Supporting Information

Designing aromatic moiety-free neutral luminescent manganese(II) halide scintillator for efficient X-ray imaging

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General Experimental Information

All solvents were used after distillation and stored over activated molecular sieves (5 Å). All reagents and chemicals were purchased from commercial sources and used without further purification. Steady-state emission experiments were measured on an Edinburgh FLS1000 spectrometer. Excited-state lifetime studies were performed with an Edinburgh FLS1000 spectrometer with a hydrogen-filled excitation source. The data were analyzed by a software package provided by Edinburgh Instruments. The absolute quantum yield of the complex was determined through an absolute method by employing an integrating sphere attached in FLS 1000 spectrometer.

The single crystals of **TPPOMnBr$_2$** were obtained by slowly evaporating the mixed solvents of CH$_2$Cl$_2$ and ethanol at room temperature. The X-ray diffraction data were collected on a Bruker D8 Venture Smart CCD Apex DUO diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) using the ω-2θ scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXT software. All calculations and molecular graphics were carried out on a computer using the SHELXT program package, Mercury and VESTA software. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference number for **TPPOMnBr$_2$** were 2336965. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +441223336033; E-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk).

Synthesis

Materials: Tri(pyrrolidin-1-yl)phosphine oxide (TPPO) (99.9%) was purchased from Bide pharmatech ltd. (Shanghai, China), $MnBr_2 \cdot 4H_2O$ (98%) was purchased from Sigma-Alrich (Shanghai, China). CH_2Cl_2 (99.9%) and EtOH (99.9%) was purchased from Energy Chemical (Shanghai, China).

TPPOMnBr₂: TPPO (2.0 g, 0.008 mmol) was dissolved in CH_2Cl_2 (30 mL) and $MnBr_2 \cdot 4H_2O$ (1.12 g, 0.004 mmol) was dissolved in EtOH (20 mL). Then they were mixed and the mixture was stirred for 12 h at room temperature. After that, the solution was removed under reduced pressure, and the single crystals suitable for SC-XRD were cultured using CH_2Cl_2 and EtOH. The synthetic yield of the complex is 80%.
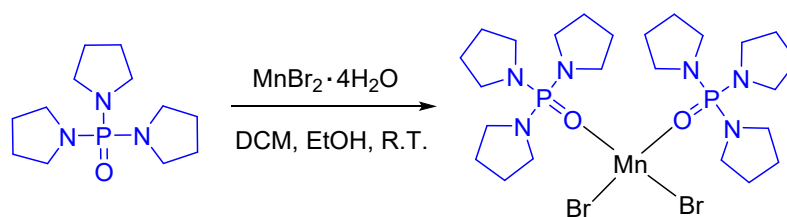
Scheme S1. Synthesis of **TPPOMnBr₂**.

Computational Methods: The first-principles calculation for the electronic structure of the complex was carried out by CASTEP, a package based on plane-wave pseudopotential density functional theory (DFT). The exchange-correlation terms in the Hamiltonian were described by the function developed by Ceperley, Alder, Perdew, and Zunger (CAPZ) in the form of local density approximation (LDA). The effective interaction between the atomic cores and valence electrons were treated by ultrasoft pseudopotentials, which allow us to employ a relatively small plane-wave basis set without compromising the computational accuracy. The kinetic energy cut off at 550 eV and intensive Monkhorst−Pack k-point mesh spanning less than $0.04/Å^3$ were chosen. To account for the effect of the delocalized d-orbitals in manganese atoms, the LDA+U method was adopted in the calculation with the UD set to 4.0 eV.

X-Ray Scintillation Characterization: The RL spectra were recorded by a QE PRO fiber-coupled fluorescence spectrometer with a Mini-X2 X-ray tube (target material: Au, P_{max} = 4 W, V_{max} = 50 kV, I_{max} = 70 μA, Amptek) as the X-ray source. The X-ray dose rates were altered by adjusting the current of the X-ray tube from 5 to 70 μA. The dose rates under different conditions were calibrated

using an X-ray ion chamber dose meter (Radcal Accu-DOSE$^+$, 10X6^{-60}).

The imaging pictures were recorded by X-ray system by manual assembly. The system consists of a Mini-X2 X-ray tube, a lens, a stage and a Nikon D850 camara. During the imaging, X-ray tube was used under an operating voltage of 50 kV and current of 70 μA. Then the imaging picture was recorded by controlling the camera exposure time to obtained clear photos.

Fabrication of Scintillation Film: The **TPPOMnBr$_2$** crystals were hand-grounded to fine powders and passed through a 200-mesh sieve to obtain a uniform ultrafine powder sample. The poly(methyl methacrylate) (PMMA) was dissolved in dry toluene at 50 °C, then the **TPPOMnBr$_2$** powder and PMMA were added into the solution at a mass ratio of 1:1 and the mixture was stirred for 12 h at room temperature. After that, the mixed solution was dropwise added onto a 3 cm × 3 cm polytetrafluoroethylene (PTFE) mold and slowly evaporated to remove toluene for 12 h at 30 °C to obtain a PMMA film suitable for X-ray imaging.

X-Ray Light Yield Measurements: The X-ray relative light yield in this work was measured by using commercial LuAG:Ce as a reference. The sample (about 100 μm in size) of **TPPOMnBr$_2$** crystal and the reference scintillator (LuAG:Ce) were set at the same position to measure the XEL spectra. The corresponding photon counting results (PC$_{measured}$) were then obtained by integrating the steady-state XEL spectra. Compared with reference LuAG:Ce,

the corresponding relative light yield was calculated according to equation (1) and (2). The equations were given as follows:

$$PC_{normalized} = \frac{PC_{measured}}{AE(d)} \quad (1)$$

$$LY_s = LY_{LUAG:Ce}\frac{PC_{normalized}(S)}{PC_{normalized}(LUAG:Ce)} \quad (2)$$

where $LY_{LuAG:Ce}$ is the light yield of LuAG:Ce (22000 photons MeV^{-1}), $PC_{normalized}$ (S) and PCnormalized (LuAG:Ce) are the photon counts of our sample and LuAG:Ce normalized to respective X-ray attenuation efficiencies.

MTF Measurements: The MTF is used to characterize the reproduction capability of the imaging contrast, defined as the ratio of the difference between the maximum and minimum gray degrees and the sum of the minimum gray scale in the image. Here, the slanted-edge method was used to calculate MTF curve. A thin tungsten sheet (1 mm) with a sharp edge was placed on top of the film, tilted about 10~20°, and an image of the tilted edge was obtained by the X-ray imaging system. According to the slanted edge contour of the image, the edge spread function (ESF) was derived in Matlab2021, and then the ESF was differentiated to obtain LSF, and its Fourier transform was carried out. The MTF can be calculated by the following equation:

$$MTF(v) = F(LSF(x)) = \frac{d(ESF(x))}{dx)} \quad (3)$$

where v is the spatial frequency and x is the position of pixels. Just as this formula, the line spread function (LSF) is the derivative of ESF and the MTF is the Fourier transform of LSF.

Table S1. Crystallographic data for **TPPOMnBr$_2$** crystal.

complex	TPPOMnBr$_2$
CCDC	2336965
Formula	C$_{24}$H$_{48}$Br$_2$MnN$_6$O$_2$P$_2$
Formula weight	729.38
Temperature/K	284.00
Crystal system	monoclinic
Space group	P2$_1$/c
a/Å	13.9678(7)
b/Å	13.3894(8)
c/Å	17.9627(10)
α/°	90
β/°	102.391(2)
γ/°	90
V/Å^3	3281.1(3)
Z	4
ρ_{calc} (g/cm^3)	1.477
μ/mm^{-1}	2.966
F (000)	1500.0
Reflections collected	59262
GOF (F^2)	1.021
R$_{int}$	0.1336
R$_{sigma}$	0.0774
R$_1$/wR$_2$ [I>=2σ (I)]	0.0547/0.1176
R$_1$/wR$_2$ [all data]	0.1076/0.1419

Table S2. Selected bond lengths (Å) and angles (º) for **TPPOMnBr$_2$**.

Br(1)–Mn(1)	2.4789(10)	Br(1)-Mn(1)-Br(2)	115.50(4)
Br(2)–Mn(1)	2.4947(9)	O(1)-Mn(1)-Br(1)	111.49(12)
Mn(1)–O(1)	2.019(3)	O(1)-Mn(1)-Br(2)	106.39(12)
Mn(1)–O(2)	2.008(3)	O(2)-Mn(1)-Br(1)	106.84(12)
P(1)–O(1)	1.485(4)	O(2)-Mn(1)-Br(2)	111.60(12)
P(2)–O(2)	1.487(4)	O(1)-Mn(1)-O(2)	104.52(16)

Table S3. Photophysical properties of **TPPOMnBr$_2$** in crystal state.

Complex	λ_{PEL}/nm	λ_{em}/nm	PLQY/%	τ/ms	FWHM/nm
TPPOMnBr$_2$	271, 277, 356, 364, 423, 439, 459	512	41.3	0.564	52
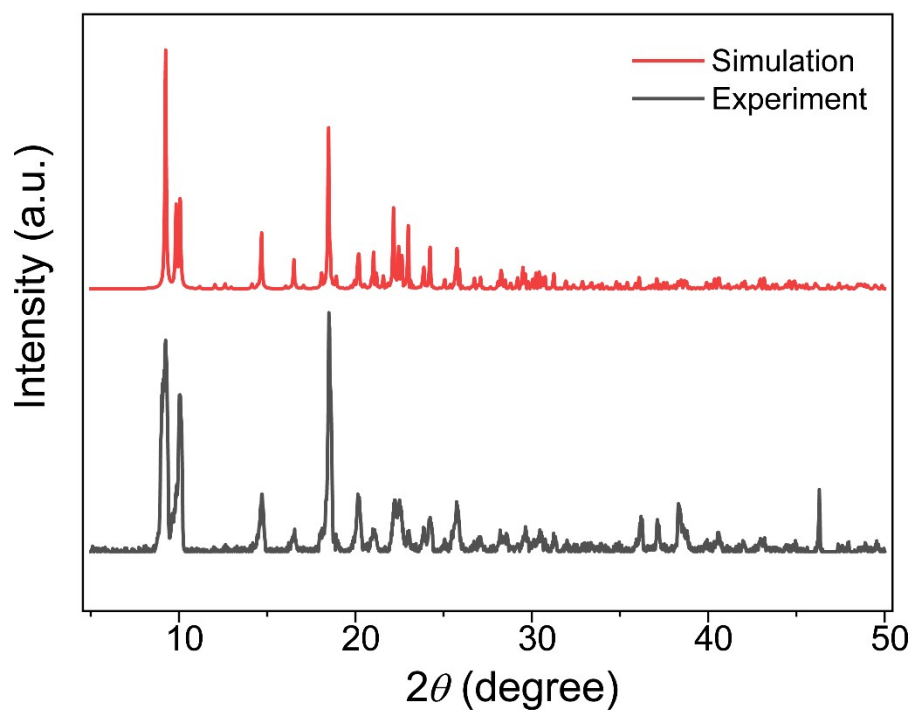
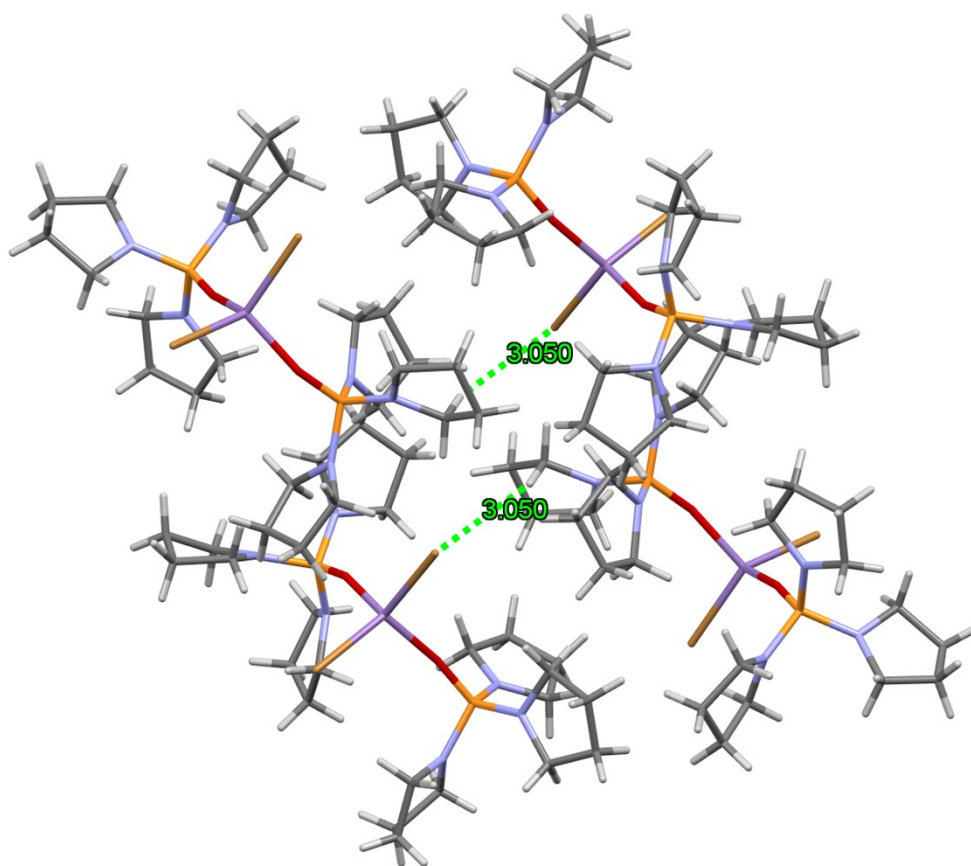**Fig. S1.** Measured and calculated PXRD of **TPPOMnBr₂**.

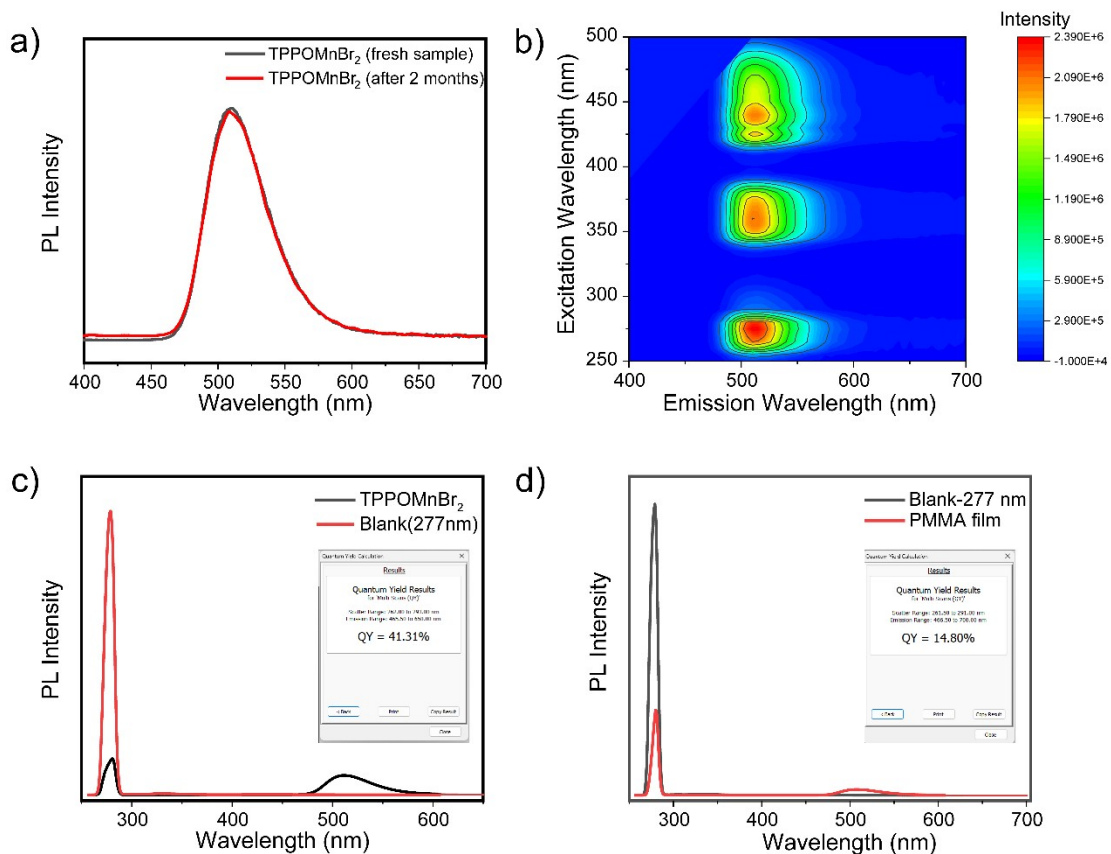**Fig. S2.** Intermolecular interactions in **TPPOMnBr₂** crystal.

Fig. S3. a) Photoluminescence spectra of **TPPOMnBr₂** crystals in fresh state and after 2 months in wet environment (λ_{ex} = 277 nm, 75% humidity). b) Excitation and emission map for photoluminescence from **TPPOMnBr₂**. PLQYs of **TPPOMnBr₂** in crystals (c) and PMMA film (d).
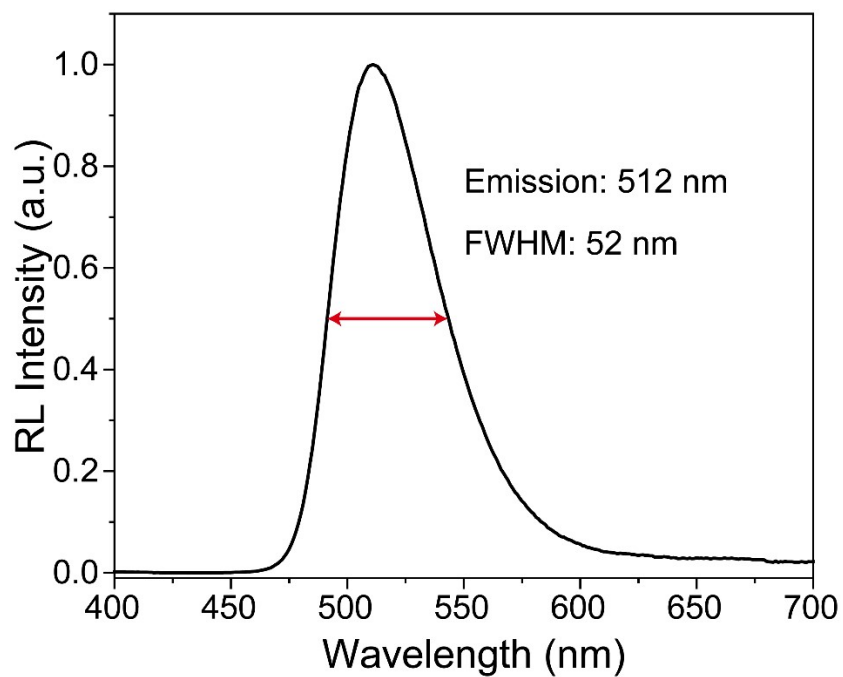
Fig. S4. RL spectrum of **TPPOMnBr$_2$** crystal under X-ray irradiation with the photon energy range of 5 to 30 keV.
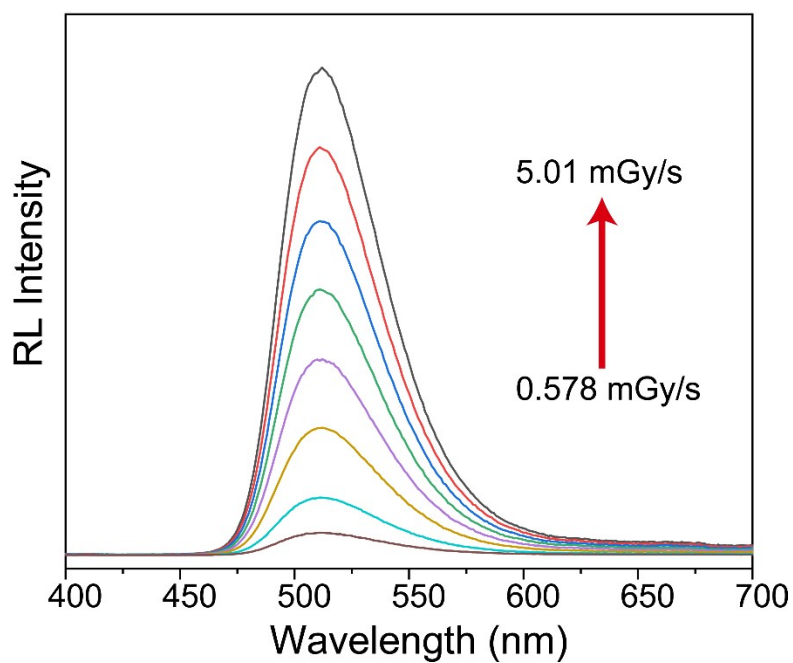
Fig. S5. RL spectra of **TPPOMnBr₂** crystal under X-ray irradiation with a dose rate range of 0.578 to 5.01 mGy/s and the photon energy range of 5 to 30 keV.
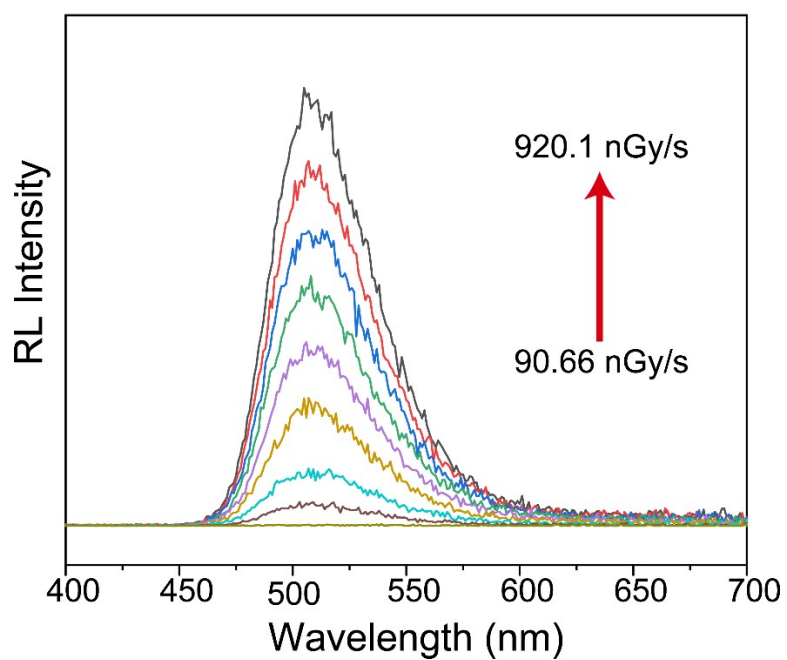
Fig. S6. RL spectra of **TPPOMnBr₂** crystal under X-ray irradiation with a dose rate range of 90.66 to 920.1 nGy/s and the photon energy range of 5 to 30 keV.