Supporting information

Tunable optoelectronic response multifunctional material: exploring switches and photoluminescence integrated in flexible thin film/crystal

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Experimental Measurement Methods

Single crystal X-ray crystallography

Variable-temperature X-ray single-crystal diffraction data of $(IPTMA)_2CdBr_4$ and $(IPTMA)_2MnBr_4$ are collected using Mo Kα radiation (λ = 0.71073 Å) on a Rigaku Saturn 724 diffractometer at ω scan mode. Data processing, including empirical absorption correction, was performed by using the Crystal Clear software package. Crystal structure at HTP, LTP for compound $(IPTMA)_2CdBr_4$ and at HTP, ITP, LTP for $(IPTMA)_2MnBr_4$ were resolved by direct method and continuous Fourier synthesis, and then refined by full-matrix least-squares methods based on F^2 with the SHELXLTL software package. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$, and the hydrogen atoms were generated geometrically at appropriate position. Moreover, calculations involving the angles and distances between some atoms were measured by DIAMOND and SHELXLTL. Crystallographic data and structure refinement of $(IPTMA)_2CdBr_4$ and $(IPTMA)_2MnBr_4$ at various temperatures is listed in Table S1 and Table S2 respectively.

Powder X-ray diffraction

Variable-temperature powder X-ray diffraction (PXRD) measurements were performed

on a Rigaku D/MAX 2000 PC X-ray diffractometer. The PXRD patterns of $(IPTMA)_2CdBr_4$ and $(IPTMA)_2MnBr_4$ were collected in the 2θ range of 5°–50° with a step size of 0.02°.

Thermal analysis measurements

Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC 214 instrument. The crystalline samples of the two compounds were measured with a rate of 10 K min^{-1} under a nitrogen atmosphere in aluminum crucibles in the temperature range from 270 K to 135 K.

Dielectric properties measurements

The complex dielectric permittivity curves were measured on an automatic impedance Tonghui 2828 analyzer from 300 K to 100 K in the frequency range from 10 kHz to 1 MHz with an applied voltage of 1.0 V. Dielectric studies were performed on pressed-powder pellets and single crystal samples, and conductive carbon/silver glue was deposited on the surface of electrode to simulate parallel plate capacitors.

Photoluminescence spectroscopic measurements

The excitation and emission spectra of $(IPTMA)_2MnBr_4$ in the solid states were measured on an Edinburgh FLS-920 fluorescence spectrometer. For photoluminescence quantum yield (PLQY) measurements, the absolute quantum efficiencies were acquired by using an integrating sphere incorporated into the Edinburgh FLS-920 fluorescence spectrometer.

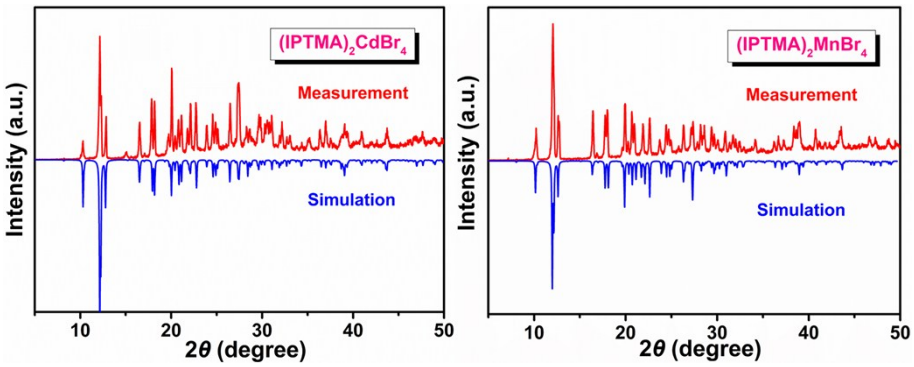

Fig. S1 Comparison between measurement and simulation PXRD of $(IPTMA)_2CdBr_4$ (left) and $(IPTMA)_2MnBr_4$ (right).

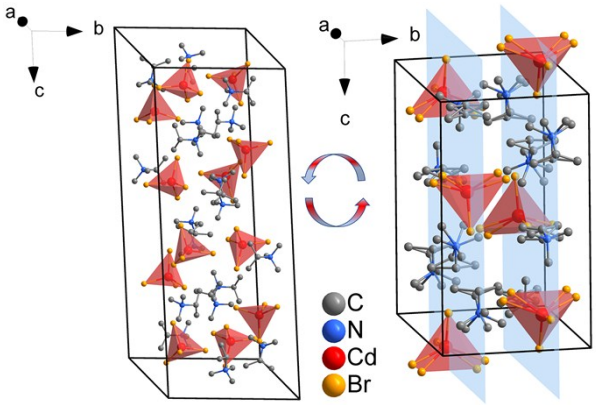

Fig. S2 Structural packing diagrams of $(IPTMA)_2CdBr_4$ at LTP (left) and HTP (right), indicating similarity of lattice framework and differences in motion state of cations and anions. All hydrogen atoms are omitted for clarity.

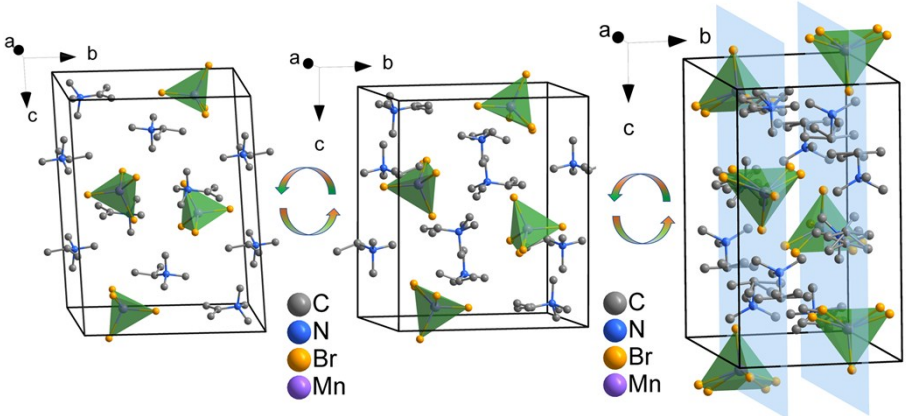

Fig. S3 Structural packing diagrams of $(IPTMA)_2MnBr_4$ at LTP (left), ITP (middle) and HTP (right), manifesting similarity of lattice framework and differences in motion state of cations and anions. All hydrogen atoms are omitted for clarity.

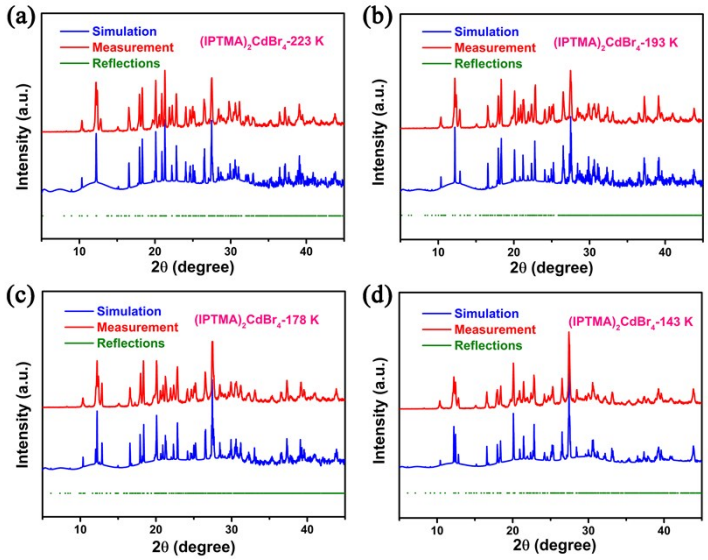

Fig. S4 Pawley refinement of PXRD data of $(IPTMA)_2CdBr_4$ at (a) 223 K, (b) 193 K, (c) 178 K and (d) 143 K. The simulated plots match well with the measured ones. As a result of the plot fitting, the structures at 223 K and 193 K and 178 K should belong to orthorhombic system. The structural refinements reveal a point group *mmm* with the most possible space group *Pnma*. At 143 K, the refinements reveal a point group 2/*m* with the most possible space group $P2_1/c$.

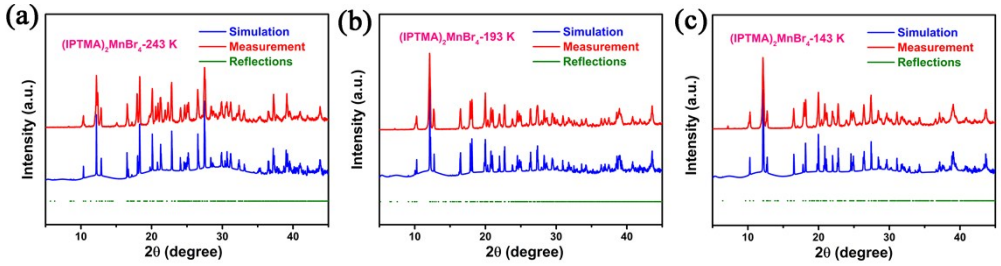

Fig. S5 Pawley refinement of PXRD data of $(IPTMA)_2MnBr_4$ at (a) 243 K, (b) 193 K and (c) 143 K. The simulated plots match well with the measured ones. The structural refinements at 243 K reveal a point group *mmm* with the most possible space group *Pnma*. At 193 K and 143 K, the refinements reveal a point group 2/*m* with the most possible space group $P2_1/c$.

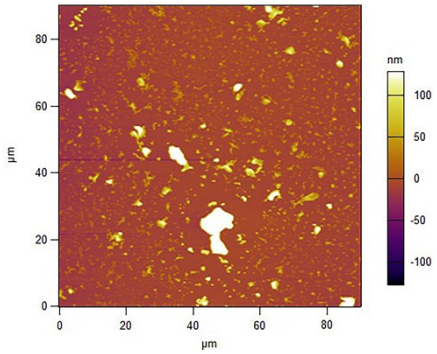

Fig. S6 The surface topography of $(IPTMA)_2MnBr_4$ thin film under a polarizing microscope.

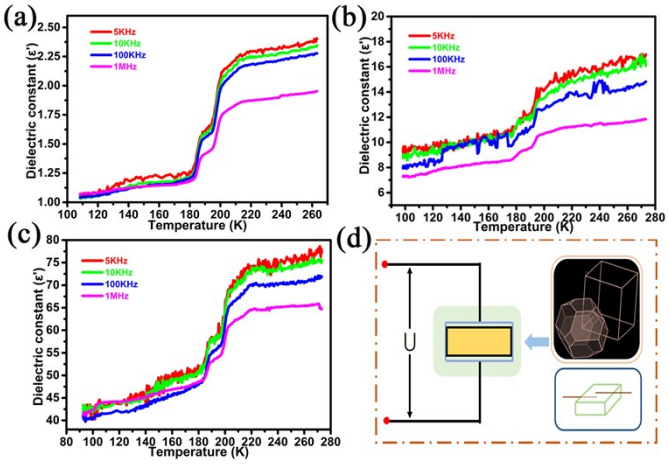

Fig. S7 The real part of the dielectric of $(IPTMA)_2CdBr_4$ measured along (a) the a-axis, (b) the b-axis, (c) the c-axis and (d) the mechanism schematic illustration of the permittivity measurement.

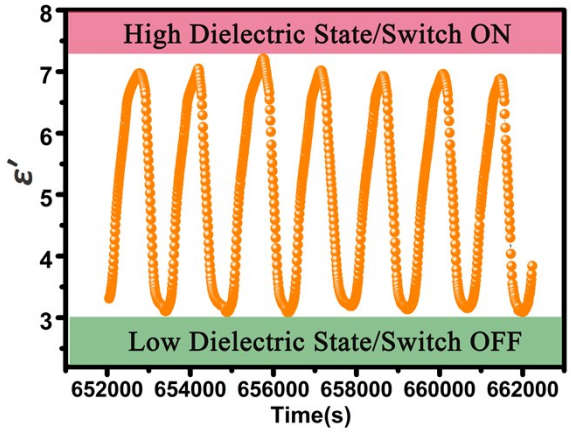

Fig. S8 Reversible switching effect of dielectric constant on single crystals of $(IPTMA)_2MnBr_4$.

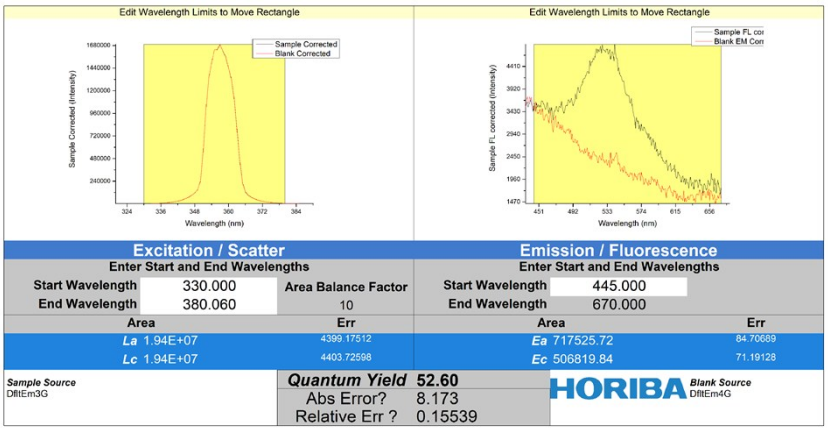

Fig. S9 The quantum yield measurement results of $(IPTMA)_2MnBr_4$.

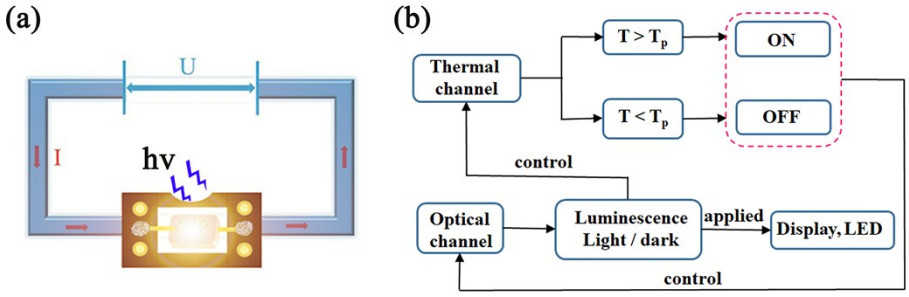

Fig. S10 (a) Schematic diagram for dielectric measurements on the electrodes made of sample. (b) Logic diagram in optoelectronic smart-controlled device.

Table S1. Crystal data and structure refinement for $(IPTMA)_2CdBr_4$.

Compound	LTP (143 K)	HTP (253 K)
Empirical formula	$C_{12}H_{32}N_2CdBr_4$	$C_{12}H_{32}N_2CdBr_4$
Formula weight	636.44	636.44
Temperature (K)	143	253
Crystal system	Monoclinic	Orthorhombic
Space group	*P*2(1)/*c*	*Pnma*
a (Å)	15.9526 (5)	13.6730 (9)
b (Å)	13.5636 (3)	9.7984 (8)
c (Å)	33.5878 (10)	16.6817 (10)
α (°)	90	90

β (°)	116.288 (3)	90
γ (°)	90	90
Volume(Å^3)	6515.9 (3)	2234.9 (3)
Z	12	4
F (000)	3672	1096
GOF	1.134	1.054
$R_1[I > 2\sigma(I)]$	0.0824	0.0784
w$R2[I > 2\sigma(I)]$	0.2056	0.2929

Table S2. Crystal data and structure refinement for $(IPTMA)_2MnBr_4$.

Compound	LTP (143 K)	ITP (193 K)	HTP (253 K)
Empirical formula	$C_{12}H_{32}N_2MnBr_4$	$C_{12}H_{32}N_2MnBr_4$	$C_{12}H_{32}N_2MnBr_4$
Formula weight	578.72	578.72	578.72
Temperature	143 K	193 K	253 K
Crystal system	Monoclinic	Monoclinic	orthorhombic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*Pnma*
a (Å)	9.8236 (13)	9.8508 (11)	13.6445 (16)
b (Å)	13.7526 (12)	13.7174 (11)	9.7917 (15)
c (Å)	18.668 (2)	16.068 (2)	16.534 (2)
α (°)	90	90	90
β (°)	120.339 (9)	91.517 (11)	90
γ (°)	90	90	90
Volume(Å^3)	2176.7 (4)	2170.5 (4)	2209.0 (5)
Z	4	4	4
GOF	1.109	1.221	1.057
$R_1[I > 2\sigma(I)]$	0.161	0.1403	0.0799
w$R2[I > 2\sigma(I)]$	0.4864	0.4428	0.2737

Table S3. Selected bond lengths [Å] for $(IPTMA)_2CdBr_4$ at LTP.

Bond lengths and angles [Å]			
Cd2—Br7	2.5907 (10)	Cd3—Br9	2.5930 (9)
Cd1—Br3	2.5675 (8)	Cd1—Br2	2.5898 (9)
Cd1—Br4	2.5857 (9)	Cd2—Br6	2.5681 (9)
Cd1—Br1	2.5876 (8)	Cd2—Br8	2.5760 (8)
Cd2—Br7	2.5907 (10)	Cd2—Br5	2.5970 (8)
Cd3—Br10	2.5686 (11)	Cd3—Br11	2.5875 (8)
Cd3—Br12	2.5757 (10)		
Br6—Cd2—Br5	108.61 (3)	Br11—Cd3—Br9	105.71 (3)
Br8—Cd2—Br5	110.12 (3)	Br12—Cd3—Br9	111.60 (4)
Br7—Cd2—Br5	110.06 (3)	Br3—Cd1—Br4	110.98 (3)
Br10—Cd3—Br12	108.37 (3)	Br3—Cd1—Br1	110.17 (3)
Br10—Cd3—Br11	111.71 (3)	Br4—Cd1—Br1	107.26 (3)
Br12—Cd3—Br11	112.76 (3)	Br3—Cd1—Br2	112.22 (3)
Br10—Cd3—Br9	106.52 (4)	Br4—Cd1—Br2	109.47 (3)
Br1—Cd1—Br2	106.53 (3)	Br6—Cd2—Br7	111.11 (4)
Br6—Cd2—Br8	109.71 (3)	Br8—Cd2—Br7	107.24 (3)

Table S4. Selected bond lengths [Å] for $(IPTMA)_2CdBr_4$ at HTP.

Bond lengths and angles [Å]			
Cd1—Br3	2.471 (6)	Cd1—Br1	2.5848 (18)
Cd1—$Br3^{i}$	2.471 (6)	Cd1—Br3'	2.673 (6)
Cd1—Br2	2.5551 (19)	Cd1—$Br3'^{i}$	2.673 (6)

Br3—Cd1—Br3^{i}	95.5 (3)	Br1—Cd1—Br3'	101.13 (14)
Br3—Cd1—Br2	110.82 (19)	Br3—Cd1—Br3'^{i}	111.75 (18)
Br3^{i}—Cd1—Br2	110.82 (19)	Br3^{i}—Cd1—Br3'^{i}	16.58 (16)
Br3—Cd1—Br1	111.35 (16)	Br2—Cd1—Br3'^{i}	105.95 (17)
Br3^{i}—Cd1—Br1	111.35 (16)	Br1—Cd1—Br3'^{i}	101.13 (14)
Br2—Cd1—Br1	115.33 (7)	Br3'—Cd1—Br3'^{i}	127.8 (2)
Br3—Cd1—Br3'	16.58 (16)	Br2—Cd1—Br3'	105.95 (17)
Br3^{i}—Cd1—Br3'	111.75 (18)		

Table S5. Selected bond lengths [Å] for $(IPTMA)_2MnBr_4$ at LTP.

Bond lengths and angles [Å]			
Br1—Mn1	2.498 (4)	Br3—Mn1	2.480 (4)
Br2—Mn1	2.483 (4)	Br4—Mn1	2.493 (4)
Br3—Mn1—Br2	111.82 (15)	Br3—Mn1—Br1	110.50 (15)
Br3—Mn1—Br4	109.62 (16)	Br2—Mn1—Br1	107.05 (15)
Br2—Mn1—Br4	108.8 (2)	Br4—Mn1—Br1	108.99 (15)

Table S6. Selected bond lengths [Å] for $(IPTMA)_2MnBr_4$ at ITP.

Bond lengths and angles [Å]			
Br1—Mn2	2.477 (3)	Mn2—Br2A	2.361 (9)
Br3—Mn2	2.495 (3)	Mn2—Br2B^{i}	2.610 (9)
Mn2—Br2A^{i}	2.361 (9)	Mn2—Br2B	2.610 (9)
Br2A^{i}—Mn2—Br2A	94.6 (4)	Br2A^{i}—Mn2—Br2B^{i}	16.1 (3)
Br2A^{i}—Mn2—Br1	111.3 (3)	Br2A—Mn2—Br2B^{i}	110.4 (2)
Br2A—Mn2—Br1	111.3 (3)	Br1—Mn2—Br2B^{i}	106.5 (3)

Br2A^{i}—Mn2—Br3	111.9 (2)	Br3—Mn2—Br2B^{i}	101.9 (2)
Br2A—Mn2—Br3	111.9 (2)	Br2A^{i}—Mn2—Br2B	110.4 (2)
Br1—Mn2—Br3	114.29 (11)	Br2A—Mn2—Br2B	16.1 (3)
Br3—Mn2—Br2B	101.9 (2)	Br1—Mn2—Br2B	106.5 (3)
Br2B^{i}—Mn2—Br2B	125.9 (4)		

Table S7. Selected bond lengths [Å] for $(IPTMA)_2MnBr_4$ at HTP.

Bond lengths and angles [Å]			
Br2—Mn1	2.4952 (12)	Mn1—Br1	2.4890 (13)
Mn1—Br4B	2.469 (2)	Mn1—Br4A	2.502 (2)
Mn1—Br3	2.4718 (11)		
Br4B—Mn1—Br3	113.61 (6)	Br1—Mn1—Br2	108.53 (5)
Br4B—Mn1—Br1	104.96 (6)	Br4B—Mn1—Br4A	9.98 (7)
Br3—Mn1—Br1	109.56 (4)	Br3—Mn1—Br4A	108.28 (7)
Br4B—Mn1—Br2	108.74 (6)	Br1—Mn1—Br4A	114.94 (7)
Br3—Mn1—Br2	111.17 (5)	Br2—Mn1—Br4A	104.30 (6)