Supporting Information

(Diisopropylammonium)$_2$MnBr$_4$: A Multifunctional Ferroelectric with Efficient Green-emission and Excellent Gas Sensing Property

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A. Experimental methods

Materials. Manganese (II) bromide hydrate (99.9%) was purchased from Alfa Aesar. Diisopropylamine (99%) was purchased from J&K Scientific Ltd. and hydrobromic acid (40%) was obtained from Aladdin Co. Ltd. (Shanghai, China). Poly (vinylidene fluoride-co-hexa-fluoropropylene) (PVDF) grains with an average molecular weight of 400,000 were obtained from Sigma-Aldrich. Organic solvents of acetone (99.5%), methanol (99.5%), ethanol (99.7%), dichloromethane (99.5%), ether (99.7%), toluene (99.5%) and formaldehyde solution (40%) were obtained from the local suppliers. All chemicals were used without further purification unless otherwise stated.

The growth of (diisopropylammonium)$_2$MnBr$_4$ single crystals. Diisopropylammonium bromide (DIPAB) crystals were first synthesized from the aqueous solution containing equal molar amounts of diisopropylamine and hydrobromic acid according the reference.[1] DIPAB (910.6 mg, 0.005 mol) was dissolved in 20 mL hydrobromic acid and then added to 10 mL aqueous solution containing 1.074 g (0.005 mol) manganese bromide. Light yellow crystals were obtained by slow evaporation of the solution. The purity of the crystals was verified by powder X-ray diffraction, as shown in Fig. S1.

Characterization

Single-crystal XRD data of the crystals were recorded with a Bruker D8 Venture. All the structures were solved by direct methods (SHELXS-9713 program) and refined by full-matrix least-squares on F2 (SHELXL-97 program) using Olex2014 software. The powder X-ray diffraction patterns of the samples were collected by using a Ni filtered Cu Kα (λ=1.5418 Å) radiation source (D/Max-2550 V, Rigaku Co.). The polycrystalline samples were prepared by grinding the single crystals for the measurement. The XRD scans were collected from 5 to 50 (2θ), with a step of 0.02 and a data collection time 0.5 s. Differential scanning calorimetry (DSC) measurements were performed on a DSC-60 instrument (Shimadzu Corporation, Japan). The heating and cooling rates were both 6 K min^{-1}. Pure aluminum was used for temperature and enthalpy calibration. The complex permittivity was measured using E4980A Precision LCR Meter with an AC voltage of 0.05 V. Ferroelectric hysteresis loops were recorded on a selected single crystal of (diisopropylammonium)$_2MnBr_4$ by using a Precision LC ferroelectric tester (Radiant Technology). Absorption measurement was recorded on Lambda 1050 UV/Vis/NIR spectrophotometer (PerkinElmer). PL spectra were recorded using 1.0 cm UV-quartz cuvettes at room temperature under ambient conditions on a Perkin-Elmer LS55 fluorescence spectrometer. The measurement of quantum efficiency was carried out on a Dual UV_NIR (HORIBA). Magnetic susceptibility data was recorded on Quantum Design physical property measurement system.

For PFM measurement, the sample was prepared by spin-coating of $DIPA_2MnBr_4$/HBr solution (0.01 M) onto a gold coated SiO_2 substrate (the thickness of gold film is about 100 nm) at a speed of 5000 rpm. Piezoresponse force microscopy was carried out using Asylum Research cypher atomic force microscope at room temperature. A conductive cantilever (HQ:NSC36/Pt) with a force constant of 1 N/m was used.

Preparation $DIPA_2MnBr_4$ / PVDF composite film

0.17 g of PVDF was first dissolved in acetone at 60 °C. 34 mg of $DIPA_2MnBr_4$ was added into the solution and the mixture was vigorously stirred at ambient temperature for 30 min. $DIPA_2MnBr_4$ / PVDF composite film was prepared by using doctor blade technique. After drying, the film with a thickness of ~200 μm was peeled off from the glass substrate and used for gas sensing.

Gas sensing

For gas sensing, the $DIPA_2MnBr_4$ / PVDF composite film was fixed in a 1.0 cm × 1.0 cm quartz cuvettes, which was then sealed by a plastic stopper. A Perkin-Elmer LS55 luminescence spectrometer with temperature controlling by using a water bath was used to record the emission of $DIPA_2MnBr_4$ / PVDF film at 525 nm at 10 °C. The vapors were injected by a micro syringe.

A glass container containing 50 ml of methanol liquid was kept at 10 °C by using a water bath. According to Antoine equation, $(\log p = A - \frac{B}{T+C}$, where, A, B and C are constants over a defined temperature range), the concentration of methanol vapor at 10 °C was calculated to be 7.4 % (wt. %, 7.14×10^4 ppm).

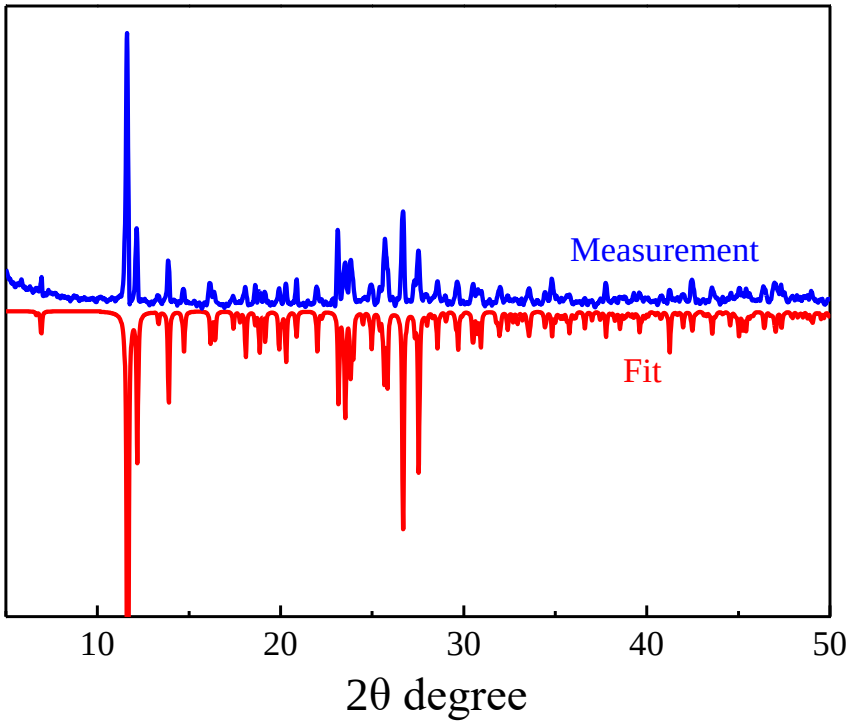

Fig. S1. Comparison of XRD patterns of measured from powders (Measurement) and fitted from single crystal structure (Fit) at room temperature, verifying the purity of the bulk phase.

Table S1. Crystallographic Data for $DIPA_2MnBr_4$.

Empirical formula	$C_{12}H_{32}Br_4MnN_2$
Temperature / K	296
Wavelength	1.54178
Formula weight /g mol^{-1}	578.94
Volume/ $Å^3$	4630.1(3)
Calc. density / g cm^{-3}	1.66094
Crystal system	Orthorhombic
Phase	*Iba2*
Hall group	*I2-2c*
a / Å	14.5214(6)
b / Å	26.5320(11)
c / Å	12.0175(5)
α / °	90
β / °	90
γ / °	90
Z	8
Dx/g·cm^{-3}	1.661
μ /mm^{-1}	12.656
F(000)	2264.0
h, k, l_{max}	17, 31, 14
T_{min},T_{max}	0.151, 0.080
θ_{max}	68.351
R	0.0513
wR2	0.1446
S	1.034

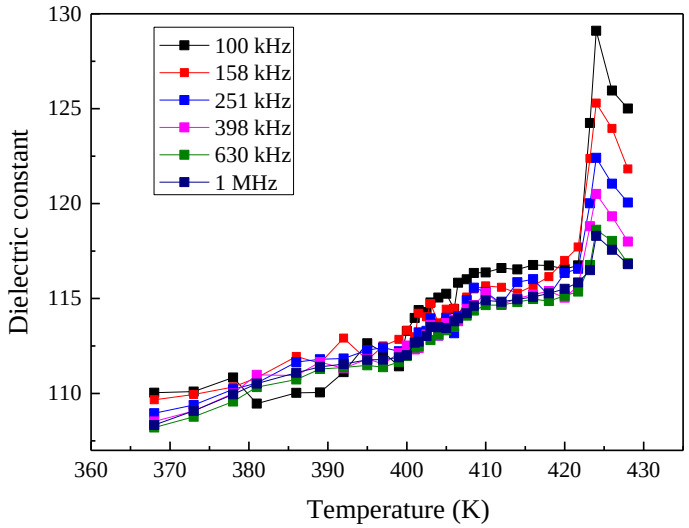

Fig. S2. The temperature-dependence of dielectric constant of $DIPA_2MnBr_4$ crystal at different frequencies.

Photoluminescence properties

Sample	Emission wavelength	Life time	Quantum Yield
$DIPA_2MnBr_4$	525 nm	1.44 ns	62.21%

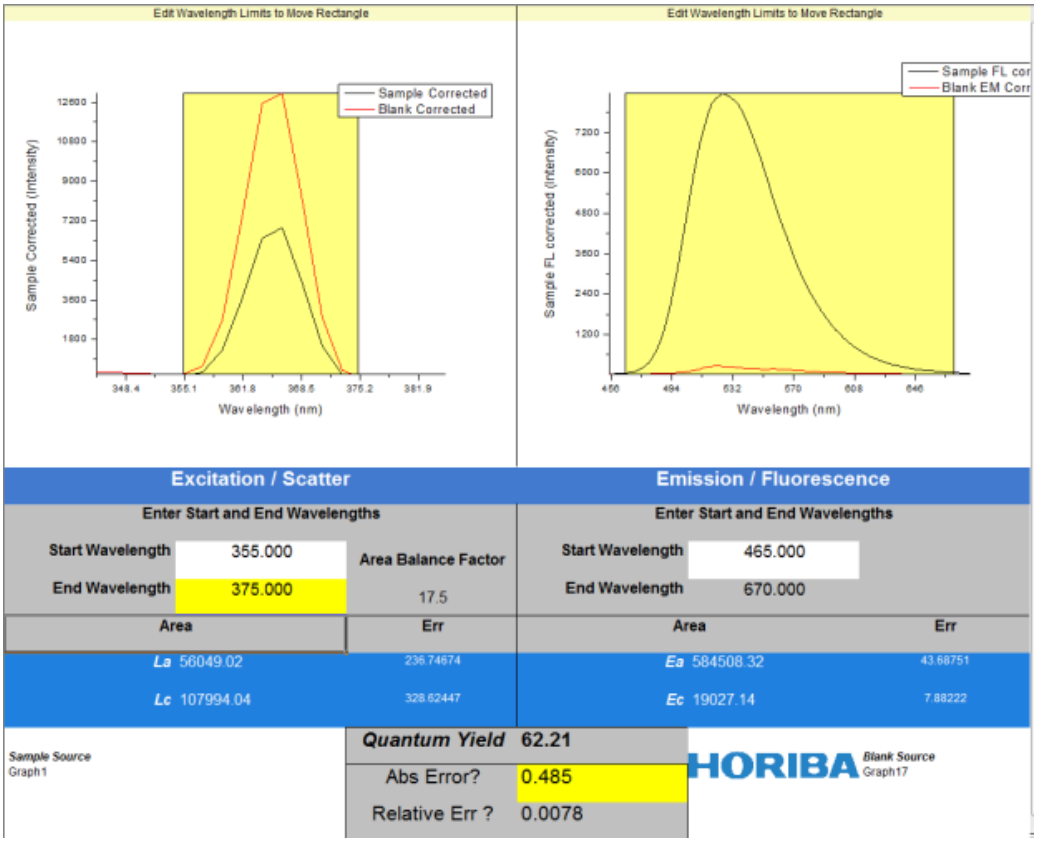

Fig. S3. The quantum yield measurement of $DIPA_2MnBr_4$ crystal.

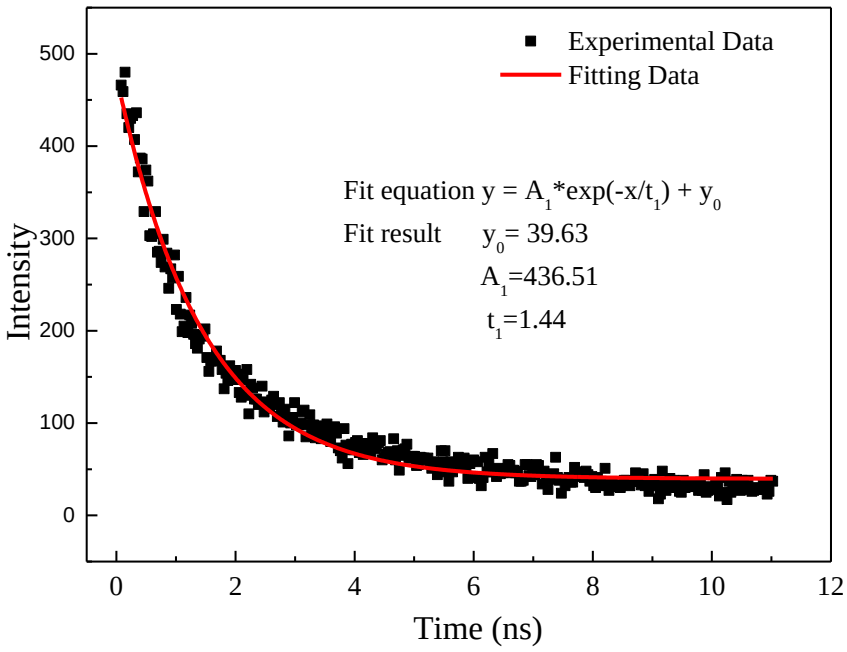

Fig. S4. The life time measurement of $DIPA_2MnBr_4$.

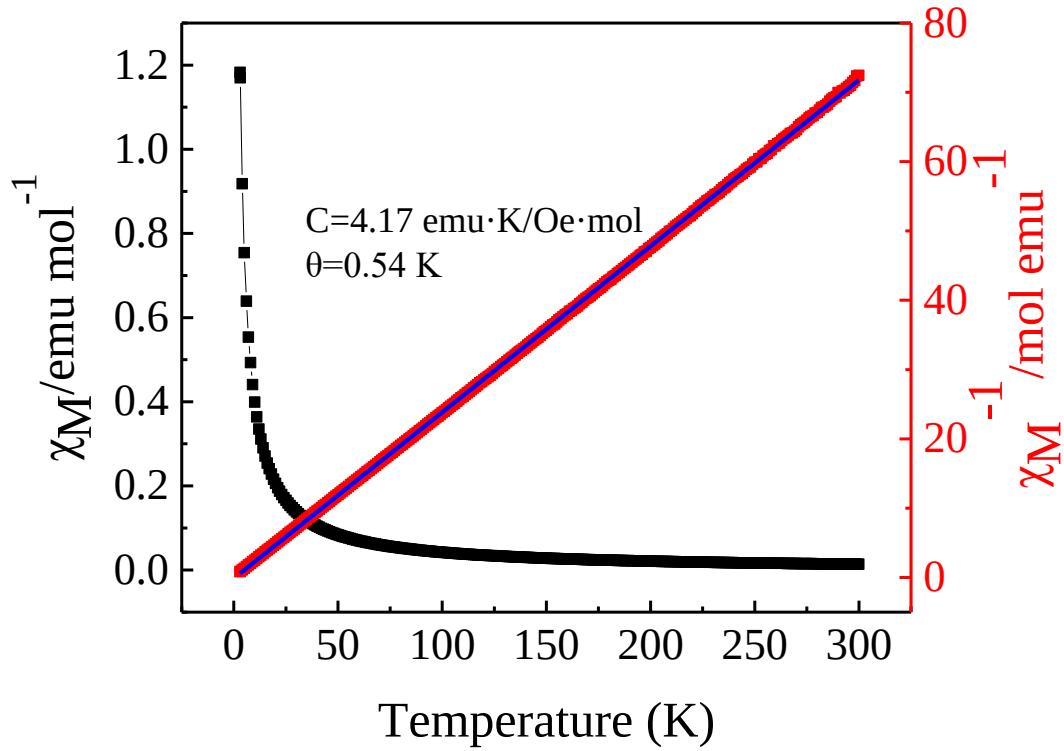

Fig. S5. The the molar magnetic susceptibility (χ_M) and inverse susceptibility (χ_M^{-1}) vs. temperature (3-300 K) plots in an applied field of 1000 Oe for $DIPA_2MnBr_4$, χ_M^{-1} obeys the Curie-Weiss law $\chi_M = C/(T-\theta)$ with C=4.17 emu K mol^{-1} and θ=0.54 K, suggesting weak ferromagnetic interactions.

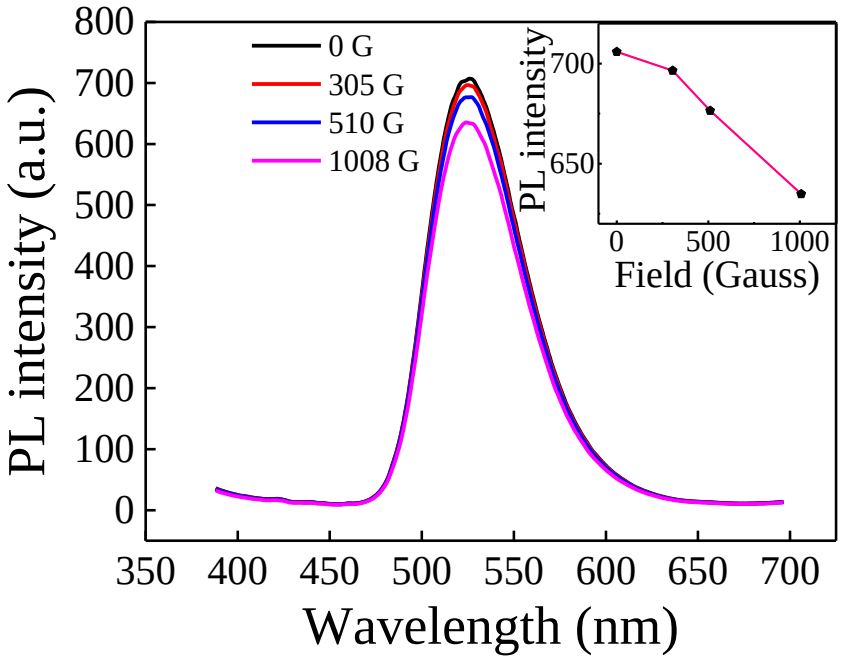

Fig. S6. Variation of PL spectrum under external magnetic field. Inset shows the PL intensity at 525 nm at different magnetic field.

[1] C. Jiang, H. Lin, C. Luo, Y. Zhang, J. Yang, H. Peng, C.-G. Duan, *J. Cryst. Growth* **2016**, *438*, 25-30.