**Supporting Information**

# Dynamic CPL switching realized in chiral Mn-based metal halides with reversible thermochromism

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## *1. Experimental*

**Materials：**

(R)-(+)-4-bromo-alpha-phenylethylamine (R-Br-MBA) (98%, 5g) and (S)-(-)-4-bromo-alpha-phenylethylamine (S-Br-MBA) (98%, 5g) were purchased from Bidepharm, $MnBr_2$ (98%, 5g) was purchased from Aladdin, and hydrobromic acid (HBr, 48 wt % in water) was purchased from Shanghai McLean Biochemical Company.

**Synthesis of (R-/S-Br-MBA)$_3$MnBr$_5$ single crystals：**

R-/S-Br-MBA (2 mmol) and $MnBr_2$ (1 mmol) were added to 3.7 mL HBr solution, and the reaction was carried out at 80 ℃ for one hour, then decreased to 60 ℃ and volatilized for one day to obtain light green crystals. Crystals were washed three times with diethyl ether and dried at 60 ℃ under vacuum overnight.

**Characterization：**

A LAMBDA 750 ultraviolet spectrometer was used to measure the UV-visible absorption spectrum of solids. Temperature-dependent PL, temperature-dependent time-resolved fluorescence spectra and temperature-dependent PLQY were measured at Edinburgh FLS980 under excitation at 365 nm. The heating rate is 20 ℃/min, and the holding time at each temperature point is 3 min. Delayed PL spectra was recorded on Edinburgh FLS980. Phosphorescence mode was operated at 1 ms delay time.

Single crystal XRD data were recorded using the Bruker D8 Venture. All structures were solved by direct methods (SHELXS-2014 program) and refined by full-matrix least square method on F2 (SHELXL-2014 program) using Olex2 software.

CCDC 2225347-2225348 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

The crystal structure of chiral Mn-based metal halide powders at room temperature has been characterized by an X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The measurement range is 5-40° and the scanning speed is 10°/min.

The solid KBr chip method was used to collect CD spectra at room temperature and 90 ℃ respectively with JASCO-J810 CD spectrometer. The scanning rate was 500 nm/min, the data pitch was 1 nm, and the bandwidth was 4 nm. CPL was tested with the circularly polarized PL spectrometer of CPL-200, and the CPL spectra at 0 ℃, 25 ℃, 60 ℃ and 90 ℃ were respectively tested with high-temperature accessories.

The SQUID-VSM magnetic measurement system was used to measure the magnetic properties of single crystal samples at 25 ℃ and 90 ℃ respectively. ESR measurements were made in the X band (~9.68 GHz) using an electron spin magnetic resonance spectrometer (JES-FA200). Continuous wave ESR spectra (~4 mW) of powder samples were collected at room temperature using unsaturated microwave power and 100 kHz magnetic field modulation at 0.1 mT.

In the argon atmosphere, the powder samples were placed in the $Al_2O_3$ crucible, and the thermogravimetric (TG) test was carried out by Q20 thermogravimetric analyzer. The temperature range was 30-800℃, and the heating rate was 10 ℃/min. The DSC

measurements were made with a TAQ2000 differential scanning calorimeter in a nitrogen atmosphere with a temperature range of 0-180 ℃ and a heating rate of 10 ℃/min.

FTIR-650 infrared spectrometer was used to measure the infrared spectrum of Mn-based metal halide crystal samples. Mn-based metal halide crystals were mixed with dried KBr at a suitable ratio, measuring the wave number range of 4000-500 $cm^{-1}$.

***2. Optical picture***

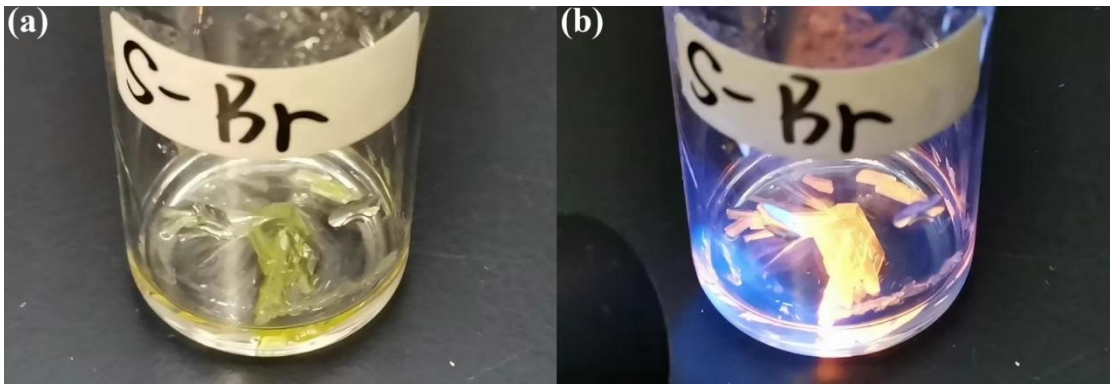


**Figure S1**. The photograph of (S-Br-MBA)$_3$MnBr$_5$ crystals under natural light (a) and UV light (b).

**Table S1. Crystal data and structural refinement for $(R\text{-}Br\text{-}MBA)_3MnBr_5$ at 300 K and 363 K.**

| Empirical formula | $C_{24}H_{33}Br_8MnN_3$ **(300 K)** | $C_{24}H_{33}Br_8MnN_3$ **(363 K)** |
|---|---|---|
| Formula weight | 1057.75 | 1057.75 |
| Temperature/K | 300 | 363 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P 1 21 1 | P 1 21 1 |
| a/Å | 14.2298(1) | 14.3055(3) |
| b/Å | 8.0337(1) | 8.0469(2) |
| c/Å | 15.9969(2) | 16.0940(3) |
| α/° | 90 | 90 |
| β/° | 94.371(1) | 94.489(2) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 1823.41(3) | 1846.98(7) |
| Z | 2 | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.927 | 1.902 |
| μ /mm$^{-1}$ | 13.348 | 13.178 |
| F(000) | 1006.0 | 1006.0 |
| Crystal size/mm$^3$ | 0.16 × 0.12 × 0.1 | 0.15 × 0.12 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2θ range for data collection/° | 5.54 to 151.43 | 5.508 to 152.17 |
| Index ranges | -17 ≤ h ≤ 17, -10 ≤ k ≤ 9, -19 ≤ l ≤ 20 | -17 ≤ h ≤ 17, -10 ≤ k ≤ 9, -20 ≤ l ≤ 20 |
| Reflections collected | 21615 | 21539 |
| Independent reflections | 7227 [$R_{int}$ = 0.0462, $R_{sigma}$ = 0.0399] | 7286 [$R_{int}$ = 0.0517, $R_{sigma}$ = 0.0451] |
| Data/restraints/parameters | 7227/673/420 | 7286/1038/481 |
| Goodness-of-fit on $F^2$ | 1.036 | 1.092 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0419, $wR_2$ = 0.1130 | $R_1$ = 0.0476, $wR_2$ = 0.1317 |
| Final R indexes [all data] | $R_1$ = 0.0435, $wR_2$ = 0.1141 | $R_1$ = 0.0531, $wR_2$ = 0.1367 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.08/-0.82 | 0.79/-0.71 |
| Flack parameter | 0.025(11) | 0.004(8) |

**Table S2. The partial bond lengths of $(R\text{-}Br\text{-}MBA)_3MnBr_5$ single crystal at 300 K and 363 K.**

| $(R\text{-}Br\text{-}MBA)_3MnBr_5$ **(300 K)** | | $(R\text{-}Br\text{-}MBA)_3MnBr_5$ **(363 K)** | |
|---|---|---|---|
| Bond | Length(Å) | Bond | Length(Å) |
| Br1-Mn1 | 2.5189(15) | Br1-Mn1 | 2.4835(17) |
| Br2-Mn1 | 2.4898(13) | Br2-Mn1 | 2.4882(16) |
| Br3-Mn1 | 2.5093(14) | Br3-Mn1 | 2.5171(18) |
| Br4-Mn1 | 2.4848(14) | Br4-Mn1 | 2.5076(17) |

**Table S3. The partial bond angles of $(R\text{-}Br\text{-}MBA)_3MnBr_5$ single crystal at 300 K and 363 K.**

| $(R\text{-}Br\text{-}MBA)_3MnBr_5$ **(300 K)** | | $(R\text{-}Br\text{-}MBA)_3MnBr_5$ **(363 K)** | |
|---|---|---|---|
| Bond | Angle(°) | Bond | Angle(°) |
| Br1-Mn1-Br2 | 110.23(5) | Br1-Mn1-Br2 | 110.72(7) |
| Br3-Mn1-Br1 | 104.94(5) | Br3-Mn1-Br1 | 103.99(6) |
| Br3-Mn1-Br2 | 112.12(5) | Br3-Mn1-Br2 | 110.11(6) |
| Br3-Mn1-Br4 | 114.20(5) | Br3-Mn1-Br4 | 105.11(6) |
| Br4-Mn1-Br1 | 103.90(5) | Br4-Mn1-Br1 | 114.03(6) |
| Br4-Mn1-Br2 | 110.91(5) | Br4-Mn1-Br2 | 112.34(7) |

***3. XRD patterns***

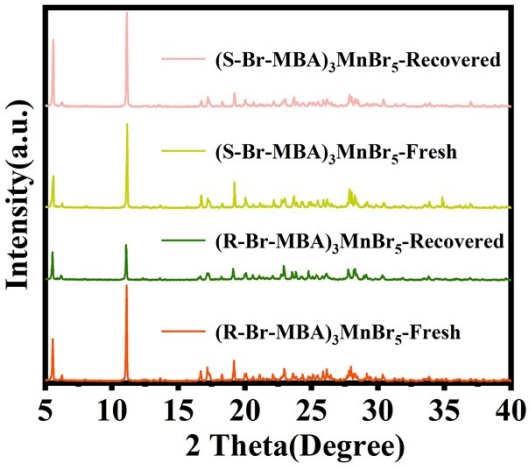


**Figure S2.** PXRD patterns of fresh sample and recovered sample.

***4. CD spectra***

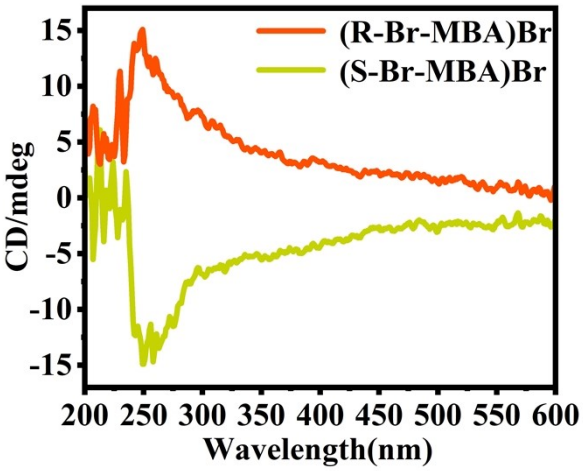


**Figure S3.** CD spectra of R-/S-Br-MBA.

***5. TG and DTG curves***

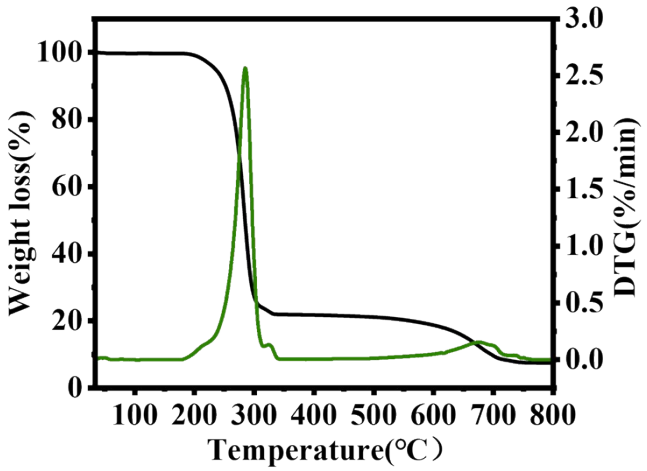


**Figure S4.** TG and DTG curves of $(S\text{-}Br\text{-}MBA)_3MnBr_5$.

***6. FTIR spectra***

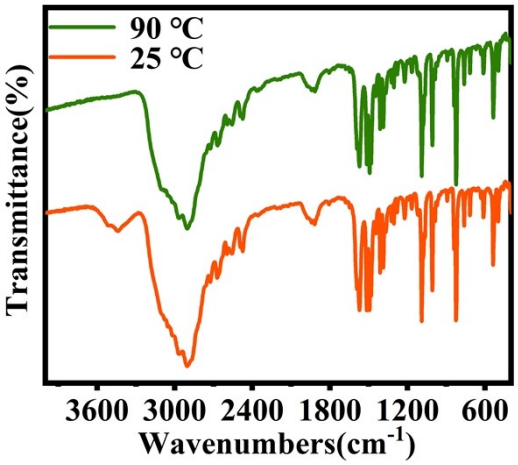


**Figure S5.** The FTIR spectra of (S-Br-MBA)$_3$MnBr$_5$ at 25 ℃ and 90 ℃.

*7. PL spectra and PLQY*

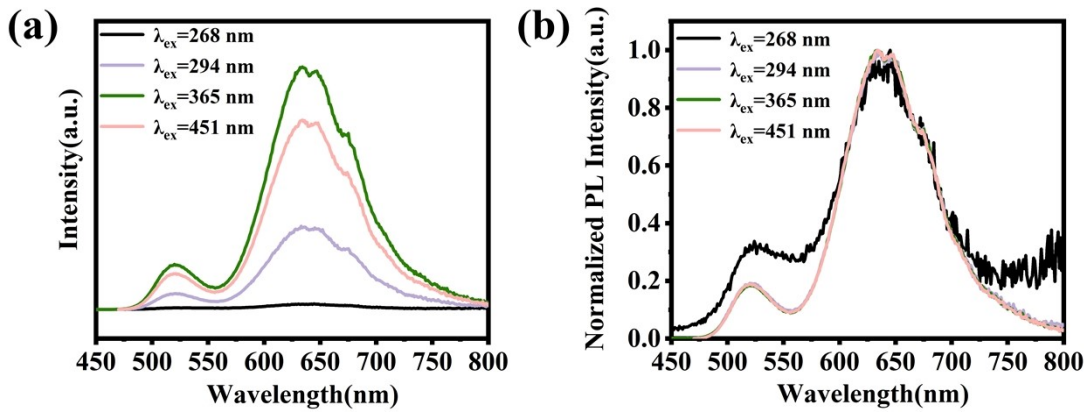


**Figure S6.** (a) PL spectra by monitoring excitation wavelengths range from 268 nm to 451 nm; (b) Normalized PL spectra.

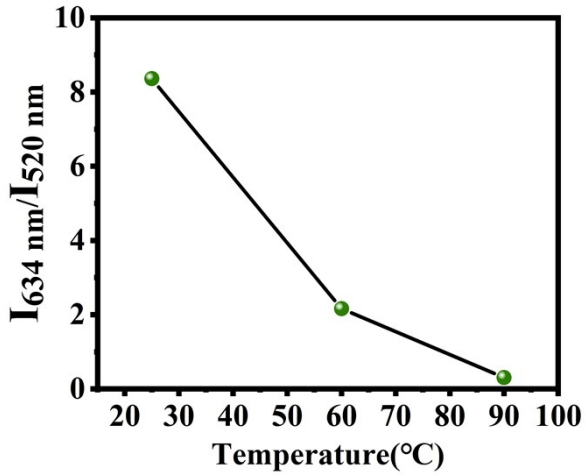


**Figure S7.** $I_{634\ nm}/I_{520\ nm}$ extracted from temperature-dependent PL spectra.

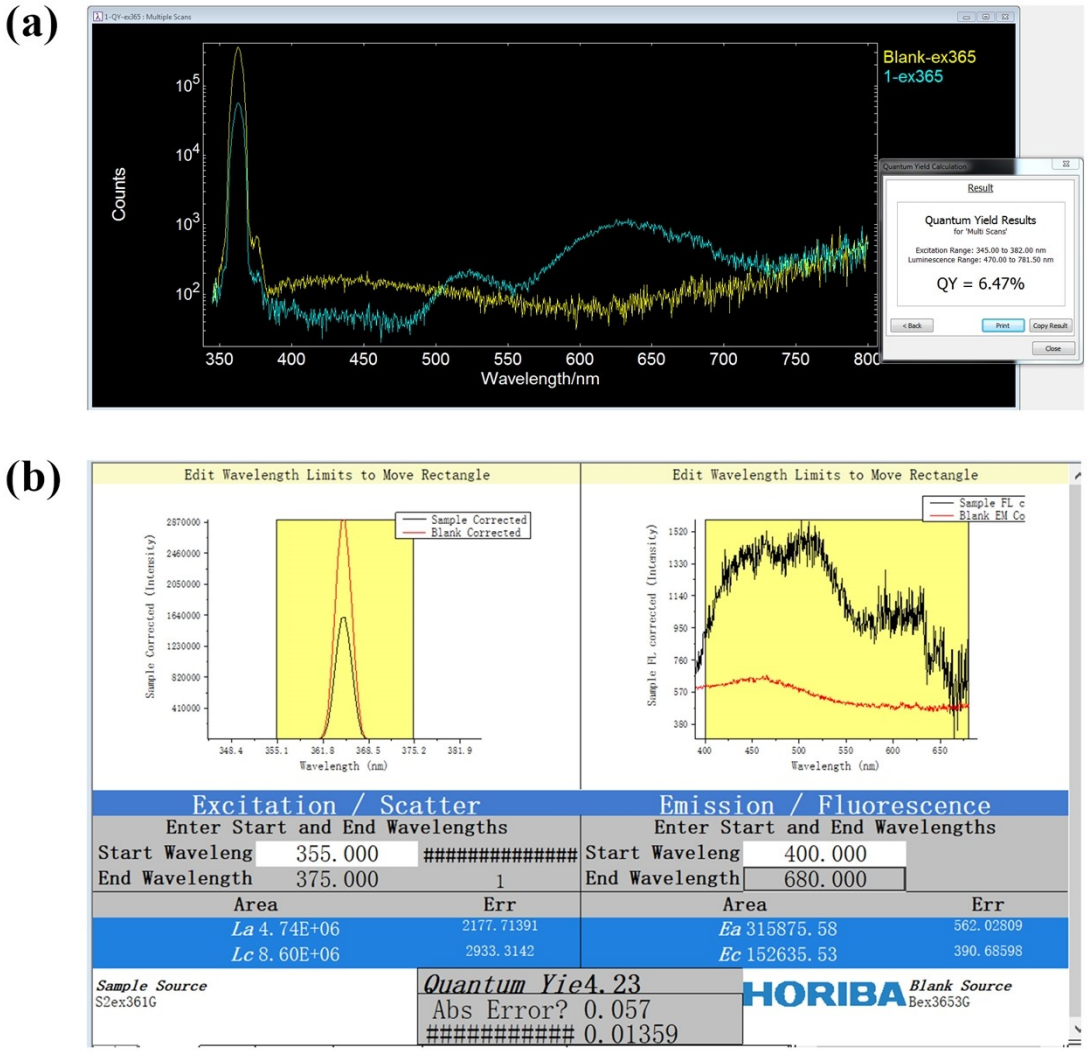


**Figure S8.** PLQY of $(R\text{-}Br\text{-}MBA)_3MnBr_5$ at (a) 25 ℃ and (b) 90 ℃.

***8.Hysteresis loops***

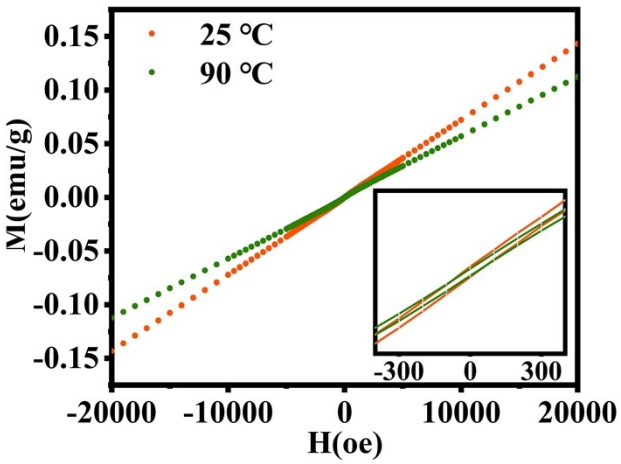


**Figure S9.** Hysteresis loops of (S-Br-MBA)$_3$MnBr$_5$ crystal at 25 ℃ and 90 ℃.

### *9. The luminescence dissymmetry factor ($g_{lum}$)*

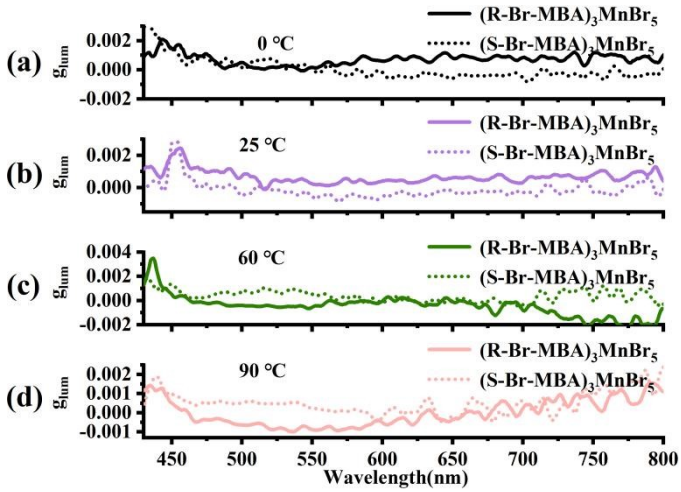


**Figure S10.** The $g_{lum}$ of (R-/S-Br-MBA)$_3$MnBr$_5$ at (a) 0 ℃, (b) 25 ℃, (c) 60 ℃ and (d) 90 ℃.