Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information

Alternating Chiral and Achiral Spacers for Constructing Two-Dimensional Chiral Hybrid Perovskites toward Circular-Polarization-Sensitive Photodetection

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Experimental

Chemicals. All starting materials, lead acetate trihydrate ($Pb(CH_3COO)_2 \cdot 3H_2O$, 99.5%, Aladdin), hydrobromic acid solution (HBr, 40% in water, Aladdin), *R*- or *S*-1-phenylpropylamine (*R*/*S*-PPA, 98%, Aladdin), *n*-pentylamine (PA, 98%, Aladdin), and N,N-dimethylformamide (DMF, 99.8%, Aladdin) for target compounds synthesis were commercial available and used without further purification.

Synthesis and Crystal Growth. *$(PA)_2PbBr_4$ (**1**)*. Microcrystals of **1** were synthesized by adding $Pb(CH_3COO)_2 \cdot 3H_2O$ (1 mmol, 379 mg) and PA (2 mmol, 174 mg) into 5 mL HBr solution (40% in water). The mixture was heated to boil under a constant magnetic stirring. After a colorless solution was obtained, the heating and stirring was stopped, and the mixture solution was left on the hotplate to cool to room temperature. Then colorless crystal plates were obtained. *(R/S-PPA)(PA)$PbBr_4$ (**2R/2S**)*. The synthesis for **2*R*** (or **2*S***) is same as that of **1** by simply replacing 50% of PA with *R*-PPA (or *S*-PPA) (*i.e.*, PA (1 mmol, 87 mg) + *R*-PPA (1 mmol, 135 mg)). After the solution cooled to room temperature, the plate-like white microcrystals of **2*R*** or **2*S*** were obtained. The bulk single crystals of **2*R*** were grown from its HBr saturated solution containing stoichiometric raw chemicals through a slow temperature-cooling process in a program-controlled oven. The temperature range is 80°C to room temperature, while the decreasing rate was 1°C per day.

Film Preparation. The films of **2*R***/**2*S*** on silica substrates were fabricated using a spin-coating technique. 0.15 g powders of **2*R*** (or **2*S***) were dissolved in 0.66 g DMF, and then 2 droplets of **2*R*** (or **2*S***) were dropped on the substrate. A rotate speed of 2,500 rpm and a holding time of 20 s were adopted. After coating, the films on silica were transferred on a hotplate of 80°C and kept for 5 min.

Single-Crystal and Powder X-Ray Diffraction (XRD). Single-crystal XRD measurements for **1**, **2*R***, and **2*S*** were performed on a Rigaku XtaLAB Synergy R HyPix diffractometer with Mo Kα (λ = 0.71073 Å). The crystal structures were solved by the direct method and refined by the full-matrix method based on F^2 using the Olex2 software. Powder XRD patterns were measured on a Rigaku Miniflex 600 X-ray diffractometer in the 2θ range from 5° to 40° with a step length of 0.02°. CCDC 2252913-2252915 contain the supplementary crystallographic data for this paper.

Optical Property Measurement. The absorption spectra of **1** and **2*R*/2*S*** powders were recorded on a PerkinElmer Lambda 950 ultraviolet-visible-near-infrared (UV-vis-NIR) spectrometer from 200 to 800 nm with an interval of 1 nm.

Circular Dichroism (CD) Measurement. The **2*R*/2*S*** films were fabricated for CD measurement. The CD spectra of **2*R*/2*S*** were measured on a Bio-Logic MOS450 CD spectrometer. The pure silica substrate was used as the reference.

Photodetection. The **2*R*** single-crystal device was used for photodetection. A two-terminal planar structure was adopted with Ag electrodes depositing on the *ab* plane (Figure **S9**). The current-voltage (*I*-*V*) traces and current-time (*I*-*t*) curves were measured on a Keithley 6517B electrometer. The Thorlabs 405 nm fiber-pigtailed laser diode was used as the light source. The incident light power was calibrated using a PM100D optical power meter of Thorlabs. The circularly polarized lights were generated by using a polarizer and quarter-wave plates (Thorlabs).

Density Functional Theory (DFT) Calculation. The single-crystal structure of **2*R*** at 300 K was used for the theoretical calculations. The DFT calculations were carried out with the CASTEP program in the Materials Studio software. The exchange-correlation effects were treated by the Perdew-Burke-Ernzerhof function (PBE) in the generalized gradient approximation (GGA). A cutoff energy of 820 eV was used, and the *k*-space integration was carried out with a Monkhorst-Pack grid of 6×6×2. The norm-conserving pseudopotential was used to describe the interactions between the ionic cores and electrons. The spin-orbital coupling was not included. The orbital electrons of Pb ($5d^{10}6s^26p^2$), Br ($4s^24p^5$), C ($2s^22p^2$), N ($2s^22p^3$), and H ($1s^1$) were regarded as valence electrons.

Figures

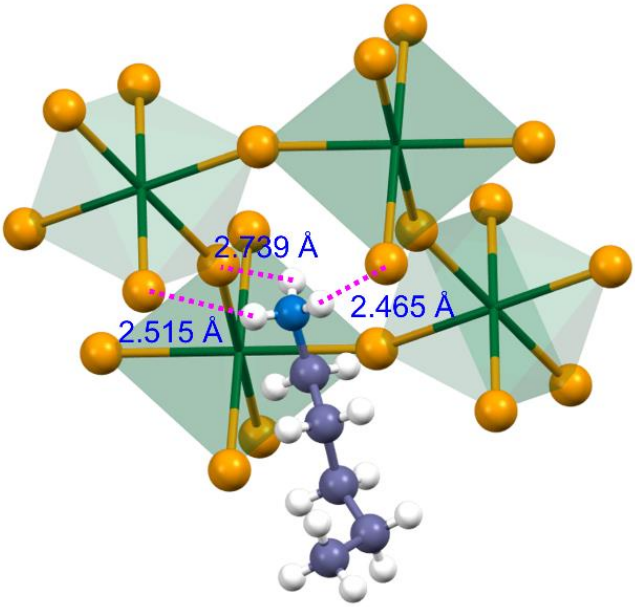

Figure S1. The hydrogen bonds in **1** crystal structure. (Pb: green, Br: yellow, N: Blue; C: Grey; H: White)

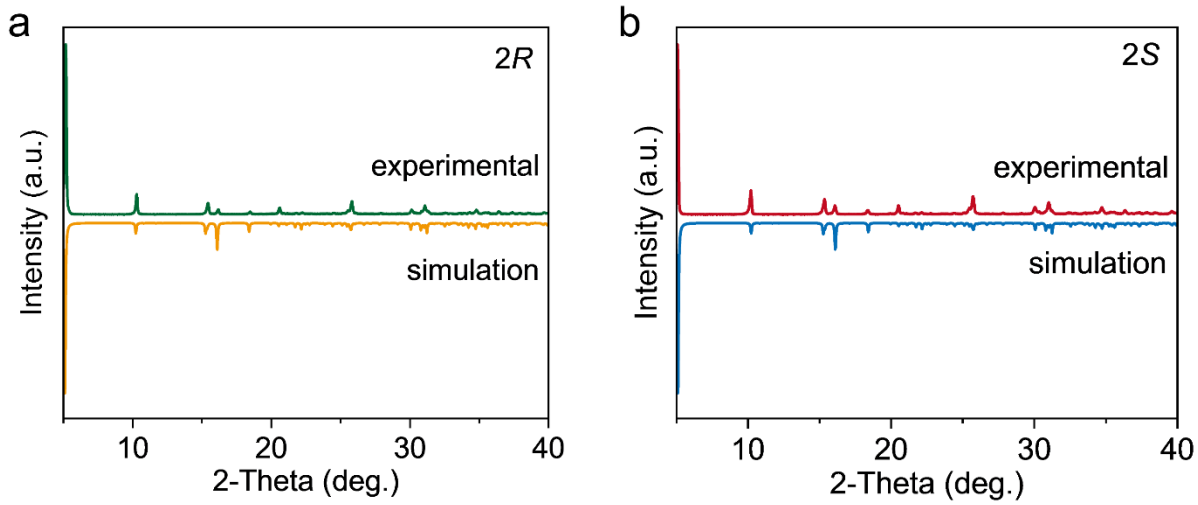

Figure S2. Experimental and simulated powder XRD patterns for (a) **2*R*** and (b) **2*S***.

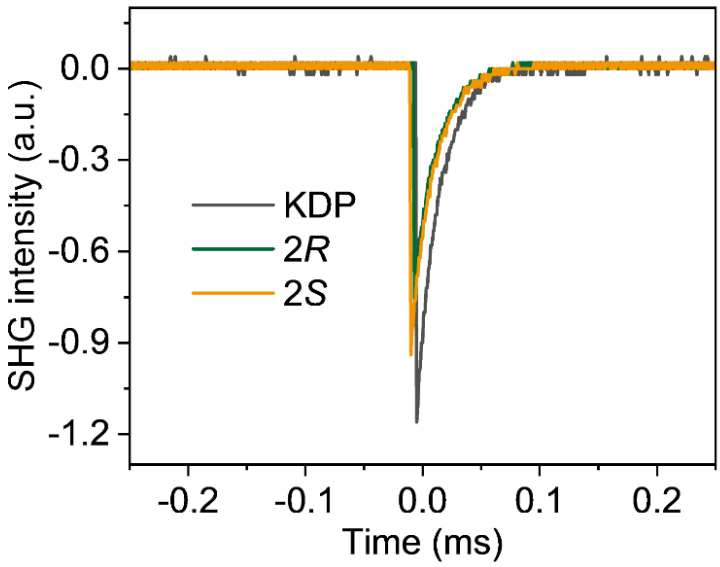

Figure S3. The SHG signals for **2*R***, **2*S***, and KH_2PO_4 (KDP) powders.

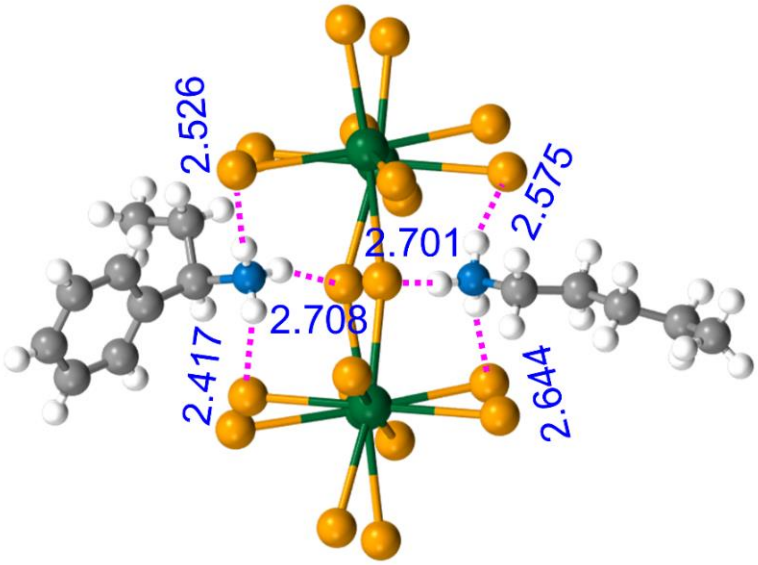

Figure S4. The hydrogen bonds in **2*R*** crystal structure (unit: Å). (Pb: green, Br: yellow, N: Blue; C: Grey; H: White)

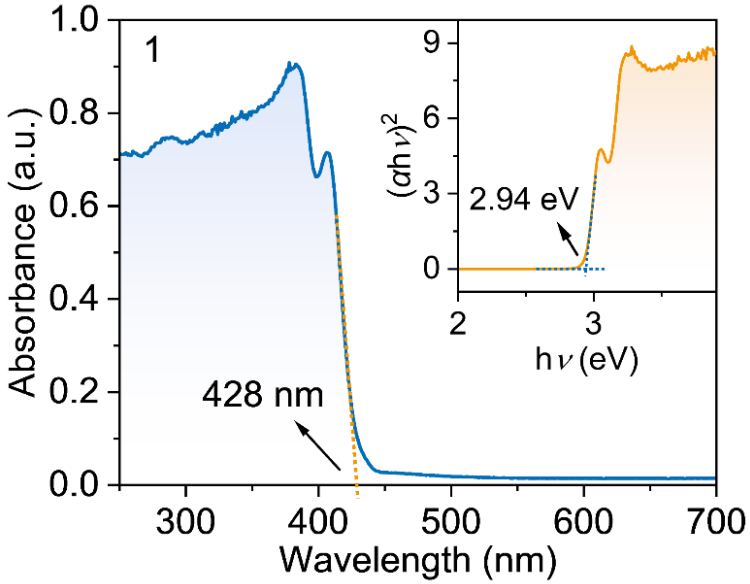

Figure S5. The absorption spectrum and estimated optical bandgap (inset) of **1**.

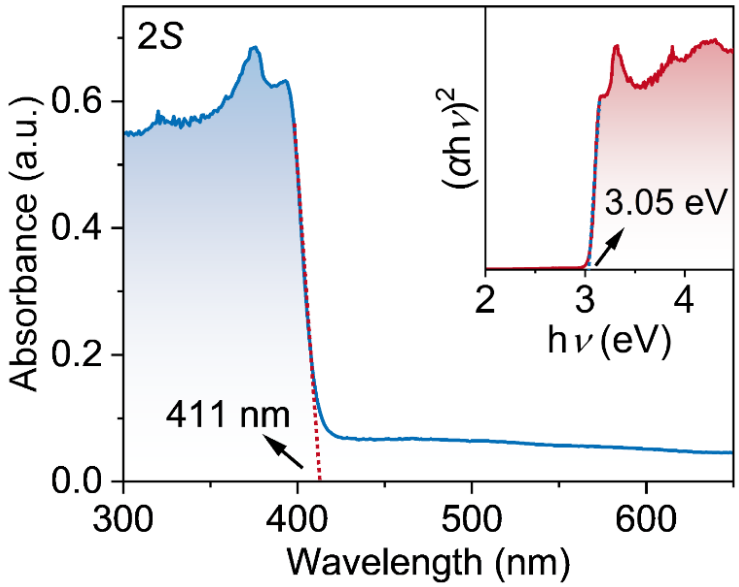

Figure S6. The absorption spectrum and estimated optical bandgap (inset) of **2*S***.

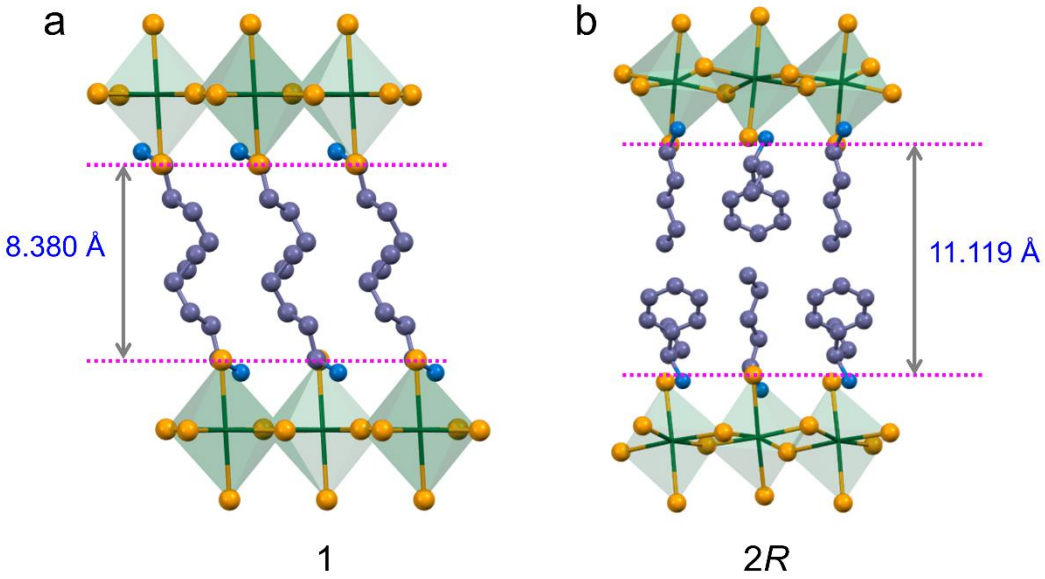

Figure S7. The interlayer distance for **1** and **2*R***. (Pb: green, Br: yellow, N: Blue; C: Grey)

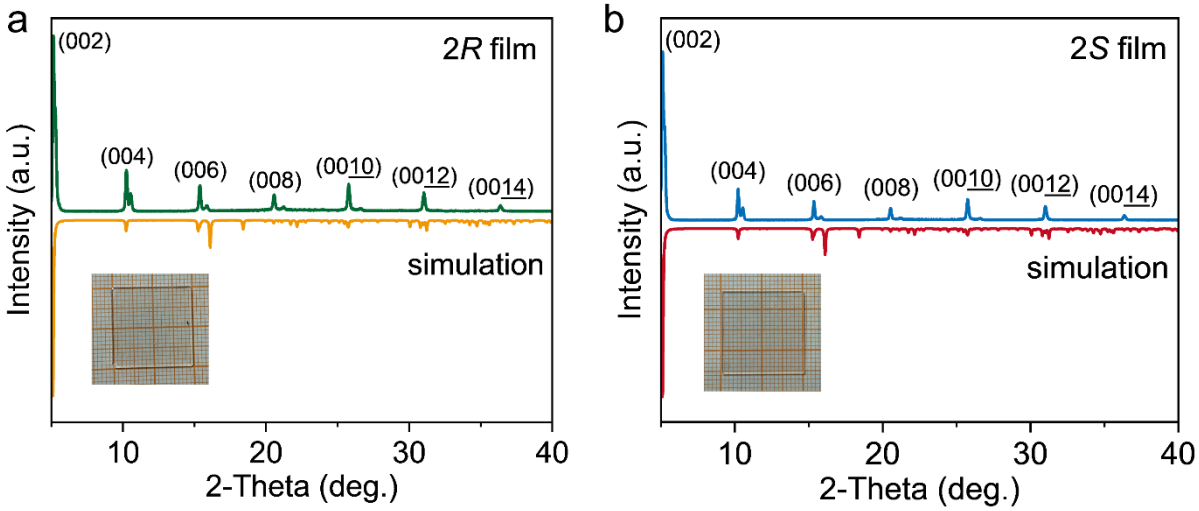

Figure S8. The PXRD patterns of **2*R*** and **2*S*** films. Insets are corresponding photons for **2*R*** and **2*S*** films, respectively.

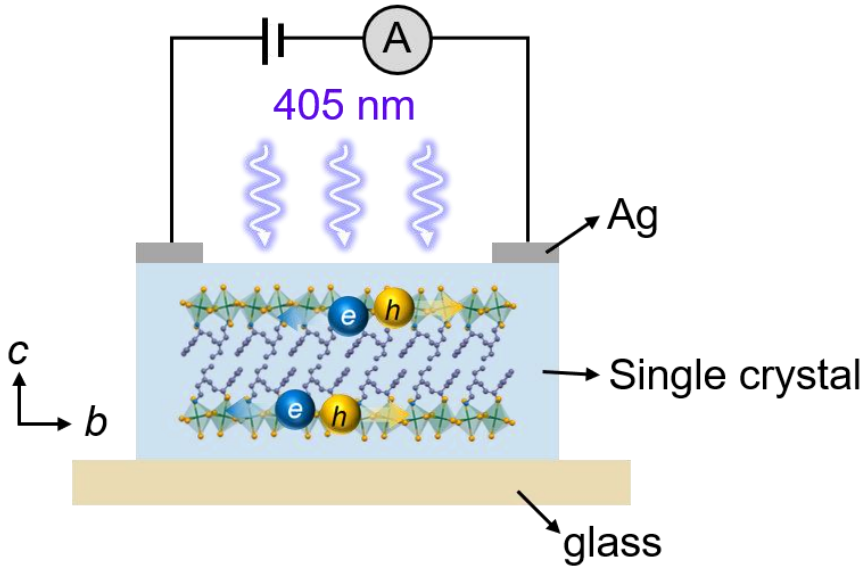

Figure S9. Schematic illustration of **2*R*** single-crystal photodetector.

Tables

Table S1. Crystal data and refinement details for **1** and **2*R*/2*S***.

Identification code	**1**	**2*R***	**2*S***
Formula	$(C_5H_{14}N)_2PbBr_4$	$(C_9H_{14}N)(C_5H_{14}N)PbBr_4$	$(C_9H_{14}N)(C_5H_{14}N)PbBr_4$
Temperature [K]	100	300	300
Weight	703.14	751.21	751.21
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	14.4011(5)	8.0160(3)	8.0152(3)
b [Å]	8.2390(2)	8.4161(4)	8.4073(3)
c [Å]	8.3208(2)	34.5711(19)	34.5750(15)
α [◦]	90	90	90
β [◦]	94.932(3)	90	90
γ [◦]	90	90	90
Volume [Å^3]	983.61(5)	2332.29(19)	2329.88(16)
ρ [g cm^{-3}]	2.374	2.139	2.142
Z	2	4	4
F(000)	648	1392	1392
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Final R indexes [$I \geq 2\sigma(I)$]	R_1=2.96%, wR_2=7.36%	R_1=4.58%, wR_2=10.48%	R_1=4.60%, wR_2=11.10%
Final R indexes [all data]	R_1=3.63%, wR_2=7.61%	R_1=6.06%, wR_2=10.99%	R_1=5.97%, wR_2=11.72%
GOF	1.051	1.051	1.107