Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

High Quantum Yield and Unusual Photoluminescence Behaviour in Tetrahedral Manganese (II) Based on Hybrid Compounds

Yan-Li Wei,[a] Jing Jing,[a] Chao Shi,[b] Heng-Yun Ye,[b] Zhong-Xia Wang[a] and Yi Zhang*[a,b]

[a] Ordered Matter Science Research Center, Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing 211189, P. R. China

[b] Chaotic Matter Science Research Center, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China

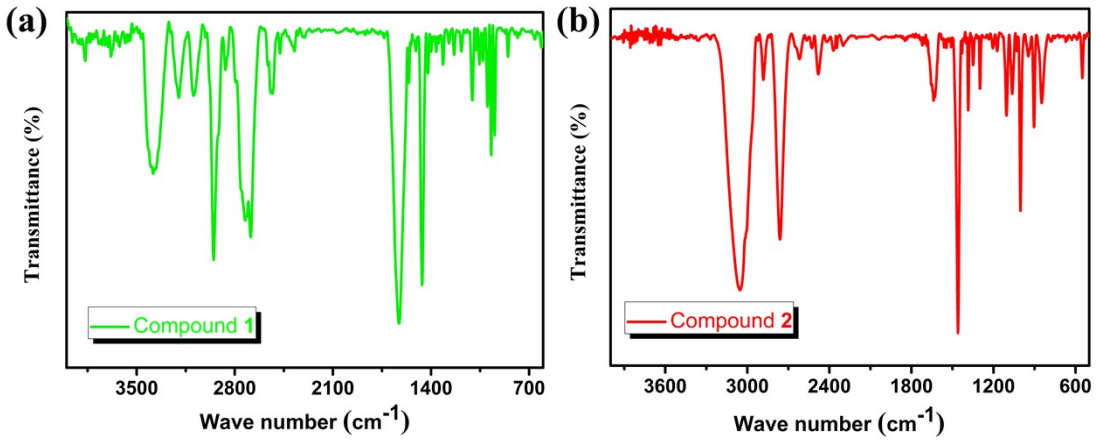


Fig. S1 Infrared (IR) spectra of solids **1** (a) and **2** (b) in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

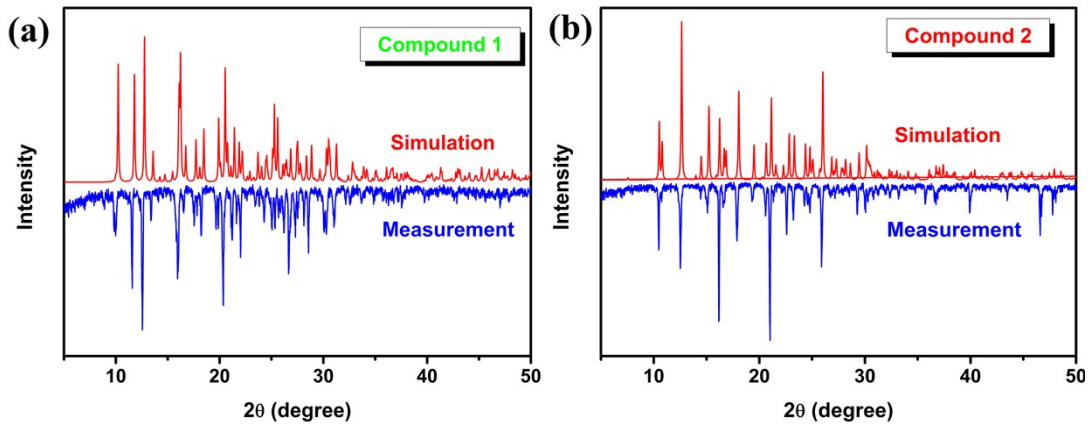


Fig. S2 Experimental powder diffraction (PXRD) patterns of compounds **1** (a) and **2** (b), which match very well with the simulated patterns in terms of the crystal structures at 293 K, respectively.

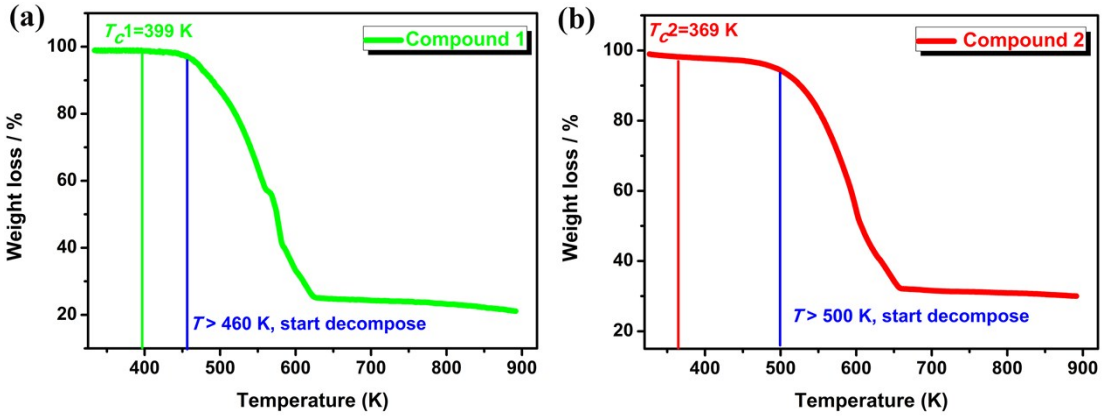


Fig. S3 TGA curves for **1** (a) and **2** (b).

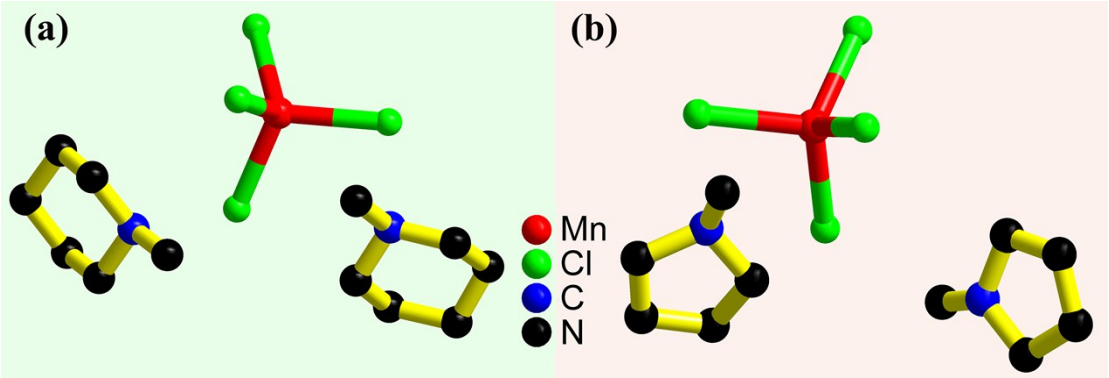


Fig. S4 The asymmetric unit of compounds **1** (a) and **2** (b).

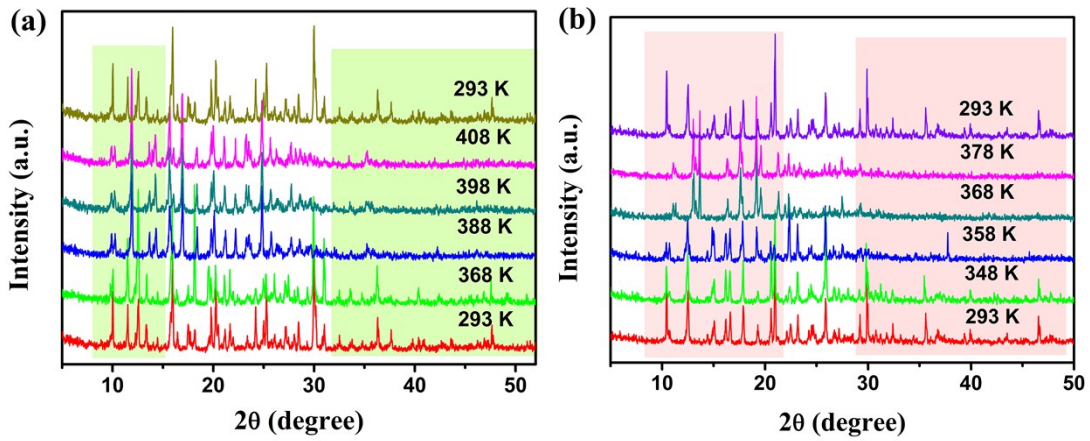


Fig. S5 Variable-temperature PXRD patterns of compounds **1** (a) and **2** (b).

Although we failed to obtain the high temperature structures of **1** and **2**, we collected cell parameters using a Rigaku CCD diffractometer with Mo-Ka radiation. The result is that the cell parameters of **1** transformed from monoclinic crystal system ($P2_1/c$) with a = 12.526(3) Å, b = 12.021(2) Å, c = 13.124(3), $\alpha = \gamma = 90.00(0)°$, β = 96.99(3)°, V=1961.5(7) in LTP to orthorhombic crystal system with a = 12.38(2) Å, b = 13.22(2) Å, c = 24.89 (4) Å, $\alpha = \beta = \gamma = 90.00(0)°$, V=4071(11) in HTP. As respect to **2**, it crystallized in the orthorhombic crystal system in both phases, but the cell parameters transformed from a = 12.0944(6) Å, b = 12.6583(6) Å, c = 23.3484(11) Å, $\alpha = \beta = \gamma = 90.00(0)°$, V=3574.5(3) in LTP to a = 9.20(4) Å, b = 13.01(6) Å, c = 15.57 (8) Å, $\alpha = \beta = \gamma = 90.00(0)°$, V=1863(15) in HTP. The change of the single crystal cell parameters were consistent with those of PXRD on polycrystalline powders **1** and **2**, which further confirmed that the high temperature unit cell parameters of **1** and **2** were valid.

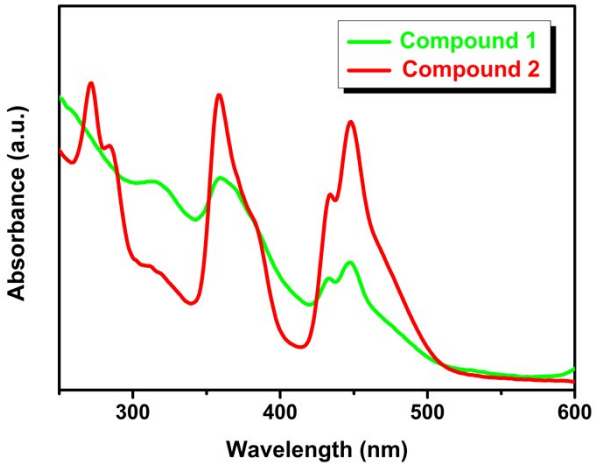
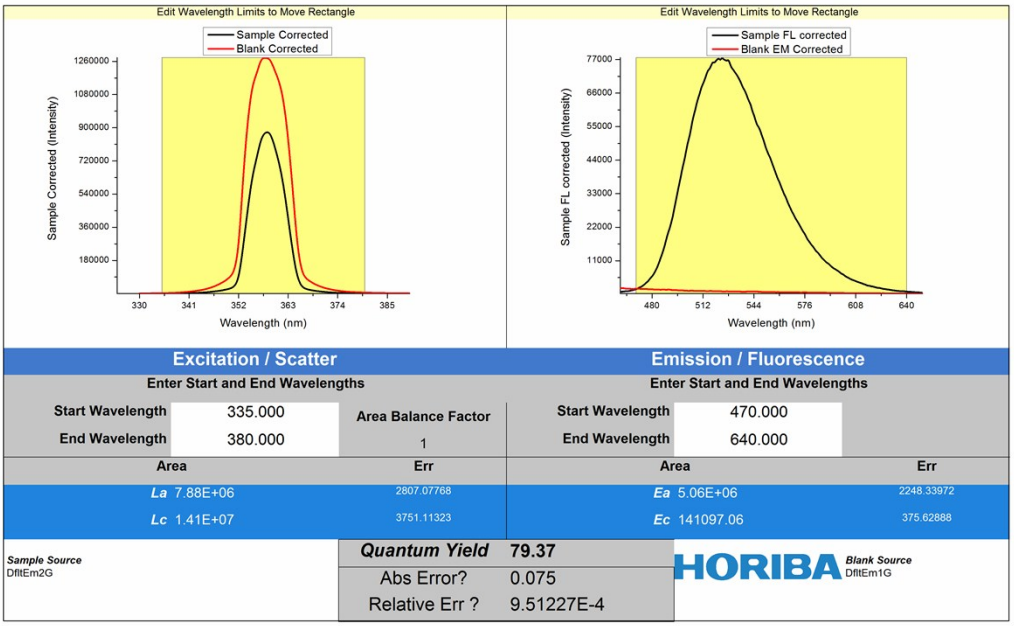


Fig. S6 The absorption spectra of compounds **1** and **2**.



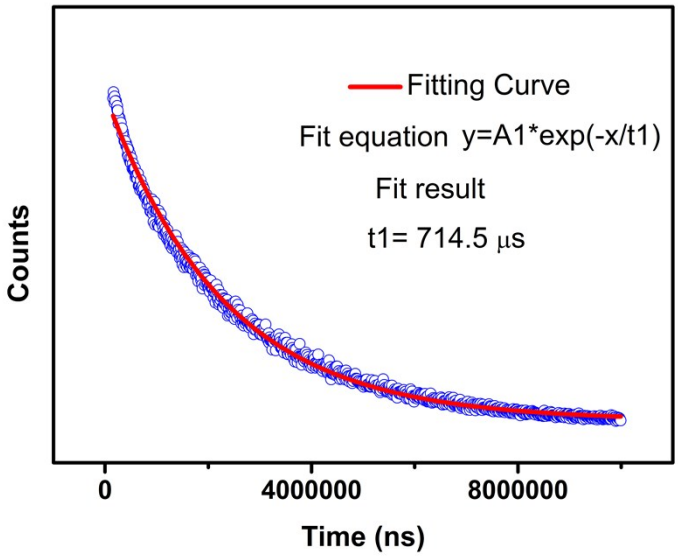
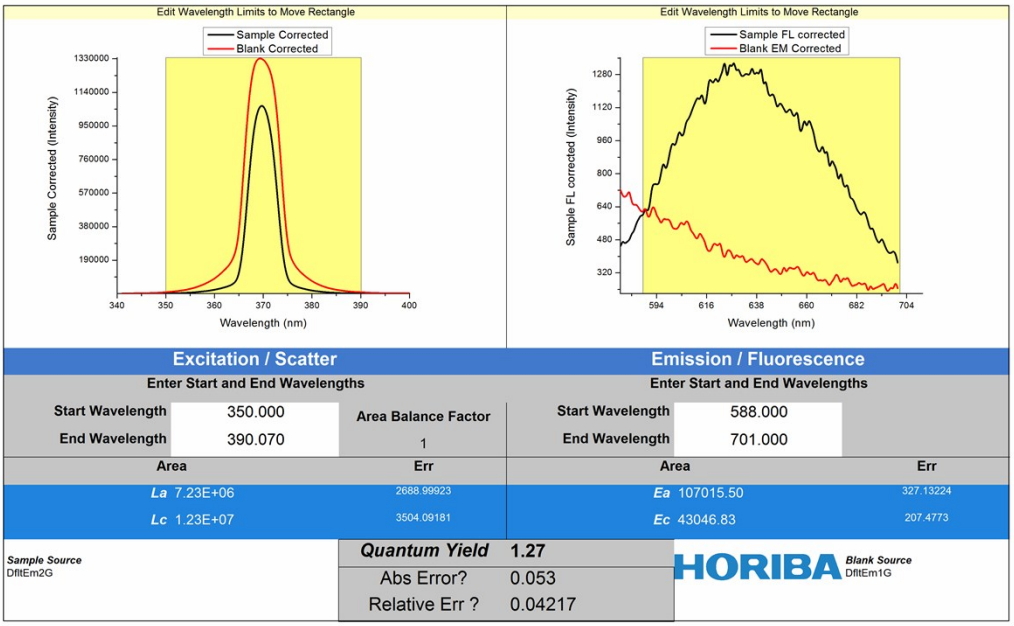


Fig. S7 The quantum yield and the lifetime of **1**.



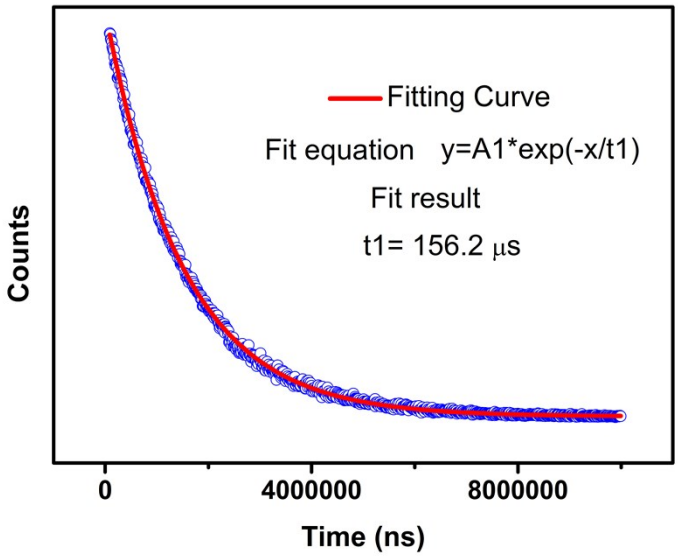


Fig. S8 The quantum yield and the lifetime of **2**.

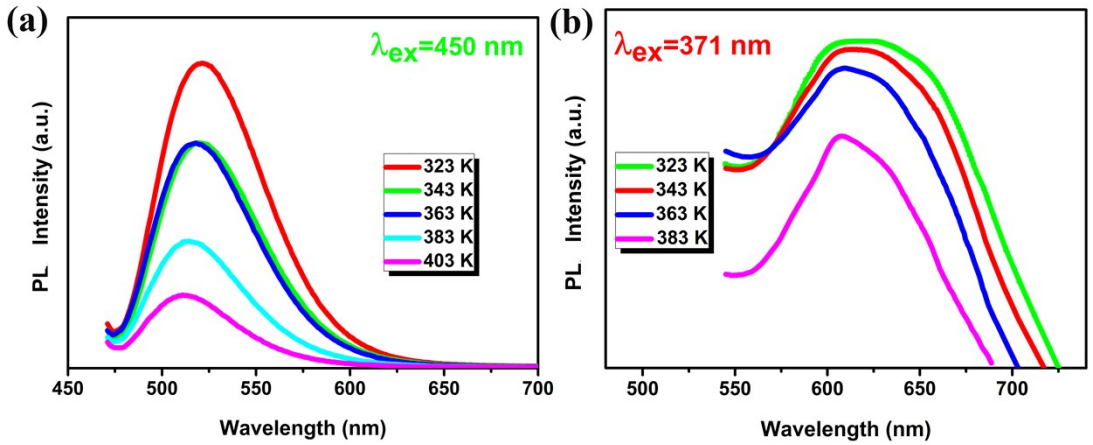


Fig. S9 Variable-temperature fluorescence spectra of **1** (a) and **2** (b).

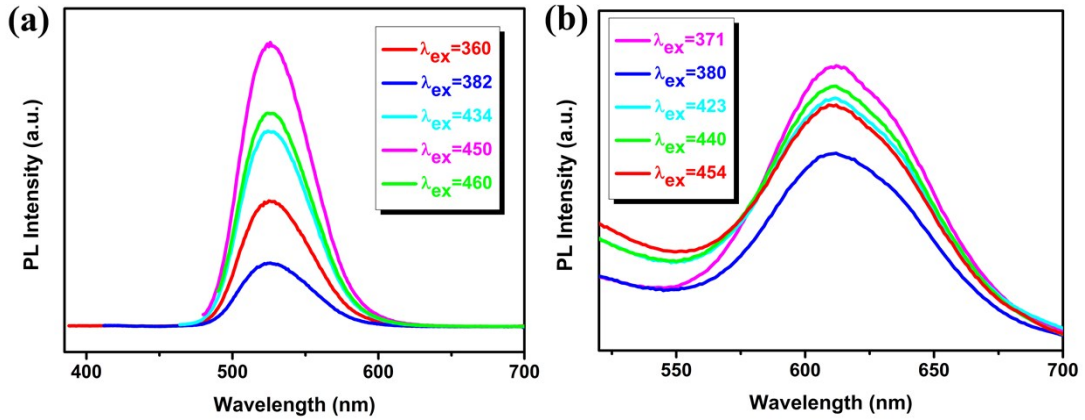


Fig. S10 The emission spectra of **1** (a) at the excitation wavelength of 360 nm, 382 nm, 434 nm, 450 nm and 460 nm and **2** (b) at 371 nm, 380 nm, 423 nm, 440 nm and 454 nm.

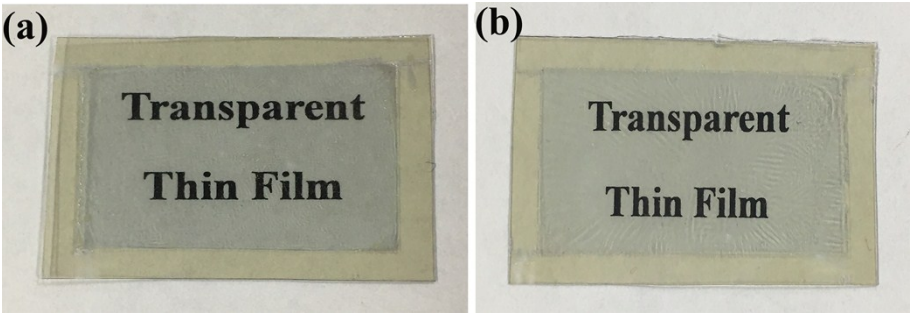


Fig. S11 Transparent thin films of **1** (a) and **2** (b) were fabricated on PET substrates plane by spin-coating method.

Table S1. Crystal data and structure refinements for compounds **1** and **2** at 293 K.

Compound	**1**	**2**
Molecular formula	$C_{12}H_{28}Cl_4MnN_2$	$C_{10}H_{24}Cl_4MnN_2$
T / K	293 K	293 K
Formula weight	397.10	369.05
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a / Å	12.526 (3)	12.0944 (6)
b / Å	12.021 (2)	12.6583 (6)
c / Å	13.124 (3)	23.3484 (11)
V / Å^3	1961.6 (7)	3574.5 (3)
Z	4	8
D_{calc} / g·cm^{-3}	1.345	1.372
μ / mm^{-1}	1.21	1.321
F (000)	828.0	1528.0
T_{min} / T_{max}	0.686 / 0.713	0.662 / 0.691
Reflns collected	13209	18550
Independent reflns	4460	3229
R_{int}	0.053	0.029
No. of parameters	172	156
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0645 / 0.0981	0.065 / 0.1770
R_1, wR_2 [all data]	0.1157 / 0.1121	0.0772 / 0.1853
GOF	1.12	1.04
$\Delta\rho$[c] / e·Å^{-3}	0.274 / -0.229	1.264 / -0.860

[a] $R_1 = \Sigma||F_o| - |F_c|| / |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2. Selected bond lengths [Å] and angles [°] for compounds **1** and **2** at 293 K.

$C_{12}H_{28}Cl_4MnN_2$			
Mn1−Cl3	2.3374 (10)	Cl3−Mn1−Cl5	115.86 (4)
Mn1−Cl5	2.3567 (11)	Cl3−Mn1−Cl4	111.32 (4)
Mn1−Cl4	2.3570 (11)	Cl5−Mn1−Cl4	104.24 (4)
Mn1−Cl2	2.3945 (11)	Cl3−Mn1−Cl2	108.13 (4)
N2−C4	1.477 (4)	Cl5−Mn1−Cl2	109.05 (4)
N2−C12	1.478 (5)	Cl4−Mn1−Cl2	107.97 (4)
N2−C13	1.496 (5)	C4−N2−C12	112.4 (3)
N1−C5	1.474 (4)	C4−N2−C13	110.8 (3)
N1−C2	1.481 (4)	C12−N2−C13	112.0 (3)
N1−C6	1.492 (4)	C5−N1−C2	111.3 (3)
C4−C7	1.510 (5)	C5−N1−C6	110.9 (3)
C2−C10	1.503 (6)	C2−N1−C6	111.4 (3)
C7−C16	1.528 (6)	N2−C4−C7	111.1 (3)

C5−C14	1.485 (6)	N1−C2−C10	110.1 (3)
C12−C15	1.483 (6)	C4−C7−C16	111.1 (4)
C9−C10	1.503 (7)	N1−C5−C14	111.2 (3)
C9−C14	1.495 (6)	C15−C12−N2	111.1 (4)
C15−C16	1.488 (7)	C10−C9−C14	110.4 (4)
		C9−C10−C2	111.4 (4)
		C5−C14−C9	112.0 (4)
		C16−C15−C12	111.0 (4)
		C15−C16−C7	110.3 (4)
$C_{10}H_{24}Cl_4MnN_2$			
Mn1−Cl4	2.3408 (16)	Cl4−Mn1−Cl5	114.20 (7)
Mn1−Cl5	2.3488 (16)	Cl4−Mn1−Cl3	113.17 (6)
Mn1−Cl3	2.3599 (14)	Cl5−Mn1−Cl3	106.05 (6)
Mn1−Cl2	2.3918 (14)	Cl4−Mn1−Cl2	106.38 (6)
C8−N2	1.457 (8)	Cl5−Mn1−Cl2	104.53 (6)
C8−C2	1.496 (10)	Cl3−Mn1−Cl2	112.29 (6)
C9−N1	1.381 (9)	N2−C8−C2	106.5 (6)
N2−C12	1.401 (9)	C12−N2−C8	118.8 (7)
N2−C1	1.501 (9)	C12−N2−C1	117.8 (7)
N1−C6	1.439 (9)	C8−N2−C1	106.2 (6)
N1−C4	1.451 (8)	C9−N1−C6	122.9 (6)
C3−C1	1.414 (11)	C9−N1−C4	122.0 (6)
C3−C2	1.510 (11)	C6−N1−C4	110.3 (6)
C6−C10	1.459 (11)	C1−C3−C2	108.8 (6)
C4−C11	1.467 (10)	C8−C2−C3	104.3 (6)
		C3−C1−N2	108.0 (6)
		N1−C6−C10	105.6 (6)
		N1−C4−C11	105.3 (6)
		C11−C10−C6	108.5 (7)
		C10−C11−C4	108.7 (7)

Table S3. Hydrogen-bond parameters (Å, °) for compounds **1** and **2** at 293 K.

	D−H···A	H···A	D···A	D−H···A
$C_{12}H_{28}Cl_4MnN_2$	N1−H1A···Cl5	2.37	3.309(3)	159.5
	N2−H2C···Cl2	2.20	3.174(3)	177.0
$C_{10}H_{24}Cl_4MnN_2$	N1−H1C···Cl3	2.69	3.651(9)	165.2
	N2−H2C···Cl2	2.35	3.330(8)	173.5