

Supporting Information

New Lead Bromide Chiral Perovskites with Ultra-Broadband White-Light Emission

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Experimental Section.

Reagents and Materials Used:

R-(+)- β -Methylphenethylamine (R-(+)- β -MPEA, 98%) was purchased from HEOWNS Company. S-(-)- β -Methylphenethylamine (S-(-)- β -MPEA, 99%) was purchased from RHN Company. Lead oxide (PbO, 99.0%), 48% aqueous hydrobromic acid (HBr), 2-propanol (GR), ethanol (GR), N, N-dimethylformamide (DMF, 99.5%), and dichloromethane (CH₂Cl₂, 99.8%) were purchased from Aladdin Reagent Ltd. Toluene (C₇H₈, 99.5%) and acetone (AR) were purchased from Damao. All the reagents were used as received without further purification.

Synthesis of (R-(+)- or S-(-)- β -MPEA)₂PbBr₄ chiral perovskite crystals:

0.1338g (3mmol) of PbO was dissolved in 4ml of a 48% HBr solution by heating to 80 °C under constant magnetic stirring. Subsequent addition of R-(+)- β -MPEA 0.1722g (0.6mmol) (or S-(-)- β -MPEA 172 ul (0.6mmol)) to the hot solution affords a clear solution and for 2h. The stirring was then discontinued, the solution was left to slowly cool to room temperature and left to stand 4h to afford crystals. The crystals were washed with dichloromethane and dried overnight with 50 °C under reduced pressure. Selected IR data (observed in KBr-pellets) for (R-(+)- β -MPEA)₂PbBr₄ : 3061 (m) , 3025(m), 2963(m), 2903(w), 2895(w), 1576(s), 1481(s), 1392(w), 986(m), 963(m), 907(w), 870(w), 839(w), 755(s), 693(s), 593(w), 530(m); (S-(-)- β -MPEA)₂PbBr₄ : 3075(m), 3025(m), 2964(m), 2897(w), 1576(s), 1476(s), 1385(w), 998(m), 971(m), 907(m), 866(m), 839(w), 757(s), 697(s), 597(w), 524(m). FTIR spectra presented small sharp peaks at 3476cm⁻¹ for our chiral perovskite crystals, indicative of intense vibration associated with the protonation of nitrogen. Moreover, the unique broad peak in range of 3300-3700 cm⁻¹ appears upon our perovskites due to preparation of perovskites in air.

Synthesis of ((rac)-MPEA)₂PbBr₄ chiral perovskite crystals:

0.1338g (3mmol) of PbO was dissolved in 4ml of a 48% HBr solution by heating to 80 °C under constant magnetic stirring. Subsequent addition of R- β -MPEA 0.0861g (0.3mmol) and S- β -MPEA 86 μ l (0.3mmol)) to the hot solution affords a clear solution and for 2h. The stirring was then discontinued, the solution was left to slowly cool to room temperature and left to stand 4h to afford crystals. The crystals were washed with dichloromethane and dried overnight with 50 °C under reduced pressure.

Fabrication of (R-(+)- and S-(-)- β -MPEA)₂PbBr₄ and ((rac)-MPEA)₂PbBr₄ chiral perovskite crystals film:

First, the clean quartz glass substrates (2*2cm²) were washed in an ultrasonic cleaner using acetone, 2-propanol, and ethanol in sequence for 15 min of each. Second, substrates were placed on a hot plate to preheating for further use. Next, as-synthesized perovskite crystals were dissolved in DMF with a certain concentration (250 mg/ml) as the precursor solution, and 70 μ l of the precursor solution was used. The continuous thin films were prepared on substrates by a spin-coating method at 2000 rpm for 30 s. Finally, the films were annealed at 65 °C for 2 minutes on a hot plate to induce crystallization.

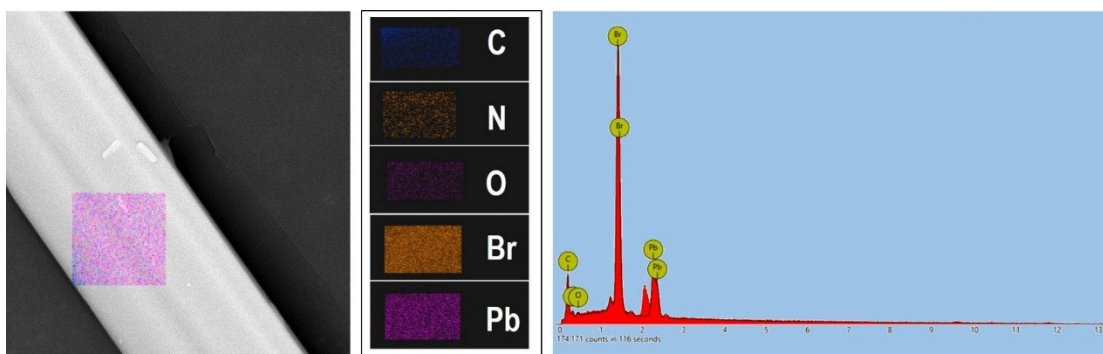
Materials Characterizations:

Thermo-gravimetry analysis (TGA) measurement was carried out using a TA instruments TG209F3 Tarsus system. The sample were heated from 35 °C to 800 °C at a rate of 10 °C min⁻¹, under a nitrogen flux of 30 ml min⁻¹ (nitrogen is used as protective gas and scavenging gas).

The PXRD analysis was performed on Bruker Powder X-Ray Diffractometer using Copper X-ray tube (standard) radiation. Infrared (IR) spectra were recorded as KBr pellets with an ALPHA spectrometer. Optical absorption spectra of perovskite crystals were measured at room temperature through absorption scan of UV-VIS-NIR Spectrofluorometer (UV-3600 Plus) while maintaining a 1 nm interval at range of 200-800 nm. The CD spectra were collected using a CD spectrometer (J-810, JASCO) at

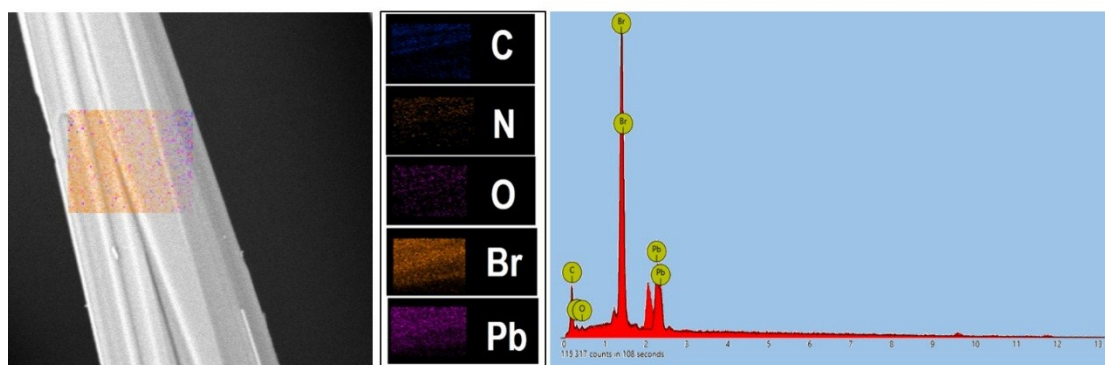
room temperature. The background was blank glass, and the spectra were obtained at a scan rate of 200 nm min⁻¹, with the data pitch being 1 nm and band width being 2 nm. Steady-state photoluminescence spectra of perovskites were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with continuous (150 W) and pulsed xenon lamps. The PLQY were acquired using an Edinburgh-steady state/transient fluorescence spectrometer FLS1000 system equipped with a xenon lamp, calibrated integrating sphere, and the Fluorescence Analysis Software Technology (FAST) package provides unsurpassed accuracy. The PLQY was calculated by the equation: $\eta_{\text{QY}} = (I_{\text{S}} - I_{\text{R}}) / (E_{\text{R}} - E_{\text{S}})$, in which I_{S} represents the luminescence emission spectrum of the sample, I_{R} is the luminescence emission spectrum from the reference (BaSO₄ powders), E_{R} is the excitation spectrum for exciting the reference, and E_{S} is the excitation spectrum for exciting the sample. Time-resolved absorption and emission data were collected at room temperature. The decay dynamics of emission and transient absorption spectra were monitored by using a pump-probe setup with an apparatus time of 2-3 ns, R928-PMT Detector, and excitation wavelength of 355 nm laser pulses with a pulse energy of 7mJ.

There is no noticeable difference in both XRD patterns among our perovskites and the previously reported one^{1, 2}, suggesting that our perovskites have the similar crystalline structures. In previously reported 2D perovskites (A₂BX₄), A site organic cations possess organic molecule of S- and R- methylbenzylamine (denoted as S-MBA and R-MBA, respectively). In our perovskites, A site organic molecule is R-(+)- and S-(-)- β -Methylphenethylamine (R-(+)- and S-(-)- β -MPEA).



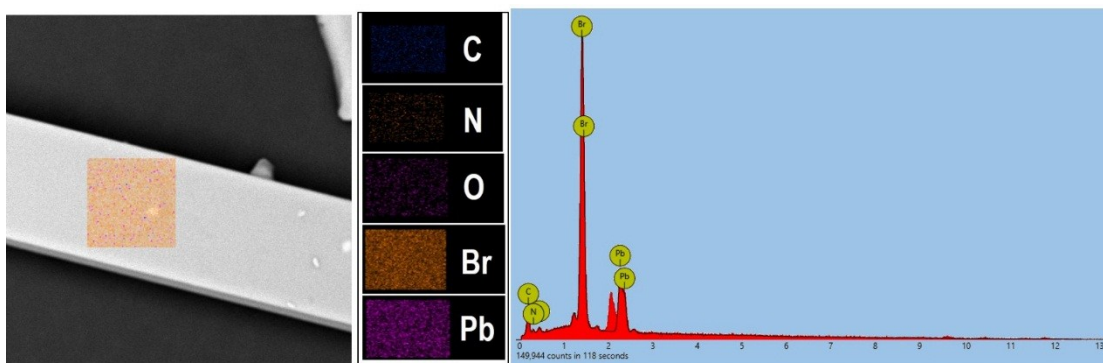
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
35	Br	Bromine	42.93	51.36
6	C	Carbon	26.92	4.84
82	Pb	Lead	12.88	39.95
7	N	Nitrogen	9.54	2.00
8	O	Oxygen	7.73	1.85

Figure S1. SEM image (scale bar is 5 μ m) and element mapping images of (R-(+)- β -MPEA)₂PbBr₄. According to related references^{3, 4}, we have further made more discussions for EDS analysis. Through analysis, the corresponding EDS spectrum of (R-(+)- β -MPEA)₂PbBr₄ give a Pb and Br heavy element atomic ratio (%) of 1.00: 3.33, which is not very close to the theoretical ratio of 1: 4. This result may be assigned to the existence of O element. The presence of O element is ascribed to the preparation in air. For light elements, we can only qualitatively confirm their existence in the crystals due to the resolution of the EDS spectrum.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
35	Br	Bromine	42.46	49.83
6	C	Carbon	25.28	4.46
82	Pb	Lead	13.26	40.35
8	O	Oxygen	9.56	2.25
7	N	Nitrogen	9.43	2.22

Figure S2. SEM image (scale bar is 30 μ m) and element mapping images of (S-(-)- β -MPEA)₂PbBr₄. Through analysis, the corresponding EDS spectrum of (S-(-)- β -MPEA)₂PbBr₄ give a Pb and Br heavy element atomic ratio (%) of 1.00: 3.20. This result is similar with EDS analysis result of (R-(+)- β -MPEA)₂PbBr₄. For light elements, we can only qualitatively confirm their existence in the crystals due to the resolution of the EDS spectrum.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
35	Br	Bromine	49.55	51.60
6	C	Carbon	16.31	2.55
82	Pb	Lead	15.59	42.11
8	O	Oxygen	13.31	2.78
7	N	Nitrogen	5.24	0.96

Figure S3. SEM image (scale bar is 10 μ m) and element mapping images of ((rac)-MPEA)₂PbBr₄. Through analysis, the corresponding EDS spectrum of ((rac)-MPEA)₂PbBr₄ give a Pb and Br heavy element atomic ratio (%) of 1.00: 3.18. This result is similar with EDS analysis result of (R-(+)- β -MPEA)₂PbBr₄. For light elements, we can only qualitatively confirm their existence in the crystals due to the resolution of the EDS spectrum.

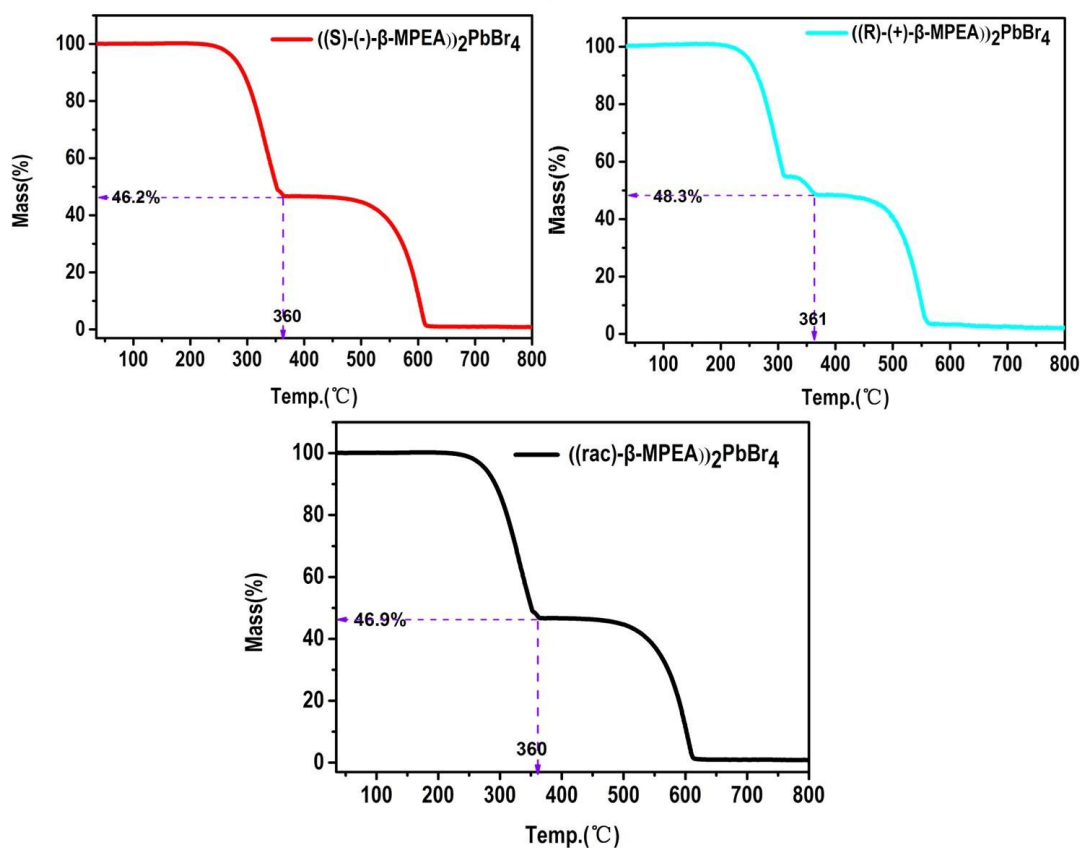
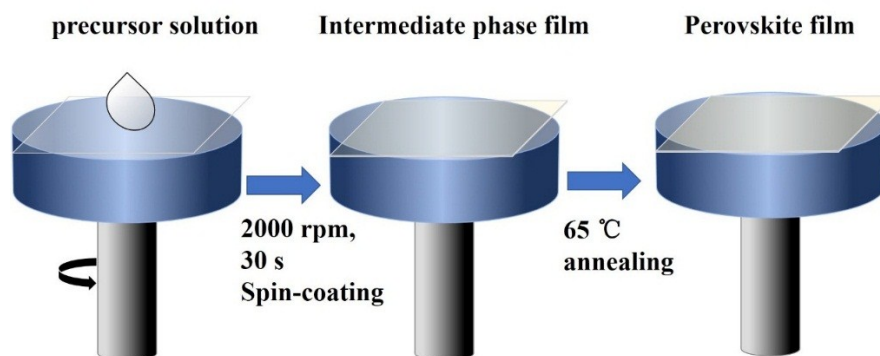


Figure S4. TGA of $(R-(+)-\beta\text{-MPEA})_2\text{PbBr}_4$, $(S-(-)-\beta\text{-MPEA})_2\text{PbBr}_4$, $((rac)\text{-MPEA})_2\text{PbBr}_4$. Minor weight loss is observed in the thermogravimetric (TG) scan at 35.0 °C below 220.0 °C, which indicates that the synthesized perovskite microcrystals is not decomposed until nearly 220.0 °C. According to the TG curve, $(S-(-)-\beta\text{-MPEA})_2\text{PbBr}_4$ shows two obvious stepwise mass losses. The first drastic weight losses is attributed to the loss of chiral molecule and 2HBr, which corresponds to a weight loss of 53.8% and agrees exactly with the organic component (theoretical value of 54.1%). When the temperature is higher than 360 °C, PbBr_2 begin to decompose and corresponds to a weight loss of 46.2% and agrees exactly with the inorganic component (theoretical value of 45.9%) in pristine-Br. $(R-(+)-\beta\text{-MPEA})_2\text{PbBr}_4$ and $((rac)\text{-MPEA})_2\text{PbBr}_4$ show similar result.



Scheme S1. The simple experimental operation diagram of synthesizing chiral perovskite thin-films.

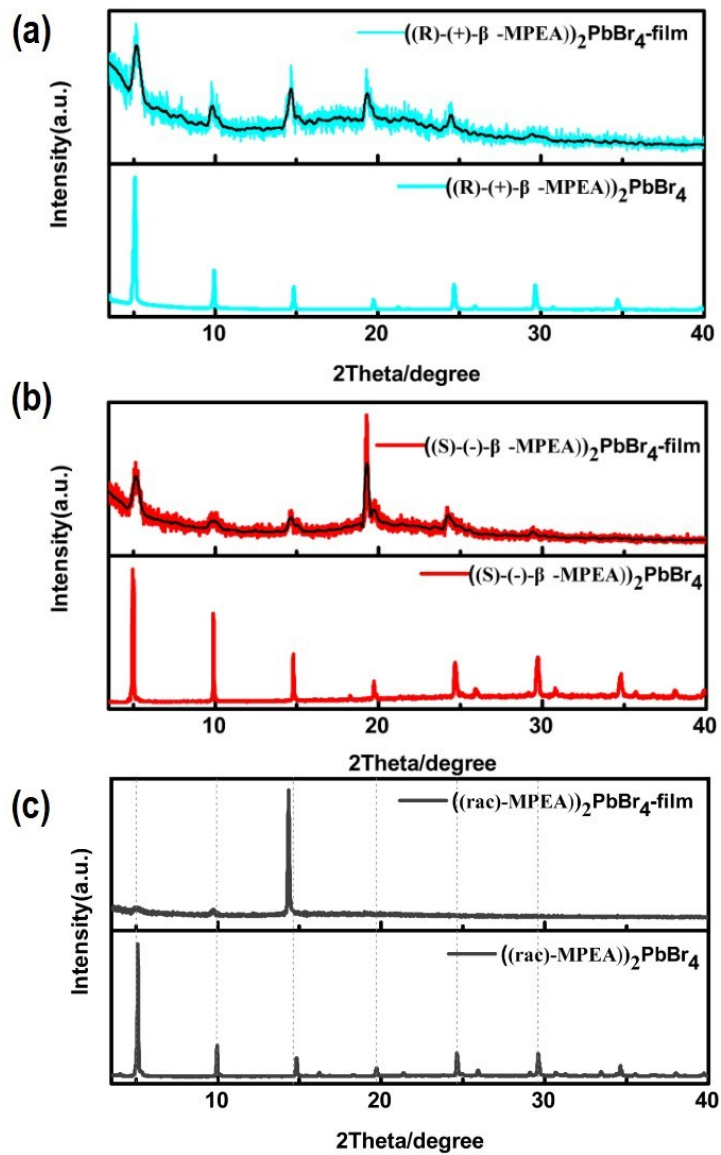


Figure S5. XRD patterns of our chiral (a) (R-(+)-β-MPEA)₂PbBr₄, (b) (S-(-)-β-MPEA)₂PbBr₄, and (c) (rac-MPEA)₂PbBr₄ powder and thin-film.

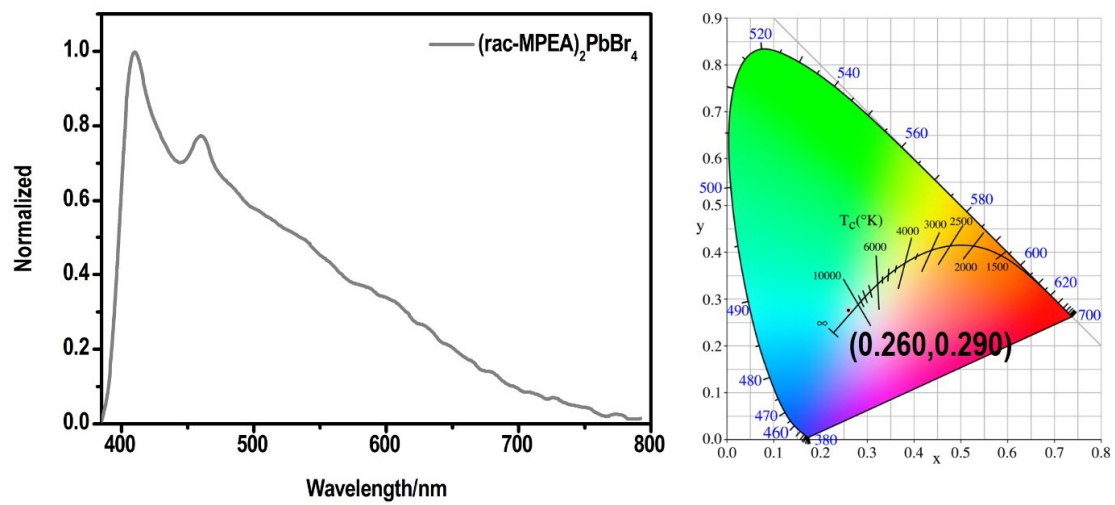


Figure S6. PL spectra of ((rac)-MPEA)₂PbBr₄ film ($\lambda_{\text{ex}}=360$ nm) (Left). CIE coordinated of the emissions of ((rac)-MPEA)₂PbBr₄ film (Right).

Table S1. Reported room-temperature PLQY (Photoluminescence Quantum Yield) and CIE Chromaticity Coordinates for white-light-emitting perovskites.

formula	ref	PLQY(%)	CIE(x,y)
(N-MEDA)PbBr ₄	5	0.5	(0.36,0.41)
(N-MEDA)PbCl _{1.2} Br _{2.8}	5	1.5	—
(EDBE)PbCl ₄	6	2	(0.33,0.39)
(PEA) ₂ PbCl ₄	7	<1	(0.37,0.42)
(CyBMA)PbBr ₄	8	1.5	(0.23,0.29)
(epz)PbBr ₄	9	0.97	(0.44,0.44)
(mpz) ₂ Pb ₃ Br ₁₀	9	0.33	(0.38,0.42)
(hmp)PbBr ₄	9	0.46	(0.41,0.39)
(hep)PbBr ₃	9	0.63	(0.52,0.41)
(hex)PbBr ₃	9	0.35	(0.54,0.40)
(4amp)PbBr ₄	9	0.54	(0.31,0.39)
C ₅ H ₁₄ N ₂ PbCl ₄ ·H ₂ O	10	1	(0.39,0.37)

N-MEDA= N¹-methylethane-1, 2-diammonium, EDBE= 2,2'-(ethylenedioxy)bis(ethylammonium), PEA= C₆H₅(CH₂)₂NH₃⁺, CyBMA= cis-1,3-bis(ammoniomethyl)cyclohexane, epz =1-ethylpiperazine, mpz= 1-methylpiperazine, hmp= homopiperazine, hep= heptamethylenimine, hex= hexamethylenimine, 4amp= 4-(aminimethyl)-piperidine

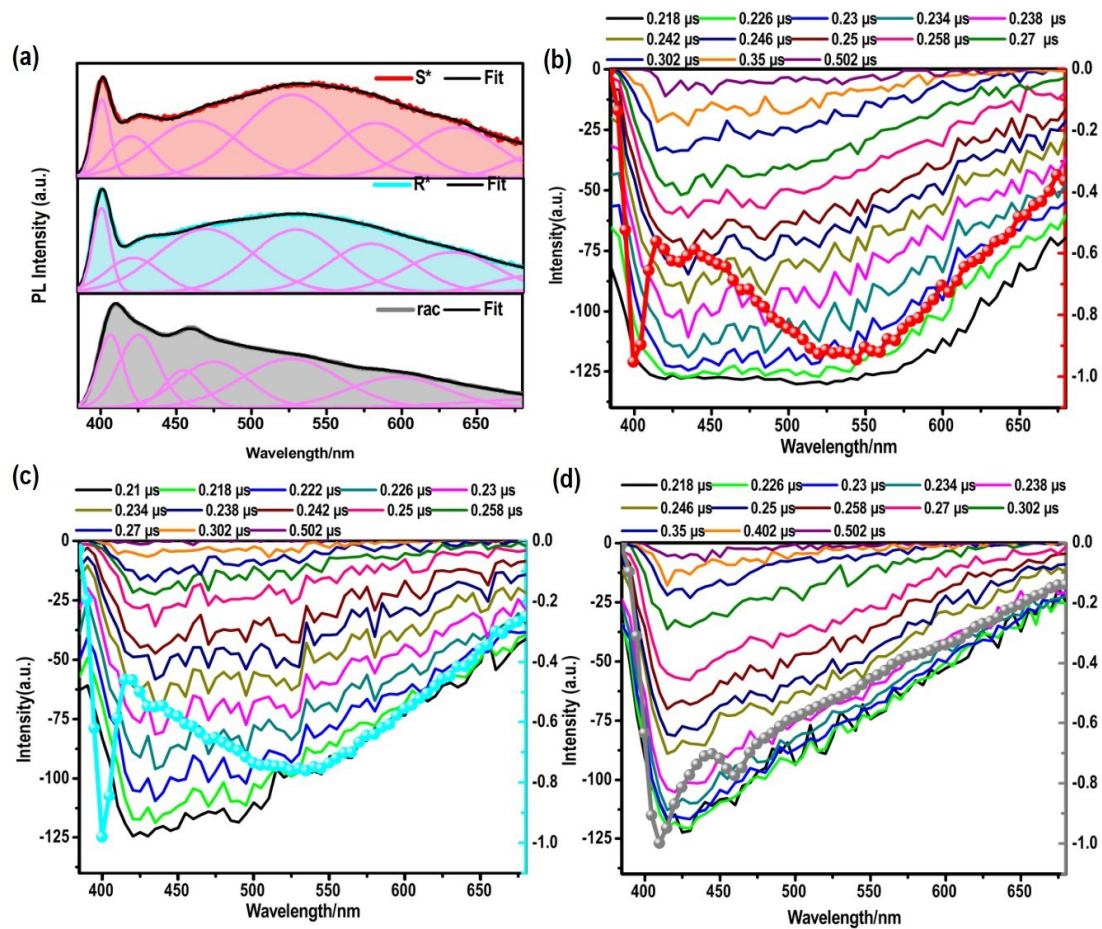


Figure S7. (a) Gaussian curve fitting analysis of the PL spectra of $(S-\beta-MPEA)_2PbBr_4$, $(R-+)\beta-MPEA)_2PbBr_4$, and $((rac)-MPEA)_2PbBr_4$ films. (general fitting=black peak). Nanosecond time-resolve PL emission (TE) spectra of (b) $(S-\beta-MPEA)_2PbBr_4$, (c) $(R-\beta-MPEA)_2PbBr_4$ and (d) $((rac)-MPEA)_2PbBr_4$ films follow the 355 nm photoexcitation, and the comparison of ns-TE spectra with correspond reverse normalized PL spectra.

Reference:

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