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Supporting Information

The Role of Halogens in Structural Diversity and Chirality Enhancement of 1D Chiral Hybrid Metal Halides

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Materials and methods

Hydrochloric acid (HCl, 37wt % in water), hydrobromic acid (HBr, 48wt % in water), and hydroiodic acid (HI, 48wt% in water) were purchased from Sigma-Aldrich (Shanghai, China), Aladdin (Shanghai, China) and Meryer, respectively. Lead chloride ($PbCl_2$, 99.99%), lead bromide ($PbBr_2$, 99.0%), and lead Iodide (PbI_2, 99.5%) were purchased from Macklin. *R*- or *S*-tetrahydro-2H-pyran-3-amine hydrochloride (*R*/*S*-3ATHP, ⩾97.0%) were purchased from Leyan.

All the analytical grade chemicals were used as received without further purification.

Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku SmartLab X-ray diffraction instrument. Thermogravimetry analyses (TGA) were conducted on a Netzsch TG 209 F3 Libra Thermo-Microbalance at a heating rate of 20 °C/minute from room temperature to 600 ºC under N_2 atmosphere. The CD spectra were measured using a JASCO J-1700 spectrometer/data system equipped with a PM-539 detector. The samples were prepared using the KBr pellet method by pressing the thoroughly ground powder containing 1% weight percentage of the crystal and KBr into a transparent pellet. Ultraviolet-vis (UV-vis) absorption spectra were performed with Shimadzu UV-2600 equipping ISR-2600Plus integrating sphere. Photoluminescence was measured on an FLS 1000 spectrometer. The emission spectrum was measured with a Xenon lamp using a solid sample holder, nF920 Nanosecond Flashlamp, and a standard integrating sphere was used to measure the lifetime and absolute quantum yield of samples. The photoluminescence quantum yields were calculated based on the equation: $\eta_{QE} = (I_S - I_R)/(E_R - E_S)$, in which I_S represents the luminescence emission spectrum of the sample, I_R represents the luminescence emission spectrum of the standard white plate, E_R is the spectrum of the excitation light from the empty integrated sphere (Teflon coating), and E_S is the excitation spectrum for exciting the sample.

Crystallographic data were collected on XtaLAB Synergy R, DW system, HyPix, with Hybrid Pixel Array Detector. Data collection, refinement, and reduction were carried out with CrysAlisPro 1.171.40.84a (Rigaku OD, 2020). SHELXL-2018 in the OLEX2 interface was used to solve the single crystal structures by direct methods. All the non-hydrogen atoms were refined anisotropically, and the positions of hydrogen atoms were generated geometrically. The X-ray crystallographic data of the compounds were deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2313113−2313120. These data can be obtained free of charge via

http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Synthesis of z-(*R*/*S*-3ATHP)$_3$PbCl$_5$: $PbCl_2$ (2 mmol) was dissolved in 20 mL HCl solution. Then *R*/*S*-tetrahydro-2H-pyran-3-amine hydrochloride (*R*/*S*-3ATHP; 6 mmol) in 10 mL HCl solution was added. After evaporation at 55 ℃ for a few days, colorless needle-like crystals z-(*R*/*S*-3ATHP)$_3$PbCl$_5$ were obtained. Yield: 62%.

Synthesis of z-(*R*/*S*-3ATHP)$_3$PbBr$_5$ and l-(*R*/*S*-3ATHP)PbBr$_3$: $PbBr_2$ (2 mmol) was dissolved in 15 mL HBr solution. Then *R*/*S*-3ATHP (2 or 6 mmol) in 8 mL HBr solution was added. After evaporation at 55 ℃ for a few days, colorless needle-like crystals z-(*R*/*S*-3ATHP)$_3$PbBr$_5$ and block crystals l-(*R*/*S*-3ATHP)$PbBr_3$ were obtained. Yield: 53.

Synthesis of l-(*R*/*S*-3ATHP)PbI$_3$: PbI_2 (2 mmol) was dissolved in 10 mL HI solution. Then *R*/*S*-3ATHP (2 mmol) in 5 mL HI solution was added. After evaporation at 55 ℃ for a few days, yellowish block crystals l-(*R*/*S*-3ATHP)PbI_3 were obtained. Yield: 54%

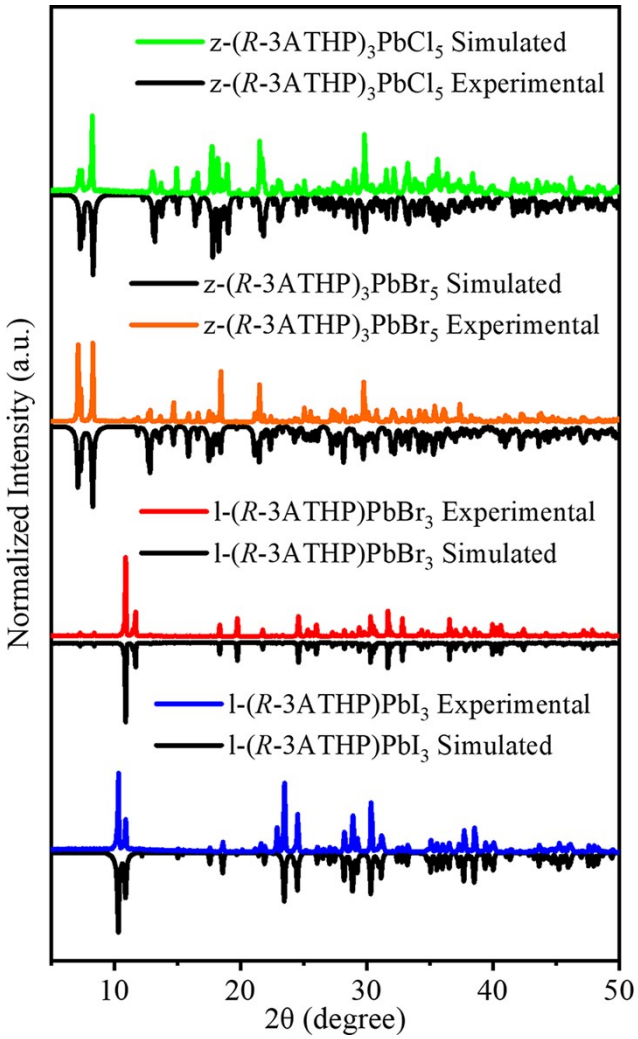

Figure S1. Measured and simulated PXRD patterns of z-(*R*-3ATHP)$_3$PbCl$_5$, z-(*R*-3ATHP)$_3$PbBr$_5$, l-(*R*-3ATHP)PbBr$_3$, and l-(*R*-3ATHP)PbI$_3$ at room temperature.

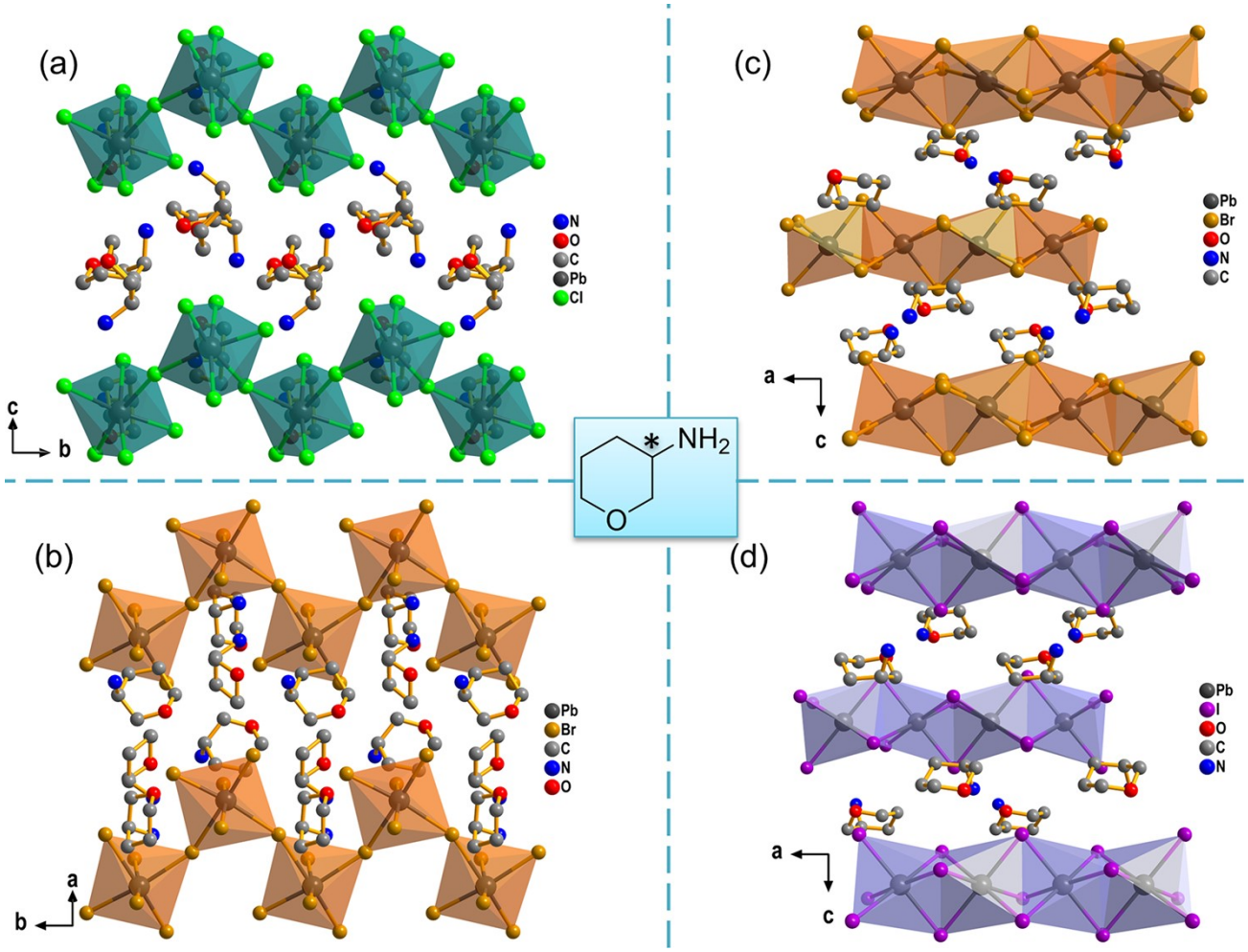

Figure S2. Crystal structures of (a) z-(*S*-3ATHP)$_3$PbCl$_5$, (b) z-(*S*-3ATHP)$_3$PbBr$_5$, (c) l-(*S*-3ATHP)PbBr$_3$, and (d) l-(*S*-3ATHP)PbI$_3$.

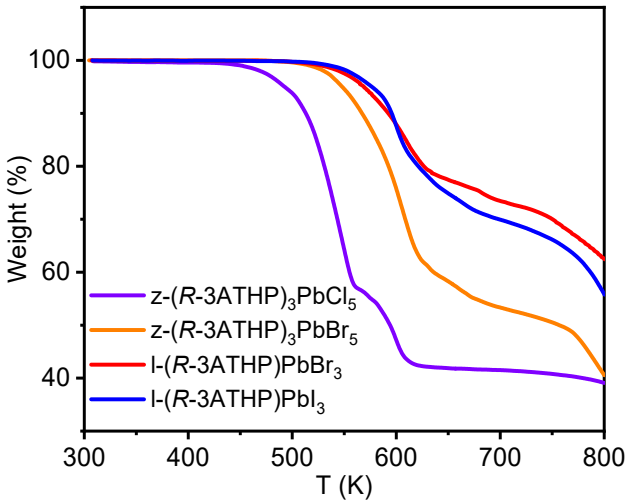

Figure S3. Thermogravimetric analysis curves of z-(*R*-3ATHP)$_3$PbCl$_5$, z-(*R*-3ATHP)$_3$PbBr$_5$, l-(*R*-3ATHP)PbBr$_3$, and l-(*R*-3ATHP)PbI$_3$.

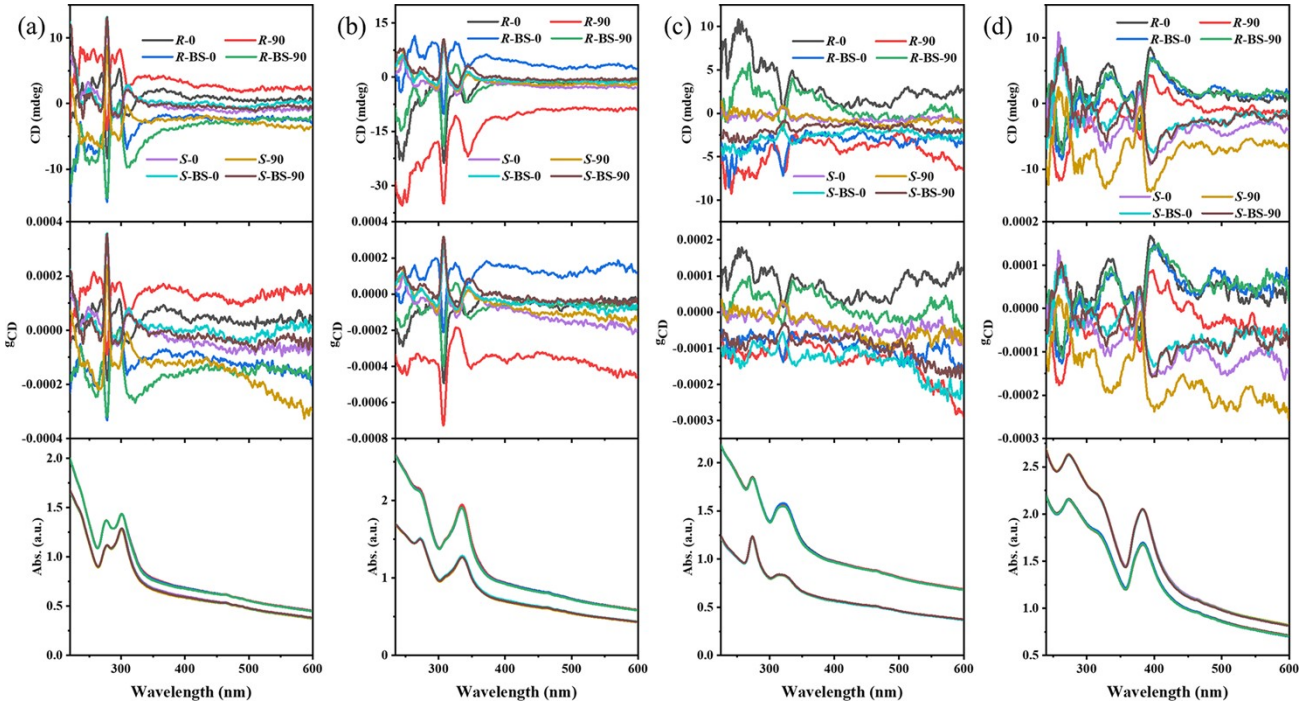

Figure S4. CD, g_{CD}, and absorption spectra of (a) z-(*R*/*S*-3ATHP)$_3$PbCl$_5$, (b) z-(*R*/*S*-3ATHP)$_3$PbBr$_5$, (c) l-(*R*/*S*-3ATHP)PbBr$_3$, and (d) l-(*R*/*S*-3ATHP)PbI$_3$. Note: 0 and 90 mean 0° and 90°, respectively; BS means a back side test by flipping the sample.

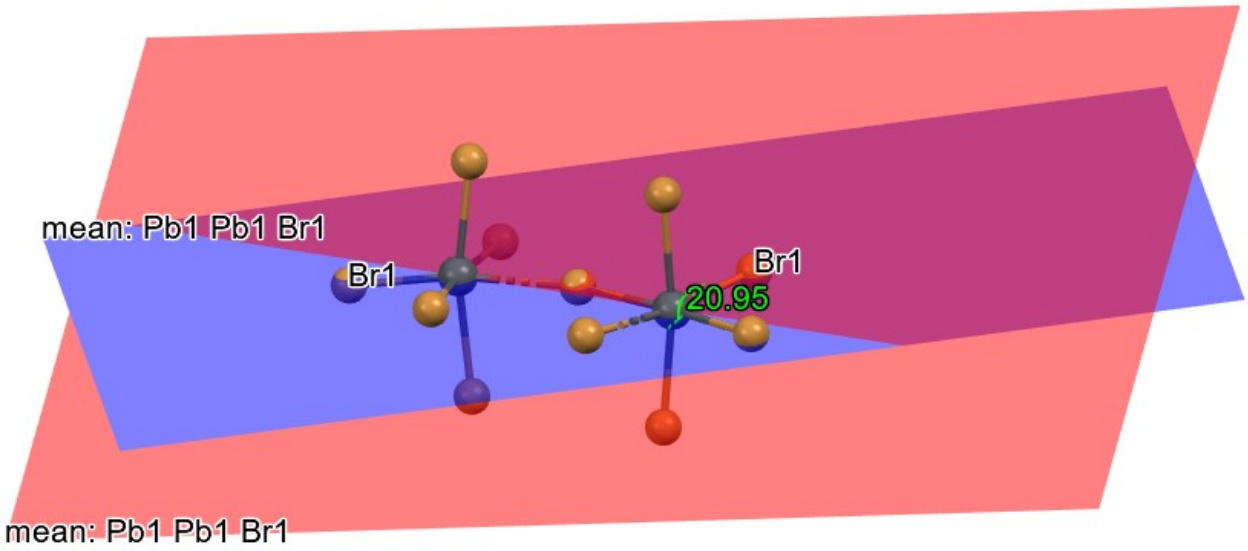

Figure S5. Example of the dihedral angle measurement of z-(*R*/*S*-3ATHP)$_3$PbBr$_5$.

Table S1. Crystallographic data and structural refinement details for zigzag crystals.

	z-(*R*-3ATHP)$_3$PbCl$_5$	**z-(*S*-3ATHP)$_3$PbCl$_5$**	**z-(*R*-3ATHP)$_3$PbBr$_5$**	**z-(*S*-3ATHP)$_3$PbBr$_5$**
CCDC No.	2313114	2313120	2313113	2313117
Chain type	zigzag	zigzag	zigzag	zigzag
Formula	$C_{15}H_{36}N_3O_3PbCl_5$	$C_{15}H_{36}N_3O_3PbCl_5$	$C_{15}H_{36}N_3O_3PbBr_5$	$C_{15}H_{36}N_3O_3PbBr_5$
Formula weight	690.91	690.91	913.21	913.21
T / K	293 (2)	293 (2)	293 (2)	293(2)
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a / Å	12.6821 (3)	12.6836(4)	12.8366 (3)	12.8323(5)
b / Å	8.1424 (2)	8.1333(3)	8.4095 (10)	8.4061(3)
c / Å	13.0057 (4)	13.0112(5)	13.2067 (3)	13.2111(4)
β / °	111.683 (3)	111.745(4)	110.073(2)	110.059(4)
V / Å^3	1247.98 (6)	1246.72(8)	1339.05 (5)	1338.63(9)
Z	2	2	2	2
D_{calc} / g·cm^{-3}	1.839	1.840	2.265	2.266
μ / mm^{-1}	7.314	7.322	13.779	13.783
F(000)	676	676	856	856
θ range /°	2.825-30.788	2.827-30.594	2.730-30.885	1.909-30.304
Reflns collected	15378	8728	34043	10640
Independent reflns (R_{int})	5964(0.0204)	4967(0.0195)	7019(0.0364)	5834(0.0238)
no. parameters	248	248	248	248
R_1[a], wR_2[b] [I>2σ(I)]	0.0159, 0.0338	0.0176, 0.0349	0.0233, 0.0397	0.0249, 0.0468
R_1, wR_2 [all data]	0.0175, 0.0340	0.0199, 0.0353	0.0284, 0.0403	0.0302, 0.0478
GOF	1.025	0.986	1.028	0.977
Δρ[c] / e·Å^{-3}	0.70, −0.49	0.449, −0.627	0.79, −0.72	0.775, −0.835

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[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.

Table S2. Crystallographic data and structural refinement details for linear crystals.

	l-(*R*-3ATHP)$PbBr_3$	**l-(*S*-3ATHP)$PbBr_3$**	**l-(*R*-3ATHP)PbI_3**	**l-(*S*-3ATHP)PbI_3**
CCDC No.	2313115	2313118	2313119	2313116
Chain type	linear	linear	linear	linear
Formula	$C_5H_{12}NOPbBr_3$	$C_5H_{12}NOPbBr_3$	$C_5H_{12}NOPbI_3$	$C_5H_{12}NOPbI_3$
Formula weight	549.08	549.08	690.05	690.05
T / K	293 (2)	293 (2)	293 (2)	293(2)
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a / Å	7.8266 (2)	7.8311(3)	8.1109 (2)	8.1132(2)
b / Å	9.7351 (3)	9.7259(4)	10.0931 (3)	10.0979(3)
c / Å	15.3312 (4)	15.3368(6)	16.2409 (4)	16.2628(4)
β / °	90	90	90	90
V / Å^3	1168.13 (6)	1168.12(8)	1329.55 (6)	1332.35(6)
Z	4	4	4	4
D_{calc} / g·cm^{-3}	3.122	3.122	3.447	3.440
μ / mm^{-1}	24.661	24.661	19.618	19.577
F(000)	976	976	1192	1192
θ range /°	2.478-30.599	2.480-30.475	2.376-30.514	2.374-30.720
Reflns collected	14333	6163	16665	11281
Independent reflns (R_{int})	2987(0.0930)	2614	3476(0.0379)	3371(0.0295)
no. parameters	102	102	102	102
R_1[a], wR_2[b] [I>2σ(I)]	0.0369, 0.0812	0.0359, 0.0735	0.0217, 0.0425	0.0237, 0.0509
R_1, wR_2 [all data]	0.0441, 0.0833	0.0444, 0.0757	0.0277, 0.0436	0.0297, 0.0521
GOF	1.008	1.011	1.001	1.029
Δρ[c] / e·Å^{-3}	1.81, −1.66	1.875, −1.157	1.04, −0.93	1.116, −0.768

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[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.

Table S3. Hydrogen bonds geometry (Å, degree) for z-(*R*-3ATHP)$_3$PbCl$_5$, z-(*R*-3ATHP)$_3$PbBr$_5$, l-(*R*-3ATHP)PbBr$_3$, and l-(*R*-3ATHP)PbI$_3$ at 293 K.

D−H···A	*d* (D−H)	*d* (H···A)	*d* (D···A)	∠D−H−A
z-(*R*-3ATHP)$_3$PbCl$_5$				
N1−H1E−Cl4^{i}	0.89	2.44	3.228(4)	148
N2−H2A−Cl1	0.89	2.53	3.330(4)	149
N2−H2B−Cl2	0.89	2.50	3.290(4)	148
N2−H2C−Cl3^{ii}	0.89	2.56	3.417(4)	163
N3−H3A−Cl3	0.89	2.46	3.294(3)	156
N3−H3B−Cl1	0.89	2.38	3.238(4)	163
N3−H3C−Cl2	0.89	2.61	3.325(4)	138
z-(*R*-3ATHP)$_3$PbBr$_5$				
N1−H1C−Br1^{i}	0.89	2.60	3.411(5)	152
N2−H2A−Br5	0.89	2.62	3.436(5)	153
N2−H2B−Br4^{iii}	0.89	2.71	3.556(5)	158
N2−H2C−Br2	0.89	2.70	3.496(5)	149
N3−H3C−Br4	0.89	2.61	3.455(4)	159
N3−H3D−Br2	0.89	2.56	3.425(5)	166
N3−H3E−Br5	0.89	2.75	3.480(5)	140
l-(*R*-3ATHP)PbBr$_3$				
N1−H1A−Br3^{iv}	0.89	2.52	3.383(8)	163
N1−H1C−Br2	0.89	2.77	3.505(8)	141
l-(*R*-3ATHP)PbI$_3$				
N1−H1A−I1^{v}	0.89	2.74	3.576(5)	158

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

Table S4. Dihedral angles between adjacent octahedra in z-(*R*-3ATHP)$_3$PbCl$_5$, z-(*R*-3ATHP)$_3$PbBr$_5$, l-(*R*-3ATHP)PbBr$_3$, and l-(*R*-3ATHP)PbI$_3$ at 293 K.

Compounds	Mean plane 1	Mean plane 2	Dihedral angle / °
z-(*R*-3ATHP)$_3$PbCl$_5$	Pb1, Cl1, Pb1	Pb1, Cl1, Pb1	4.28
	Pb1, Cl2, Pb1	Pb1, Cl2, Pb1	2.91
	Pb1, Cl3, Pb1	Pb1, Cl3, Pb1	7.18
	Pb1, Cl4, Pb1	Pb1, Cl4, Pb1	12.76
	Pb1, Cl5, Pb1	Pb1, Cl5, Pb1	1.36
	Pb1, Cl5, Pb1	Pb1, Cl5, Pb1	0.89

z-(*R*-3ATHP)$_3$PbBr$_5$	Pb1, Br1, Pb1	Pb1, Br1, Pb1	20.95
	Pb1, Br2, Pb1	Pb1, Br2, Pb1	3.53
	Pb1, Br3, Pb1	Pb1, Br3, Pb1	1.54
	Pb1, Br4, Pb1	Pb1, Br4, Pb1	6.25
	Pb1, Br5, Pb1	Pb1, Br5, Pb1	0.19
l-(*R*-3ATHP)PbBr$_3$	Pb1, Br3, Pb1	Pb1, Br3, Pb1	1.00
	Pb1, Br1, Pb1	Pb1, Br1, Pb1	1.65
	Pb1, Br2, Pb1	Pb1, Br2, Pb1	2.66
	Pb1, Br3, Pb1	Pb1, Br3, Pb1	1.18
	Pb1, Br1, Pb1	Pb1, Br1, Pb1	1.18
	Pb1, Br2, Pb1	Pb1, Br2, Pb1	2.67
	Pb1, Br3, Pb1	Pb1, Br3, Pb1	1.49
l-(*R*-3ATHP)PbI$_3$	Pb1, I1, Pb1	Pb1, I1, Pb1	0.32
	Pb1, I2, Pb1	Pb1, I2, Pb1	0.16
	Pb1, I3, Pb1	Pb1, I3, Pb1	0.15
	Pb1, I1, Pb1	Pb1, I1, Pb1	0.33
	Pb1, I2, Pb1	Pb1, I2, Pb1	0.17
	Pb1, I3, Pb1	Pb1, I3, Pb1	0.16