Electronic Supplementary Information

Functionalized triphenylphosphine oxide-based manganese(II) complexes for luminescent printing

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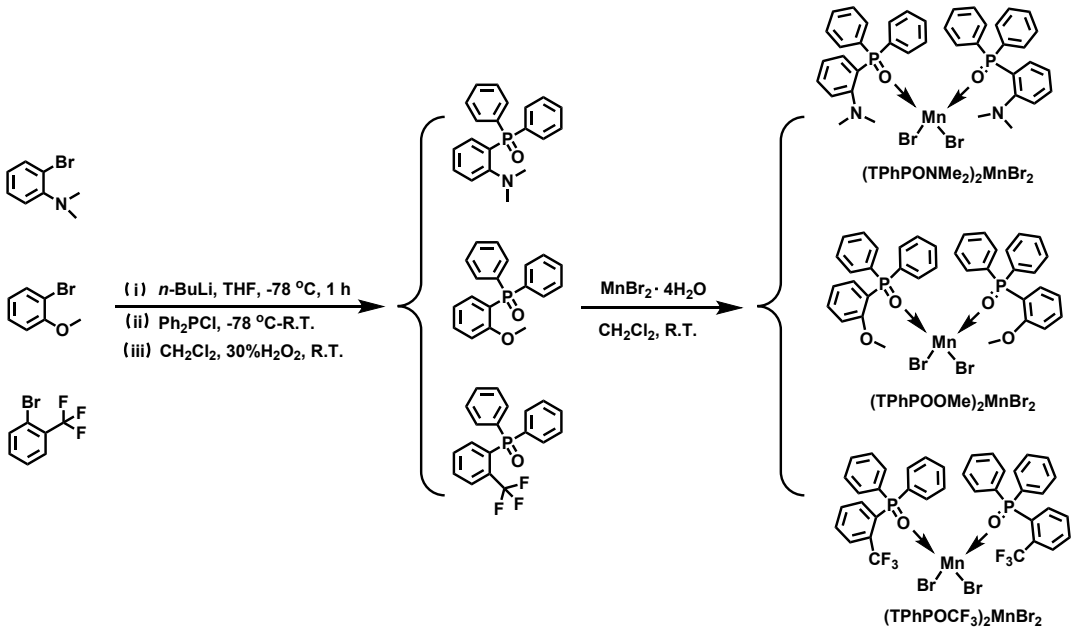

Scheme S1. The synthetic routes for neutral manganese(II) complexes ($(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$)).

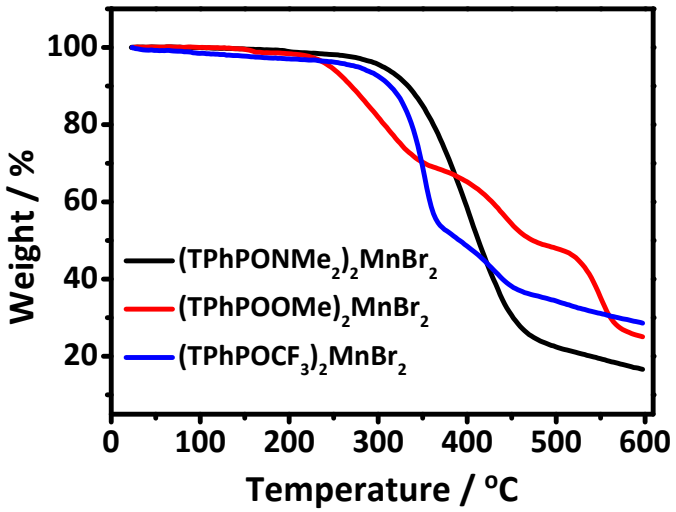

Fig. S1. The TGA curves of complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$ recorded at a heating rate of 10 °C min^{-1}.

Thermal stability. Thermogravimetric analysis (TGA) curves showed that the decomposition temperatures (T_d) of $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$ were 304.6 °C, 247.1 °C, and 277.2 °C, respectively. The high T_d values indicated that these neutral manganese complexes possessed high thermal stability.

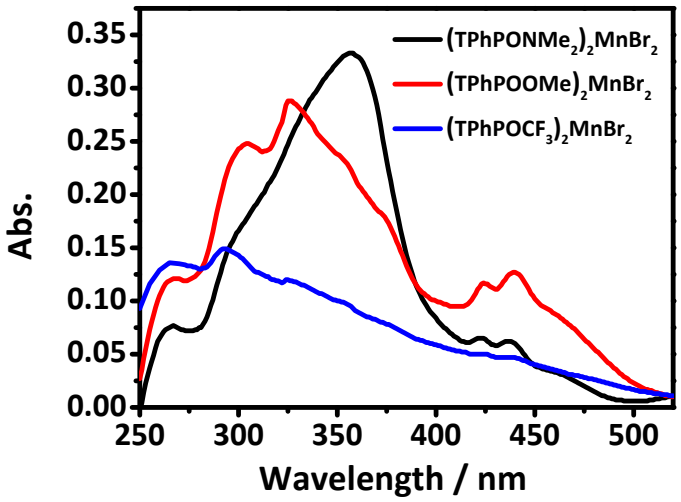

Fig. S2. The UV-vis absorption of complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$ in solid state at room temperature.

Absorption spectra. They share the similar UV-vis absorption spectra in solids with wide absorption range from 250 to 480 nm, including intra-ligand π-π* transitions (below 300 nm), typical intra-configurational *d–d* electron transition of Mn(II) in tetrahedral environment from quartet states ^4E, $^4A_1$ (G) and ^4E (D) to ground state $^6A_1$ (S) (320-480 nm).

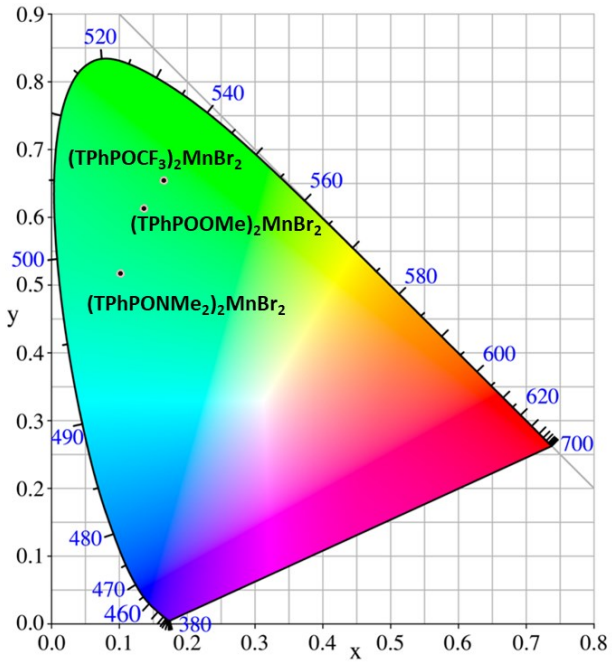

Fig. S3. The 1931 Commission Internationale de L'Eclairage (CIE) chromaticity diagram of complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$.

CIE 1931 chromaticity diagram. The CIE coordinates were used to indicate the emission color changes of manganese(II) complexes by varying the substituents. The emission color changed from (0.102, 0.517) to (0.137, 0.614) and (0.166, 0.655).

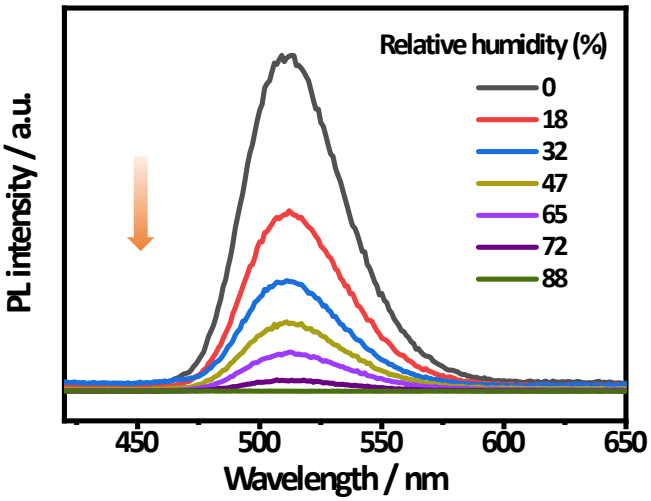

Fig. S4. The PL spectral changes of $(TPhPOCF_3)_2MnBr_2$ films at various humidity under 300 nm excitation.

Moisture sensitivity. The PL intensity decreased significantly when the relative humidity (RH) increased. At high RH of 88%, the emission of complex was fully quenched, indicating the destruction of coordination environmental caused by water.

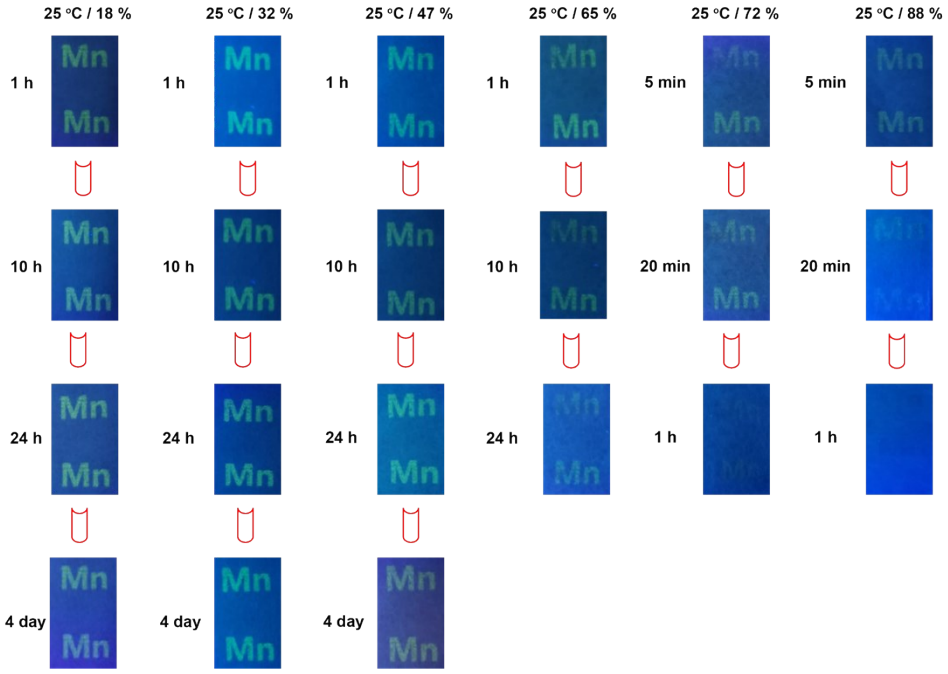

Fig. S5. The luminescent “Mn” characters on security paper at various humidity of 18%, 32%, 47%, 65%, 72%, and 88% for different time at room temperature.

Moisture sensitivity. The luminescent “Mn” characters kept almost unchanged for 4 days under the 47% humidity. Although the luminescent characters of “Mn” became a little blurry when the security paper was stored under the 65% humidity for 1 days, it can also be clearly discerned by naked-eyes. However, when the security paper was stored at 72% and 88% humidity for 1 h, the luminescence of “Mn” characters was fully quenched. These results indicated that the recorded information on security paper can be retained for a long time at a relatively high humidity.

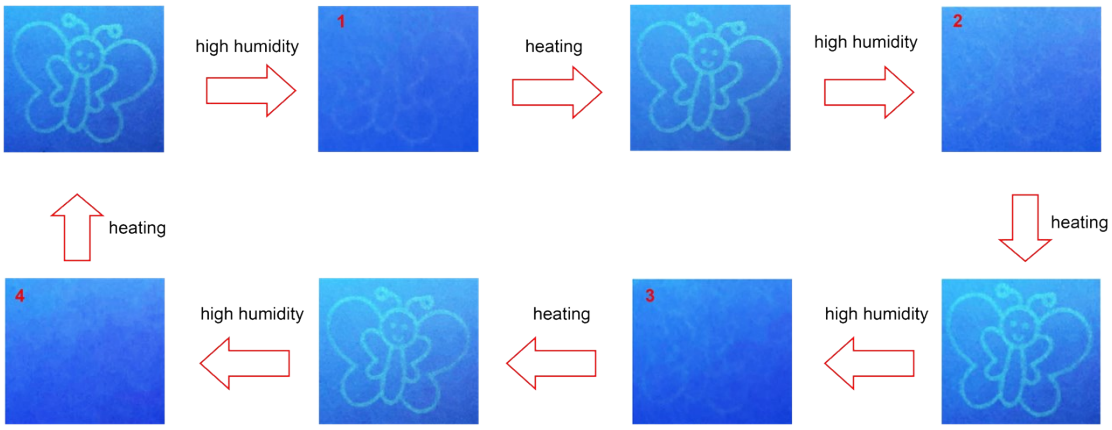

Fig. S6. The reversible luminescence quenching and recovering experiments of manganese(II) complexes on paper under 72% humidity.

Moisture sensitivity. The printed information disappeared under 72% humidity, which will benefit the information protection, and further recovered after heating with a blower for about 3 min. This kind of reversible information protection method is favorable. More importantly, this luminescence quenching and recovering experiments could be repeatable for multiple cycles without notable changes by the naked eye. The result indicates that moisture does not limit the application.

Table S1. Crystallographic data for complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$.

Complex	$(TPhPONMe_2)_2MnBr_2$	$(TPhPOOMe)_2MnBr_2$	$(TPhPOCF_3)_2MnBr_2$
CCDC	2056436	2056437	2056435
Formula	$C_{40}H_{40}Br_2MnN_2O_2P_2$	$C_{38}H_{34}Br_2MnO_4P_2$	$C_{38}H_{28}Br_2F_6MnO_2P_2$
Formula weight	857.44	831.35	907.33
Temperature (K)	299.24	301.27	300,35
Radiation (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	16.8598(17)	18.152(5)	11.8485(17)
b (Å)	12.7324(13)	11.553(3)	14.0394(19)
c (Å)	18.1108(16)	18.905(5)	23.466(4)
β (°)	93.791(3)	109.307(7)	98.906(4)
V (Å^3)	3879.3(7)	3741.7(17)	3856.4(10)
Z	4	4	4
$\rho_{(calc)}$ (g/cm^3)	1.468	1.476	1.5627
F (000)	1740.0	1676.0	1804.9
μ(mm^{-1})	2.519	2.611	2.558
Reflections collected	34366	33268	33678
R(int)	0.0486	0.0914	0.0512
GOF	1.012	1.019	1.119
R_1/wR_2 [$I>2\sigma(I)$]	0.0407, 0.0862	0.0509, 0.1134	0.0543, 0.1198
R_1/wR_2 (all data)	0.0835, 0.1020	0.0992, 0.1336	0.0954, 0.1471

Table S2. The selected bond lengths and angles of complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$.

Complex	$(TPhPONMe_2)_2MnBr_2$		$(TPhPOOMe)_2MnBr_2$		$(TPhPOCF_3)_2MnBr_2$	
Bond lengths(Å)	Br1-Mn1	2.4911(6)	Br1-Mn1	2.4654(8)	Br1-Mn1	2.4720(8)
	Br2-Mn1	2.4815(6)	Br2-Mn1	2.4896(8)	Br2-Mn1	2.4658(8)
	Mn1-O1	2.0166(19)	Mn1-O1	2.036(2)	Mn1-O1	2.045(3)
	Mn1-O2	2.037(2)	Mn3-O2	2.040(2)	Mn1-O2	2.008(3)
Bond angles (°)	Br2-Mn1-Br1	116.39(2)	Br1-Mn1-Br2	115.53(3)	Br2-Mn1-Br1	115.00(3)
	O1-Mn1-Br1	104.70(6)	O1-Mn1-Br1	107.64(7)	O1-Mn1-Br1	108.46(8)
	O1-Mn1-Br2	111.31(6)	O1-Mn1-Br2	113.57(8)	O1-Mn1-Br2	108.90(8)
	O1-Mn1-O2	105.26(8)	O1-Mn1-O2	102.55(11)	O2-Mn1-Br1	102.66(9)
	O2-Mn1-Br1	108.12(6)	O2-Mn1-Br1	110.33(8)	O2-Mn1-Br2	116.67(10)
	O2-Mn1-Br2	110.36(6)	O2-Mn1-Br2	106.43(8)	O2-Mn1-O1	104.38(12)

Table S3. The intra-/inter-molecular interactions of complexes $(TPhPONMe_2)_2MnBr_2$, $(TPhPOOMe)_2MnBr_2$, and $(TPhPOCF_3)_2MnBr_2$ existed in crystal.

$(TPhPONMe_2)_2MnBr_2$	$(TPhPOOMe)_2MnBr_2$	$(TPhPOCF_3)_2MnBr_2$
C—H···π	C—H···π	C—F···π
2.990 Å	2.980 Å	3.326 Å
2.760 Å		3.491 Å
2.940 Å		3.662 Å
2.960 Å		3.442 Å
2.980 Å		