Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Large In-Plane Anisotropic 2D Perovskite Toward High Linearly Polarized Light Response

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Synthesis. All the analytical grade chemicals were used as received without further purification. Stoichiometric amounts of lead iodide (5 mmol, 2.31 g) and *Rac*/*R*/*S*-piperidine-3-carboxylic acid (10 mmol, 1.29 g) were dissolved in a concentrated aqueous HI solution. A clear solution was obtained after continuous stirring for 1 hour at 353 K. Plate crystal crystals were obtained by slowly cooling (l.5 K/day) the above solution to room temperature.

General characterizations. Room temperature X-ray diffraction data were collected on a Rigaku SmartLab X-ray diffractometer. The diffraction patterns were obtained in the 2θ range of 5−50° with a step size of 0.02°. Ultraviolet-vis (UV-vis) absorption spectra were performed with Shimadzu UV-2600 equipping ISR-2600Plus integrating sphere.

***I-V* measurement.** *I-V* measurement was conducted using a PDA FS380 Source meter. The light intensity was quantified by a photodetector (PM100A, Thorlabs).

Device fabrication. The crystal used to assemble the polarization photodetector device was measured as 3×4×1 mm^3. Electrodes were prepared on the (100) surface of the single crystal along the *c*-axis. The effective area of the photodetector device was determined to be 0.4 mm^2 using a high-definition digital camera.

DFT calculation. VASP code was used to conduct DFT calculations. The projector augmented wave method and the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation were used to define the ion-electron interactions and the exchange-correlation interactions, respectively. Van der Waals interactions were assessed by employing Grimme's dispersion-corrected semi-empirical DFT-D3 method[1]. The cutoff of energy was set to 500 eV and a 4×4×2 Gamma centered grid of k-points was used. VASPKIT was used to perform Post-processing analysis[2].

Single-crystal X-ray Diffraction. Crystallographic data of the **1*Rac***/**1*R***/**1*S*** were collected on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Mo Kα radiation and an XtaLAB

Synergy R, DW system, HyPix diffractometer. Rigaku CrysAlisPro software was used to collect data, refine cells, and reduce data. SHELXL-2018 in the OLEX2 interface was used to solve the single crystal structures by direct methods[3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. The X-ray crystallographic data of **1*Rac*/1*R*/1*S*** were deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2265467-2265469. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

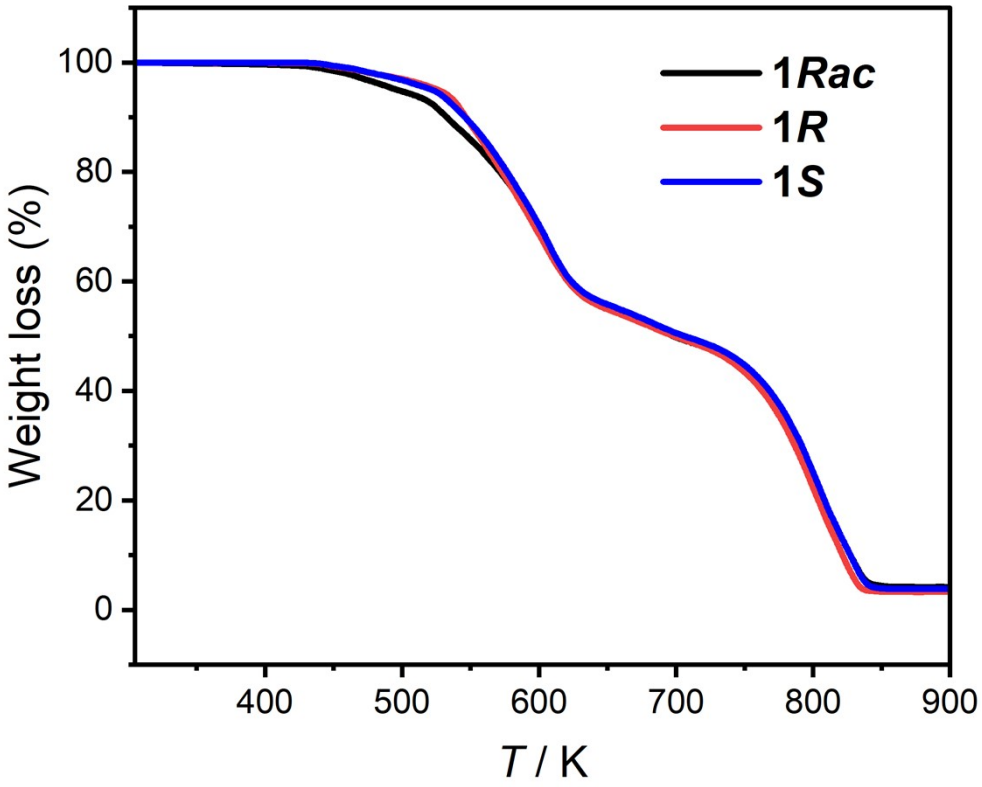

Fig. S1 TGA measurement of **1*Rac*/1*R*/1*S*.**

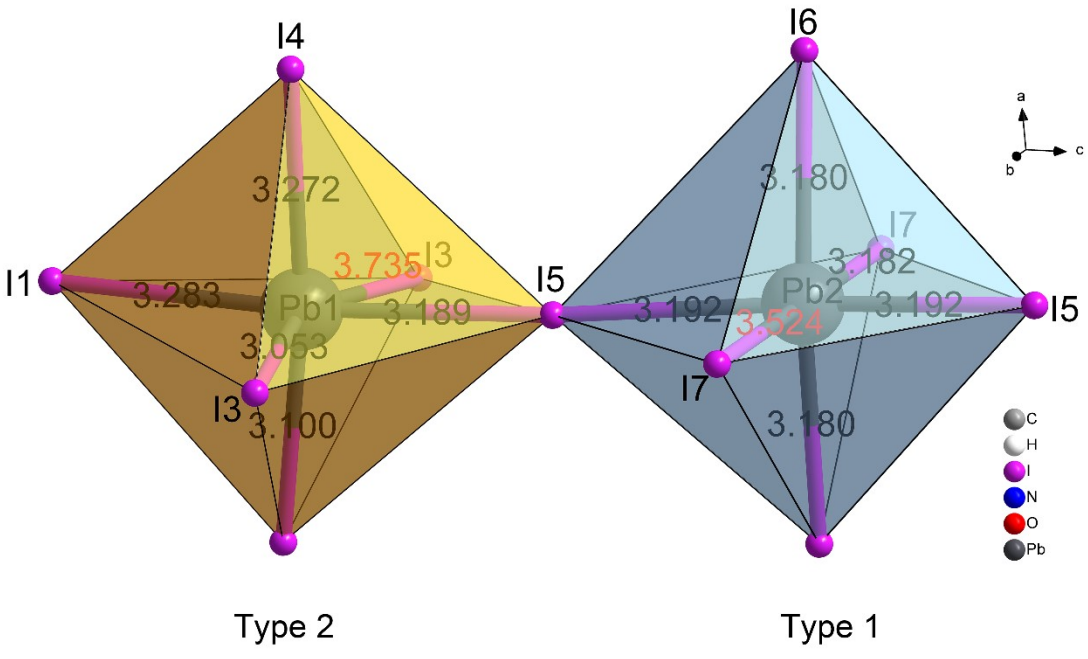

Fig. S2 Two types of $[PbI_6]^{4-}$ octahedrons showing different degrees of distortion in **1*R***.

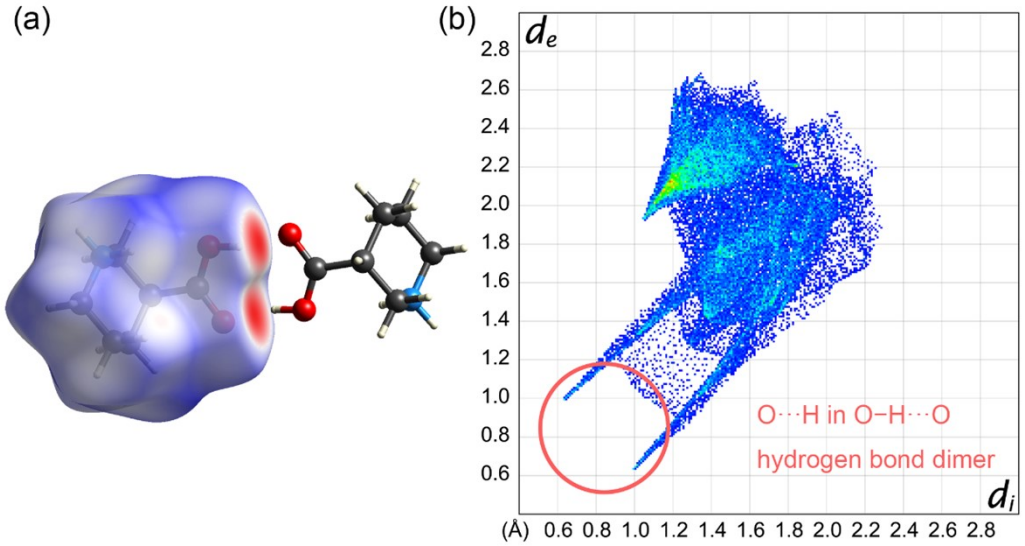

Fig. S3 Hirshfeld surfaces and 2D fingerprint plots for cations in dimer O···H–O hydrogen bond of **1*Rac.***

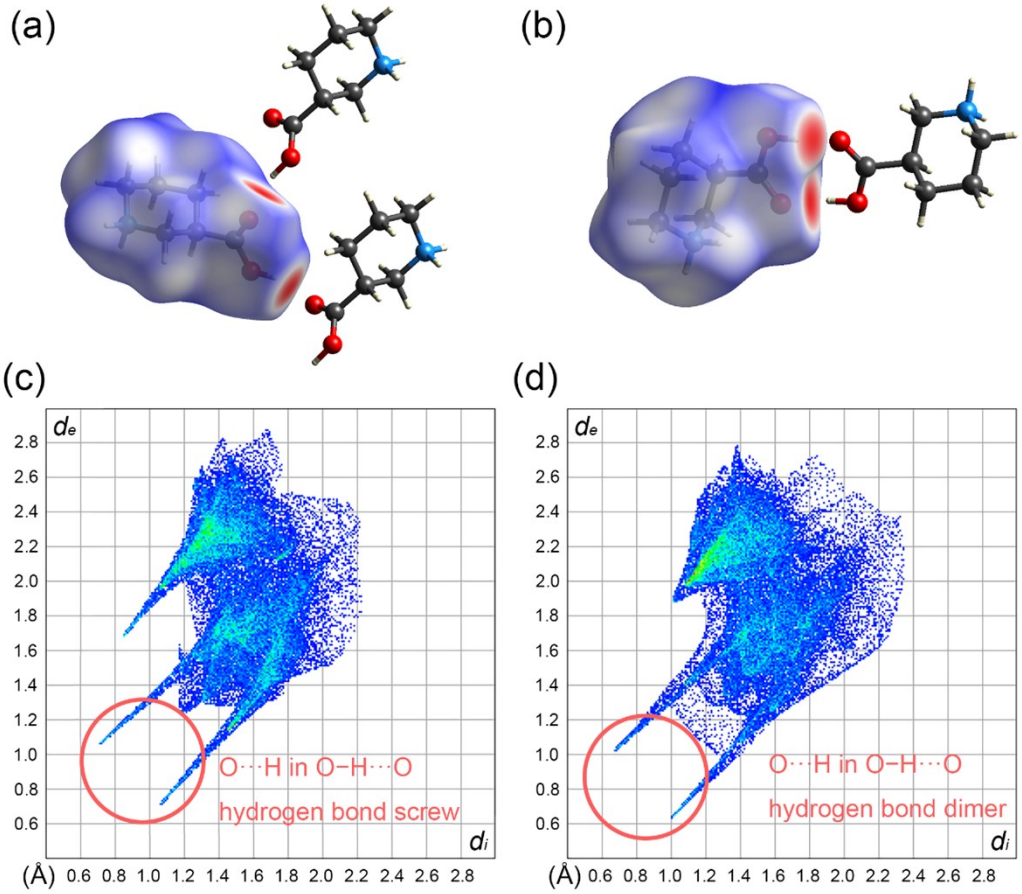

Fig. S4 Hirshfeld surfaces and fingerprint plots for cations in dimer and helical chain O···H–O hydrogen bond of **1*R***, respectively.

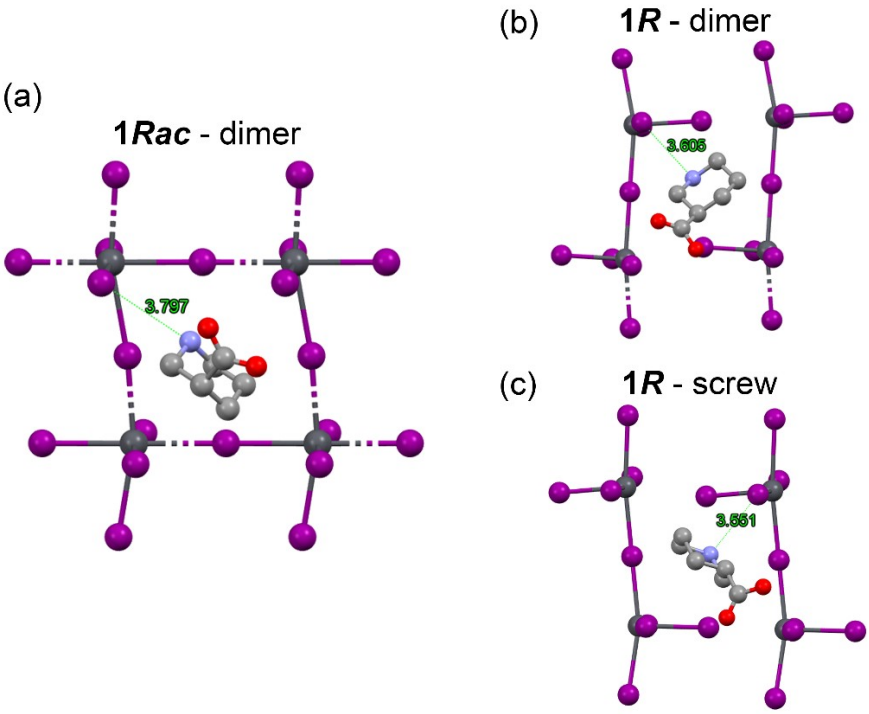

Fig. S5 (a) Shortest N···I distance in the crystal structure of **1*Rac*** and (b, c) **1*R*.**

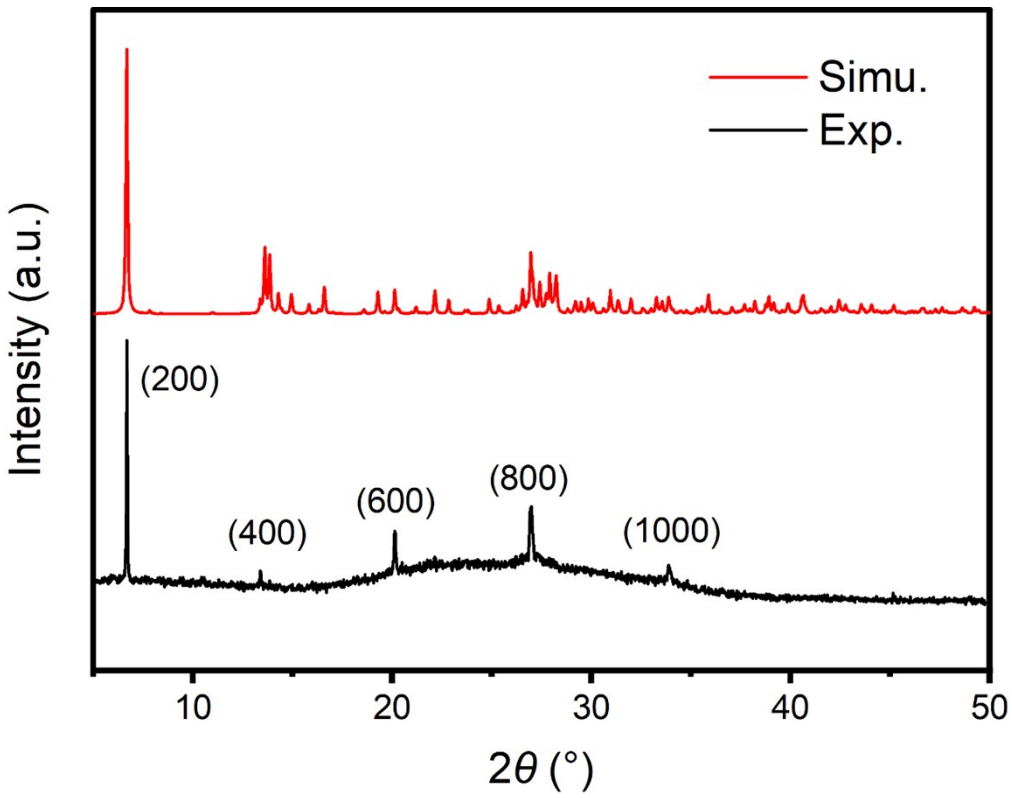

Fig. S6 Single crystal orientation for **1*R***.

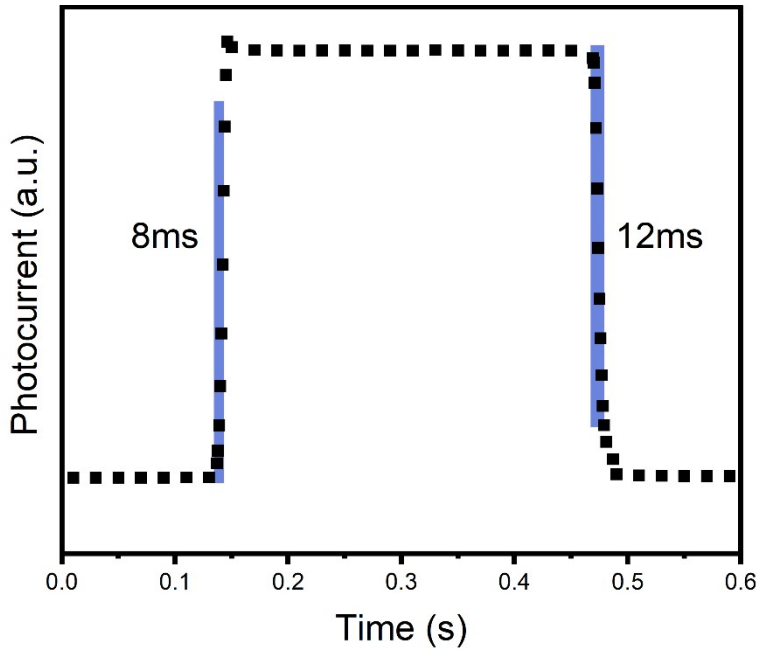

Fig. S7 Response time for **1*R*** under 405 nm polarized light irradiation.

Table S1 Crystallographic data and structural refinement details for **1*Rac*/1*R*/1*S*.**

	1*Rac*	**1*R***	**1*S***
Formula	$C_{12}H_{24}I_4N_2O_4Pb$	$C_{36}H_{72}I_{12}N_6O_{12}Pb_3$	$C_{36}H_{72}I_{12}N_6O_{12}Pb_3$
Formula weight	975.12	2925.36	2925.36
Crystal system	orthorhombic	Monoclinic	Monoclinic
space group	*Pnma*	*C*2	*C*2
a / Å	13.0681(6)	26.5063(9)	26.4701(9)
b / Å	26.5774(15)	6.7057(2)	6.7028(2)
c / Å	6.5224(3)	19.2086(7)	19.2218(6)
α / °	90	90	90
β / °	90	94.165(3)	94.167(3)
γ / °	90	90	90
V / Å^3	2265.33(19)	3405.2(2)	3401.39(19)
Z	4	2	2
Flack parameter	/	0.003(2)	-0.014(5)
D_{calc} / g·cm^{-3}	2.859	2.853	2.856
μ / mm^{-1}	12.915	12.888	12.902
Reflns. collected	27504	20057	12748
Obsd. reflns. [$I>2\sigma(I)$]	1969	6919	5867
R_{int}	0.0929	0.0248	0.0342
R_1[a]/wR_2[b] [$I>2\sigma(I)$]	0.0411/0.0696	0.0268/0.0333	0.0317/0.0634
R_1/wR_2 (all data)	0.0896/0.0800	0.0509/0.0521	0.0406/0.0658

GOF	1.030	1.074	0.960
$\Delta\rho^c$ / e·Å^{-3}	1.002/-1.134	0.848/-1.210	0.775/-1.596

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2 Hydrogen bonds for **1*Rac*/1*R*/1*S***.

D—H···A	D—H / Å	H···A / Å	D···A / Å	D—H···A / Å
1Rac				
O1—H1···O2^{i}	0.82	1.80	2.604(11)	166.9
N1—H1A···I2^{iii}	0.89	3.16	3.796(6)	130.2
N1—H1B···I2^{iv}	0.89	3.23	4.012(8)	147.9
C2—H2···O2^{ii}	0.98	2.46	3.387(11)	158.1
C4—H4A···I2^{v}	0.97	3.12	3.901(7)	138.5
C4—H4B···I2^{iv}	0.97	3.10	3.968(7)	150.0
C5—H5B···I3^{v}	0.97	3.29	3.959(8)	127.5
C6—H6A···I2^{iii}	0.97	3.31	3.901(8)	121.5
C6—H6B···I2^{vi}	0.97	3.25	4.145(9)	155.1

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*+1/2, −*y*, *z*+1/2; (iii) *x*−1, *y*, *z*; (iv) *x*−1, *y*, *z*−1; (v) *x*−1/2, *y*, −*z*+1/2; (vi) *x*−1/2, *y*, −*z*+3/2.

1R				
C2—H2···I4	0.98	3.29	4.090(7)	140
C5—H5B···I6^{iii}	0.97	3.14	4.042(10)	156
C6—H6A···I6	0.97	3.15	3.970(9)	143
C6—H6B···I6^{iii}	0.97	3.31	4.178(11)	150
C8—H8···O4^{iv}	0.98	2.59	3.551(11)	168

C10—H10A···I4	0.97	3.15	3.813(9)	127
C10—H10B···I4^{v}	0.97	3.18	4.019(9)	146
C11—H11A···I1^{v}	0.97	3.22	3.875(10)	126
C11—H11B···I1	0.97	3.32	3.998(10)	129
C12—H12A···I2^{i}	0.97	3.29	4.167(9)	151
C12—H12B···I2^{vi}	0.97	3.24	3.796(9)	118
C16—H16A···I6^{vii}	0.97	3.28	3.945(9)	127
C16—H16B···I2^{viii}	0.97	3.28	4.070(10)	140
C17—H17B···I6^{vii}	0.97	3.25	3.848(9)	122
C17—H17B···I7^{ix}	0.97	3.26	3.951(9)	130
C18—H18A···I2^{ix}	0.97	3.21	4.043(9)	146
N1—H1B···I4	0.89	2.67	3.551(8)	170
N2—H2A···I1^{v}	0.89	3.15	3.713(7)	123
N2—H2A···I2^{vi}	0.89	2.99	3.664(7)	134
N2—H2B···I4^{v}	0.89	3.18	3.968(7)	149
N2—H2B···O4	0.89	2.49	3.034(9)	120
N3—H3C···I6^{x}	0.89	2.90	3.606(8)	137
N3—H3D···I3^{viii}	0.89	3.08	3.907(7)	156
O1—H1···O2^{x}	0.82	1.95	2.727(8)	158
O3—H3···O6	0.82	1.87	2.674(9)	167
O5—H5···O4	0.82	1.81	2.623(9)	170

Symmetry codes: (i) −x, y, −z; (iii) x, y+1, z; (iv) −x−1/2, y+1/2, −z; (v) x, y−1, z; (vi) −x, y−1, −z; (vii) −x−1/2, y−3/2, −z−1; (viii) x−1/2, y−3/2, z; (ix) x−1/2, y−1/2, z; (x) −x−1/2, y−1/2, −z−1.

1S

C2—H2···I4	0.98	3.31	4.107(10)	140
C5—H5A···I6^{iii}	0.97	3.13	4.043(13)	157
C6—H6A···I6^{iii}	0.97	3.30	4.170(13)	150
C6—H6B···I6	0.97	3.15	3.966(12)	143
C8—H8···O4^{iv}	0.98	2.58	3.544(14)	168
C10—H10A···I4^{iii}	0.97	3.15	3.818(12)	128
C10—H10B···I4	0.97	3.17	4.014(12)	147
C11—H11A···I1^{iii}	0.97	3.30	3.987(13)	129
C11—H11B···I1	0.97	3.21	3.857(13)	125
C12—H12A···I2^{i}	0.97	3.23	3.786(12)	118
C12—H12B···I2^{v}	0.97	3.30	4.167(12)	150
C16—H16A···I6^{vi}	0.97	3.29	3.946(12)	126
C16—H16B···I2^{vii}	0.97	3.28	4.083(12)	141
C17—H17A···I6^{vi}	0.97	3.24	3.841(12)	122
C17—H17A···I7^{viii}	0.97	3.27	3.951(12)	129
C18—H18B···I2^{viii}	0.97	3.20	4.033(11)	145
N1—H1B···I4	0.89	2.68	3.558(10)	168
N2—H2A···I4	0.89	3.17	3.958(9)	149
N2—H2A···O4	0.89	2.50	3.039(12)	120
N2—H2B···I1	0.89	3.13	3.696(10)	123
N2—H2B···I2^{i}	0.89	2.99	3.665(9)	134
N3—H3C···I3^{vii}	0.89	3.09	3.917(9)	156
N3—H3D···I6^{ix}	0.89	2.90	3.603(10)	137

O1—H1···O2^{vi}	0.82	1.94	2.719(11)	159
O3—H3···O6	0.82	1.86	2.660(13)	164
O5—H5···O4	0.82	1.86	2.618(11)	154

Symmetry codes: (i) −x+1, y, −z+1; (iii) x, y−1, z; (iv) −x+3/2, y−1/2, −z+1; (v) −x+1, y−1, −z+1; (vi) −x+3/2, y+1/2, −z+2; (vii) x+1/2, y+1/2, z; (viii) x+1/2, y−1/2, z; (ix) −x+3/2, y−1/2, −z+2.

Table S3 Bond angles and bond lengths for I−Pb inorganic sheets in **1*Rac*/1*R.***

Bond angles	Angle / °	Bond lengths	Length / Å
1*Rac*			
I3—Pb1—I3^{i}	179.76(3)	Pb1—I3^{i}	3.2709(7)
I3^{i}—Pb1—I1	99.687(18)	Pb1—I3	3.2515(7)
I3—Pb1—I1	80.553(18)	Pb1—I2^{ii}	3.1851(6)
I2^{ii}—Pb1—I3^{i}	86.389(13)	Pb1—I2	3.1851(6)
I2—Pb1—I3^{i}	86.389(13)	Pb1—I1	3.4194(7)
I2 ^{ii}—Pb1—I3	93.625(13)	Pb1—I1^{iii}	3.1684(7)
I2—Pb1—I3	93.624(13)		
I2^{ii}—Pb1—I2	170.30(2)		
I2^{ii}—Pb1—I1	87.420(12)		
I2—Pb1—I1	87.420(12)		
I1^{iii}—Pb1—I3	86.298(18)		
I1^{iii}—Pb1—I3^{i}	93.462(19)		
I1^{iii}—Pb1—I2	93.446(12)		
I1^{iii}—Pb1—I2^{ii}	93.447(12)		
I1^{iii}—Pb1—I1	166.852(12)		

Symmetry codes: (i) +x, +y, 1+z; (ii) +x, 1/2-y, +z; (iii) -1/2+x, +y, 3/2-z.

1*R*

I1—Pb1—I3^{iii}	94.988 (19)	I1—Pb1	3.2834(3)
I2—Pb1—I1	86.012 (12)	I1—Pb1^{i}	3.2833(3)
I2—Pb1—I3^{iii}	79.714 (16)	I2—Pb1	3.1004(6)
I2—Pb1—I5	96.469 (18)	I3—Pb1	3.0533(7)
I3—Pb1—I1	97.46 (2)	I3—Pb1^{ii}	3.7346(7)
I3—Pb1—I2	88.293 (18)	I4—Pb1	3.2718(6)
I3—Pb1—I4	86.521 (18)	I5—Pb1	3.1893(6)
I3—Pb1—I5	90.41 (2)	I5—Pb2	3.1921(6)
I4—Pb1—I1	88.944 (13)	I6—Pb2	3.1797(6)
I4—Pb1—I3^{iii}	106.631 (16)	I7—Pb2	3.1815(10)
I5—Pb1—I3^{iii}	77.85 (2)	I7—Pb2^{iii}	3.5242(10)
I5—Pb1—I4	89.339 (18)		
I5—Pb2—I7^{ii}	82.96 (2)		
I5^{iv}—Pb2—I7^{ii}	82.96 (2)		
I6^{iv}—Pb2—I5	87.445 (16)		
I6^{iv}—Pb2—I5^{iv}	94.142 (16)		
I6—Pb2—I5	94.139 (16)		
I6—Pb2—I5^{iv}	87.445 (16)		
I6—Pb2—I7^{ii}	96.472 (13)		
I6^{iv}—Pb2—I7^{ii}	96.472 (13)		
I6—Pb2—I7	83.528 (13)		
I6^{iv}—Pb2—I7	83.528 (13)		

I7—Pb2—I5	97.04 (2)
I7—Pb2—I5^{iv}	97.04 (2)

Symmetry codes: (i) −x, y, −z; (ii) x, y+1, z; (iii) x, y−1, z; (iv) −x, y, −z−1.

Table S4 Comparison of working conditions for 2D perovskite polarization photodetectors.

	ω	Bias / V	Incident light / nm	Reference
This work	8	-0.2	405	/
$(Cl\text{-}PMA)_2CsAgBiBr_7$	1.3	0	405	53
$(i\text{-}AA)_2CsPb_2Br_7$	7.2	0	405	52
$(BPA)_2PbBr_4$	6.8	0	377	51
$(i\text{-}BA)_2(MA)Pb_2Cl_7$	2.5	0	266	50
$(BA)_2(GA)Pb_2I_7$	2.2	/	520	49
$(FPEA)_2PbI_4$	2.1	/	520	28
$(BA)_2(FA)Pb_2I_7$	1.96	0	637	29
$(BA)_2(DMA)Pb_2Br_7$	1.43	/	405	48
$(i\text{-}BA)_2(DMA)Pb_2Br_7$	1.4	/	405	47
$Cs_2[C(NH_2)_3]Pb_2Br_7$	1.3	/	405	46
$(s\text{-}BA)_2(MA)Pb_2I_7$	1.16	/	520	45
$(IA)_2(DMA)Pb_2Br_7$	1.15	/	405	44

Reference

[1] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104.

[2] V. Wang, N. Xu, J.-C. Liu, G. Tang, W.-T. Geng, *Comput. Phys. Commun.* **2021**, 267, 108033.

[3] a) G. M. Sheldrick, *Acta Crystallogr C Struct Chem* **2015**, 71, 3; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339.