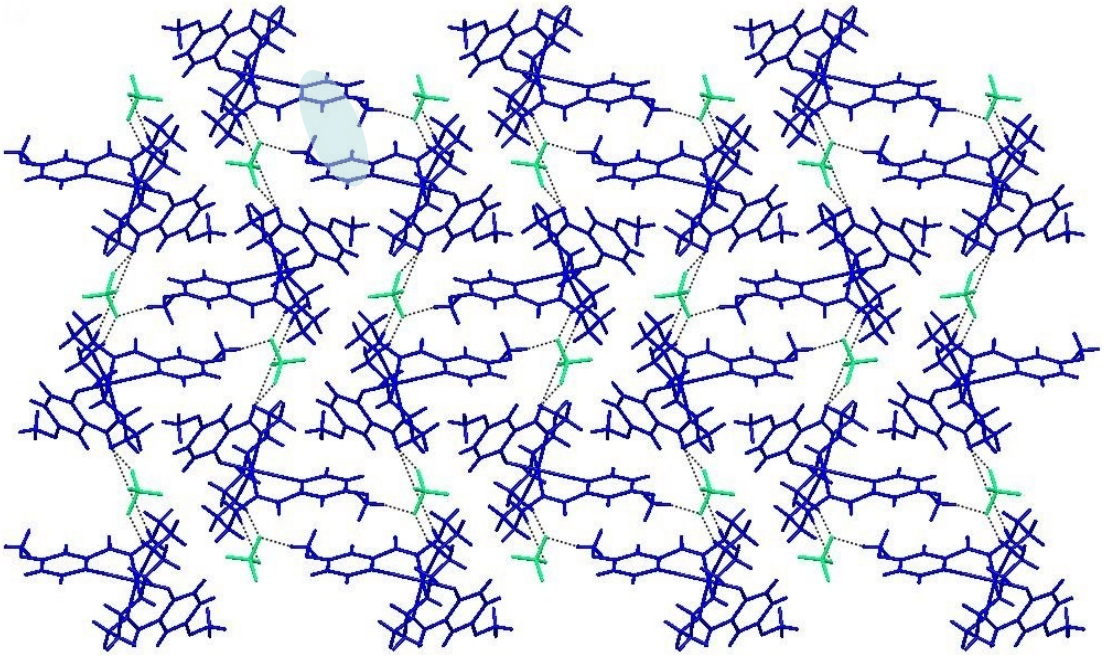

Figure S7. Crystal packing of compound **2** at 293 K, viewed along the *a* axis, showing the network of links mediated by BF_4^- anions. The stacking between phenyl groups from ligands of the neighbor cation is shown in the light blue background.

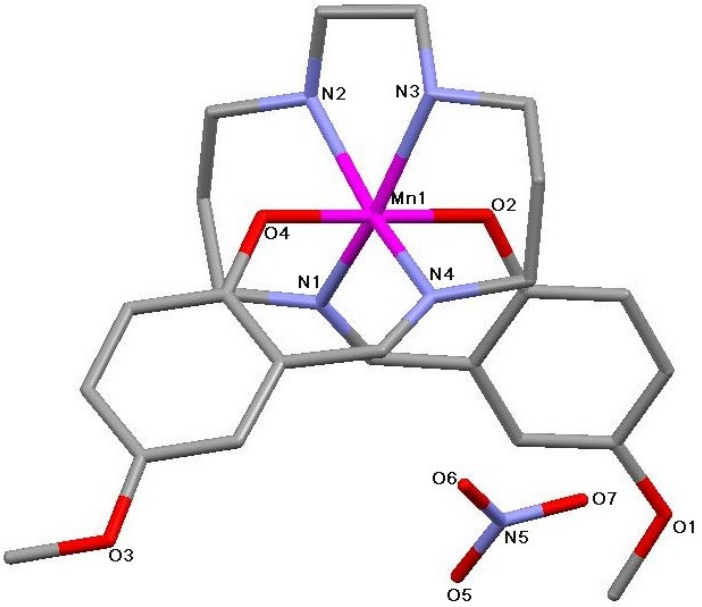

Figure S8. The molecular structure for compound **3** at 293 K, hydrogen atoms have been omitted for clarity.

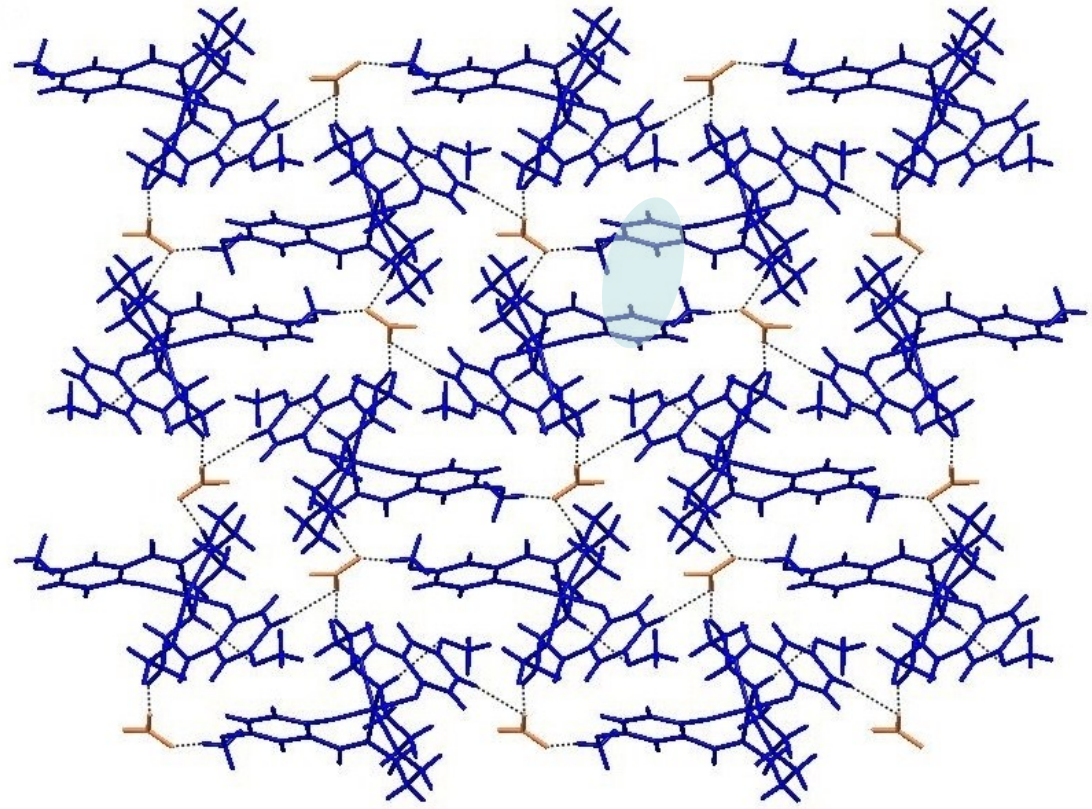

Figure S9. Crystal packing of compound **3** at 293 K, viewed along the *a* axis, showing the network of links mediated by NO_3^- anions. The stacking between phenyl groups from ligands of the neighbor cation is shown in the light blue background.

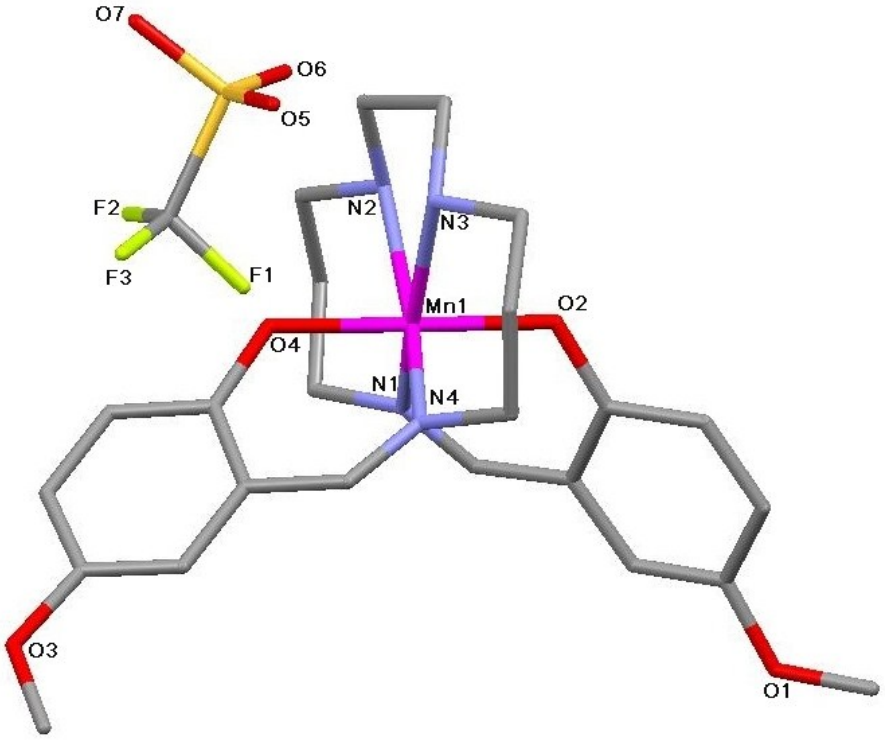

Figure S10. The molecular structure for compound **4** at 293 K, hydrogen atoms have been omitted for clarity.

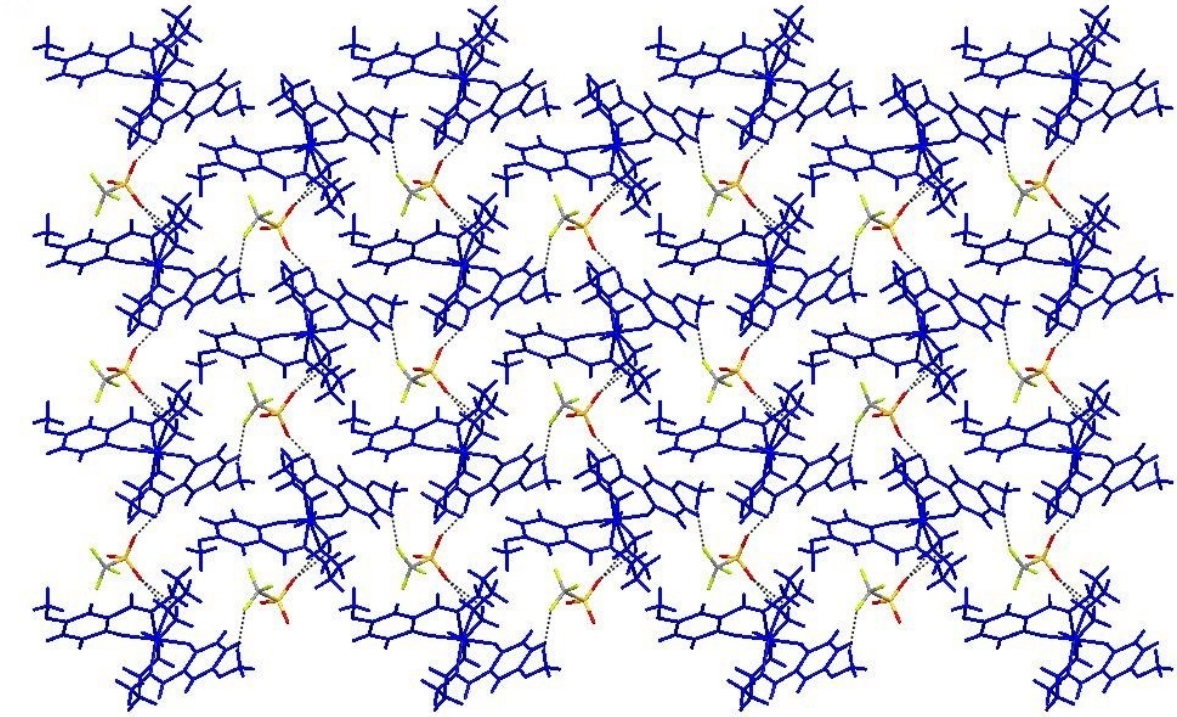

Figure S11. Crystal packing of compound **4** at 293 K, viewed along the *b* axis, showing the network of links mediated by the $CF_3SO_3^-$ anions.

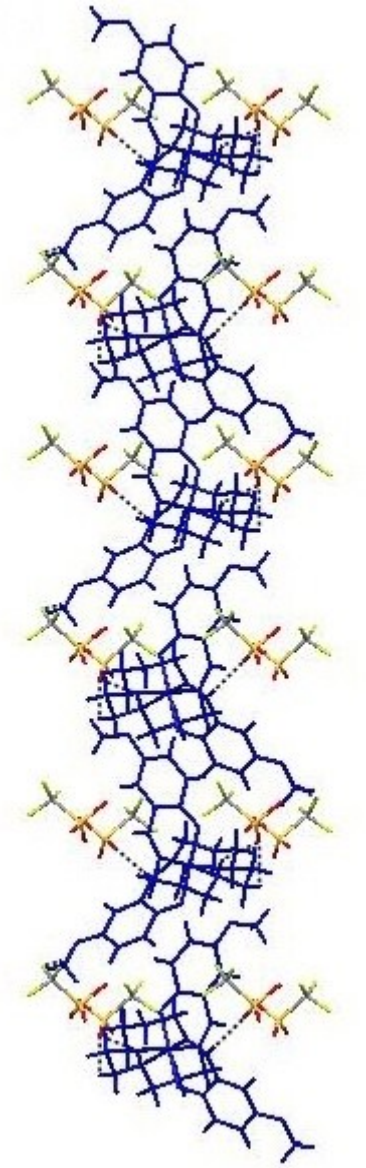

Figure S12. The chain structure of complex **4**, viewed along the *a* axis at 293 K.