## **Supporting Information**

## ThermoinducedStructural-TransformationandThermochromicLuminescenceinOrganicManganeseChloride Crystals

Meng-En Sun, <sup>a</sup> Yao Li, <sup>a</sup> Xi-Yan Dong, <sup>a, b</sup> Shuang-Quan Zang <sup>a, \*</sup>

<sup>a</sup>College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China.

E-mail: zangsqzg@zzu.edu.cn

<sup>b</sup>College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454000,

China

## **Materials and Methods**

**Materials.** All reagents and solvents used were of commercially available reagent grade and were used without any additional purification.

## **Characterization**

Thermogravimetric analysis (TGA) of the compounds were performed on a SDT 2960

thermal analyzer from room temperature to 400°C at a heating rate of 5°C/min under

nitrogen atmosphere. UV-vis absorption spectra was recorded with a U-2000 spectrophotometer. Powder X-ray diffraction (PXRD) data were collected at room temperature in air using X'Pert PRO diffractometer (Cu K $\alpha$ ,  $\lambda = 1.54178$  Å). For better peaking, the PXRD data for the heat treated samples was de-baseline treated with X'Pert HighScore Plus. Simulated powder patterns were calculated by Mercury software using the crystallographic information file (CIF) from single-crystal x-ray experiment.

Differential Scanning Calorimeter (DSC). DSC analyses of the compound were

performed on a DSC Q25 thermal analyzer from room temperature to 150  $^\circ\!{\rm C}$  and cool

to room temperature at a heating rate of  $5^{\circ}$ C/min under nitrogen atmosphere.

Single-Crystal X-ray Diffraction Analysis (SCXRD). SCXRD measurements were performed on a Rigaku XtaLAB Pro diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.7107$  Å) at 293K for Data collection and reduction were performed using the program CrysAlisPro. The intensities were corrected for absorption using empirical method implemented in SCALE3 ABSPACK scaling algorithm. The crystal structures are visualized by DIAMOND 3.2.

**Luminescence measurements.** Luminescence microscopy images were recorded on an Olympus BX53 microscope, and measurements were carried out using a HORIBA FluoroLog-3 fluorescence spectrometer. Luminescence decay were measured on HORIBA Scientific Fluorolog-3 spectrofluorometer equipped with phosphor lamp, operating in time-correlated single photon counting mode (TCSPC) with a resolution time of 200 ps. The photoluminescent quantum efficiency in powder form was measured using an integrating sphere on a HORIBA Scientific Fluorolog-3 spectrofluorometer.



**Figure S1**. View of an individual  $[Mn_2Cl_9]^{5-}$  anion and nearest neighbor  $C_4NOH_{10}^+$  cations in compound  $(C_4NOH_{10})_5Mn_2Cl_9C_2H_5OH$  (1). N–H···Cl hydrogen-bonding interactions between  $C_4NOH_{10}^+$  and  $[Mn_2Cl_9]^{5-}$ (black dash line) the N–H···Cl (N–H···Cl angles) are 3.205 Å (147.92°), 3.198 Å (171.57°), 3.340 Å (138.89°), 3.337 Å (134.29°), 3.556 Å (128.49°), 3.287 Å (147.64°), 3.218 Å (163.40°), 3.410 Å (169.02°), 3.359 Å (111.03°), 3.217 Å (158.78°), 3.335 Å (172.82°), 3.155 Å (154.96°) and 3.278 Å (154.27°), respectively. O–H···Cl hydrogen-bonding interactions between  $[Mn_2Cl_9]^{5-}$  and  $C_2H_5OH$  (green dash line); the O–H···Cl (O–H···Cl angles) are 3.226 Å (155.42°).



**Figure S2.** X-Ray powder diffraction (PXRD) patterns of compound 1 crystals powder (blue line) and simulated from single-crystal data (red line).



Figure S3. X-Ray powder diffraction (PXRD) patterns of compound 2 crystals powder (blue line) and simulated from single-crystal data (red line).



**Figure S4.** UV-vis diffuse reflectance spectra of solid-state compounds 1 (red line), 2 (green line) and  $C_4NOH_{10}Cl$  (turquoise line).



Figure S5. Excitation spectra (monitored at 620 nm) (dotted line) and emission spectra (excited at 420 nm) (solid line) of solid-state compound 1 at R.T.. Em = Emission, Ex = Excitation. The intensity of peaks was normalized.



Figure S6. Excitation spectra (monitored at 520 nm) (dotted line) and emission spectra (excited at 430 nm) (solid line) of solid-state compound 2 at R.T.. Em = Emission, Ex = Excitation. The intensity of peaks was normalized.



Figure S7. Representative time-resolved photoluminescence decays ( $\lambda_{Ex} = 420 \text{ nm}$ ) of solid-state compound 1 at R.T..



**Figure S8**. Representative time-resolved photoluminescence decays ( $\lambda_{Ex} = 430$  nm) of solid-state compound **2** at R.T..



Figure S9. The excited wavelength-dependent emission spectra of solid-state compound 1 at R.T..



Figure S10. The excited wavelength-dependent emission spectra of solid-state compound 2 at R.T..



Figure S11. The luminescence spectra of solid-state compound 2 (black line,  $\lambda_{Ex} = 360$  nm) and thermal treated compound 1 (red line,  $\lambda_{Ex} = 360$  nm). The intensity of peaks was normalized.



Figure S12. TGA plot of compounds 1 (red line), 2 (green line) and  $C_4NOH_{10}Cl$  (turquoise line).

15.64 00.01(10)	373.00 149.99(10)
00.01(10)	149,99(10)
rtharhamhia	( - • )
	monoclinic
212121	$P2_{1}/c$
0.0363(6)	6.5440(2)
0.0218(13)	16.1548(4)
1.2177(15)	14.6769(4)
0	90
0	95.619(3)
0	90
838.8(4)	1544.14(7)
	4
.584	1.604
.326	1.539
896.0	764.0
0.71073	0.71073
.946 to 58.396	3.76 to 57.894
6494	12384
196/0/399	3588/0/154
.028	1.045
$R_1 = 0.0407, wR_2 = 0.0849$	$R_1 = 0.0225, wR_2 =$
	0.0570
$R_1 = 0.0522, wR_2 = 0.0873$	$R_1 = 0.0254, wR_2 =$
	0.0582
0.03(2)	
867428	1867436
	rthorhombic $2_12_12_1$ $0363(6)$ $0.0218(13)$ $1.2177(15)$ $0$ <t< td=""></t<>

 Table S1. Single crystal X-ray diffraction data of compounds 1 and 2 crystals.

 $R_1 = \sum ||F_0| - |F_c| \sum / ||F_0|. \ wR_2 = \left[ \sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2 \right]$ 

**Table S2**. Atomic positions of compound 1. All non-hydrogens were refined with anisotropic displacement parameters, while the hydrogens were refined with isotropic displacement parameters.

Atom	X	у	Z	U(eq)
Mn1	1756.0(8)	4200.3(4)	6848.2(4)	10.45(17)
Mn2	1501.7(8)	2489.6(4)	6924.7(4)	10.61(17)
Cl1	2122.0(14)	4851.1(6)	7849.2(6)	13.8(3)
Cl2	-203.3(13)	4986.5(6)	6508.0(6)	13.2(3)
Cl3	3845.0(14)	4734.7(6)	6247.3(6)	14.8(3)
Cl4	-161.5(13)	3401.3(6)	7373.0(5)	12.0(2)

Cl5	3575.2(13)	3309.7(6)	3309.7(6) 7226.7(5)	
Cl6	1465.4(13)	3299.5(6)	5896.5(5)	12.3(2)
Cl7	1800.7(14)	1910.5(6)	7980.0(6)	14.3(3)
C18	-567.7(14)	1770.1(6)	6617.2(6)	15.2(3)
C19	3566.4(13)	1799.0(5)	6407.6(6)	12.4(2)
01	2969(4)	3087.3(19)	9837.2(17)	21.4(9)
O2	-3366(4)	4449.7(18)	8428.5(18)	24.0(9)
O3	2253(4)	5121.0(18)	4564.3(18)	19.5(9)
O4	7624(4)	3511.0(19)	5219.1(17)	19.4(9)
05	-3629(4)	2321.2(18)	8460.0(18)	22.6(9)
O6	-4518(5)	5563(2)	5145.5(19)	29.6(10)
N1	2269(4)	3441(2)	8570.3(19)	11.6(9)
N2	-1877(5)	5461(2)	7734(2)	18.8(10)
N3	267(5)	4035(2)	4660(2)	14.0(9)
N4	5064(5)	3160(2)	5917(2)	13.7(9)
N5	-1864(5)	1261(2)	7983(2)	15.9(10)
C1	1485(6)	3040(3)	9613(3)	21.4(12)
C2	1187(6)	3531(2)	9090(2)	14.6(11)
C3	3816(5)	3458(3)	8814(2)	13.3(11)
C4	3998(6)	2955(3)	9338(2)	19.0(12)
C5	-3680(6)	4544(3)	7777(3)	25.6(14)
C6	-3441(6)	5258(3)	7590(3)	20.7(12)
C7	-1490(6)	5302(3)	8402(2)	17.5(11)
C8	-1829(6)	4584(3)	8541(3)	19.5(12)
C9	1074(6)	5132(3)	5016(2)	17.0(11)
C10	-229(6)	4734(3)	4782(3)	15.1(11)
C11	1571(6)	4016(3)	4224(2)	17.1(11)
C12	2769(6)	4451(3)	4481(3)	18.3(12)
C13	6199(6)	3546(3)	4933(3)	19.6(12)
C14	5159(6)	3041(3)	5226(2)	18.6(12)
C15	6561(6)	3168(2)	6216(2)	15.9(11)
C16	7520(6)	3666(3)	5875(2)	16.6(11)
C17	-2128(6)	2247(3)	8646(3)	19.6(12)
C18	-1662(6)	1519(2)	8634(2)	18.8(12)
C19	-3409(6)	1370(3)	7758(3)	20.1(12)
C20	-3816(7)	2100(3)	7823(3)	23.4(13)
C21	-3473(7)	5819(3)	5581(3)	22.5(12)
C22	-2369(6)	6228(3)	5220(3)	23.0(13)

Atom	X	у	Z	U(eq)
Mn1	-4397.5(3)	6625.5(2)	2758.6(2)	18.08(7)
Cl1	-5535.5(6)	6413.6(2)	1200.3(2)	28.64(9)
Cl2	-707.1(5)	6713.3(2)	2852.8(2)	21.94(8)
C13	-5205.1(5)	5468.0(2)	3648.9(2)	20.79(8)
Cl4	-5451.0(5)	7819.8(2)	3491.3(3)	28.33(9)
01	-333.9(14)	4185.2(6)	657.7(6)	19.4(2)
02	450.5(14)	3946.5(6)	4133.2(7)	24.3(2)
N1	599.8(17)	4763.1(7)	2487.6(8)	19.7(2)
N2	-1012.5(18)	2579.0(7)	5097.4(8)	22.9(3)
C1	1715(2)	4424.8(9)	989.0(9)	20.2(3)
C2	2108(2)	4276.7(9)	2001.5(9)	21.3(3)
C3	-1544(2)	4555.8(9)	2110.2(10)	22.5(3)
C4	-1772(2)	4682.1(9)	1088.5(10)	22.0(3)
C5	1834(2)	3309.3(9)	4474.8(11)	26.6(3)
C6	748(2)	2491.7(9)	4526.1(11)	26.4(3)
C7	-2390(2)	3270.0(9)	4749.7(11)	23.6(3)
C8	-1151(2)	4050.2(9)	4724.0(10)	23.5(3)

**Table S3**. Atomic positions of compound **2**. All non-hydrogens were refined with anisotropic displacement parameters, while the hydrogens were refined with isotropic displacement parameters.

Table S4. Selected bond lengths (Å) and bond angles (°) for compounds 1 and 2.

(C.	4NOH10)5N	/In <sub>2</sub> Cl <sub>10</sub> ·EtOH	(1)		(C <sub>4</sub> NOF	$I_{10}$ ) <sub>2</sub> MnCl <sub>4</sub> ( <b>2</b>	)
Bond len	Sond lengths (Å) Bond Angles (°)		Bond lengths (Å)		Bond Angles (°)		
Mn1-Cl1	2.5137(14)	Cl1-Mn1-Cl3	96.25(5)	Mn1-Cl1	2.3600(4)	Cl1-Mn1-Cl2	106.469(15)
Mn1-Cl2	2.4765(14)	Cl1-Mn1-Cl4	92.56(5)	Mn1-Cl2	2.4096(4)	Cl1-Mn1-Cl3	110.705(15)
Mn1-Cl3	2.5167(14)	Cl1-Mn1-Cl5	90.66(4)	Mn1-Cl3	2.3703(4)	Cl3-Mn1-Cl2	106.926(14)
Mn1-Cl4	2.6080(14)	Cl1-Mn1-Cl6	169.63(5)	Mn1-Cl4	2.3450(4)	Cl4-Mn1-Cl1	118.994(16)
Mn1-Cl5	2.5548(13)	Cl2-Mn1-Cl1	90.62(5)			Cl4-Mn1-Cl2	105.264(14)
Mn1-Cl6	2.7201(14)	Cl2-Mn1-Cl3	96.80(5)			Cl4-Mn1-Cl3	107.750(15)
Mn2-Cl4	2.5487(14)	Cl2-Mn1-Cl4	92.26(5)				
Mn2-Cl5	2.5725(14)	Cl2-Mn1-Cl5	174.41(5)				
Mn2-Cl6	2.7184(13)	Cl2-Mn1-Cl6	97.82(4)				
Mn2-Cl7	2.5360(14)	Cl3-Mn1-Cl4	167.28(5)				
Mn2-Cl8	2.4489(14)	Cl3-Mn1-Cl5	88.47(5)				
Mn2-Cl9	2.5681(13)	Cl3-Mn1-Cl6	88.75(4)				
		Cl4-Mn1-Cl6	81.15(4)				
		Cl5-Mn1-Cl4	82.25(4)				
		Cl5-Mn1-Cl6	80.37(4)				
		Cl4-Mn2-Cl5	83.07(4)				
		Cl4-Mn2-Cl6	82.25(4)				
		Cl4-Mn2-Cl9	166.75(5)				
		Cl5-Mn2-Cl6	80.09(4)				
		Cl7-Mn2-Cl4	93.48(5)				
		Cl7-Mn2-Cl5	89.67(4)				
		Cl7-Mn2-Cl6	169.29(5)				
		Cl7-Mn2-Cl9	93.08(4)				
		Cl8-Mn2-Cl4	94.04(5)				
		Cl8-Mn2-Cl5	176.35(5)				
		Cl8-Mn2-Cl6	97.35(5)				
		Cl8-Mn2-Cl7	92.73(5)				
		Cl8-Mn2-Cl9	97.14(5)				
		Cl9-Mn2-Cl5	85.47(4)				
		Cl9-Mn2-Cl6	89.26(4)				
		Mn1-Cl5-Mn2	84.18(4)				
		Mn2-Cl4-Mn1	83.58(4)				
		Mn2-Cl6-Mn1	84.18(4)				

$(C_4 \text{NOH}_{10})_5 \text{Mn}_2$	$Cl_{10}$ ·EtOH (1)	$(C_4 NOH_{10})_2 MnCl_4$ (2)		
Excitation	Lifetime	Excitation	Lifetime	
wavelength (nm)	(ms)	wavelength (nm)	(ms)	
360	4.74	350	3.34	
380	4.61	380	3.36	
420	4.84	400	3.32	
440	4.82	430	3.36	
500	4.78	470	3.35	
530	4.83	490	3.31	

 Table S5. The excited wavelength-dependent emission decay time for compounds 1 and 2.