

Supporting Information
For
Broadband photoluminescence and nonlinear chiroptical
properties in chiral 2D halide perovskites

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Experimental section

Reagents and materials used:

(R)-1-(3-bromophenyl)ethylamine (R-3BrMBA, 98%) was purchased from Kaiwei Chemical Reagent Ltd. (S)-1-(3-bromophenyl)ethylamine (S-3BrMBA, 98%) was purchased from Leyan Chemical Reagent Ltd. Hydrobromic acid (HBr, 48wt.% in water, 99.99% metals basis), lead bromide (PbBr₂, 99.999% metals basis), isopropyl alcohol (99.8%) chlorobenzene (ACS), dimethyl sulfoxide (DMSO, Anhydrous) and N, N-dimethylformamide (DMF, 99.8%) were purchased from Aladdin Reagent Ltd. Cesium bromide (CsBr, 99.9% trace metals basis) was purchased from Sigma-Aldrich. Ethanol anhydrous (99.5%) and deionized water were purchased from Macklin Reagent Ltd. Ether absolute (AR) and acetone (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received without further purification.

Synthesis of (R- or S-3BrMBA)₂PbBr₄ chiral perovskite crystals:

183.5 mg (0.5 mmol) of PbBr₂ and 151 μL of (R)-1-(3-bromophenyl)ethylamine (1 mmol) or (S)-1-(3-Bromophenyl)ethylamine) were separately dissolved in 8 mL of a 48% HBr solution by heating to 90 °C for 2 h under constant magnetic stirring, and then heated to 140 °C for an additional 0.5 h with stirring to produce a clear colorless solution. Thereafter, the solution was quickly transferred into an oven set at 110 °C, which subsequently cools to room temperature at a rate of 1.0 °C/h to obtain bulk single crystal. The obtained single crystals were filtered and washed three times with ether and then dried in a vacuum chamber at room temperature.

Fabrication of (R- and S-3BrMBA)₂PbBr₄ chiral perovskite crystals film:

First, the quartz glass substrates ($15 \times 15 \text{ mm}^2$) were washed in an ultrasonic cleaner using deionized water, acetone, 2-propanol, and ethanol in sequence for 20 min of each, respectively. Second, substrates were treated with oxygen plasma for 5 min for further use. The perovskite thin-film fabrication was performed in a nitrogen-filled glovebox. First, 40 mg of as-synthesized perovskite crystals or powders were dissolved in 200 μL of DMF to prepare precursor solutions. The precursor was stirred at room temperature for 3 h. After that, the precursor solution was spin-coated onto the glass substrates with a rotation speed of 4000 rpm for 40 s, after which they were annealed at 80 °C for 10 min, and the whole deposition process was carried out in a nitrogen atmosphere. The obtained perovskite thin films were stored inside the glove box filled with nitrogen for further characterization.

Fabrication of CsPbBr₃ perovskite film:

The perovskite precursor solution, prepared by 36.7 mg (0.2 mmol) PbBr₂, and 23.3 mg (0.2 mmol) CsBr dissolved in 500 μL DMSO, was fully stirred for 3 h. The perovskite precursor solution was then spin-coated onto clean quartz glass substrates at 4000 rpm for 60 s. During the spin coating process, chlorobenzene (100 μL) was poured on the spinning substrate 45 s prior to the end of the program. Then, the film was heated at 80 °C for 10 min, and the whole deposition process was carried out in a nitrogen atmosphere. The obtained perovskite thin films were stored inside the glove box filled with nitrogen for further characterization.

Structural characterization:

Single-crystal X-ray diffraction (SCXRD) was performed on a Bruker D8 diffractor with Mo K_α radiation ($\lambda = 0.71071 \text{ \AA}$). Crystal structures of R- and S-3BrMBA₂PbBr₄ were solved by direct methods and then refined by the full-matrix least-squares refinements on F^2 using a SHELXLTL 97 software package. The specific analytical data are presented in **Tables S1–S6**.

Materials characterizations:

Powder X-ray diffraction measurements were performed on a Smart Lab 3KW instrument (Rigaku) with a Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) source. The diffraction patterns were collected in the 2θ range of 3°–50° with a step size of 0.01°. Surface morphologies were characterized using FEI Inspect F50 field emission scanning electron microscope (SEM) at an accelerating voltage of 3 kV. Optical absorption spectra of perovskite thin films were measured at room temperature through absorption scan of UV–VIS–NIR Spectrofluorometer (UV-3600 Plus) while maintaining a 0.5 nm interval at range of 200–800 nm. The CD spectra were collected using a circular dichroism spectrometer (Model 420SF, Aviv Biomedical Inc., America) at room temperature. The background was blank quartz glass, and the spectra were obtained at a scan rate of 200 nm/min, with the data pitch being 1 nm and band width being 2 nm.

The steady-state photoluminescence (PL) spectra of perovskites were carried out on LabRAM HR800 Raman system (Horiba Jobin Yvon) with a 325 nm laser. The time-resolved photoluminescence (TRPL) spectroscopy was carried out on a home-built system. A 385 nm pulsed laser was used as the excitation source, which was frequency doubled by a BBO crystal from an fs-laser source (Chameleon Compact OPO, center wavelength: 770 nm, repetition rate: 80 MHz). The pump light was focused by a microscopy objective (50 $\times$, NA: 0.5). For the laser power-dependent photoluminescence, a continuously variable attenuator was used to change the exciting power. The time-resolved photoluminescence (TRPL) spectra and laser power-dependent photoluminescence were obtained with a HORIBA iHR320 spectrophotometer, and a 400 nm long-pass filter (MEFH10-400LP, Lbtek) was placed in front of the spectrometer to filter out the excess laser. TRPL decay kinetics were collected and analyzed using a TCSPC (Pico Quant PicoHarp 300) module (SPC130) and a SPAD detector (IDQ, id100) with an instrument response function $\sim$ 200 ps. The PLE spectra was obtained at room temperature on an Fluorolog spectrofluorometer (Horiba Jobin Yvon). Circularly polarized luminescence (CPL) spectra were recorded by the JASCO CPL spectrophotometer (CPL-300) coupled with a 325 nm excitation source.

SHG measurements were carried out in a reflection geometry through our home-built micro-area nonlinear optical characterization system. The pump pulses were supplied by Spectra-Physics Solstice Maitai HP (100fs, 80MHz, 680–1060 nm), which were focused onto the chiral perovskite crystals via an microscopy objective (50 $\times$, NA: 0.5). The spot radius of the fs pulses on the samples was $\sim$ 10 μ m at 840 nm. During the measurement, a broadband ultrafast variable attenuator (Newport VA-BB) was employed to control the incident power of the laser pulses. The SHG signals were collected by a HORIBA iHR320 spectrophotometer, and a 750 nm short-pass filter (MEFH10-750SP, Lbtek) is placed in front of the spectrometer to filter out the excess laser. For linear polarization-resolved SHG measurements, a linear polarizer (FLP25-NIR-M, Lbtek) and a half waveplate (AHWP10-SNIR, Lbtek) were placed in the incident light path to rotate the polarization direction of the laser pulses. For circular polarization-resolved SHG measurements, the half waveplate was replaced by a quarter-waveplate (AQWP20-SNIR, Lbtek) and placed in the incident light path to modulate excitation polarization between left circular polarization (σ^-) and right circular polarization (σ^+) states.

Supplement figures:

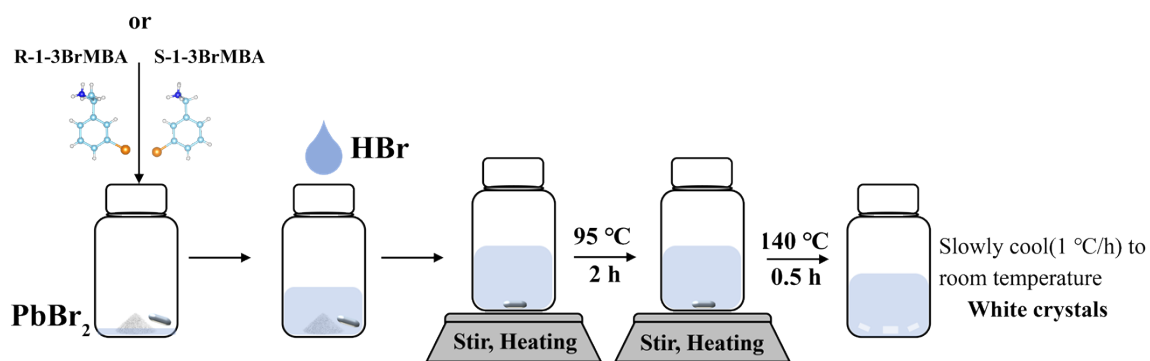


Fig. S1: The schematic diagram of synthesis of R- or S-3BrMBA₂PbBr₄ chiral perovskite crystals.

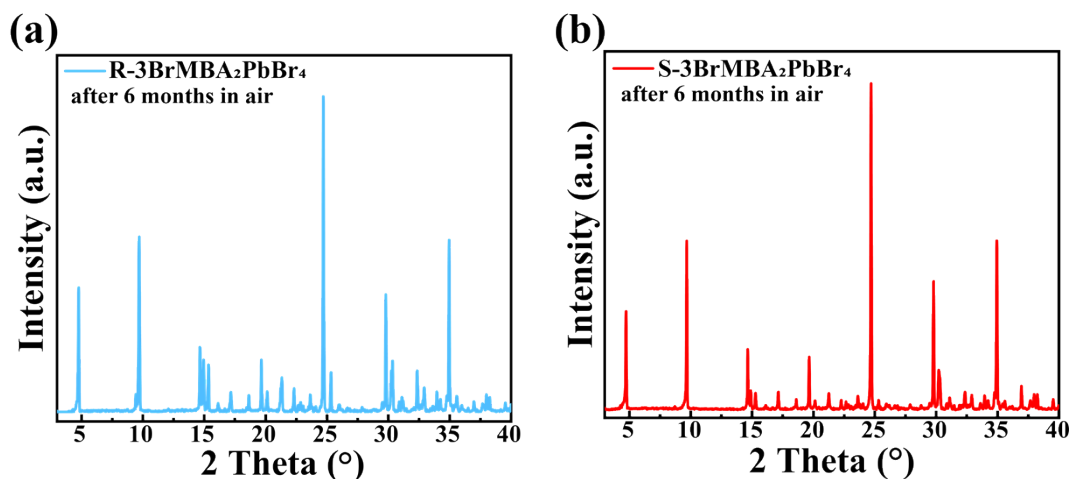


Fig. S2: PXRD patterns of the R- and S-3BrMBA₂PbBr₄ single crystals stored for 6 months. The crystals were stored in ambient conditions.

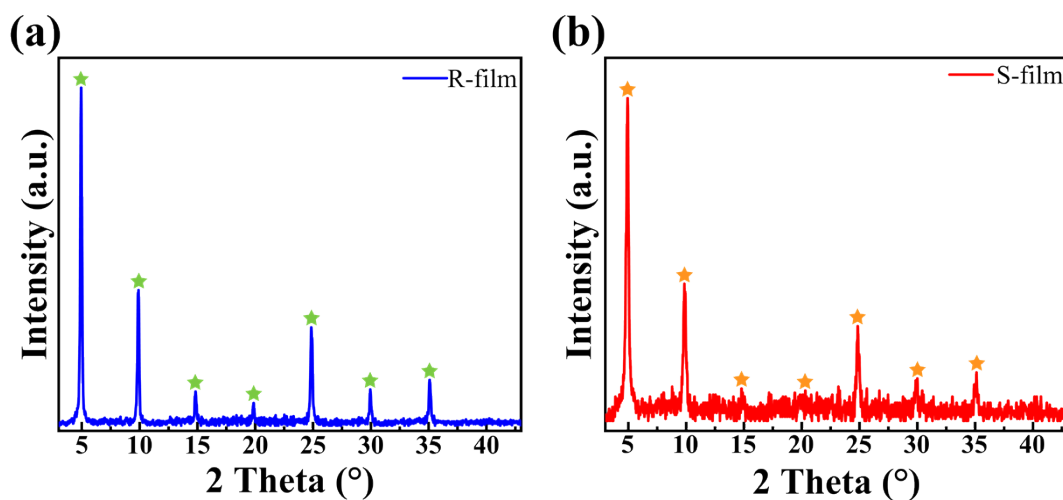


Fig. S3: XRD patterns of R-3BrMBA₂PbBr₄ and S-3BrMBA₂PbBr₄ thin films.

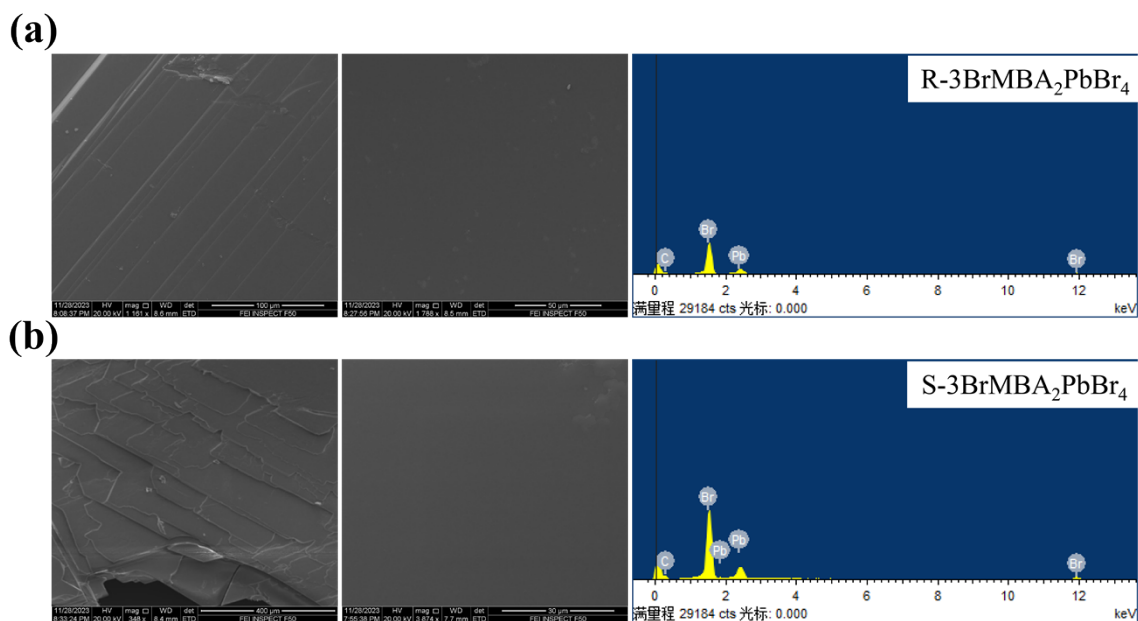


Fig. S4: SEM-EDS images of (a) R-3BrMBA₂PbBr₄ and (b) S-3BrMBA₂PbBr₄ bulk crystals.

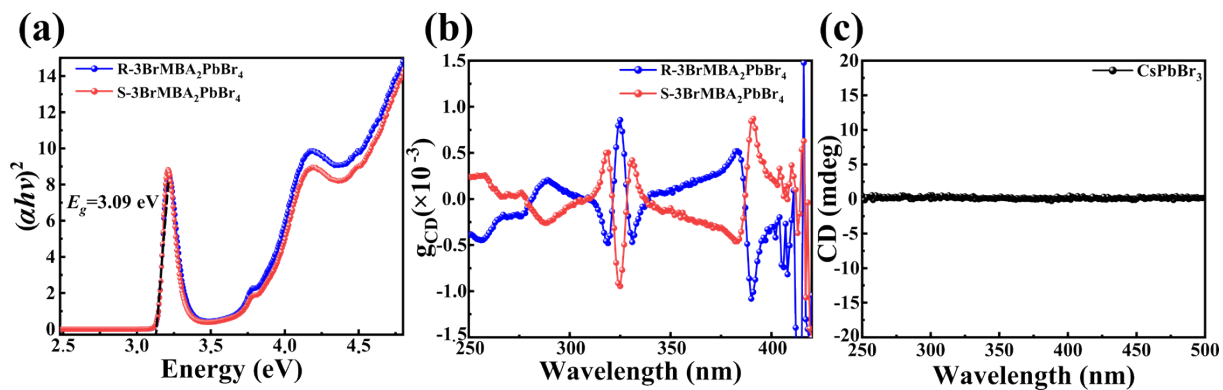


Fig. S5: (a) The bandgap of R- and S-3BrMBA₂PbBr₄ determined from a Tauc-plot. (b) The g_{CD} spectra of R- and S-3BrMBA₂PbBr₄ films. (c) The Circular dichroism (CD) spectra of achiral CsPbBr₃ films range from 200 to 500 nm.

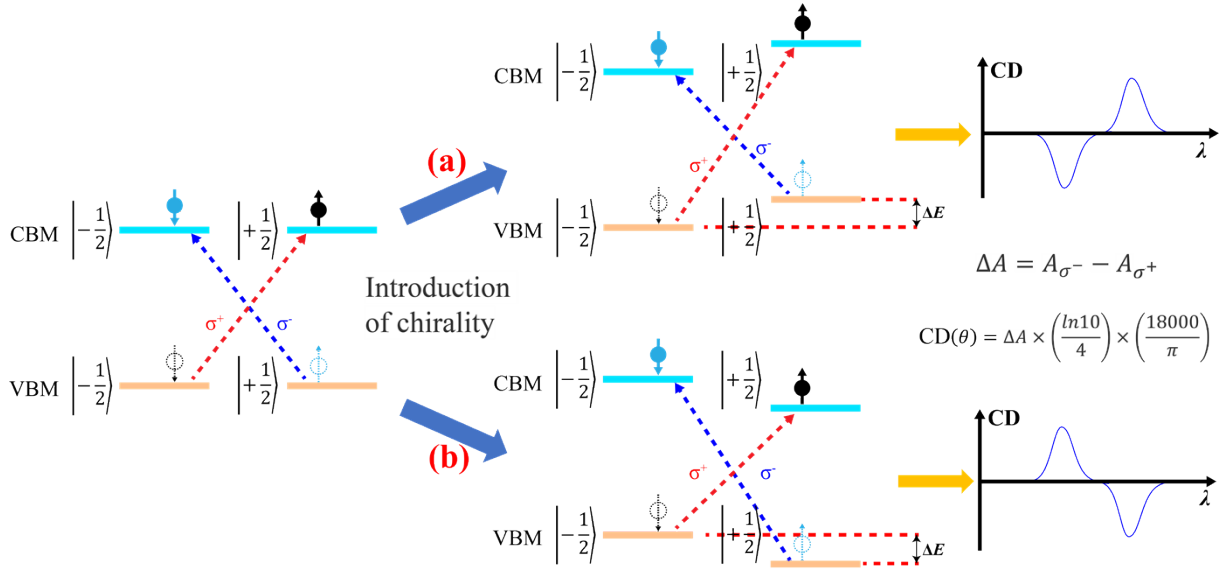


Fig. S6: Schematic illustration of energy diagram perturbation by chirality leading to asymmetric CD spectra.

The microscopic physical mechanism for the sign change in the CD signal of chiral halide perovskites is illustrated in **Fig. S6**. The valence band maximum (VBM) and conduction band minimum (CBM) of halide perovskites are both composed of quantum states with total angular momentum quantum number $J = 1/2$ and magnetic quantum number $m_j = \pm 1/2$ ^[1], where the magnetic quantum number represents the spin state of the electrons. This unique band structure primarily originates from the spin-orbit coupling phenomenon of lead ions within the perovskite structure^[2]. More precisely, Perovskite absorbs σ^+ corresponds to transitions from the VBM state $\left| -\frac{1}{2} \right\rangle$

to the CBM state $\left| +\frac{1}{2} \right\rangle$, while the absorption of σ^- corresponds to the transition from VBM $\left| +\frac{1}{2} \right\rangle$ to CBM $\left| -\frac{1}{2} \right\rangle$. This selection rule for band-edge optical transitions provides a crucial theoretical foundation for a deep understanding of circular dichroism.

When the energy bands of halide perovskite undergo chiral perturbation, analogous to the effect of a weak magnetic field, the degeneracy of energy levels with different magnetic quantum numbers is lifted. For left-handed chirality (path a in **Fig. S6**), electrons with spin-up (i.e., the $\left| +\frac{1}{2} \right\rangle$ energy levels in VB and CB) possess relatively higher energy. This results in a difference in the photon energy required for absorption of σ^- and σ^+ light. Therefore, the absorption peak for σ^+ has a higher energy, while the absorption peak for σ^- has lower energy, resulting in an asymmetric CD signal. For right-handed chirality, the changes in the band edge energy levels of perovskite are opposite (path b in **Fig. S6**), thus producing an opposite CD signal^[1, 3, 4].

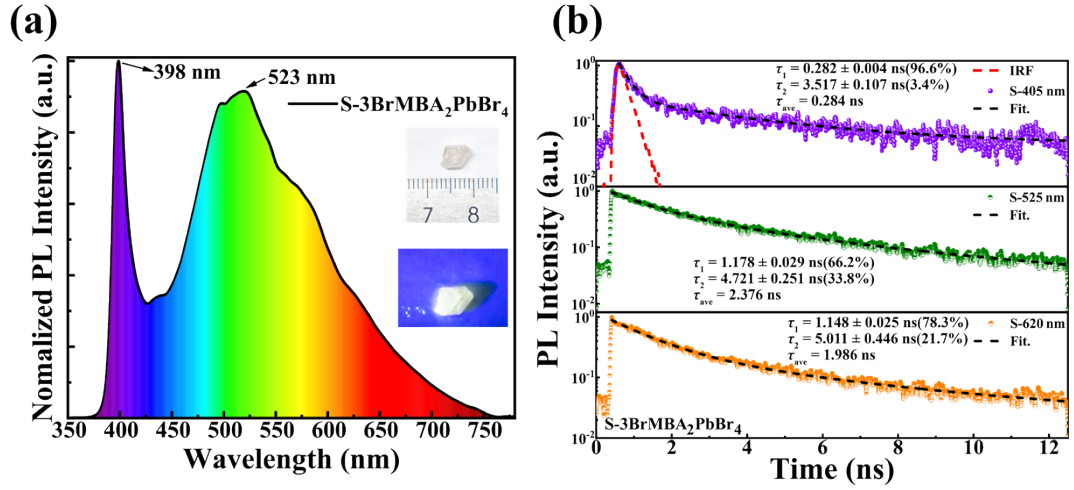


Fig. S7: (a) PL spectra of S-3BrMBA₂PbBr₄ single crystal ($\lambda_{\text{exc}} = 325$ nm). Inset: the optical image under ambient light (up) and UV light (down, 365 nm). (b) Time-resolve photoluminescence (TRPL) spectra decays and fittings of the S-3BrMBA₂PbBr₄ single crystal emission at 405, 525 and 620 nm.

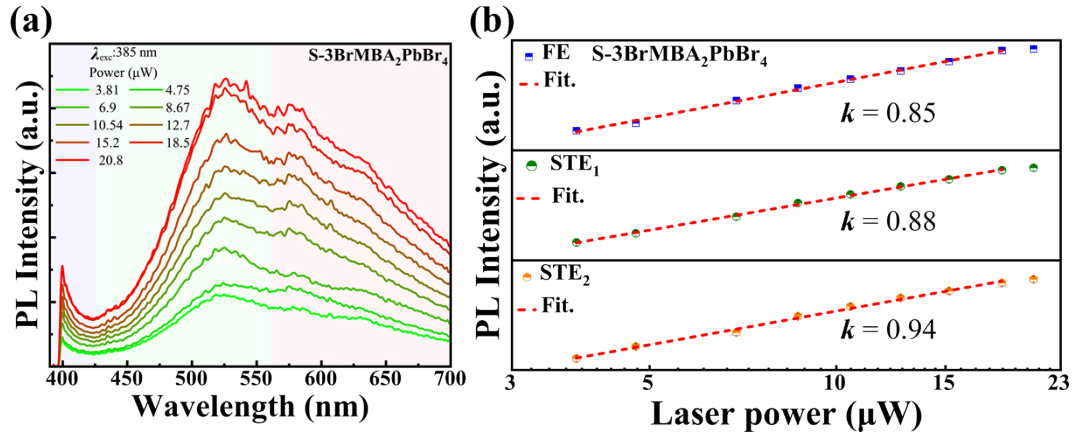


Fig. S8: (a) Power-dependent PL spectra of S-3BrMBA₂PbBr₄ single crystal obtained at various excitation powers of a 385 nm laser at room temperature. (b) The integrated PL intensity as a function of excitation power of S-3BrMBA₂PbBr₄ single crystal for FE (top), STE₁ (middle), and STE₂ (bottom).

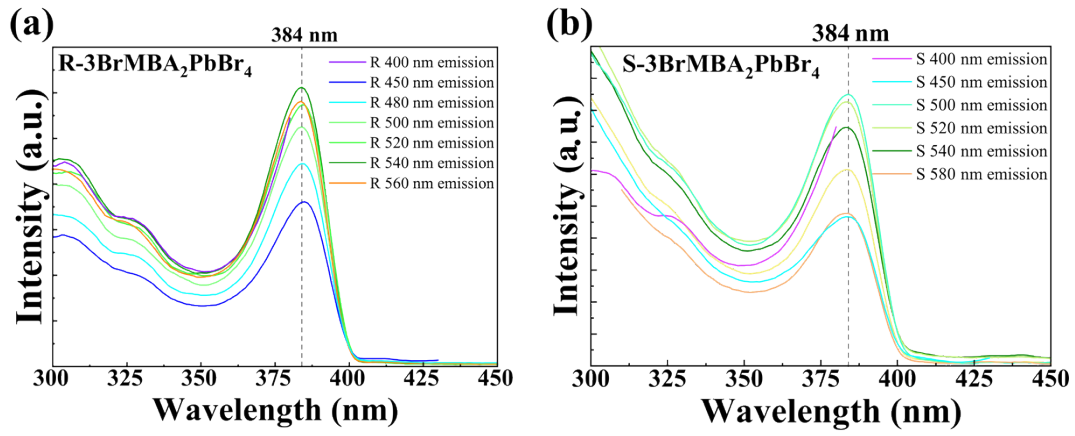


Fig. S9: Photoluminescence excitation spectra (PLE) for the different wavelengths emissions of (a) R-3BrMBA₂PbBr₄ and (b) S-3BrMBA₂PbBr₄ thin film.

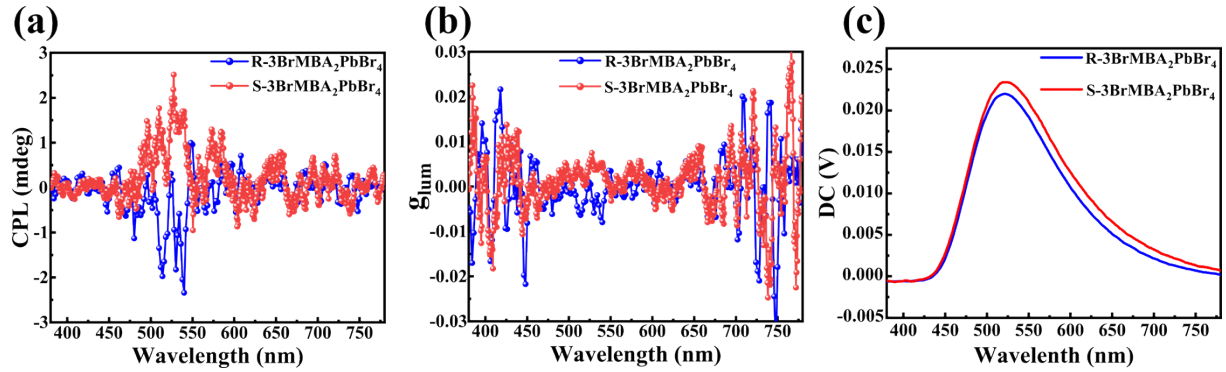


Fig. S10: (a) CPL spectra of R- and S-3BrMBA₂PbBr₄ at 325 nm excitation. (b) CPL g_{lum} versus wavelength of R- and S-3BrMBA₂PbBr₄ excited at 325 nm. (c) DC values of R- and S-3BrMBA₂PbBr₄.

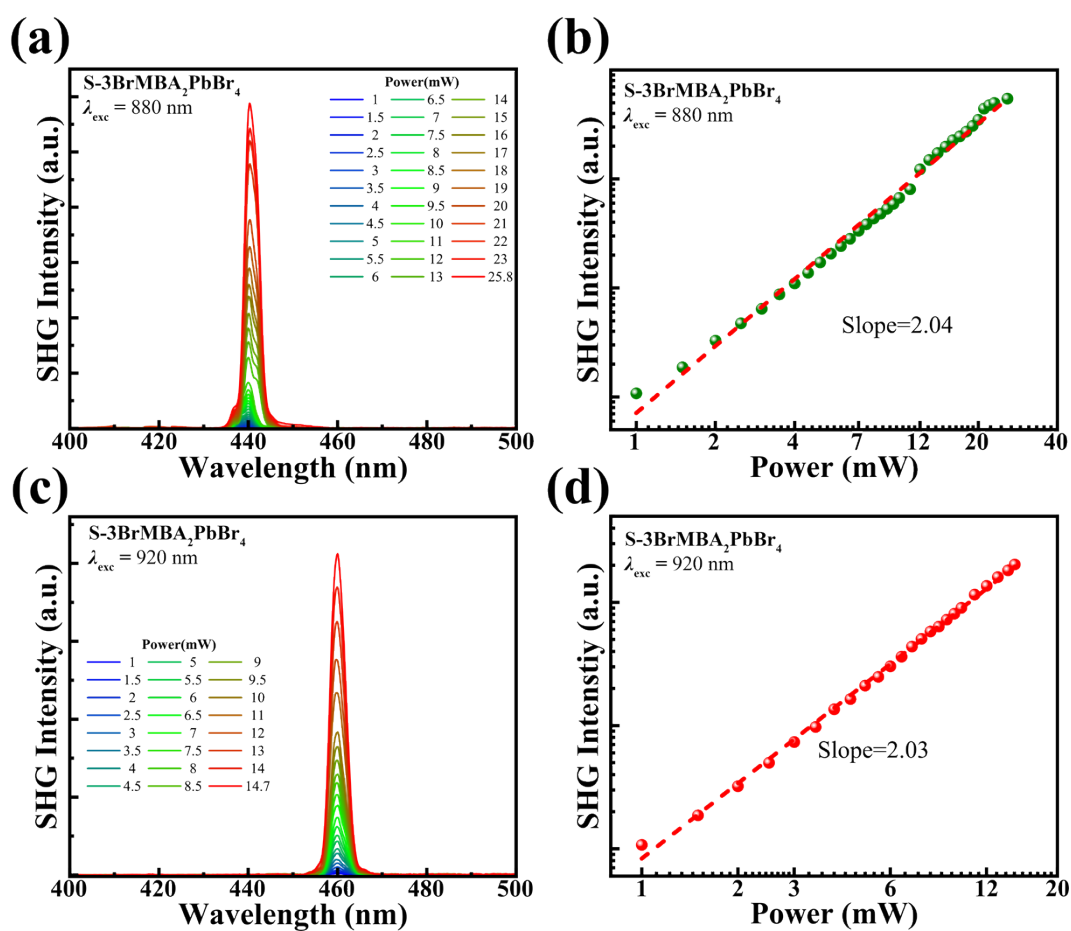


Fig. S11: The SHG spectra of S-3BrMBA₂PbBr₄ under various excitation power. (a, c) Excitation and detection wavelengths are 880(920) and 440(460) nm, respectively. (b, d) Logarithmic plot of SHG intensity as function of the incident power. The solid line is a linear fit with a slope of 1.92(20.3).

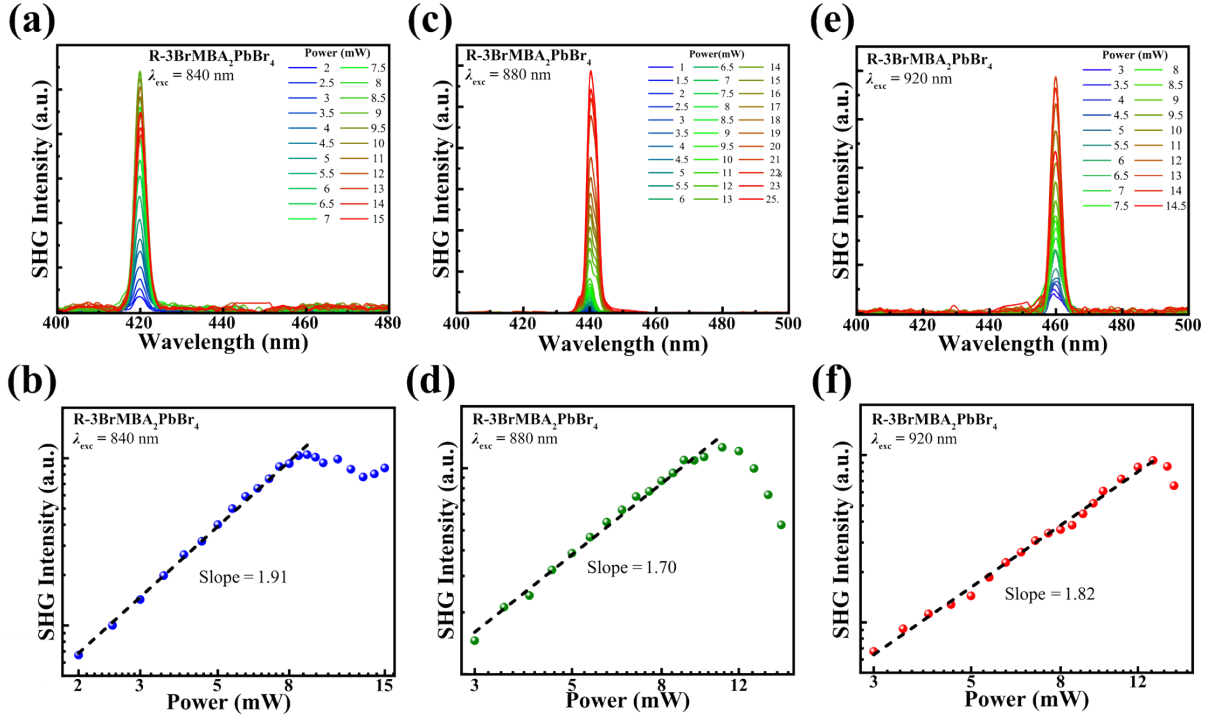


Fig. S12: The SHG spectra of R-3BrMBA₂PbBr₄ under various excitation power. (a, d) Excitation wavelengths are 840 nm and logarithmic plot of SHG intensity as function of the incident power with a slope of 1.91. (b, e) Excitation wavelengths are 880 nm and logarithmic plot of SHG intensity as function of the incident power with a slope of 1.70. (c, f) Excitation wavelengths are 920 nm and logarithmic plot of SHG intensity as function of the incident power with a slope of 1.82.

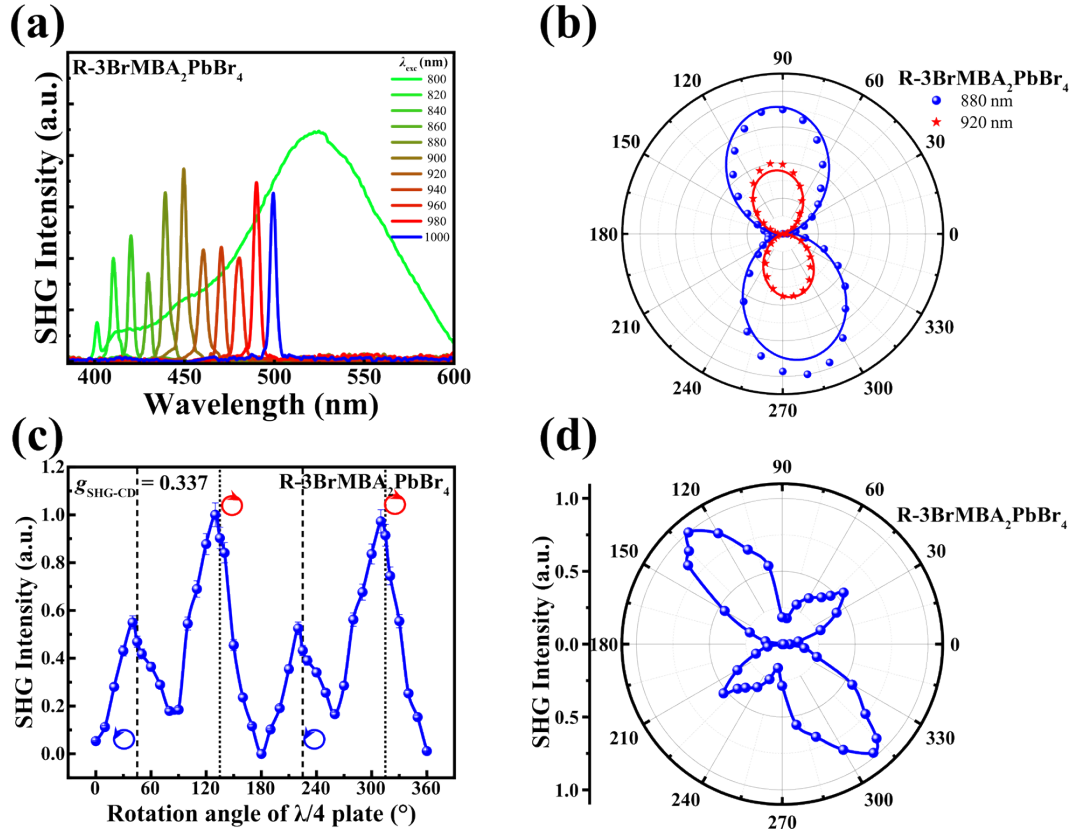


Fig. S13: Nonlinear optical responses of the chiral R-3BrMBA₂PbBr₄ perovskite single crystal. (a) The SHG intensity of the R-3BrMBA₂PbBr₄ crystal pumped at various wavelengths. (b) The polarization dependence spectra with selected excitation wavelength, the curves represent the $\cos 2\theta$ fit for SHG. (c) SHG intensity as a function of the rotation angle of the quarter-waveplate. The excitation and detection wavelengths are 840 and 420 nm, respectively. (d) Polar SHG intensity plots of the R-3BrMBA₂PbBr₄ crystal as a function of polarization angle.

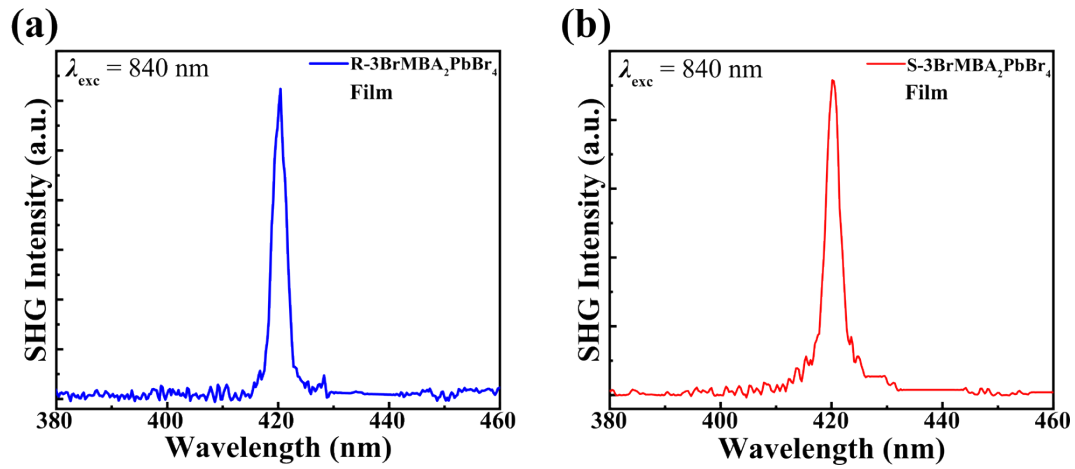


Fig. S14: The SHG intensity of the (a) R-3BrMBA₂PbBr₄ and (b) S-3BrMBA₂PbBr₄ thin film pumped at 840 nm.

Table S1: Crystallographic data for R-3BrMBA₂PbBr₄ and S-3BrMBA₂PbBr₄.

Identification code	R-3BrMBA ₂ PbBr ₄	S-3BrMBA ₂ PbBr ₄
Empirical formula	C ₁₆ H ₂₂ Br ₆ N ₂ Pb	C ₁₆ H ₂₂ Br ₆ N ₂ Pb
Formula weight	929.00	929.00
Temperature/K	296.15	296.15
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁
<i>a</i> /Å	8.7980(11)	8.7793(7)
<i>b</i> /Å	7.8893(9)	7.8782(5)
<i>c</i> /Å	18.020(3)	17.9737(14)
α /°	90	90
β /°	97.505(4)	97.480(2)
γ /°	90	90
Volume/Å ³	1240.0(3)	1232.57(16)
<i>Z</i>	2	2
ρ_{calc} g/cm ³	2.488	2.503
μ /mm ⁻¹	16.473	16.573
<i>F</i> (000)	848.0	848.0
Crystal size/mm ³	0.12 × 0.1 × 0.08	0.12 × 0.1 × 0.08
Radiation	Mo <i>K</i> _α (λ = 0.71073)	Mo <i>K</i> _α (λ = 0.71073)
2 θ range for data collection/°	4.56 to 50.188	4.68 to 50.19
Index ranges	−10 ≤ <i>h</i> ≤ 10, −9 ≤ <i>k</i> ≤ 8, −21 ≤ <i>l</i> ≤ 21	−10 ≤ <i>h</i> ≤ 10, −9 ≤ <i>k</i> ≤ 9, −21 ≤ <i>l</i> ≤ 21
Reflections collected	19652	21993
Independent reflections	4093 [<i>R</i> _{int} = 0.0830, <i>R</i> _{sigma} = 0.0892]	4300 [<i>R</i> _{int} = 0.0724, <i>R</i> _{sigma} = 0.0854]
Data/restraints/parameters	4093/121/207	4300/7/207
Goodness-of-fit on <i>F</i> ²	1.025	1.006
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0475, <i>wR</i> ₂ = 0.0805	<i>R</i> ₁ = 0.0510, <i>wR</i> ₂ = 0.0914
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0906, <i>wR</i> ₂ = 0.0942	<i>R</i> ₁ = 0.0946, <i>wR</i> ₂ = 0.1064
Largest diff. peak/hole /eÅ ⁻³	0.87/−1.56	1.97/−1.06
Flack parameter	0.069(18)	0.07(2)

Table S2: Bond Lengths for R-3BrMBA₂PbBr₄.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1	Br3	3.037(2)	Pb1	Br5	2.976(2)
Pb1 ¹	Br3	3.193(2)	Pb1 ²	Br5	3.037(2)
Pb1	Br4	2.979(2)	Pb1	Br6	2.990(2)
$\Delta d = 6.08 \times 10^{-4}$					

$$^1 1 - X, 1/2 + Y, 1 - Z; ^2 -X, 1/2 + Y, 1 - Z; ^3 1 - X, -1/2 + Y, 1 - Z; ^4 -X, -1/2 + Y, 1 - Z$$

Table S3: Bond Lengths for S-3BrMBA₂PbBr₄.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1 ¹	Br3	3.038(3)	Pb1 ²	Br5	3.187(2)
Pb1	Br3	2.966(2)	Pb1	Br5	3.029(3)
Pb1	Br4	2.983(2)	Pb1	Br6	2.973(3)
$\Delta d = 6.23 \times 10^{-4}$					

$$^1 1 - X, -1/2 + Y, 1 - Z; ^2 -X, -1/2 + Y, 1 - Z; ^3 1 - X, 1/2 + Y, 1 - Z; ^4 -X, 1/2 + Y, 1 - Z$$

Table S4: Bond Angles for R-3BrMBA₂PbBr₄.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br3	Pb1	Br3 ³	85.10(3)	Br5	Pb1	Br4	97.52(7)
Br4	Pb1	Br3 ³	85.79(6)	Br5	Pb1	Br5 ⁴	83.90(3)
Br4	Pb1	Br3	89.25(6)	Br5	Pb1	Br6	90.70(6)
Br4	Pb1	Br5 ⁴	89.90(6)	Br6	Pb1	Br3 ³	87.15(6)
Br5	Pb1	Br3	88.96(7)	Br6	Pb1	Br3	101.06(6)
Br5 ⁴	Pb1	Br3 ³	102.14(7)	Br6	Pb1	Br5 ⁴	80.88(6)
$\sigma^2 = 45.33$							

$$^1 1 - X, 1/2 + Y, 1 - Z; ^2 -X, 1/2 + Y, 1 - Z; ^3 1 - X, -1/2 + Y, 1 - Z; ^4 -X, -1/2 + Y, 1 - Z$$

Table S5: Bond Angles for S-3BrMBA₂PbBr₄.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br3	Pb1	Br3 ³	83.88(3)	Br4	Pb1	Br5	101.11(7)
Br3	Pb1	Br4	90.70(7)	Br4	Pb1	Br5 ⁴	87.25(6)
Br3	Pb1	Br5	89.06(8)	Br5	Pb1	Br5 ⁴	85.16(3)
Br33	Pb1	Br5 ⁴	101.99(8)	Br6	Pb1	Br3 ³	89.88(7)
Br3	Pb1	Br6	97.36(7)	Br6	Pb1	Br5 ⁴	85.81(7)
Br4	Pb1	Br3 ³	80.82(7)	Br6	Pb1	Br5	89.25(6)
$\sigma^2 = 44.87$							

$$^1_1 - X, -1/2 + Y, 1 - Z; ^2_2 - X, -1/2 + Y, 1 - Z; ^3_1 - X, 1/2 + Y, 1 - Z; ^4_2 - X, 1/2 + Y, 1 - Z$$

Table S6: Bond Angles for R- and S-3BrMBA₂PbBr₄.

R-3BrMBA ₂ PbBr ₄				S-3BrMBA ₂ PbBr ₄			
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Pb1	Br3	Pb1 ¹	143.57(8)	Pb1	Br3	Pb1 ¹	157.55(10)
Pb1	Br5	Pb1 ²	157.71(9)	Pb1	Br5	Pb1 ²	143.68(10)
$\Delta\beta = 14.14$				$\Delta\beta = 13.87$			

References:

- [1] Ahn J, Ma S, Kim J Y, et al. Chiral 2D organic inorganic hybrid perovskite with circular dichroism tunable over wide wavelength range. *J Am Chem Soc*, 2020, 142(9), 4206
- [2] Shamsi J, Urban A S, Imran M, et al. Metal halide perovskite nanocrystals: Synthesis, post-synthesis modifications, and their optical properties. *Chem Rev*, 2019, 119(5), 3296
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- [4] Yang L S, Lin E C, Hua Y H, et al. Circularly polarized photoluminescence of chiral 2D halide perovskites at room temperature. *Acs Appl Mater Inter*, 2022, 14(48), 54090