Electronic Supplementary Information

Chiral Three-Dimensional Organic-Inorganic Lead Iodide Hybrid Semiconductor

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Experimental Section

Starting Materials. $Pb(AcO)_2 \cdot 3H_2O$(99.9%), hydroiodic acid (57% in H_2O, distilled, H_3PO_2 stabilized, 99.95%), hypophosphorous acid solution (50% in H_2O) were purchased from Macklin. 3-(1-aminoethyl)pyridine (97%), (*R*)-1-(pyridin-3-yl)ethanamine (97%), (*S*)-1-(pyridin-3-yl)ethanamine (97%), 2-(1-aminoethyl)pyridine (97%), (*R*)-1-(pyridin-2-yl)ethanamine (97%), and (*R*)-1-(pyridin-2-yl)ethanamine (97%) were purchased from Bide-Pharmatech Company Limited. All reagents were commercially available and were used as received without further purification.

Synthesis.

Synthesis of 3*R*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then (*R*)-1-(pyridin-3-yl)ethanamine (202.8 mg, 3 mmol) was added and a red solid formed. Continue stirring and heating up to 80 °C, the red precipitate dissolved, and the solution turned yellow. The yellow solution was volatilized under constant temperature at 80 °C. Five days later, millimeter-sized red plate crystals were obtained, with a yield of about 40%. **Anal. Calcd.** for $C_7H_{12}N_2Pb_2I_6$ (**3*R***): C: 6.47%, H: 0.93%, N: 2.15%. **Found**: C: 6.63%, H: 0.77%, N: 2.10%.

Synthesis of 3*S*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then (*S*)-1-(pyridin-3-yl)ethanamine (202.8 mg, 3 mmol) was added and the solution was volatilized under constant temperature at 80 °C. Five days later, millimeter-sized red plate crystals were obtained, with a yield of about 43%. **Anal. Calcd.** for $C_7H_{12}N_2Pb_2I_6$ (**3*S***): C: 6.47%, H: 0.93%, N: 2.15%. **Found**: C: 6.60%, H: 0.75%, N: 2.09%.

Synthesis of 3*Rac*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then 1-(pyridin-3-yl)ethanamine (202.8 mg, 3 mmol) was added and the clear solution was volatilized under constant temperature at 80 °C. Five days later, millimeter-sized red plate crystals were obtained, with a yield of about 42%. **Anal. Calcd.** for $C_7H_{12}N_2Pb_2I_6$ (**3*Rac***): C: 6.47%, H: 0.93%, N: 2.15%. **Found**: C: 6.56%, H: 0.74%, N: 2.12%.

Synthesis of 2*R*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then (*R*)-1-(pyridin-2-yl)ethanamine (202.8 mg, 3 mmol) was added and the clear solution was evaporated at 80°C to yield red crystals.

Synthesis of 2*S*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then (*S*)-1-(pyridin-2-yl)ethanamine (202.8 mg, 3 mmol) was added and the clear solution was evaporated at 80°C to yield red crystals.

Synthesis of 2*Rac*. $Pb(AcO)_2$ (6.83g, 18 mmol) was dissolved in 57% HI (70 mL, 25 °C) solution, stirred to clear, and then added to 3.0 mL 50% H_3PO_2 solution. Then 1-(pyridin-2-yl)ethanamine (202.8 mg, 3 mmol) was added and the clear solution was evaporated at 80°C to yield red crystals.

Single crystal and PXRD measurements . Suitable size of single-crystals of titled compounds were selected for single-crystal X-ray diffraction analysis. Crystallographic data 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 cell, and reduce data. SHELXL-2018 with the OLEX2 interface was used to solve the structures by direct methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically. The crystal structures generated in this study have been deposited in the Cambridge Crystallographic Data Center under accession code CCDC: 2323588-2323597 can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Physical property measurements.

IR spectra were measured on a Nicolet5700 spectrometer.

Elemental analysis (EA) of C, H, and N was performed on UNICUBE-Elementar elemental analyzer.

The UV-VIS diffuse reflectance experiments of single crystal powder samples were carried out on Shimazu UV-2600 UV-Vis absorption spectrometer equipped with ISR-2600Plus integrating sphere. The bandgap value is estimated from the Kubelka-Munk equation:

$$\alpha/S = (1-R)^2/(2R) \qquad \text{(E1)}$$

where R is the reflectance, and α and S are the absorption and scattering coefficients, respectively.

Circular dichroism (CD) spectra were measured using single crystal powder with a JASCO J-1500 MIF CD spectrometer at room temperature.

***I-V* measurement.** *I*−*V* curves were performed by a PDA FS380 Source meter. Simulated AM 1.5 G irradiation was produced by a CEL-S500/350 solar simulator (Ceaulight, 350 W) with an AM1.5 filter. The light intensity was measured and calibrated by a Si photodetector connected with a power meter (CEL-NP2000-2A, Ceaulight). A THORLABS 565 nm pigtailed laser diode (LP 565L3) was used for visible light illumination. The incident light intensity was measured by light power meter.

CPL-sensitive direct photodetection performance measurement. Laser diodes with wavelength of 565 nm (ML 565L3, Thorlabs) were used for light source. Circularly polarized light was obtained by a linear polarizer (Thorlabs) and a quarter-wave plate (Thorlabs). The light intensity was measured and calibrated by a Si photodetector connected with a power meter (PM100A, Thorlabs). The current signals were collected using a PDA FS380 Source meter.

(1) Anisotropy factor (g_{CD}) is defined by:

$$g_{CD} = \frac{\mathrm{CD[mdeg]}}{32930 \times Absorbance} = \frac{\Delta \mathrm{A}}{\mathrm{Absorbance}} \qquad \text{(S1)}$$

where ΔA is the difference between the left-handed (A_L) and right-handed (A_R) absorptions of CPL ($\Delta A = A_L - A_R$).

(2) Anisotropy factor (g_{Iph}) is defined by:

$$g_{\mathrm{Iph}} = \frac{2\left|I_{\mathrm{ph}}^{\mathrm{R}} - I_{\mathrm{ph}}^{\mathrm{L}}\right|}{I_{\mathrm{ph}}^{\mathrm{R}} + I_{\mathrm{ph}}^{\mathrm{L}}} \qquad \text{(S2)}$$

where I_{ph}^{R} and I_{ph}^{L} are the photocurrents under R- and L-CPL illumination, respectively).

(3) Responsivity (R) is calculated through:

$$R_{\lambda} = \frac{I_{\mathrm{p}} - I_{\mathrm{d}}}{\mathrm{S}P_{\lambda}} \qquad \text{(S3)}$$

(4) Detectivity (D^*) is calculated through:

$$D^* = \frac{R_\lambda}{\sqrt{2eI_d/S}} \qquad \text{(S4)}$$

S is the detector area with a value of 0.003cm^2, and e is the quantity of electric charge with a value of $1.602176634\times10^{-19}$ C.

Computational details. The Vienna ab initio simulation package was used for DFT calculations. The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation was employed to express the exchange-correlation interaction. Grimme's dispersion-corrected semi-empirical DFT-D3 method was adopted to evaluate van der Waals interactions. The energy cutoff was set to 500 eV and a 3×3×2 grid of k-points was used.

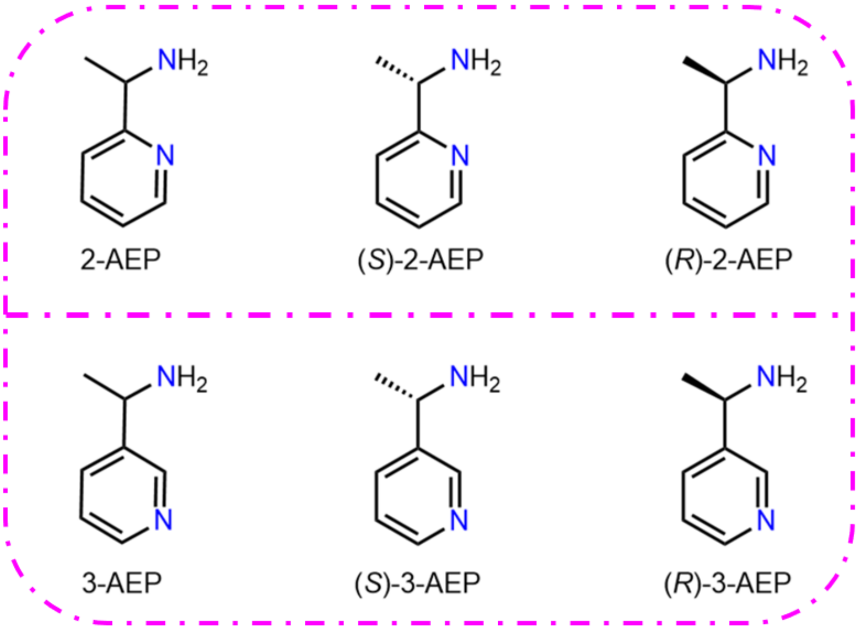

Fig. S1 Diagram of the chiral cation used by compound **2*R*/*S*/*Rac*** and **3*R*/*S*/*Rac***.

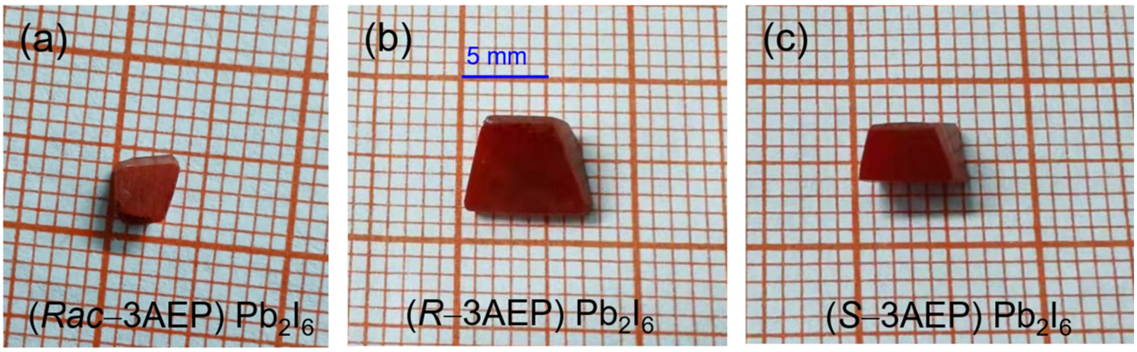

Fig. S2 Bulk single crystals of (a) **3*Rac***, (b) **3*R***, and (c) **3*S***.

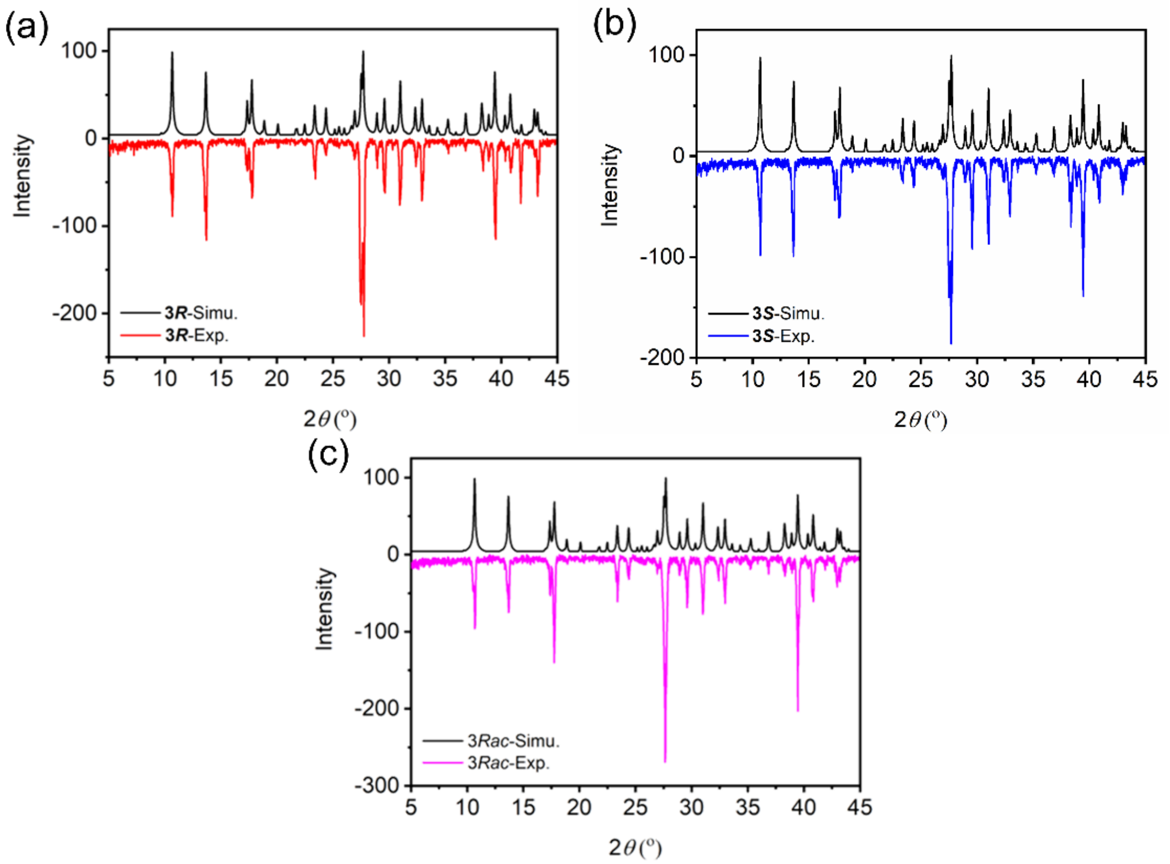

Fig. S3 PXRD patterns of (a) **3*R***, (b) **3*S***, and (c) **3*Rac*** at 298 K.

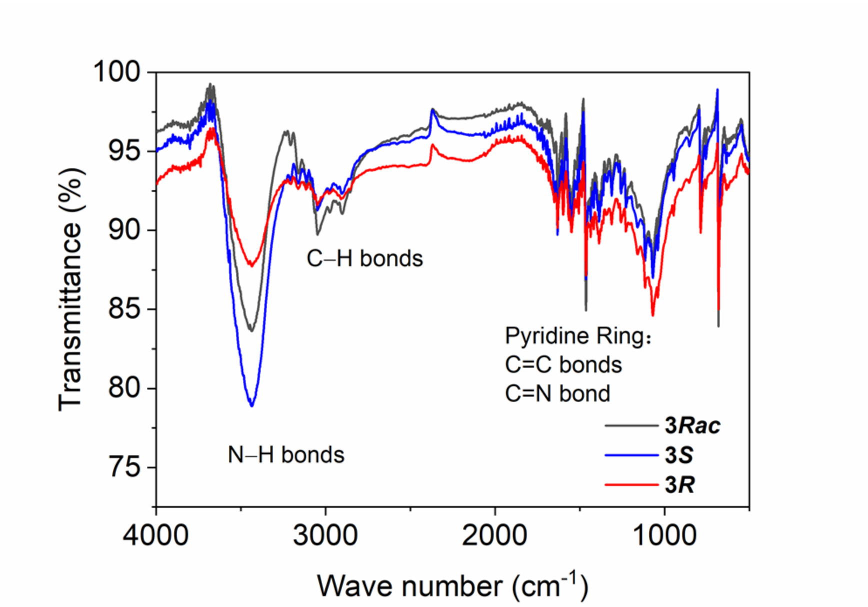

Fig. S4 IR spectra of **3*Rac*/*R*/*S*** showing the spectral ranges of 500-4000 cm^{-1}.

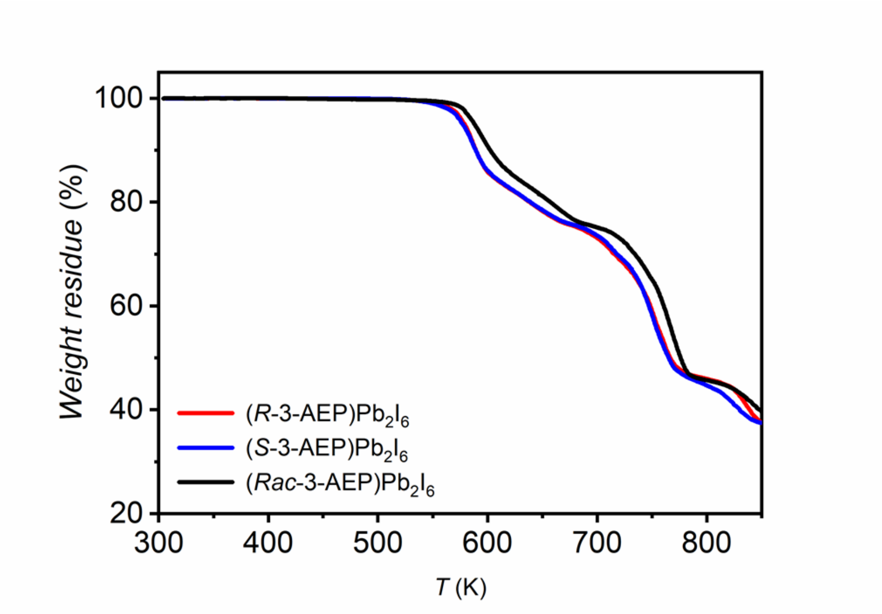

Fig. S5 Thermogravimetric analysis (TGA) curves of **3*Rac***, **3*S***, and **3*R*** recorded on a NETZSCH TG 209F3 apparatus under air atmosphere, showing a good thermal stability up to about 575 K.

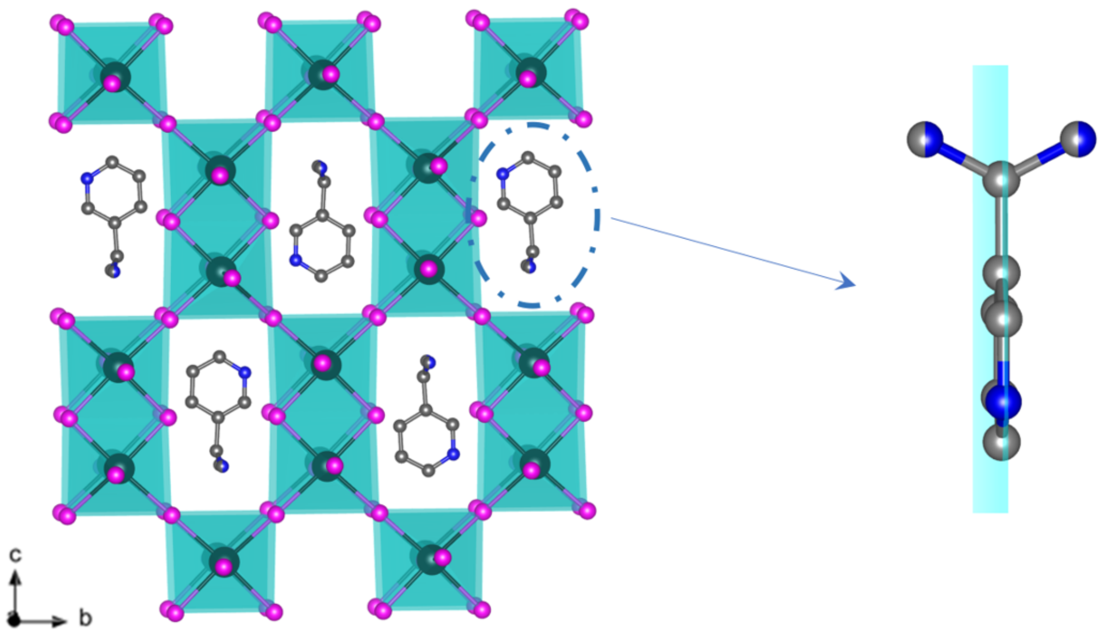

Fig. S6 The structure of 3*Rac* and *Rac*-3AEP in LTP.

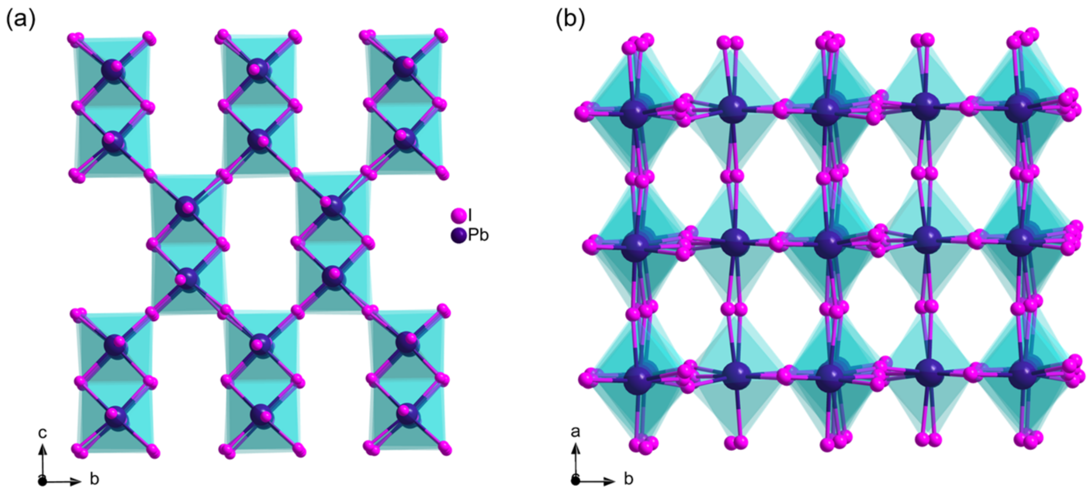

Fig. S7 (a, b) Inorganic framework 3D connectivity. Purple, and magenta spheres represent Pb, and I, respectively.

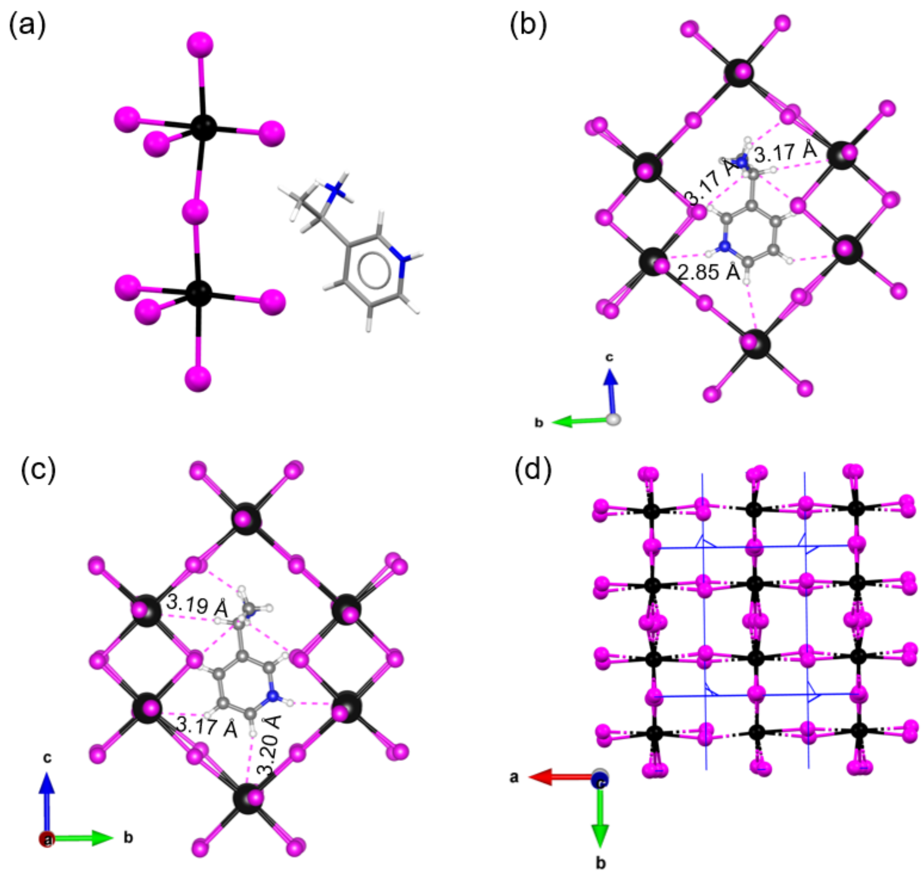

Fig. S8 Crystal strucute of **3*R***. (a) Asymmetric unit of **3*R*** at (a) 240 K. (b, c) N−H···halogen interactions between the organic cations and inorganic layers of **3*R*** at 240 K. (d) Top view of the inorganic sublattice showing 2_1 screw axes (green) he corner-sharing octahedral bridging iodine atoms and twisted Pb-I planes along the *a* and *c* directions, respectively. Purple, and magenta spheres represent Pb, and I, respectively.

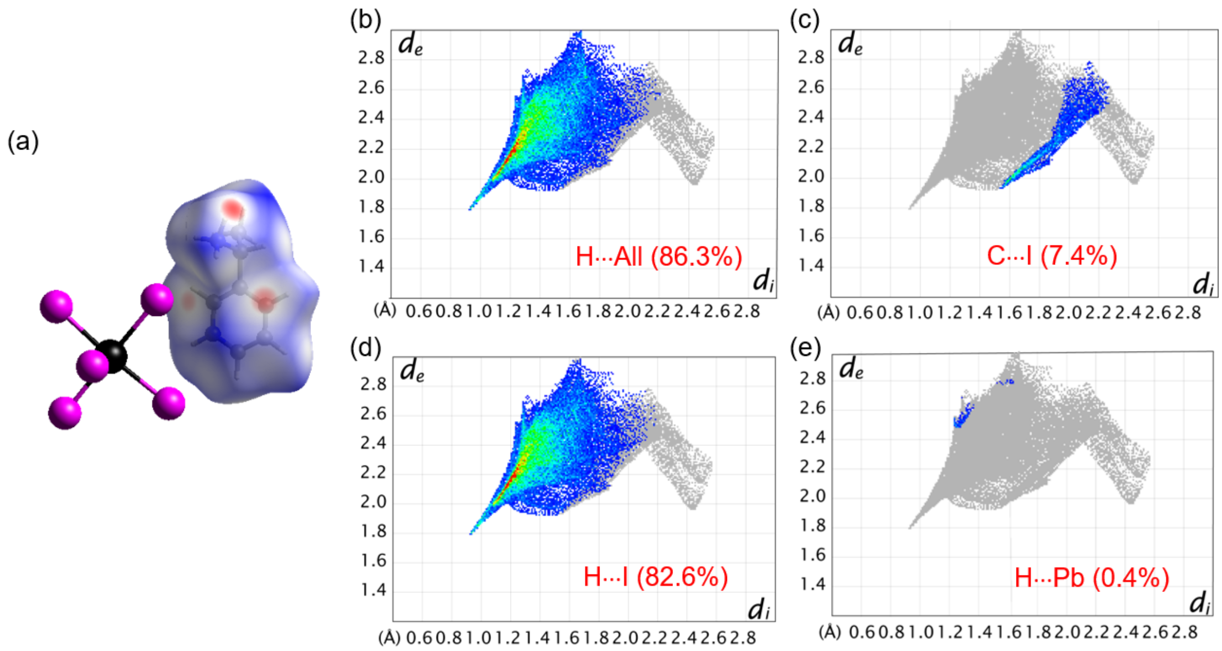

Fig. S9 (a) 3D *d*norm surface and (b-d) 2D fingerprint plots of **3*R*** at 240 K. Red, white and blue regions of the Hirshfeld surfaces indicate positive (close contact), neutral and negative isoenergies, respectively. Note: The d_i and d_e represent the distances from the Hirshfeld surface to the nearest nucleus inside (or internal, d_i) and outside (or external, d_e) the surface. The d_{norm} surface is the set of normalized distances for all atoms and surfaces.

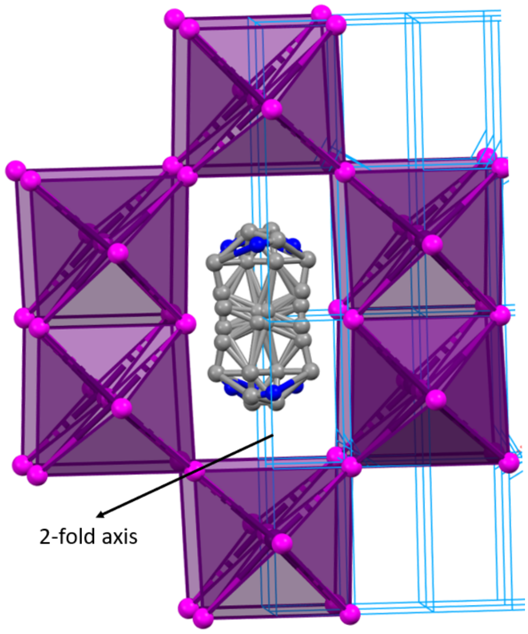

Fig. S10 Crystal structures of **3*R*** at 425 K, showing the disordered 3AEP molecule with 2-fold screw axes (indigo).

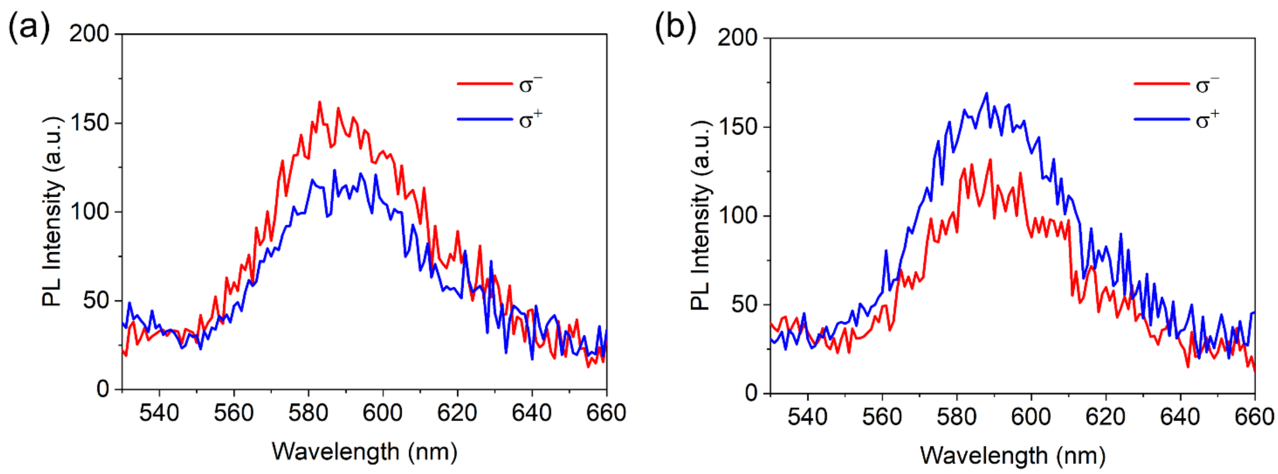

Fig. S11 Circularly polarized light excited photoluminescence spectra of (a) **3*R*** and (b) **3*S*** upon L-CPL (σ^+) and R-CPL (σ^-) excitation at 510 nm and 298 K.

Table S1. Summary space groups of 3D lattices formed by dimers of metal halide octahedra

Compound	Crystal system	Space Group	Ref (DOI)
$(3AMPY)Pb_2I_6$	monoclinic	*Im*	10.1021/jacs.0c00101
$(3AMPY)PbSnI_6$	monoclinic	*Im*	10.1021/jacs.0c00101
$(4AMPY)Pb_2I_6$	monoclinic	*Ia*	10.1021/jacs.0c00101
$(3AMPY)Sn_2I_6$	monoclinic	*Im*	10.1021/jacs.0c00101
$(3AMPY)_{0.5}(4AMPY)_{0.5}Sn_2I_6$	monoclinic	*Im*	10.1021/jacs.0c00101
$(4AMPY)Sn_2I_6$	monoclinic	*Im*	10.1021/jacs.0c00101
$(TMAEA)Pb_2Cl_6$	orthorhombic	*Pma*2	10.1021/jacs.0c00375
$(dmpz)Pb_2Br_6$	orthorhombic	*Pbam*	10.1002/anie.202005012
$(Hmpz)Pb_2Br_6$	orthorhombic	*Pbam*	10.1002/anie.202005012
$(Hepz)Pb_2Br_6$	orthorhombic	*Cmmm*	10.1002/anie.202005012
$(Hppz)Pb_2Br_6$	orthorhombic	*Amm*2	10.1002/anie.202005012
$(H_2apy)Pb_2Br_6$	orthorhombic	*Iba2*	10.1002/anie.202005012
$(H_2dap)Pb_2Br_6$	orthorhombic	*Pnma*	10.1002/anie.202005012
$(dmpz)Pb_2I_6$	orthorhombic	*Pbam*	10.1002/anie.202005012
$(EATMP)Pb_2Br_6$	monoclinic	*Pc*	10.1021/jacs.0c09586
$(1,4BDA)Pb_2Br_6$	monoclinic	$P2_1/c$	10.1021/jacs.1c11803
$(NMPA)Pb_2Br_6$	orthorhombic	*Pba*2	10.1021/jacs.1c11803
$(TMEA)Pb_2Br_6$	orthorhombic	*Pma*2	10.1021/jacs.1c11803
$(DMEA)Pb_2Br_6$	orthorhombic	*Pbca*	10.1021/jacs.1c11803
$(M_2pda)Pb_2I_6$	orthorhombic	*Pbam*	10.1039/d2qi01651f
$(Mpda)Pb_2I_6$	orthorhombic	*Pbam*	10.1039/d2qi01651f
$(H_2bda)Pb_2I_6$	monoclinic	$P2_1/c$	10.1039/d2qi01651f
$(NMPDA)Pb_2I_4Br_2$	orthorhombic	*Pbam*	10.1002/smll.202305990
(*R*-3AEP)Pb_2I_6	orthorhombic	$C222_1$	This work
(*S*-3AEP)Pb_2I_6	orthorhombic	$C222_1$	This work
(*Rac*-3AEP)Pb_2I_6	orthorhombic	*Cmca*	This work
(*R*-2AEP)Pb_2I_6	orthorhombic	$C222_1$	This work
(*S*-2AEP)Pb_2I_6	orthorhombic	$C222_1$	This work
(*Rac*-2AEP)Pb_2I_6	orthorhombic	*Cmca*	This work

Note: 3AMPY = 3-(ammoniomethyl)pyridin-1-ium, 4AMPY = 4-(ammoniomethyl)pyridin-1-ium, Dmpz = *N*,*N*'-dimethylpyrazinium, Hmpz = *N*-hydro-*N*'-methylpyrazinium, Hepz = *N*-hydro-*N*'-

ethylpyrazinium, Hppz = *N*-hydro-*N*'-isopropylpyrazinium, H_2apy = *N*,*N*'-dihydro-3-amidinopyridinium, H_2dap = *N*,*N*'-dihydro-1,3-propanediammonium, EATMP = 2-(aminoethyl)-trimethylphosphanium, 1,4BDA = 1,4-butanediammonium, NMPA = *N*,*N*′-dimethyl-1,3-propanediammonium, TMEA = 2-(aminoethyl)trimethylammonium, DMEA = *N*,*N*-dimethylethylenediammonium, M_2pda = *N*,*N*′-dimethyl-1,3-propanediammonium, Mpda = *N*-methyl-1,3-propanediammonium, H_2bda = 1,4-butylenediammonium, NMPDA = *N*,*N*′-dimethyl-1,3-propanediammonium, 3-AEP = 3-(1-ammonioethyl)pyridin-1-ium, 2-AEP = 2-(1-ammonioethyl)pyridin-1-ium.

Table S2. Selected hydrogen bonds for (R-3AEP)Pb_2I_6 and (S-3AEP)Pb_2I_6.

D−H···A	D−H / Å	H···A / Å	D···A / Å	∠DHA / °
(R-3AEP)Pb_2I_6-245 K				
N(1)−H(1A)···I(5)^{i}	0.90	2.90	3.66(2)	143.5
N(1)−H(1B)···I(3)^{ii}	0.90	3.22	3.94(2)	139.1
N(1)−H(1B)···I(7)	0.90	3.17	3.72(2)	121.6
N(2)−H(2B)···I(4)^{ii}	0.87	2.85	3.674(9)	158.4
C(1)−H(1E)···I(8)^{iii}	0.97	3.19	4.03(2)	146.5
C(2)−H(2A)···I(4)^{i}	0.99	3.17	4.16(2)	176.9
C(5)−H(5)···I(9)^{iii}	0.94	3.17	3.929(10)	138.7
C(6)−H(6)···I(4)^{iii}	0.94	3.20	4.115(9)	164.3
Symmetry codes: (i) 1−X, 1−Y, −1/2+Z; (ii) 1/2+X, 1/2−Y, 1−Z; (iii) 1/2+X, 1/2+Y, +Z.				
(S-3AEP)Pb_2I_6-240 K				
C(1)−H(1B)···I(4)^{ii}	0.96	3.24	4.06(3)	144.6
C(2)−H(2)···I(4)^{i}	0.98	3.15	4.12(2)	177.6
C(5)−H(5)···I(9)^{iv}	0.93	3.16	3.923(12)	140.6
C(6)−H(6)···I(4)^{iv}	0.93	3.19	4.097(10)	165.7
N(1)−H(1D)···I(9)^{v}	0.89	3.16	3.96(3)	150.4
N(1)−H(1E)···I(6)^{i}	0.89	3.11	3.69(3)	124.1
N(1)−H(1F)···I(2)	0.89	3.27	3.78(3)	118.8
N(2)−H(2A)···I(4)^{iii}	0.86	2.87	3.671(11)	156.5
Symmetry codes: (i) x+1, y, z; (ii) −x+1, y−1/2, −z; (iii) −x+1, y−1/2, −z+1; (iv) −x, y−1/2, −z+1; (v) −x, y−1/2, −z.				

Table S3. Crystallographic data and refinement parameters for (R-3AEP)Pb_2I_6

	240 K	298 K	425 K
Formula	$C_7H_{12}N_2Pb_2I_6$	$C_7H_{12}N_2Pb_2I_6$	$C_7H_{12}N_2Pb_2I_6$
Formula weight	1299.97	1299.97	1299.97
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	$C222_1$	$C222_1$	$C222$
a / Å	12.9493(3)	12.9629(3)	9.4786(5)
b / Å	18.7108(5)	18.7955(5)	17.723(10)
c / Å	17.6439(5)	17.6714(5)	6.5033(4)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V / Å^3	4274.97(13)	4305.53(19)	1092.50(11)
Z	8	8	2
Flack parameter	-0.016(16)	−0.019(5)	0.36(4)^d
D_{calc} / g·cm^{-3}	4.040	4.011	3.952
μ / mm^{-1}	24.385	24.212	23.855
total reflns	19778	59812	12319
obsd reflns ($I > 2\sigma(I)$)	3771	6128	1443
R_{int}	0.038	0.0746	0.0073
$R_1{}^a$ /$wR_2{}^b$ ($I > 2\sigma(I)$)	0.0606, 0.1713	0.0488, 0.1343	0.0327, 0.0723
R^1/wR^2 (all data)	0.0692, 0.1785	0.0767, 0.1492	0.0557, 0.0770
GOF	1.064	1.12	1.059
$\Delta\rho^c$ / e·Å^{-3}	5.19/−4.67	3.01/−5.38	1.35/−1.50

^{a} $R_1 = \Sigma| |F_o| - |F_c| | / |F_o|$. ^{b} $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2] / \Sigma w(F_o{}^2)^2]^{1/2}$. ^{c} Maximum and minimum residual electron density. ^{d} The Flack test results become meaningless as the compounds become weak anomalous scatterers in the high-temperature high-disorder phase.

Table S4. Crystallographic data and refinement parameters for (S-3AEP)Pb_2I_6

	245 K	298 K	425 K
Formula	$C_7H_{12}N_2Pb_2I_6$	$C_7H_{12}N_2Pb_2I_6$	$C_7H_{12}N_2Pb_2I_6$
Formula weight	1299.97	1299.97	1299.97
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	$C222_1$	$C222_1$	$C222$
a / Å	12.9335(5)	12.9621(7)	9.4743(7)
b / Å	18.7439(8)	18.7875(13)	17.730(12)
c / Å	17.6358(8)	17.6666(9)	6.5088(4)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V / Å^3	4273.3(3)	4302.3(4)	1093.35(13)
Z	8	8	2
Flack parameter	-0.01(4)	0.41(2)[d]	0.52(5)[d]
D_{calc} / g·cm^{-3}	4.041	4.011	3.949
μ / mm^{-1}	24.395	24.230	23.836
total reflns	15592	11819	6242
obsd reflns ($I > 2\sigma(I)$)	5320	5064	1443
R_{int}	0.066	0.025	0.0073
R_1[a] /wR_2[b] ($I > 2\sigma(I)$)	0.0684, 0.1748	0.0424, 0.0952	0.0414, 0.1052
R^1/wR^2 (all data)	0.0900, 0.1865	0.0791, 0.1058	0.0566, 0.1096
GOF	1.02	1.075	1.107
$\Delta\rho^c$ / e·Å^{-3}	4.88/−4.82	1.96/−2.71	1.82/−1.74

[a] $R_1 = \Sigma| |F_o| - |F_c| | / |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density. [d] The Flack test results become meaningless as the compounds become weak anomalous scatterers in the high-temperature high-disorder phase.

Table S5. Bond angles and bond lengths of (*R*-3AEP)Pb_2I_6 and (*S*-3AEP)Pb_2I_6.

Bond angles	Angle / °	Bond lengths	Length / Å
(*R*-3AEP)Pb_2I_6-245 K			
Pb(1)–I(1)–Pb(1)^{i}	163.50(8)	I(1)–Pb(1)	3.1766(6)
Pb(1)^{ii}–I(2)–Pb(1)	93.69(5)	I(1)–Pb(1)^{i}	3.1767(6)
Pb(1)^{ii}–I(3)–Pb(1)	90.59(5)	I(2)–Pb(1)^{ii}	3.1451(12)
Pb(2)^{iii}–I(4)–Pb(1)	172.33(4)	I(2)–Pb(1)	3.1451(12)
Pb(2)–I(5)–Pb(1)	171.70(4)	I(3)–Pb(1)^{ii}	3.2282(14)
Pb(2)–I(6)–Pb(2)^{iv}	169.16(11)	I(3)–Pb(1)	3.2282(14)
Pb(2)^{v}–I(7)–Pb(2)	88.23(4)	I(4)–Pb(1)	3.2418(14)
Pb(2)^{v}–I(8)–Pb(2)	91.33(4)	I(4)–Pb(2)^{iii}	3.2281(14)
Pb(2)–I(9)–Pb(1)^{iii}	165.91(6)	I(5)–Pb(1)	3.2233(16)
I(1)–Pb(1)–I(3)	170.70(9)	I(5)–Pb(2)	3.1315(15)
I(1)–Pb(1)–I(4)	85.91(5)	I(6)–Pb(2)^{iv}	3.1983(6)
I(1)–Pb(1)–I(5)	98.09(4)	I(6)–Pb(2)	3.1983(6)
I (1)–Pb(1)–I(9)^{vi}	91.83(5)	I(7)–Pb(2)^{v}	3.2455(13)
I(2)–Pb(1)– I (1)	89.09(2)	I(7)–Pb(2)	3.2455(13)
I(2)–Pb(1)–I(3)	87.86(3)	I(8)–Pb(2)^{v}	3.1584(13)
I(2)–Pb(1)–I(4)	89.78(2)	I(8)–Pb(2)	3.1584(13)
I(2)–Pb(1)–I(5)	171.76(5)	I(9)–Pb(1)^{iii}	3.2822(16)
I(2)–Pb(1)–I(9)^{vi}	88.52(3)	I(9)–Pb(2)	3.2614(15)
I(3)–Pb(1)–I(4)	85.29(2)		
I(3)–Pb(1)–I(9)^{vi}	96.86(3)		
I(4)–Pb(1)–I(9)^{vi}	177.19(3)		
I(5)–Pb(1)–I(3)	84.42(4)		
I(5)–Pb(1)–I(4)	86.73(6)		
I(5)–Pb(1)– I (9)^{vi}	95.26(6)		
I(4)^{vi}–Pb(2)– I (7)	91.62(2)		
I(4)^{vi}–Pb(2)–I(9)	176.08(4)		
I(5)–Pb(2)–I(4)^{vi}	92.17(6)		
I(5)–Pb(2)–I(6)	92.09(4)		

I(5)–Pb(2)–I(7)	176.00(6)
I(5)–Pb(2)–I(8)	91.25(4)
I(5)–Pb(2)– I (9)	89.25(2)
I(6)–Pb(2)–I(4) ^{vi}	88.04(5)
I(6)–Pb(2)–I(7)	86.74(2)
I(6)–Pb(2)–I(9)	88.26(6)
I(7)–Pb(2)–I(9)	86.88(3)
I(8)–Pb(2)–I(4) ^{vi}	87.50(2)
I(8)–Pb(2)–I(6)	174.53(5)
I(8)–Pb(2)–I(7)	90.22(3)
I(8)–Pb(2)–I(9)	96.12(3)

Symmetry codes:(i): +X, −Y, 1−Z; (ii) 1−X, +Y, 3/2−Z; (iii) −1/2+X, 1/2−Y, 1−Z; (iv) 1+X, 1−Y, 1−Z; (v) 1−X, +Y, 1/2−Z; (vi) 1/2+X, 1/2−Y, 1−Z.

(*R*-3AEP)Pb_2I_6-298 K

I(1)–Pb(1)–I(2)	88.73(2)	I(1)–Pb(1)	3.1641(11)
I(1)–Pb(1)–I(3)	88.68(2)	I(2)–Pb(1)	3.1822(6)
I(1)–Pb(1)–I(4)	90.259(18)	I(3)–Pb(1)	3.2771(13)
I(1)–Pb(1)–I(5)	87.70(3)	I(4)–Pb(1)	3.2402(12)
I(1)–Pb(1)–I(6)	173.48(4)	I(5)–Pb(1)	3.2178(12)
I(2)–Pb(1)–I(3)	91.40(4)	I(6)–Pb(1)	3.2025(15)
I(2)–Pb(1)–I(4)	86.73(4)	I(3) ^{ii} –Pb(2)	3.2695(12)
I(2)–Pb(1)–I(5)	171.85(4)	I(4) ^{ii} –Pb(2)	3.2258(12)
I(2)–Pb(1)–I(6)	97.43(4)	I(6)–Pb(2)	3.1503(14)
I(4)–Pb(1)–I(3)	177.87(3)	I(7)–Pb(2)	3.1733(11)
I(5)–Pb(1)–I(3)	95.84(3)	I(8)–Pb(2)	3.1926(5)
I(5)–Pb(1)–I(4)	85.96(19)	I(9)–Pb(2)	3.2281(12)
I(6)–Pb(1)–I(3)	93.29(5)		
I(6)–Pb(1)–I(4)	87.96(5)		
I(6)–Pb(1)–I(5)	85.92(3)		
I(4)^{i}–Pb(2)–I(3)^{ii}	177.27(3)		

I(4)^{i}–Pb(2)–I(9)	91.666(19)
I(6)–Pb(2)–I(3)^{ii}	89.96(6)
I(6)–Pb(2)–I(4)^{i}	90.70(5)
I(6)–Pb(2)–I(7)	89.84(3)
I(6)–Pb(2)–I(8)	93.66(4)
I(6)–Pb(2)–I(9)	177.50(5)
I(7)–Pb(2)–I(3)^{ii}	95.24(3)
I(7)–Pb(2)–I(4)^{i}	87.409(19)
I(7)–Pb(2)–I(8)	174.69(6)
I(7)–Pb(2)–I(9)	89.43(3)
I(8)–Pb(2)–I(3)^{ii}	88.76(5)
I(8)–Pb(2)–I(4)^{i}	88.56(5)
I(8)–Pb(2)–I(9)	87.24(2)
I(9)–Pb(2)–I(3)^{ii}	87.72(2)
Pb(1)–I(1)–Pb(1)^{iii}	93.30(8)
Pb(1)^{iv}–I(2)–Pb(1)	165.83(5)
Pb(1)^{ii}–I(3)–Pb(1)	167.91(5)
Pb(2)^{iii}–I(4)–Pb(1)	172.67(3)
Pb(2)–I(5)–Pb(1)^{iii}	91.30(4)
Pb(2)–I(6)–Pb(1)	175.30(8)
Pb(2)^{v}–I(7)–Pb(2)	91.56(4)
Pb(2)–I(8)–Pb(2)^{vi}	170.28(9)
Pb(2)^{v}–I(9)–Pb(2)	89.58(4)

Symmetry codes:(i) 1/2+X, 1/2−Y, 1−Z; (ii) −1/2+X, 1/2−Y, 1−Z; (iii) 1−X, +Y, 3/2−Z; (iv) +X, −Y, 1−Z; (v) 1−X, +Y, 1/2−Z; (vi) +X, 1−Y, 1−Z.

(*R*-3AEP)Pb_2I_6-425 K

I(1)–Pb(1)–I(1)^{i}	179.28(5)	Pb(1)–I(1)	3.2517(2)
I(2)^{ii}–Pb(1)–I(1)	90.8(2)	Pb(1)–I(1)^{i}	3.25171(19)
I(2)–Pb(1)–I(1)^{i}	90.8(2)	Pb(1)–I(2)^{ii}	3.1813(4)
I(2)–Pb(1)–I(1)	88.7(2)	Pb(1)–I(2)	3.1813(4)

I(2)^{ii}–Pb(1)–I(1)^{i}	88.7(2)	Pb(1)–I(3)	3.1984(7)
I(2)–Pb(1)–I(2)^{ii}	96.333(16)	Pb(1)–I(3)^{iii}	3.1984(7)
I(2)^{ii}–Pb(1)–I(3)	88.055(14)		
I(2)^{ii}–Pb(1)–I(3)^{iii}	175.51(6)		
I(2)–Pb(1)–I(3)	175.51(6)		
I(2)–Pb(1)–I(3)^{iii}	88.055(14)		
I(3)^{iii}–Pb(1)–I(1)^{i}	90.259(17)		
I(3)–Pb(1)–I(1)	90.259(17)		
I(3)–Pb(1)–I(1)^{i}	90.259(17)		
I(3)^{iii}–Pb(1)–I(1)	90.259(17)		
I(3)^{iii}–Pb(1)–I(3)	87.58(3)		
Pb(1)^{iv}–I(1)–Pb(1)^{i}	179.28(5)		
Pb(1)–I (2)–Pb(1)^{iv}	177.9(4)		
Pb(1)^{iii}–I (3)–Pb(1)	92.42(3)		

Symmetry codes:(i) 1−X,1−Y,+Z; (ii) +X, +Y, 1+Z; (iii) 1−X, +Y, 1−Z;(iv) +X, +Y, 1+Z; (v) 3/2−X, 3/2−Y, +Z.

(*S*-3AEP)Pb_2I_6-245 K

Pb(1)–I(1)–Pb(1)^{i}	163.50(8)	I(1)–Pb(1)	3.2253(16)
Pb(1)^{ii}–I(2)–Pb(1)	93.69(5)	I(1)–Pb(1)^{i}	3.2253(16)
Pb(1)^{ii}–I(3)–Pb(1)	90.59(5)	I(2)–Pb(1)	3.1494(15)
Pb(2)^{iii}–I(4)–Pb(1)	172.33(4)	I(2)–Pb(1)^{i}	3.1495(15)
Pb(2)–I(5)–Pb(1)	171.70(4)	I(3)–Pb(1)	3.1763(8)
Pb(2)–I(6)–Pb(2)^{iv}	169.16(11)	I(3)–Pb(1)^{ii}	3.1763(8)
Pb(2)^{v}–I(7)–Pb(2)	88.23(4)	I(4)–Pb(1)	3.2370(19)
Pb(2)^{v}–I(8)–Pb(2)	91.33(4)	I(4)–Pb(2)^{iii}	3.2238(19)
Pb(2)–I(9)–Pb(1)^{iii}	165.91(6)	I(5)–Pb(1)	3.221(2)
I(1)–Pb(1)–I(3)	170.70(9)	I(5)–Pb(2)	3.1302(19)
I(1)–Pb(1)–I(4)	85.91(5)	I(6)–Pb(2)	3.1604(16)
I(1)–Pb(1)–I(5)	98.09(4)	I(6)–Pb(2)^{iv}	3.1604(16)
I (1)–Pb(1)–I(9)^{vi}	91.83(5)	I(7)–Pb(2)	3.2395(16)

I(2)–Pb(1)– I (1)	89.09(2)	I(7)–Pb(2)^{iv}	3.2396(16)
I(2)–Pb(1)–I(3)	87.86(3)	I(8)–Pb(2)	3.1945(7)
I(2)–Pb(1)–I(4)	89.78(2)	I(8)–Pb(2)^{v}	3.1946(7)
I(2)–Pb(1)–I(5)	171.76(5)	I(9)–Pb(1)^{iii}	3.270(2)
I(2)–Pb(1)–I(9)^{vi}	88.52(3)	I(9)–Pb(2)	3.262(2)
I(3)–Pb(1)–I(4)	85.29(2)		
I(3)–Pb(1)–I(9)^{vi}	96.86(3)		
I(4)–Pb(1)–I(9)^{vi}	177.19(3)		
I(5)–Pb(1)–I(3)	84.42(4)		
I(5)–Pb(1)–I(4)	86.73(6)		
I(5)–Pb(1)– I (9)^{vi}	95.26(6)		
I(4)^{vi}–Pb(2)– I (7)	91.62(2)		
I(4)^{vi}–Pb(2)–I(9)	176.08(4)		
I(5)–Pb(2)–I(4)^{vi}	92.17(6)		
I(5)–Pb(2)–I(6)	92.09(4)		
I(5)–Pb(2)–I(7)	176.00(6)		
I(5)–Pb(2)–I(8)	91.25(4)		
I(5)–Pb(2)– I (9)	89.25(2)		
I(6)–Pb(2)–I(4)^{vi}	88.04(5)		
I(6)–Pb(2)–I(7)	86.74(2)		
I(6)–Pb(2)–I(9)	88.26(6)		
I(7)–Pb(2)–I(9)	86.88(3)		
I(8)–Pb(2)–I(4)^{vi}	87.50(2)		
I(8)–Pb(2)–I(6)	174.53(5)		
I(8)–Pb(2)–I(7)	90.22(3)		
I(8)–Pb(2)–I(9)	96.12(3)		

Symmetry codes:(i): 1+X, +Y, 1+Z; (ii) 1−X, 1/2+Y, 1−Z; (iii) 1−X, −1/2+Y, 1−Z; (iv) −1+X, +Y, −1+Z

(*S*-3AEP)Pb_2I_6-290 K

I(1)–Pb(1)–I(4)	85.44(3)	I(1)–Pb(1)	3.1641(11)

I(1)–Pb(1)–I(9)^{vi}	96.64(4)	I(2)–Pb(1)	3.1822(6)
I(2)–Pb(1)–I(1)	87.91(4)	I(3)–Pb(1)	3.2771(13)
I(2)–Pb(1)–I(3)	88.93(3)	I(4)–Pb(1)	3.2402(12)
I(2)–Pb(1)–I(4)	89.87(3)	I(5)–Pb(1)	3.2178(12)
I(2)–Pb(1)–I(5)	172.15(6)	I(6)–Pb(1)	3.2025(15)
I(2)–Pb(1)–I(9)^{vi}	88.61(3)	I(3)^{ii}–Pb(2)	3.2695(12)
I(3)–Pb(1)–I(1)	170.99(6)	I(4)^{ii}–Pb(2)	3.2258(12)
I(3)–Pb(1)–I(4)	86.12(6)	I(6)–Pb(2)	3.1503(14)
I(3)–Pb(1)–I(5)	98.00(5)	I(7)–Pb(2)	3.1733(11)
I(3)–Pb(1)–I(9)^{vi}	91.71(6)	I(8)–Pb(2)	3.1926(5)
I(7)–Pb(1)–I(9)^{vi}	177.37(4)	I(9)–Pb(2)	3.2281(12)
I(9)–Pb(1)–I(1)	84.69(4)		
I(9)–Pb(1)–I(4)	86.95(8)		
I(9)–Pb(1)–I(9)^{vi}	94.83(8)		
I(4)^{vi}–Pb(2)–I(7)	91.64(3)		
I(4)^{vi}–Pb(2)–I(9)	176.38(4)		
I(5)–Pb(2)–I(4)^{vi}	91.85(8)		
I(5)–Pb(2)–I(6)	90.89(5)		
I(5)–Pb(2)–I(7)	176.42(8)		
I(5)–Pb(2)–I(8)	92.52(5)		
I(5)–Pb(2)–I(9)	89.41(8)		
I(6)–Pb(2)–I(4)^{vi}	87.53(3)		
I(6)–Pb(2)–I(7)^{i}	90.03(4)		
I(6)–Pb(2)–I(8)	174.79(6)		
I(6)–Pb(2)–I(9)	95.85(4)		
I(7)–Pb(2)–I(9)	87.06(3)		
I(8)–Pb(2)–I(4)^{vi}	88.42(7)		
I(8)–Pb(2)–I(7)	86.81(3)		
I(8)–Pb(2)–I(9)	88.13(7)		
Pb(1)^{i}–I(1)–Pb(1)	90.68(5)		
Pb(1)–I(2)–Pb(1)^{i}	93.51(6)		

Pb(1)–I(3)–Pb(1)^{ii}	164.14(11)
Pb(2)^{iii}–I(4)–Pb(1)	172.48(5)
Pb(2)–I(5)–Pb(1)	172.50(12)
Pb(2)^{iv}–I(6)–Pb(2)	91.39(5)
Pb(2)^{v}–I(7)–Pb(2)^{iv}	88.56(5)
Pb(2)^{v}–I(8)–Pb(2)^{v}	170.00(14)
Pb(2)–I(9)–Pb(1)^{iii}	166.46(7)

Symmetry codes:(i) 1/2+X, 1/2−Y, 1−Z; (ii) −1/2+X, 1/2−Y, 1−Z; (iii) 1−X, +Y, 3/2−Z; (iv) +X, −Y, 1−Z; (v) 1−X, +Y, 1/2−Z; (vi) +X, 1−Y, 1−Z.

(*S*-3AEP)Pb_2I_6-425 K

I (1)–Pb(1)– I (1)^{i}	87.81(3)	Pb(1)–I(1)	3.2015(9)
I (1)^{i}–Pb(1)– I (2)	90.20(2)	Pb(1)–I(1)^{i}	3.2015(9)
I (1)^{i}–Pb(1)– I (2)^{ii}	90.20(2)	Pb(1)–I(2)^{ii}	3.2544(19)
I (1)^{iii}–Pb(1)– I (2)	90.20(2)	Pb(1)–I(2)	3.2544(19)
I (1)–Pb(1)– I (2)	90.20(2)	Pb(1)–I(3)	3.1827(4)
I (2)^{ii}–Pb(1)– I (2)^{i}	179.46(6)	Pb(1)–I(3)^{iii}	3.2015(4)
I (3)^{iii}–Pb(1)– I (1)	175.82(2)		
I (3)–Pb(1)– I (1)^{i}	175.82(2)		
I (3) –Pb(1)– I (1)	88.003(17)		
I (3)^{iii} –Pb(1)– I (1)	88.003(17)		
I (3)–Pb(1)– I (2)^{ii}	89.8(3)		
I (3)^{iii} –Pb(1)– I (2)^{ii}	89.8(3)		
I (3)^{iii}–Pb(1)– I (2)	89.8(3)		
I (3)–Pb(1)– I (2)	89.8(3)		
I(3)–Pb(1)–I(3)^{iii}	96.180(17)		
Pb(1)^{ii}–I(1)–Pb(1)^{i}	92.19(3)		
Pb(1)– I (2)–Pb(1)^{iv}	179.46(6)		
Pb(1)^{ii}– I (3)–Pb(1)^{v}	179.9(5)		

Symmetry codes: 1−X, 1−Y, +Z; (ii) +X, Y, 1+Z; (iii) 1−X, +Y, −1−Z.

Table S6. Summary of the chiroptical properties of chiral lead halide-based semiconductors.

Dimension	Compound	g_{CD}	g_{Iph}	*R* (A/W)	D^* (Jones)	*λ* (nm)	Ref (DOI)
1D	(*R*/*S*-PEA)PbI_3	1.9×10^{-2}	9.7×10^{-2}	1.2×10^{-1}	7.1×10^{11}	395	10.1038/s41467-019-09942-z
	(*R*/*S*-1/2-NEA)PbI_3	NA	2.9×10^{-1}	9×10^{-2}	3.8×10^{11}	405	10.1021/acs.chemmater.1c03622
2D	(*R*/*S*-MBA)$_2$$PbI_4$	0.004	1.0×10^{-1}	NA	NA	486	10.1021/acsnano.0c05980
	(*R*/*S*-BPEA)$_2$$PbI_4$	2.0×10^{-3}	1.3×10^{-1}	2.1×10^{-3}	3×10^{11}	520	10.1021/jacs.1c07183
	(*R*/*S*-3AMP)$PbBr_4$	1.8×10^{-3}	2.0×10^{-1}	4.2×10^{-2}	1.2×10^{12}	430	10.1002/adma.202204119
	(*R*/*S*-VPEA)$_2$$PbI_4$	NA	2.2×10^{-1}	1.6	2.2×10^{13}	490	10.1002/adfm.202306199
2D Nanowires	(*R*/*S*-MBA)$_2$$PbI_4$	NA	1.5×10^{-1}	47.1	1.2×10^{13}	505	10.1021/jacs.1c02675
Quasi-2D	(*S*/*R*-2-NEA)$MAPb_2I_7$	5×10^{-3}	1.5×10^{-1}	15.7	NA	405	10.1021/acsnano.1c09521
3D	(*R*/*S*-BPEA)$EA_6Pb_4Cl_{15}$ (Cavity formed by six octahedra)	7.6×10^{-5}	2.8×10^{-1}	1.8×10^{-3}	4.7×10^{10}	320	10.1002/anie.202307034
	(*R*/*S*-3AEP)Pb_2I_6 (Cavity formed by two octahedra)	4.1×10^{-6}	8.0×10^{-2}	0.25	3.2×10^{12}	565	Our work

Note: PEA and MBA = phenylethylammonium, 1/2-NEA = 1/2-(naphthyl)ethylammonium, BPEA = 1-(4-bromophenyl)ethylammonium; MA = methylammonium, 3AMP = 3-(aminomethyl)-piperidine divalent cation, VPEA = 1-(4-vinylphenyl)ethanammonium, EA = ethylammonium