Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Halogen regulation strategy triggers NLO and dielectric dual switches with green fluorescence

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Experimental Measurement

Powder X-ray Diffraction. The powder X-ray diffraction (PXRD) measurement is performed on a Rigaku D/MAX 2000 PC X-ray diffractometer at room temperature. The diffraction pattern is recorded in the 2θ range of 5–50° with a step size of 0.02°. As shown in Fig. S1, the PXRD pattern obtained at 298 K is very consistent with the simulated pattern based on the crystal structure at room temperature, indicating the phase purity of the primary crystals of these two compounds.

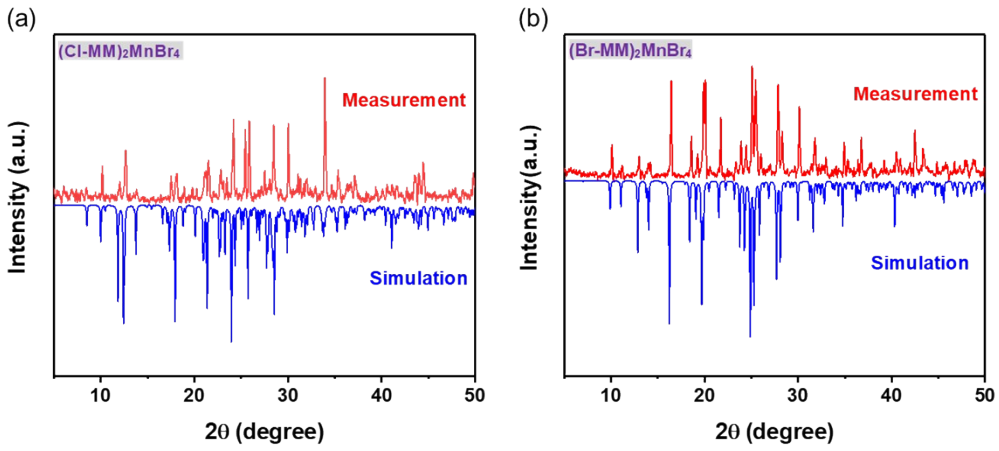


Fig. S1 PXRD measurement and simulation diagram of $(Cl\text{-}MM)_2MnBr_4$ (a) and $(Br\text{-}MM)_2MnBr_4$ (b).

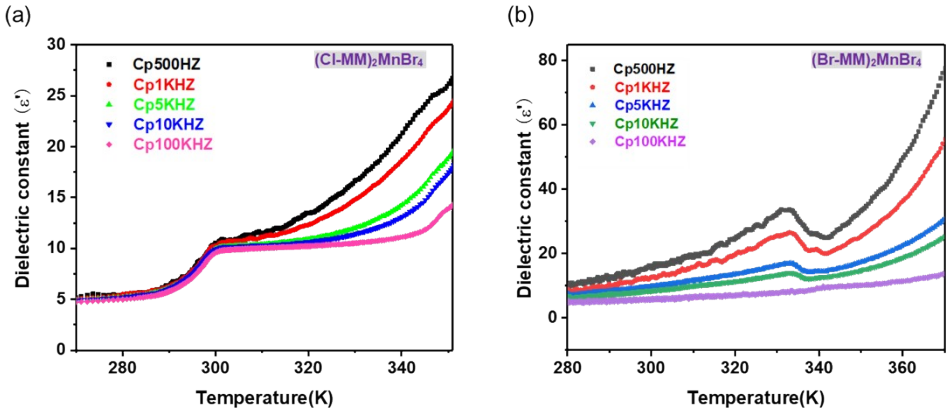


Fig. S2 Curves of the temperature-dependent real part (ε') of the dielectric constant of $(Cl\text{-}MM)_2MnBr_4$ (a) and $(Br\text{-}MM)_2MnBr_4$ (b) at different frequencies

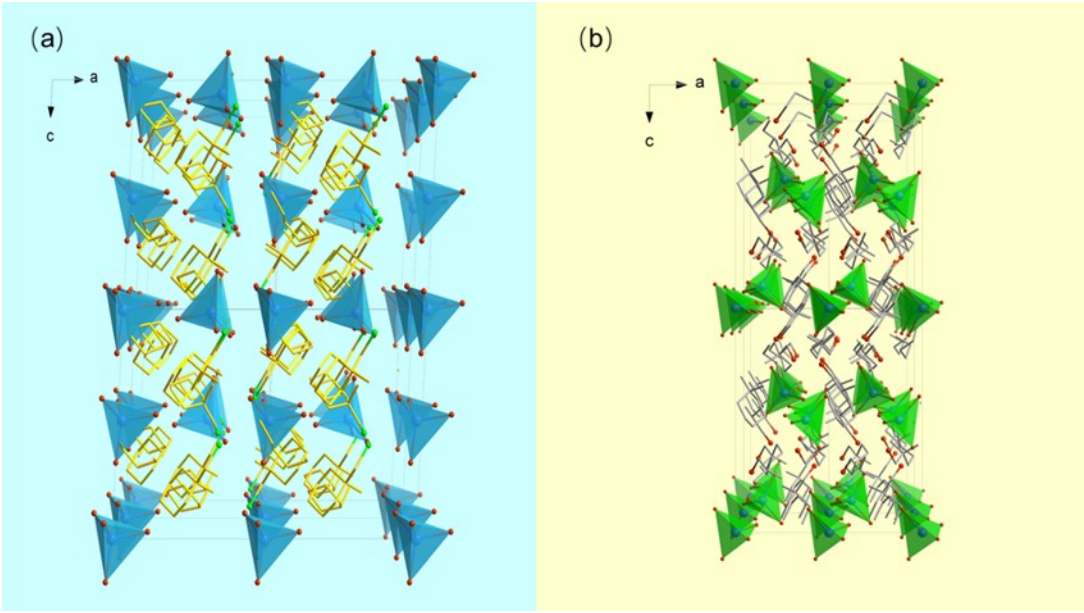
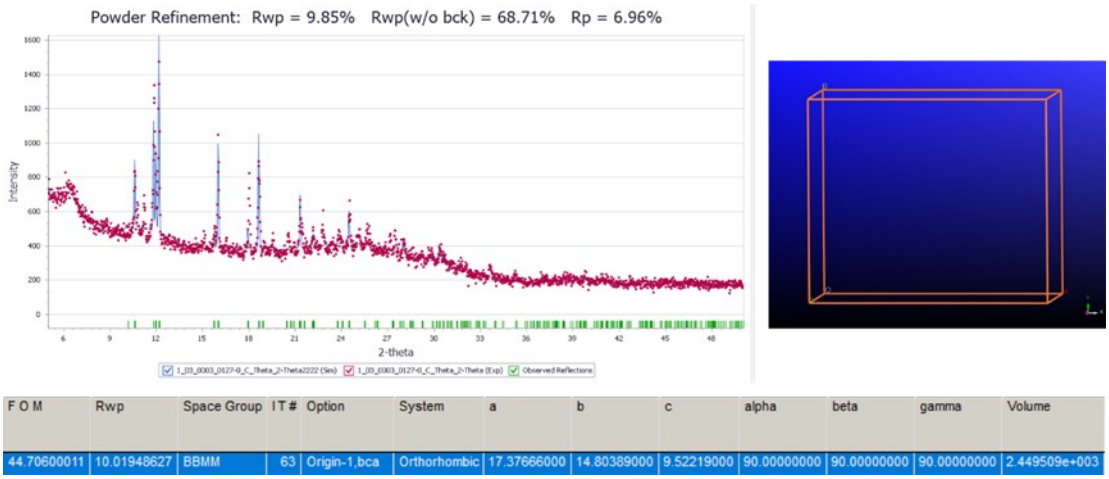
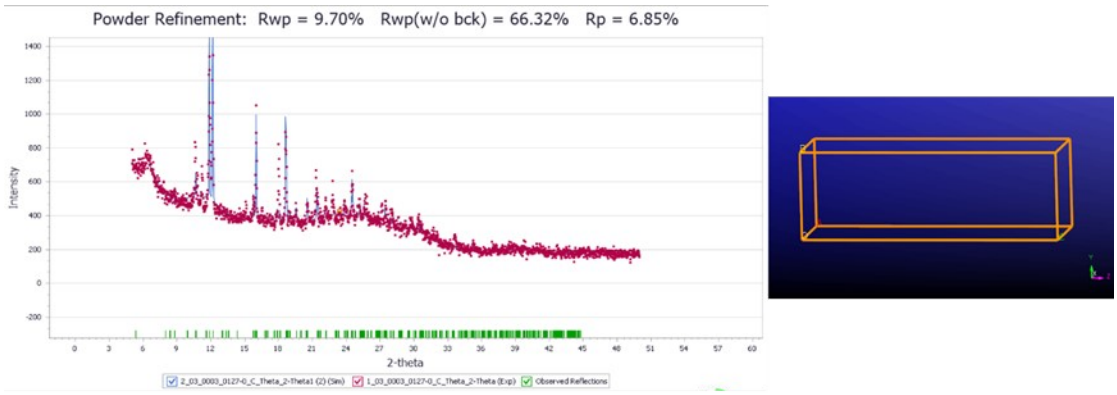


Fig. S3 The unit cell packing diagrams of (a) $(Cl\text{-}MM)_2MnBr_4$ and (b) $(Br\text{-}MM)_2MnBr_4$ viewed from the b-axis direction, all hydrogen atoms are omitted for convenience of observation.



F O M	Rwp	Space Group	I T #	Option	System	a	b	c	alpha	beta	gamma	Volume
44.70600011	10.01948627	BBMM	63	Origin-1,bca	Orthorhombic	17.37666000	14.80389000	9.52219000	90.00000000	90.00000000	90.00000000	2.449509e+003

Fig. S4 The simulation result of the PXRD data obtained by (Cl-MM)$_2$MnBr$_4$ at 400 K in Material Studio, it is inferred that its high temperature phase is in the orthorhombic system (the unit cell is located on the upper right), and its space group may be *Cmcm*.



F O M	Rwp	Space Group	I T #	Option	System	a	b	c	alpha	beta	gamma	Volume
18.98192246	10.13077845	I4/MMM	139	Origin-1	Tetragonal	10.54672200	10.54672200	33.19476100	90.00000000	90.00000000	90.00000000	3.692364e+003

Fig. S5 The simulation result of the PXRD data obtained by (Br-MM)$_2$MnBr$_4$ at 400 K in Material Studio, it is inferred that its high temperature phase is in the tetragonal system (the unit cell is located on the upper right), and its space group may be *I4/mmm*

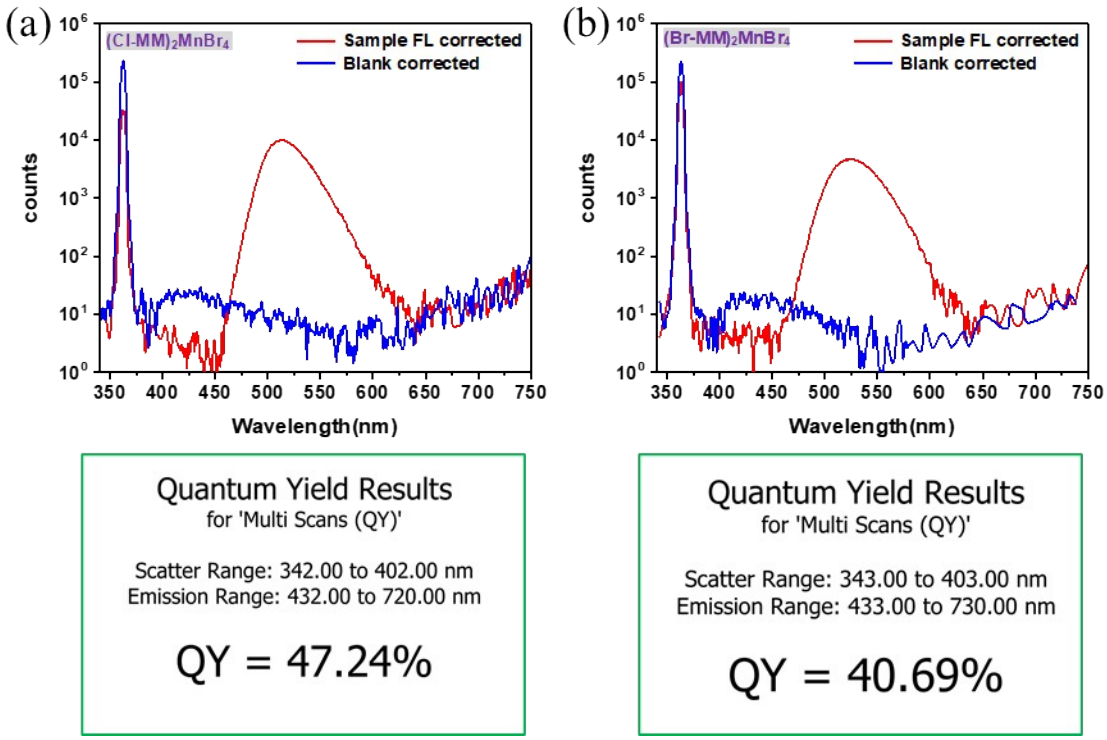


Fig. S6 Photoluminescence quantum yield measurement curves and results of (Cl-MM)$_2$MnBr$_4$ (a) and (Br-MM)$_2$MnBr$_4$ (b).

Table S1. Crystal data and structure refinement for (Cl-MM)$_2$MnBr$_4$ at 299 K and 343 K.

(Cl-MM)$_2$MnBr$_4$	RTP (299 K)	ITP (343 K)
Empirical formula	$C_{12}H_{26}Br_4Cl_2MnN_2O_2$	$C_{12}H_{25}Br_4Cl_2MnN_2O_2$
Formula weight	675.83	674.802
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.3974(5)	10.4211(4)
b/Å	16.8596(7)	16.8859(7)
c/Å	12.8924(6)	12.9516(6)
α/°	90	90
β/°	93.508(4)	93.546(4)
γ/°	90	90
Volume/Å^3	2255.75(18)	2274.73(17)
Z	4	4
F (000)	1308.0	1340.0
Goodness-of-fit on F^2	1.041	1.011

R_1 [I>=2σ (I)]	0.1048	0.0710
wR_2 [I>=2σ (I)]	0.2892	0.1793

Table S2. Crystal data and structure refinement for $(Br\text{-}MM)_2MnBr_4$

Compound	$(Br\text{-}MM)_2MnBr_4$
Empirical formula	$C_{12}H_{26}Br_6MnN_2O_2$
Formula weight	764.69
Temperature/K	297.09(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.4580(3)
b/Å	17.8292(8)
c/Å	17.8808(8)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2377.61(17)
Z	4
F (000)	1448.9
Goodness-of-fit on F^2	0.960
R_1 [I>=2σ (I)]	0.0516
wR_2 [I>=2σ (I)]	0.1047