Structural descriptor for enhanced spin-splitting in 2D hybrid perovskites

Manoj K. Jana,[1] Ruyi Song,[2] Yi Xie,[1,3] Rundong Zhao,[1,6] Peter C. Sercel,[4,5] Volker Blum[1,2]* and David B. Mitzi[1,2]*

[1]*Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, USA.*

[2]*Department of Chemistry, Duke University, Durham, NC 27708, USA.*

[3]*University Program in Materials Science and Engineering, Duke University, Durham, NC 27708, USA.*

[4]*Center for Hybrid Organic Inorganic Semiconductors for Energy, Golden, CO, 80401 USA*

[5]*Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA, USA.*

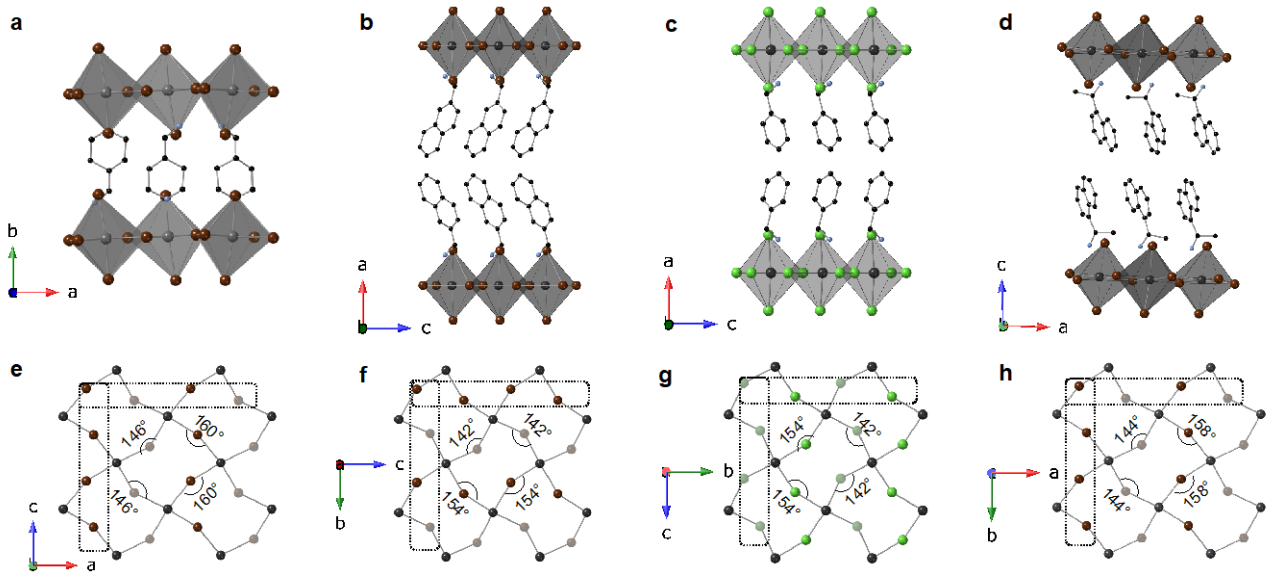
[6]*Current affiliation: School of Physics, Beihang University, Beijing 100191, China*

**e-mail: david.mitzi@duke.edu; volker.blum@duke.edu*

Contents

Noncentrosymmetric		Centrosymmetric	
PG	SG	PG	SG
C_1	P1	C_i	P-1
C_2	$P2_1$, C2	C_{2h}	$P2_1/a$, $P2_1/b$, $P2_1/c$,
C_s	Pn, Pc, Cn, Cm, Cc, Ic		$P2_1/m$, $P2_1/n$, C2/c, C2/m
C_{2v}	$Pca2_1$, $Cmc2_1$	D_{2h}	Pbca, Pnma, Cmca
D_2	$P2_12_12_1$	D_{4h}	$P4_2/ncm$

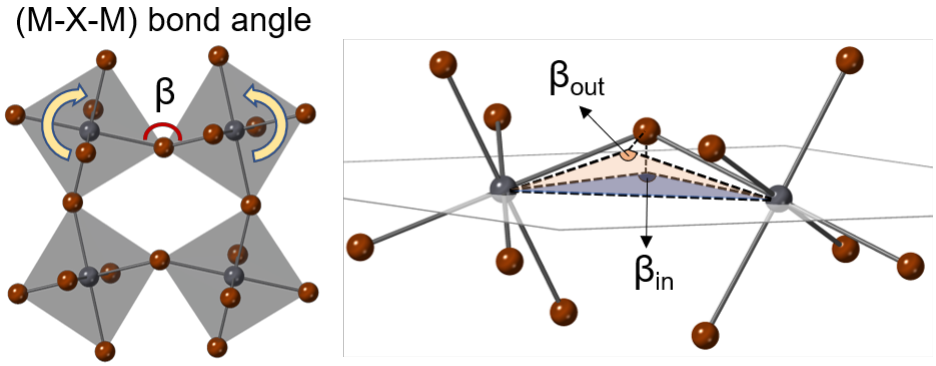
Supplementary Figure 1 | Crystal space groups (SGs) and point groups (PGs) observed frequently among known 2D MHPs. 2D chiral MHPs crystallize in Sohncke groups denoted in grey.



Supplementary Figure 2 | a-d, Schematic single-crystal X-ray structures of (**a**) [4-AMP]$PbBr_4$, (4AMP: 4-(aminomethyl)piperidine), (**b**) $[NMA]_2PbBr_4$ (NMA: 1-(2-naphthyl)methanammonium), (**c**) $[PMA]_2PbCl_4$ (PMA: phenylmethylammonium), (**d**) $[S\text{-}1\text{-}1\text{-}NEA]_2PbBr_4$ (S-1-1-NEA : S-(−)-1-(1-naphthyl)ethylammonium). In each case, all H atoms are omitted for visual clarity. **e-h**, In-plane views of perovskite layers corresponding to panels (**a-d**) showing the equatorial Pb-X-Pb bond angles (β). Axial X atoms are omitted for clarity. The two distinct equatorial X atoms associated with widely disparate β angles are distinguished by shaded and solid spheres. The dashed rectangles differentiate the individual rows comprised of the same type of equatorial X atoms from the rows comprising alternating types of equatorial X atoms, highlighting the local geometry fluctuation along one of the in-plane directions. Grey, brown, purple, green, blue, black, and pink spheres denote Pb, Br, I, Cl, N, C, and H atoms, respectively.

Supplementary Note 1: Structural distortions in 2D MHPs

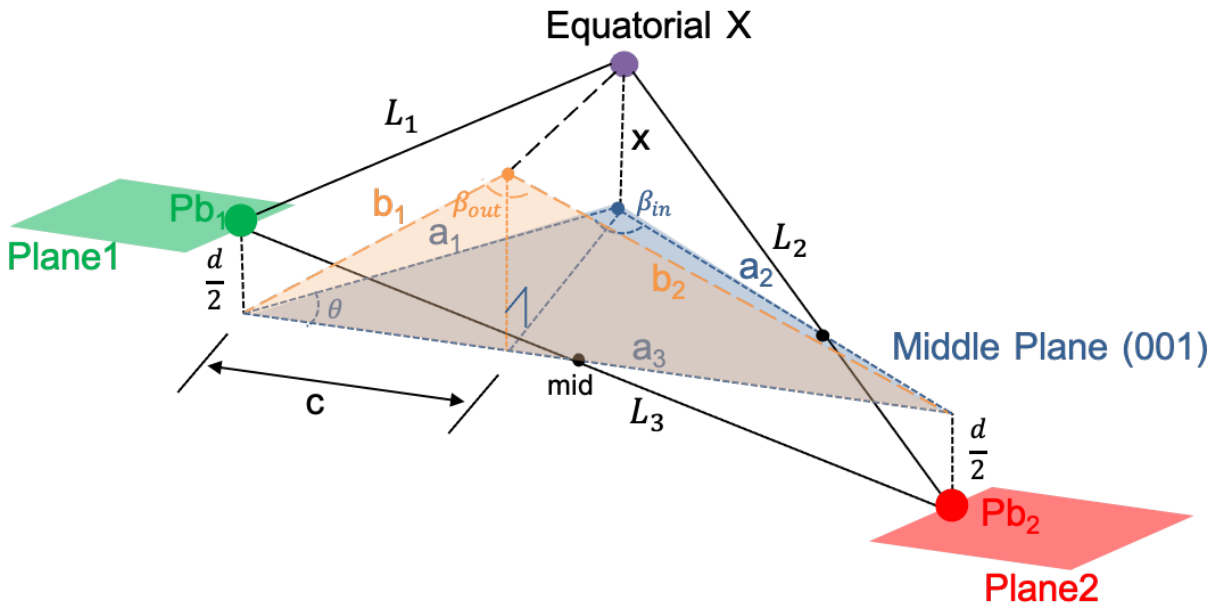
In 3D AMX_3 perovskite structures (where A=$CH_3NH_3^+$, $CH(NH_2)NH_2^+$, Cs^+, Rb^+; M=Pb^{2+}, Sn^{2+}, Ge^{2+}; X=Cl^-, Br^-, I^-), the corner-sharing MX_6 octahedra create cuboctahedral voids that host the A-site cations. The maximum allowed radius of the A-site cation is 2.60 Å in the largest possible scenario where M=Pb^{2+} and X=I^-, according to the Goldschmidt tolerance criterion for a perfect cubic perovskite.[1,2] With larger cations, the 3D perovskite structure collapses to low-dimensional variants. ⟨100⟩-oriented 2D MHPs with general formula $A'_2A_{n-1}B_nX_{3n+1}$ are conceptually obtained by excising the parent 3D AMX_3 every n^{th} plane along ⟨100⟩-direction and incorporating the larger A' spacer cations in-between the resulting slabs.[2] Here, we focus on the single-layer (n=1) members of 2D MHPs (M=Pb^{2+}) wherein each anionic perovskite layer of corner-sharing $[MX_4]^{2-}$ octahedra alternates with a bilayer (monolayer) of A'^+ (A'^{2+}) organic cations, coupled with specific hydrogen bonding interactions between the organic ammonium head groups and the nearest halogen atoms.



Supplementary Figure 3 | Schematic (left) showing a tilting distortion of corner-sharing MX_6 octahedra in ⟨100⟩-oriented MHPs, that leads to an equatorial (bridging) M-X-M bond angle (β) of < 180°. Schematic (right) showing the in-plane (β_{in}) and out-of-plane (β_{out}) components of β, which are determined by projecting the equatorial X atom onto a horizontal plane (blue) formed by coplanar M atoms, and onto a plane (yellow) perpendicular to the horizontal plane, respectively.

a) Interoctahedral distortions: The allowed cross-sectional area of the organic cation in 2D MHPs is given by the maximum area enclosed by the four axial halogens of neighboring corner-sharing MX_6 octahedra (~ 40 $Å^2$, for example, in 2D lead iodide perovskites[1,2]). As the cross-sectional area of the organic cation increases, the MX_6 octahedra will tilt to accommodate the

larger cation and allow for an optimal packing of organic cations to meet the charge-density requirements, and such tilting of octahedra causes equatorial (bridging) M-X-M bond angles (β) to decrease from the ideal (undistorted structure) 180° value (Supplementary Figure 3). The in-plane tilting component (β_{in}) is determined by projecting the equatorial X atom onto the horizontal plane consisting of M atoms. The out-of-plane tilting component (β_{out}) is found by projecting the equatorial X atom onto a plane normal to the horizontal plane.[3]



Supplementary Figure 4 | Schematic showing the displacement of adjacent Pb atoms (denoted as Pb_1 and Pb_2) with respect to (100) plane (blue), and the various parameters used for calculating the in-plane (β_{in}) and out-of-plane (β_{in}) components of octahedral tilting distortions.

In some of the lead perovskites studied here, the adjacent Pb atoms are not strictly coplanar, but are slightly displaced by the same distance in opposite directions with respect to the horizontal crystallographic (100) plane. In this case, to accurately determine β_{in} and β_{out}, a triangle is formed within the (100) plane by projecting the two adjacent Pb atoms (denoted as Pb_1 and Pb_2) and the equatorial X atom onto the (100) plane as shown in Supplementary Figure 4. a_1, a_2, and a_3 denote the three lengths of the as-formed triangle, which are mathematically expressed as:

$$a_1 = \sqrt{{L_1}^2 - (x - \frac{d}{2})^2}$$

$$a_2 = \sqrt{{L_2}^2 - (x + \frac{d}{2})^2}$$

$$a_3 = 2 \times \sqrt{(\frac{L_3}{2})^2 - (\frac{d}{2})^2} = \sqrt{{L_3}^2 - d^2}$$

where L_1, L_2, and L_3 denote the distances connecting Pb_1, Pb_2 and X, d is the vertical distance between Pb_1 and Pb_2, and x is the perpendicular distance between equatorial X and the (100) plane (Supplementary Figure 4). Using a_1, a_2 and a_3, β_{in} can be calculated as follows:

$$\beta_{in} = \arccos\left(\frac{\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}^2 + \sqrt{{L_2}^2 - (x + \frac{d}{2})^2}^2 - \sqrt{{L_3}^2 - d^2}^2}{2\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}\sqrt{{L_2}^2 - (x + \frac{d}{2})^2}}\right)$$

$$\beta_{in} = \arccos\left(\frac{{L_1}^2 + {L_2}^2 - {L_3}^2 - 2x^2 + \frac{d^2}{2}}{2\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}\sqrt{{L_2}^2 - (x + \frac{d}{2})^2}}\right)$$

β_{out} can be calculated by projecting X onto a plane (yellow) perpendicular to (100) and forming a triangle with the (100)-plane projected points of Pb_1 and Pb_2. b_1, b_2, and a_3 are the three lengths of this triangle sides (Supplementary Figure 4), which can be derived as follows:

$$\theta = \arccos\left(\frac{\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}^2 + \sqrt{{L_3}^2 - d^2}^2 - \sqrt{{L_2}^2 - (x + \frac{d}{2})^2}^2}{2\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}\sqrt{{L_3}^2 - d^2}}\right)$$

$$\theta = \arccos\left(\frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}\sqrt{{L_3}^2 - d^2}}\right)$$

$$c = a_1 \times \cos\theta$$

$$c = \sqrt{{L_1}^2 - (x - \frac{d}{2})^2} \times \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_1}^2 - (x - \frac{d}{2})^2}\sqrt{{L_3}^2 - d^2}}$$

$$c = \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}}$$

$$b_1 = \sqrt{c^2 + x^2}$$

$$b_1 = \sqrt{(\frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}$$

$$b_2 = \sqrt{(a_3 - c)^2 + x^2}$$

$$b_2 = \sqrt{(a_3 - \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}$$

Using b_1 and b_2, β_{out} can be calculated as follows:

β_{out}

$$= \arccos(\frac{\sqrt{(\frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}^2 + \sqrt{(a_3 - \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}^2 - {a_3}^2}{2\sqrt{(\frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}\sqrt{(a_3 - \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}})^2 + x^2}})$$

$$\beta_{out} = \arccos(\frac{2(c^2 + x^2 - a_3 c)}{2\sqrt{c^2 + x^2}\sqrt{(a_3 - c)^2 + x^2}})$$

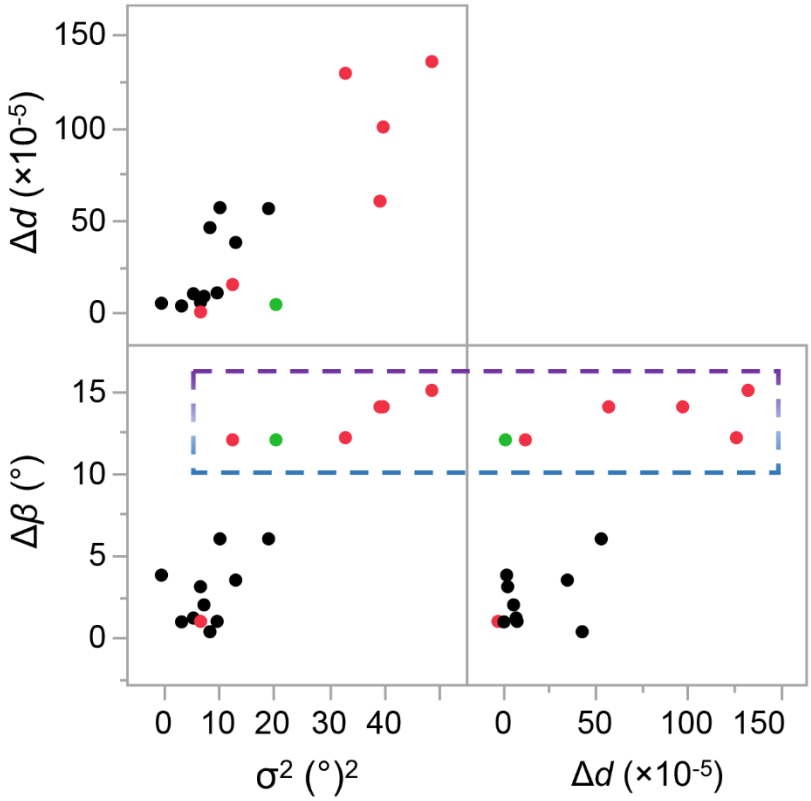
where

$$a_3 = \sqrt{{L_3}^2 - d^2}$$

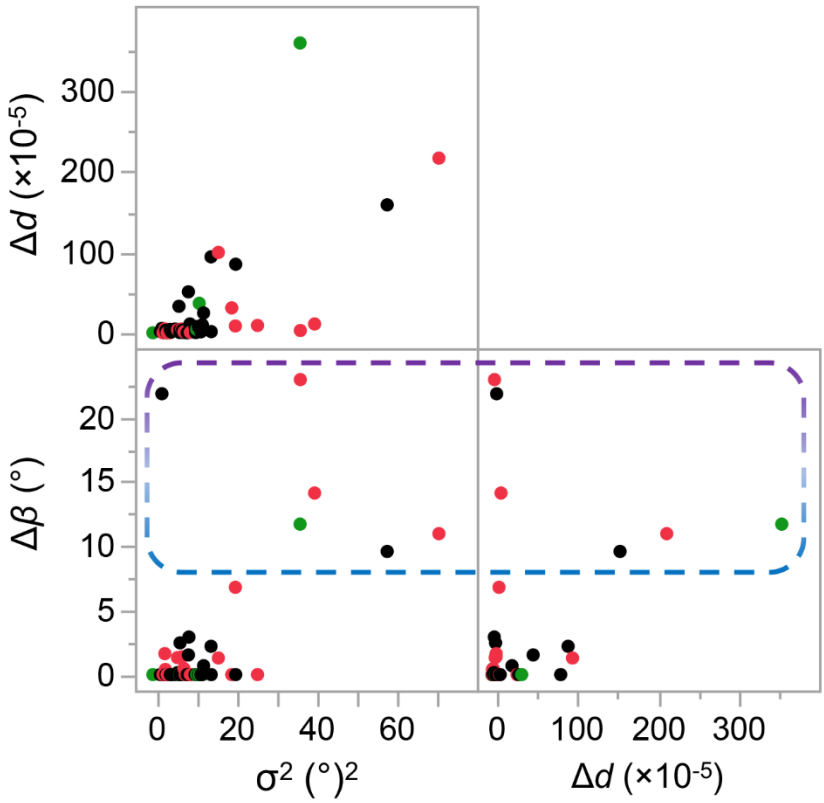
$$c = \frac{{L_1}^2 + {L_3}^2 - {L_2}^2 + 2dx - d^2}{2\sqrt{{L_3}^2 - d^2}}$$

Note that when the adjacent Pb atoms are coplanar (i.e., d =0), the picture is simplified to the one shown in Supplementary Figure 3 (right panel). For the MHPs studied here, d is either equal or very close to zero.

b) Intraoctahedral distortions: Intraoctahedral distortion within a single MX_6 octahedron, on the other hand, is quantified using metrics such as bond length distortion, $\Delta d = \left(\frac{1}{6}\right)\Sigma(d_i - d_0)^2/d_0{}^2$ (where d_i denotes the six M-X bond lengths and d_0 is the mean M-X bond length), and bond angle variance, $\sigma^2 = \Sigma_{i=1}^{12}(\theta_i - 90)^2/11$ (where θ_i denotes the individual *cis* X-M-X bond angles).[4]



Supplementary Figure 5 | Scatterplot matrix of intraoctahedral distortions (Δd and σ^2) and interoctahedral tilting distortion ($\Delta\beta$), corresponding to X-ray single-crystal structures of chiral and noncentrosymmetric MHPs listed in Table 1 in the main text. Black, red, and green data points denote, respectively, lead iodide, lead bromide, and lead chloride MHPs. The dashed rectangle encompasses MHPs (based on X = Br, Cl) with a large $\Delta\beta$ (> 11°), all of which also exhibit a sizeable spin-splitting (see Supplementary Figures 8-13).



Supplementary Figure 6 | Scatterplot matrix of intraoctahedral distortions (Δd and σ^2) and interoctahedral tilting distortion ($\Delta\beta$), corresponding to X-ray single-crystal structures of > 70 MHPs with centrosymmetric global space groups. Black, red, and green data points denote, respectively, lead iodide, lead bromide, and lead chloride MHPs. The dashed rectangle encompasses MHPs with a large $\Delta\beta$ (> 10º). See **Supplementary Table 1** for the list of MHPs, the corresponding values of distortions, and space groups.

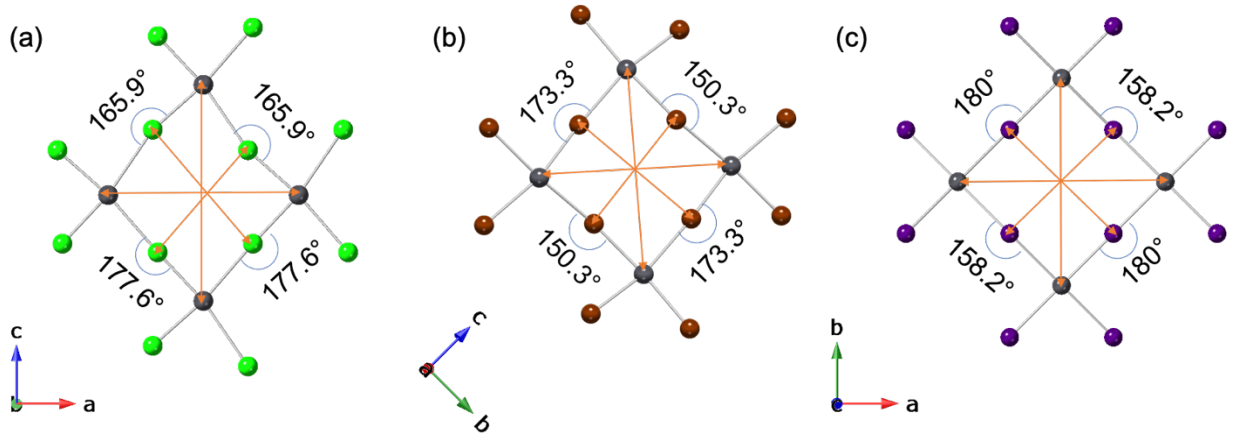
Supplementary Table 1 | Survey of inter- and intra-octahedral distortions in known 2D ⟨100⟩-oriented $[PbX_4]^{2-}$ based perovskites with centrosymmetric global space groups. Crystal structure data were obtained at ambient temperatures unless otherwise mentioned in parentheses.

Organic spacer cation	X	Space group	Intraoctahderal distortions[a]		Interoctahedral distortions		Ref.
			Δd ($\times 10^{-5}$)	σ^2 $(°)^2$	β, β' (°)	$\Delta\beta$ (°)	
2-naphthylmethylammonium (NMA)	Cl	*Pbam*	0.12	0.03	148.02	0	5
2-fluoroethylammonium (173K) [b]	Cl	*Pnma*	360	36.94	177.60 165.90	11.70	6
cyclopropylammonium (173K)	Cl	$P2_1/c$	0.55	6.73	146.71	0	7
cyclobutylammonium (173K)	Cl	$P2_1/c$	4.35	11.02	148.23	0	7
cyclopentylammonium (173K)	Cl	*Cmca*	36.70	11.66	154.81	0	7
3-(2-ammonioethyl)anilinium (AEA)	Br	$P2_1/c$	8.52	20.72	144.33 151.12	6.79	3
1, 4-butanediammonium (BDA)	Br	*P-1*	4.81	7.27	148.41 149.79	1.38	3
histammonium (HIS) (100K) [c]	Br	$P2_1/c$	2.92	37.01	173.26 150.32	22.94	3
2-methyl-1,5-pentanediammonium (MPenDA)	Br	$C2/c$	0.04	2.58	147.40	0	3
1,8-diaminooctane (OdA)	Br	$P2_1/c$	0.07	3.60	148.21	0	3
n-butylammonium (BA)	Br	*Pbca*	0.67	9.42	154.82	0	3
phenethylammonium (PEA)	Br	*P-1*	99.90	16.46	150.82 152.11	1.29	8
3-(dimethylamino)-1-propylamine (DMAPA) [c]	Br	$P2_1/c$	11	40.58	170.90 156.78	14.12	9
1-(1-naphthyl)ethylammonium (Rac-NEA)	Br	$P2_1/c$	31	19.80	152.53	0	10
N^1-methylpropane-1,3-diammonium (NMPDA) (100K)	Br	$P2_1/c$	4.92	3.03	164.27 162.64	1.63	11
cyclopropylammonium (173K)	Br	$P2_1/c$	0.16	4.24	146.29	0	7

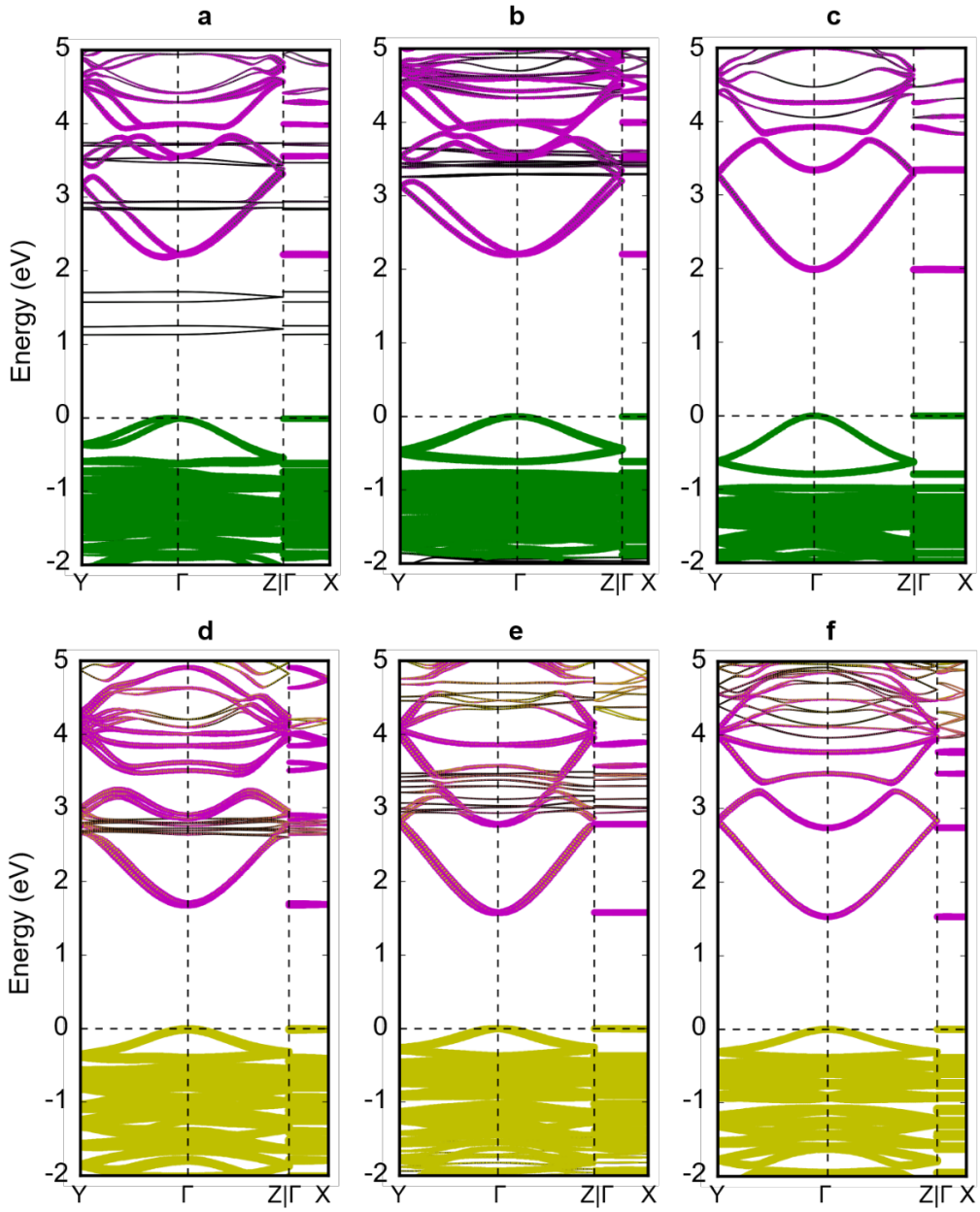
cyclobutylammonium (173K)	Br	$P2_1/c$	2.10	8.46	148.60	0	7
cyclopentylammonium (173K)	Br	$P2_1/c$	9.20	26.27	153.60	0	7
3,4-dichlorobutan-1-ammonium (BEA-Cl_2) (100K)	Br	*P*-1	1.26	7.81	145.41 145.88	0.47	12
3,4-dibromobutan-1-ammonium (BEA-Br_2) (100K)	Br	*P*-1	3.87	6.21	149.12 147.80	1.32	12
but-3-en-1-ammonium (BEA)	Br	$P2_1/c$	0.29	3.20	151.01	0	13
but-3-yn-1-ammonium (BYA) (100K)	Br	$P2_1/c$	1.30	8.17	145.91	0	13
(E)-3,4-diiodobut-3-en-1-ammonium (BYA-I_2) (100K)	Br	*P*-1	0.28	3.16	146.44 146.04	0.40	12
N,N-dimethylphenylene-p-diammonium (DPDA) (100K) [c]	Br	$P2_1/n$	217	71.73	176.88 165.92	10.96	14
benzylammonium (BzA)	I	*Pbca*	1.28	12.08	158.43	0	15
4-iodobenzylammonium (4-I-BzA) (100K)	I	$P2_1/c$	3.07	10.81	156.11	0	16
4-fluorobenzylammonium (4-F-BzA) (106K)	I	$P2_1/n$	24.70	12.75	158 158.69	0.69	16
2-(1-cyclohexenyl)ethylammonium (173K)	I	*P*-1	94.4	14.62	148.72 150.92	2.20	17
1,4-bis-(ammoniomethyl)cyclohexane (173K)	I	$P2_1/c$	3.42	7.45	153.14	0	18
2-ethanolammonium (173K)	I	$P2_1/c$	4.77	2.37	159.10	0	19
3-propanolammonium (173K)	I	$P2_1/c$	33	6.57	163.68	0	19
2-bromoethylammonium (173K)	I	*Pnma*	51	8.94	177.23 175.70	1.53	19
2-iodoethylammonium (173K)	I	$P2_1/c$	4.16	4.41	147.25	0	19
3-iodopropylammonium (173K)	I	$P2_1/c$	2.59	12.17	148.76	0	19
4-iodobutylammonium (173K)	I	$P2_1/c$	0.36	10.77	147.02	0	19
5-iodopentylammonium (173K)	I	$P2_1/c$	1.64	8.99	154.36	0	19
6-iodohexylammonium (173K)	I	*Pbca*	10	12.43	160.98	0	19
5,5‘-bis(ammoniumethylsulfanyl)-2,2‘-bithiophene (BAEST)	I	*P*-1	4.23	6.85	149.40 151.87	2.47	20

1-methylbutylammonium (1-Me-ba)	I	$P2_1/c$	7.63	11.46	153.90	0	21
1-methylhexylammonium (1-Me-ha)	I	$P2_1/c$	7.87	10.63	153.87	0	21
1-methylpropylammonium (1-Me-pa) [c]	I	$P4_2/ncm$	5.58	2.3	180 158.16	21.84	21
2-ethylhexylammonium (2-Et-ha)	I	$P2_1/c$	1.06	4.67	153.98	0	21
cyclopropylammonium (173K)	I	$P2_1/c$	1.79	1.89	147.16	0	22
cyclobutylammonium (173K)	I	$P2_1/c$	0.52	6.82	147.27	0	22
cyclopentylammonium (173K)	I	$P2_1/c$	4.72	5.61	154.57	0	22
cyclohexylammonium (173K)	I	*Pbca*	11	9.33	154.79	0	22
dodecylammonium (DA)	I	$P2_1/a$	85.20	20.80	150.67	0	23
1,6-diaminohexane (HdA) (200K)	I	$P2_1/c$	3.27	3.30	148.31	0	24
1,8-diaminooctane (OdA) (200K)	I	$P2_1/c$	0.42	7.68	147.45	0	24
benzodiimidazolium (Bdi)	I	$C2/m$	0.02	8.63	180	0	25
naphthalene-O-propylammonium	I	$P2_1/c$	1.49	14.67	146.87	0	26
naphthalene-O-hexylammonium	I	$P2_1/c$	2.65	9.07	146.14 149.06 148.60	2.92	27
MeO-naphthalene-O- ethylammonium	I	*Pbca*	0.06	4.79	155.56	0	27
MeO-naphthalene-O-hexylammonium	I	*P*-1	2.14	6.20	154.46 154.31	0.15	27
perylene-O-ethylammonium	I	$P2_1/c$	0.15	3.47	155.23	0	26
N,N-dimethylphenylene-p-diammonium (DPDA) (100K) [c]	I	$P2_1/n$	159	58.77	176.64 167.06	9.58	14

[a] Average values are reported.
[b] In this MHP, $\Delta\beta = 11.7°$ along one in-plane direction and $\Delta\beta = 0°$ along the other in-plane direction similar to chiral MHPs in Fig. 2f, g in the main text; the isolated inorganic layers are nominally noncentrosymmetric (see **Supplementary Figure 7a**)
[c] These MHPs exhibit $\Delta\beta > 9°$; however, equal β angles are found on opposite sides of the squares formed by Pb atoms in the structure so that an inversion center is retained (see **Supplementary Figures 7b and c**).

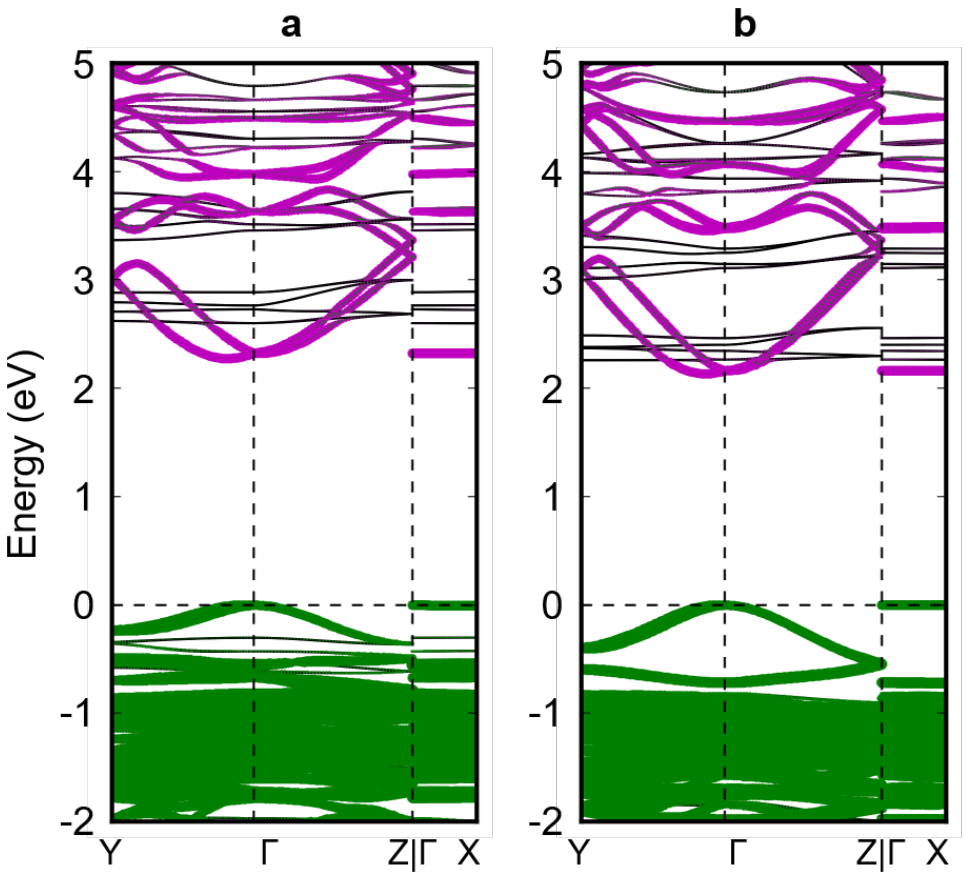


Supplementary Figure 7 | a-c, In-plane views of perovskite layers in **(a)** 2-fluoroethylammonium lead chloride (centrosymmetric, *Pnma*), (**b**) histammonium lead bromide (centrosymmetric, $P2_1/c$) and (**c**) 1-methylpropylammoium lead iodide (centrosymmetric, $P4_2/ncm$). The equatorial Pb-X-Pb bond angles, β, are shown in each panel. The layers shown in **(b)** and **(c)** possess inversion symmetry. The layer shown in **(a)** does not have inversion symmetry; however, there is an inversion center between adjacent inorganic layers in this structure.

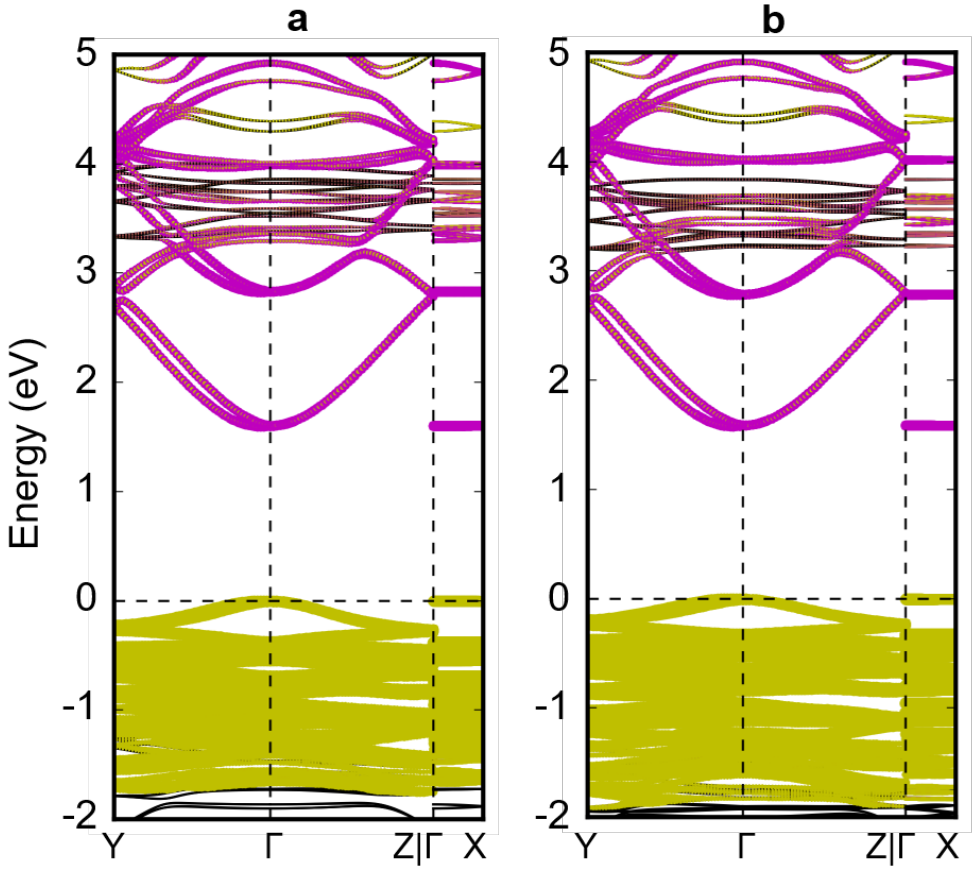


Supplementary Figure 8 | **a-f,** DFT-PBE+SOC electronic band structures of chiral [S-4-NO_2-MBA]$_2$$PbBr_4$·$H_2O$ (**a**), [R-4-Cl-MBA]$_2$$PbBr_4$ (**b**), [S-2-Me-BuA]$_2$$PbBr_4$ (**c**), [S-4-NH_3-MBA] PbI_4 (**d**), [R-4-Cl-MBA]$_2$$PbI_4$ (**e**), and [S-MHA]$_2$$PbI_4$ (**f**) along the k-paths shown in Figure **3b** of the main text. Experimental atomic coordinates were used for band structure calculations. Pb-, Br-, I- and organic-derived electronic states are highlighted in purple, green, yellow, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges (which is known to be captured faithfully already at the DFT-PBE+SOC

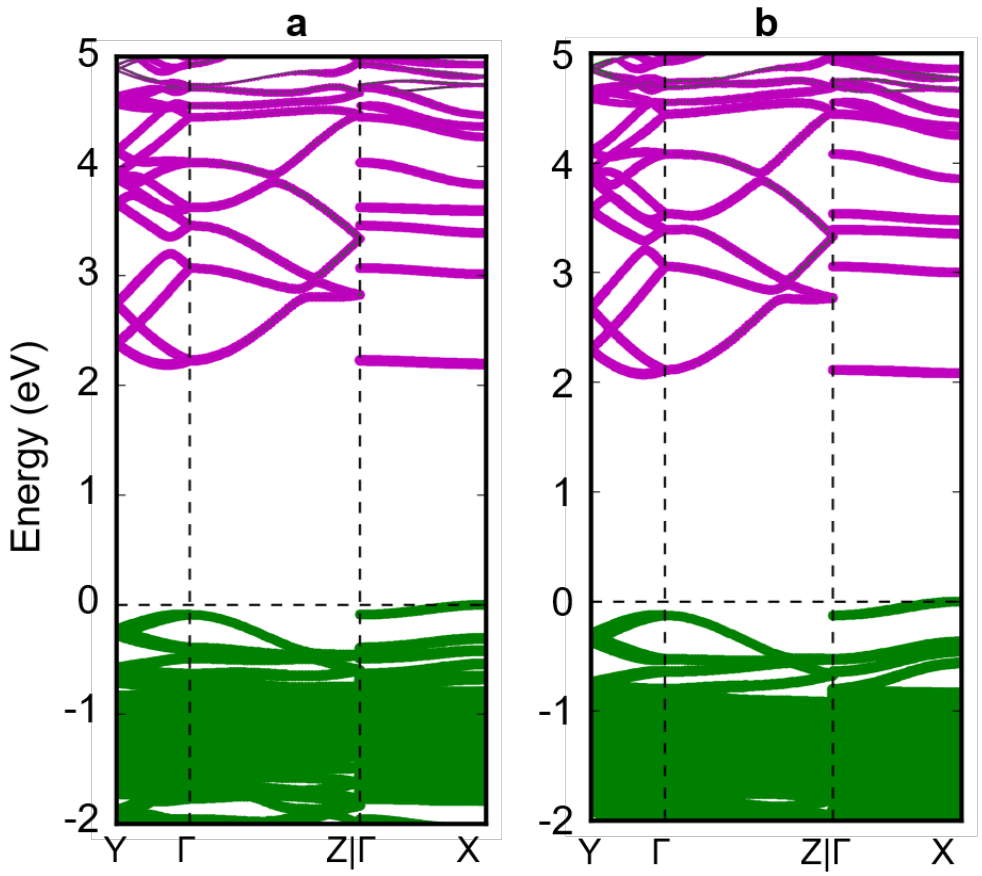
level of theory), not the alignment of energy levels or the exact fundamental gap. In preparing **Supplementary Figures 8-13**, attention was paid to relative energy band structure shifts between experimentally derived and computationally optimized geometries. The observed band structure differences can be traced to seemingly small changes in geometry between experiment and computation. For example, small experimental (XRD) uncertainties in bond lengths associated with light-element aromatic rings can translate into noticeable changes of the molecular electronic structure and also shifts with respect to the inorganic-derived bands. The key point of this paper, which is the correlation between observed Rashba-Dresselhaus spin splitting and inorganic layer geometry, remains unaffected by these differences.



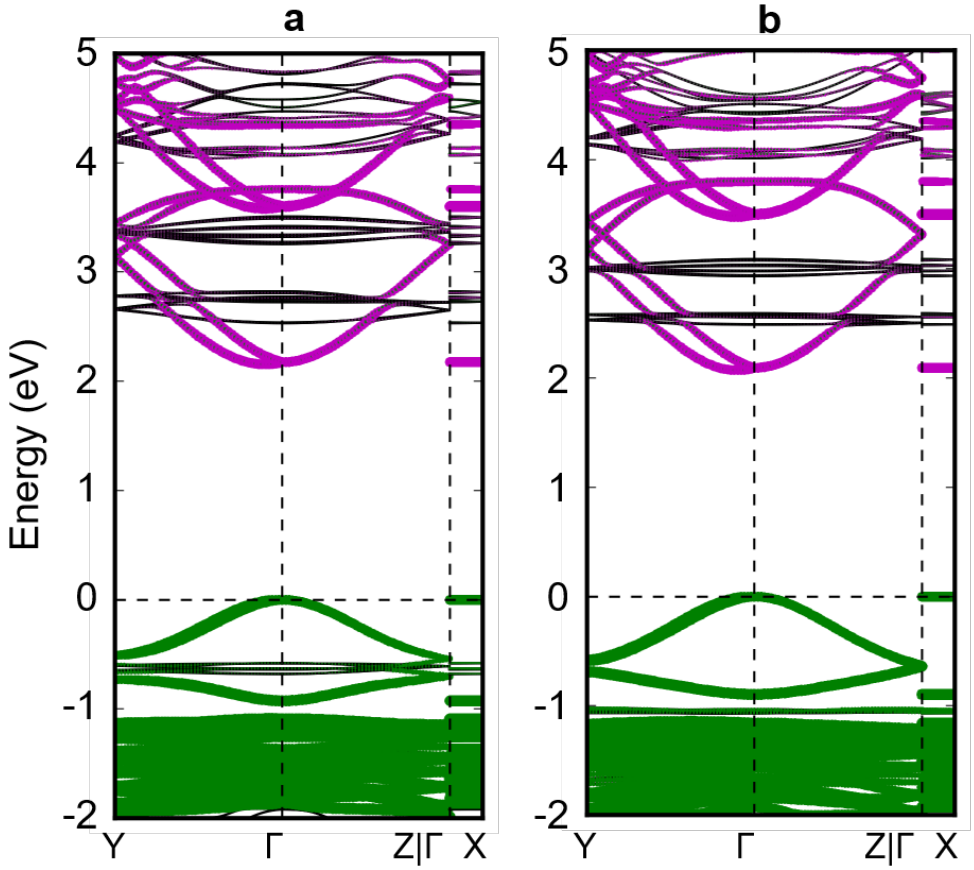
Supplementary Figure 9 | **a,b,** DFT-PBE+SOC electronic band structures of chiral [S-1-1-NEA]$_2$PbBr$_4$ using computationally relaxed (**a**) and experimental (**b**) atomic coordinates. Pb-, Br-, and organic-derived electronic states are highlighted in purple, green, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges (which is known to be captured faithfully already at the DFT-PBE+SOC level of theory), not the alignment of energy levels or the exact fundamental gap. See caption of **Supplementary Figure 8** for further comments regarding observed band structure changes related to experimental and computational geometries.



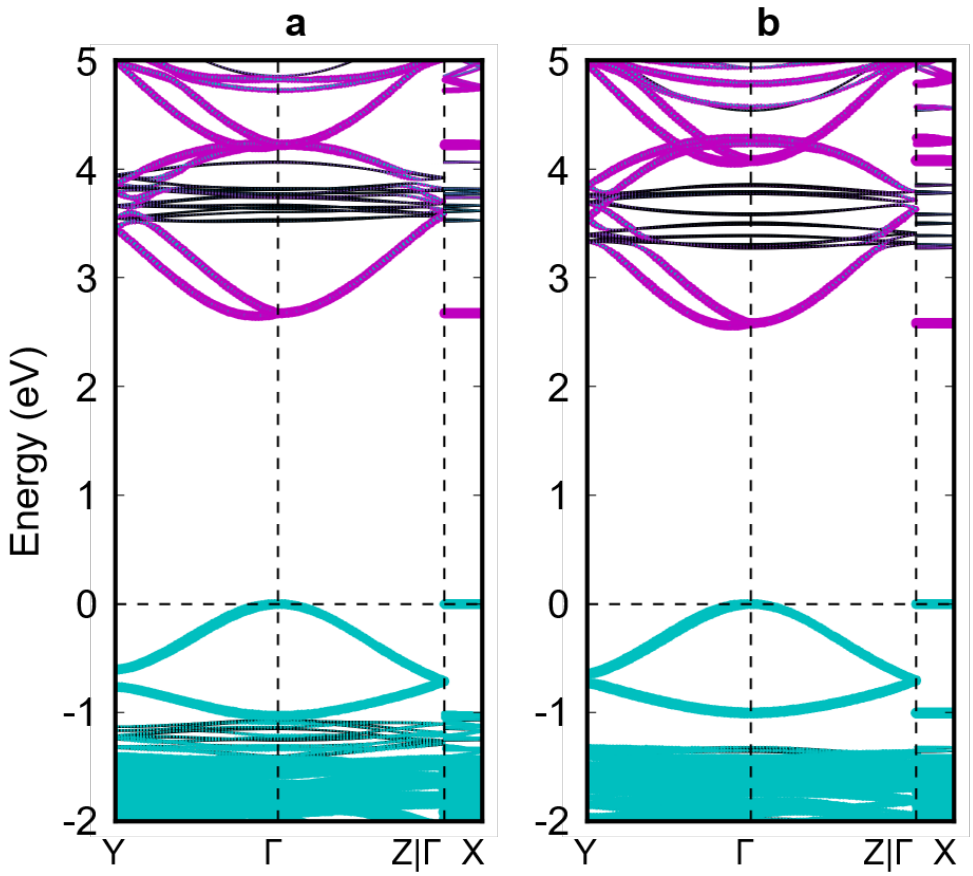
Supplementary Figure 10 | **a,b,** DFT-PBE+SOC electronic band structures of chiral [S-MBA]$_2$PbI$_4$ using computationally relaxed (**a**) and experimental (**b**) atomic coordinates. Pb-, I-, and organic-derived electronic states are highlighted in purple, yellow, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges, not the alignment of energy levels or the exact fundamental gap. See caption of **Supplementary Figure 8** for further comments regarding observed band structure changes related to experimental and computational geometries.



Supplementary Figure 11 | **a,b,** DFT-PBE+SOC electronic band structures of achiral [4AMP]$PbBr_4$ using computationally relaxed (**a**) and experimental (**b**) atomic coordinates. Pb-, Br-, and organic-derived electronic states are highlighted in purple, green, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges, not the alignment of energy levels or the exact fundamental gap. See caption of **Supplementary Figure 8** for further comments regarding observed band structure changes related to experimental and computational geometries.



Supplementary Figure 12 | **a,b,** DFT-PBE+SOC electronic band structures of achiral $[NMA]_2PbBr_4$ using computationally relaxed (**a**) and experimental (**b**) atomic coordinates. Pb-, Br-, and organic-derived electronic states are highlighted in purple, green, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges, not the alignment of energy levels or the exact fundamental gap. See caption of **Supplementary Figure 8** for further comments regarding observed band structure changes related to experimental and computational geometries.



Supplementary Figure 13 | **a,b,** DFT-PBE+SOC electronic band structures of achiral $[PMA]_2PbCl_4$ using computationally relaxed (**a**) and experimental (**b**) atomic coordinates. Pb-, Cl-, and organic-derived electronic states are highlighted in purple, blue, and black colors, respectively. Note that the focus of these plots is the degree of SOC near the inorganic-derived conduction band edges, not the alignment of energy levels or the exact fundamental gap. See caption of **Supplementary Figure 8** for further comments regarding observed band structure changes related to experimental and computational geometries.

Supplementary Table 2 | Metrics of intra- and inter-octahedral distortions and computed spin-splitting parameters of select chiral and achiral 2D MHPs corresponding to Fig. 5 in the main text.

Experimental geometries	σ^2 (^{o}^{2})	Δd (10^{-5})	$\Delta\beta$ (^{o})	$\Delta\beta_{in}$ (^{o})	$\Delta\beta_{out}$ (^{o})	Max. D_{in} (^{o})	Max. D_{out} (^{o})	$\Delta E^{\pm}$ (eV)	k_0 (Å^{-1})	α (eV.Å)
$[R\text{-}4\text{-}Cl\text{-}MBA]_2PbBr_4$	49.64	135.3	14.862	12.186	11.857	34.637	15.461	0.044	0.031	0.709
$[S\text{-}1\text{-}1\text{-}NEA]_2PbBr_4$	40.17	62	13.922	15.602	2.15	36.044	9.9	0.108	0.049	1.102
$[S\text{-}4\text{-}NO_2\text{-}MBA]_2PbBr_4{\cdot}H_2O$	34	129.4	12.127	12.097	0.232	31.226	3.833	0.137	0.049	1.398
$[S\text{-}2\text{-}Me\text{-}BuA]_2PbBr_4$	7.77	0.191	0.237	0.173	1.084	27.093	1.988	0	0	0
$[S\text{-}MBA]_2PbI_4$	20.1	56.44	5.857	5.852	0.29	28.55	0.32	0.033	0.02	0.825
$[S\text{-}4\text{-}NH_3\text{-}MBA]PbI_4$	14.13	38	3.482	4.544	0.129	28.883	20.292	0.009	0.015	0.3
$[R\text{-}4\text{-}Cl\text{-}MBA]_2PbI_4$	12.74	34.74	3	2.952	0.1125	28.195	1.527	0.012	0.014	0.429
$[S\text{-}MHA]_2PbI_4$	10.77	10.48	0.826	0.91	0.01	26.46	3.148	0	0	0
$[NMA]_2PbBr_4$	13.57	15.44	11.67	11.67	0	38.044	0	0.082	0.038	1.079
$[PMA]_2PbCl_4$	21.42	4.22	12.26	12.26	0	37.971	0	0.092	0.047	0.979
$[4AMP]PbBr_4$	40.83	104.9	13.77	14.198	1.929	33.497	4.816	0.14	0.049	1.429

Relaxed geometries	σ^2 (^{o}^{2})	Δd (10^{-5})	$\Delta\beta$ (^{o})	$\Delta\beta_{in}$ (^{o})	$\Delta\beta_{out}$ (^{o})	Max. D_{in} (^{o})	Max. D_{out} (^{o})	$\Delta E^{\pm}$ (eV)	k_0 (Å^{-1})	α (eV.Å)
$[R\text{-}4\text{-}Cl\text{-}MBA]_2PbBr_4$	64	140.5	17.074	13.911	14.066	38.258	17.986	0.062	0.039	0.795
$[S\text{-}1\text{-}1\text{-}NEA]_2PbBr_4$	57.03	65.72	18.648	21.056	4.526	42.632	11.899	0.185	0.063	1.468
$[S\text{-}4\text{-}NO_2\text{-}MBA]_2PbBr_4{\cdot}H_2O$	50.24	77.82	7.624	8.192	1.407	34.897	7.362	0.06	0.035	0.857
$[S\text{-}2\text{-}Me\text{-}BuA]_2PbBr_4$	8.36	11.46	0.353	0.338	1.769	30.879	2.833	0	0	0
$[S\text{-}MBA]_2PbI_4$	20.96	19.37	5.867	5.901	0.04	31.709	1.386	0.03	0.02	0.75
$[S\text{-}4\text{-}NH_3\text{-}MBA]PbI_4$	17.59	16.31	0.329	1.309	2.412	30.085	23.446	0.002	0.007	0.143
$[R\text{-}4\text{-}Cl\text{-}MBA]_2PbI_4$	15.3	187.88	1.221	1.262	0.8875	34.622	3.059	0	0	0
$[S\text{-}MHA]_2PbI_4$	12.91	7.1	0.609	0.704	0.07	29.876	4.157	0.003	0.007	0.214
$[NMA]_2PbBr_4$	11.61	26.24	12.216	12.216	0	41.51	0	0.075	0.038	0.987
$[PMA]_2PbCl_4$	21.32	20.3	14.527	14.527	0	42.68	0	0.11	0.063	0.873
$[4AMP]PbBr_4$	49.81	74.81	15.3	15.64	2.086	37.663	4.792	0.142	0.052	1.365

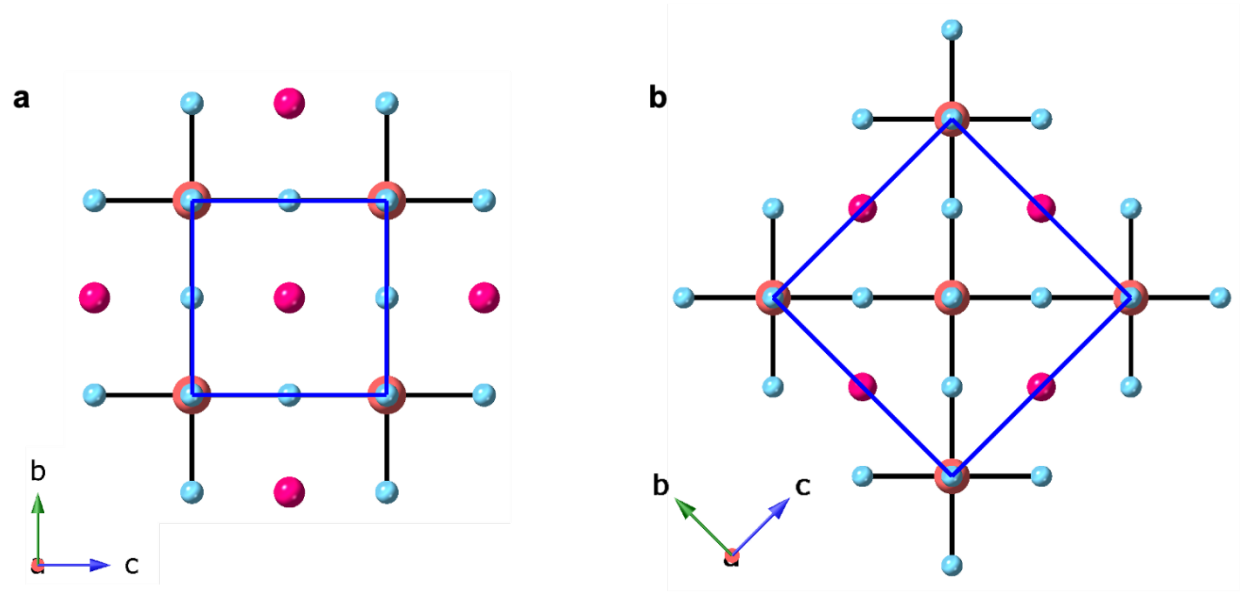
Supplementary Note 2: First-principles simulations of 2D Cs_2PbBr_4 models

For a broader investigation of the structural origin and evolution of spin-splitting in 2D MHPs, we have systematically constructed multiple series of idealized 2D Cs_2PbBr_4 perovskite models starting from an undistorted (1 × 1) perovskite square lattice (Supplementary Figure 14a). In all the models, there is a single $[PbBr_4]^{2-}$ layer spanning the *a-b* plane within the unit cell, and rows of Cs^+ cations lie on either side of the $[PbBr_4]^{2-}$ layer along the *c*-direction. In the undistorted (1 × 1) lattice, Pb-Br bond lengths are fixed to 3 Å (based on the average value found in $CsPbBr_3$), while equatorial Pb-Br-Pb (β) and axial Br-Pb-Br bond angles are 180º. Interoctahedral tilting distortions represent a good starting point for the study, as multiple previous reports emphasize their dominant role in affecting band dispersions and bandgaps for 2D MHPs. Generating a pure interoctahedral tilting distortion while maintaining all Pb-Br bond lengths equal to 3 Å (i.e., $\Delta d = 0$ and $\sigma^2 = 0$) necessitates a $(\sqrt{2} \times \sqrt{2})$-R45° perovskite lattice (using Wood's notation[28]) with respect to the underlying lattice of squares formed by the Pb-sites (Supplementary Figure 14b), which is indeed frequently observed within 2D MHPs. Two individual sets of $(\sqrt{2} \times \sqrt{2})$-R45° models have been constructed (Supplementary Figure 15) by tilting the adjacent $PbBr_6$ octahedra symmetrically (i.e., to the same degree) exclusively along in-plane or out-of-plane directions of the perovskite layer, giving rise to β_{in} or β_{out} values that increase from 140º (largest distortion) to 180º (zero distortion). In each case, symmetric tilting engenders a single β_{in} or β_{out} value within the perovskite lattice.

Based on earlier structural characterization of chiral NEA_2PbBr_4,[10] we have created additional sets of $(\sqrt{2} \times \sqrt{2})$-R45° models by introducing asymmetric tilting for adjacent $PbBr_6$ octahedra exclusively along in-plane or out-of-plane directions (Supplementary Figure 16). In each case, two disparate β angles (140º≤β≤160º) are thus generated within the perovskite lattice, with in-plane or out-of-plane disparity between adjacent bond angles ($\Delta\beta_{in}$ or $\Delta\beta_{out}$) ranging from 5º to 20º in each set of models (Supplementary Figure 16). Whereas the undistorted (1 × 1) and $(\sqrt{2} \times \sqrt{2})$-R45° models (Supplementary Figure 14) both correspond to the P4/mmm space group (a = b ≠ c), asymmetrically distorted $(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 models constructed with $\Delta\beta_{in}$ or $\Delta\beta_{out}$, exhibit a reduced orthorhombic symmetry (a ≠ b ≠ c). The conventional space groups and point groups for the asymmetrically distorted models are listed in Supplementary Table 3. $\Delta\beta_{in}$

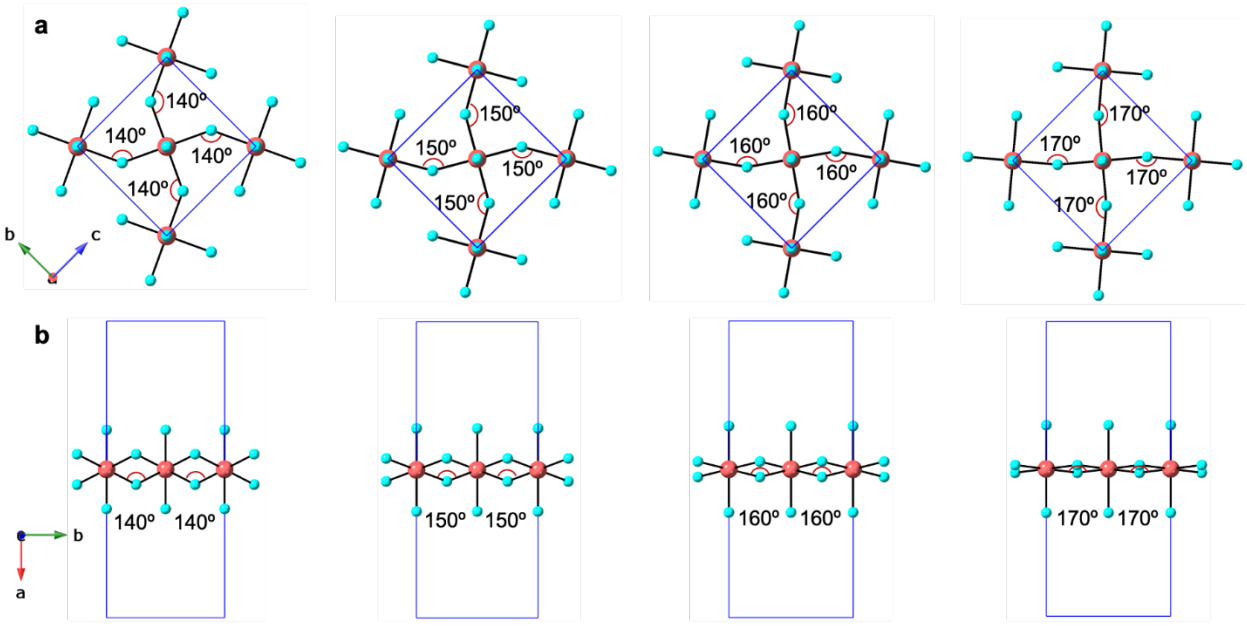
always creates a local formal dipole about Pb sites leading to a noncentrosymmetric polar P$mc2_1$ space group. On the other hand, $\Delta\beta_{out}$ can be introduced with and without a resulting local formal dipole about Pb sites leading to noncentrosymmetric polar P$ma2$ and nonpolar P222_1 space groups, respectively (Supplementary Figure 16b,c). See Supplementary Tables 4-6 for the formal dipole analysis for representative models.

Note that $\Delta\beta_{in}$ or $\Delta\beta_{out}$ are always accompanied by non-zero intraoctahedral distortions, Δd and σ^2, whose values are either similar or much smaller compared with those found in experimental MHPs (see Table 1 in the main text). Importantly, the corresponding values of Δd and σ^2 are similar between the sets of models with pure $\Delta\beta_{in}$ and pure $\Delta\beta_{out}$, thereby allowing us to isolate and compare the dominant effects of $\Delta\beta_{in}$ versus $\Delta\beta_{out}$ on the associated electronic band structures.

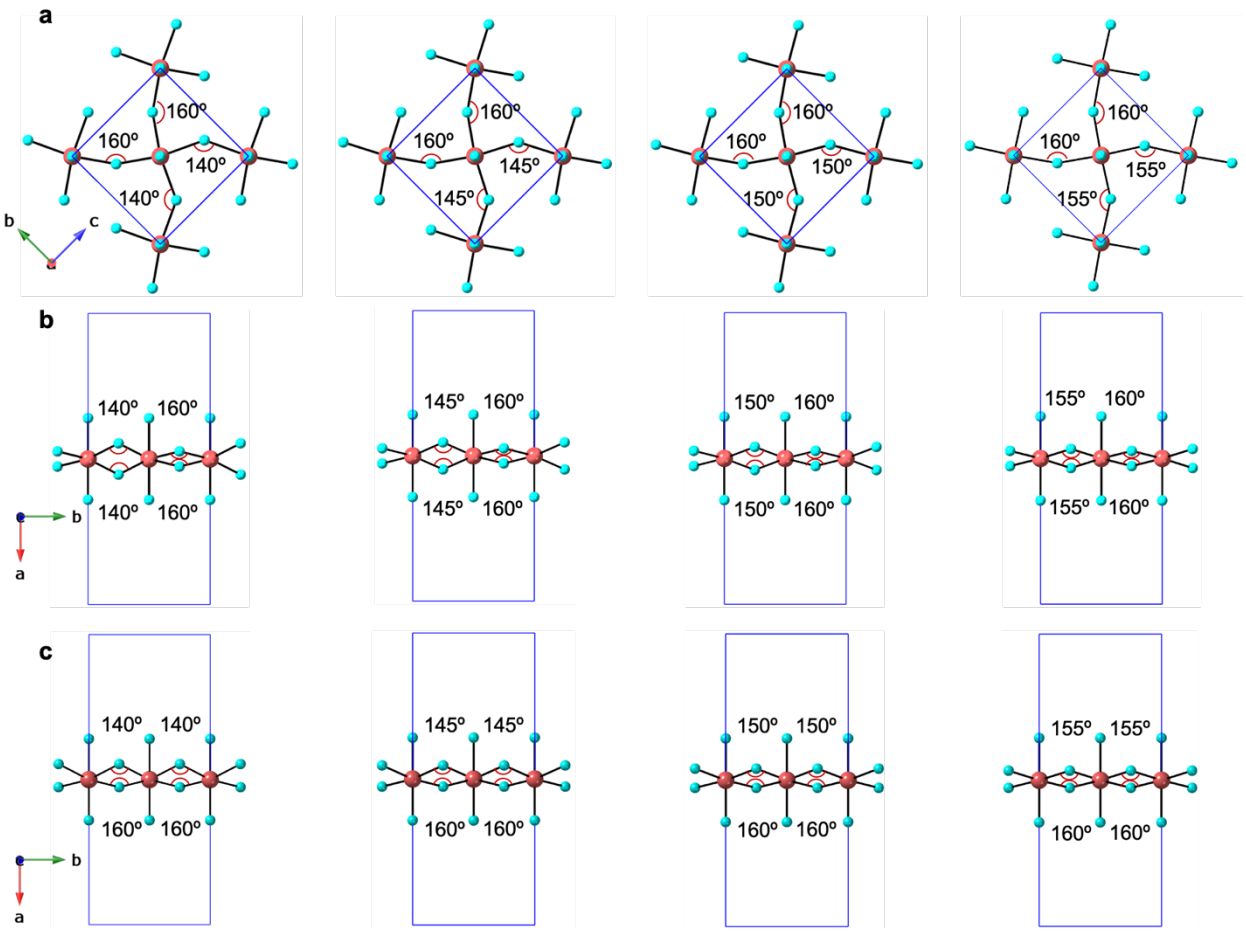


Supplementary Figure 14 | **a**, Undistorted (1 × 1) perovskite square lattice. **b**, Undistorted ($\sqrt{2} \times \sqrt{2}$)-R45° perovskite lattice (using Wood's notation[28,29]). Cs, Pb, and Br atoms are denoted by pink, orange and cyan spheres, respectively.

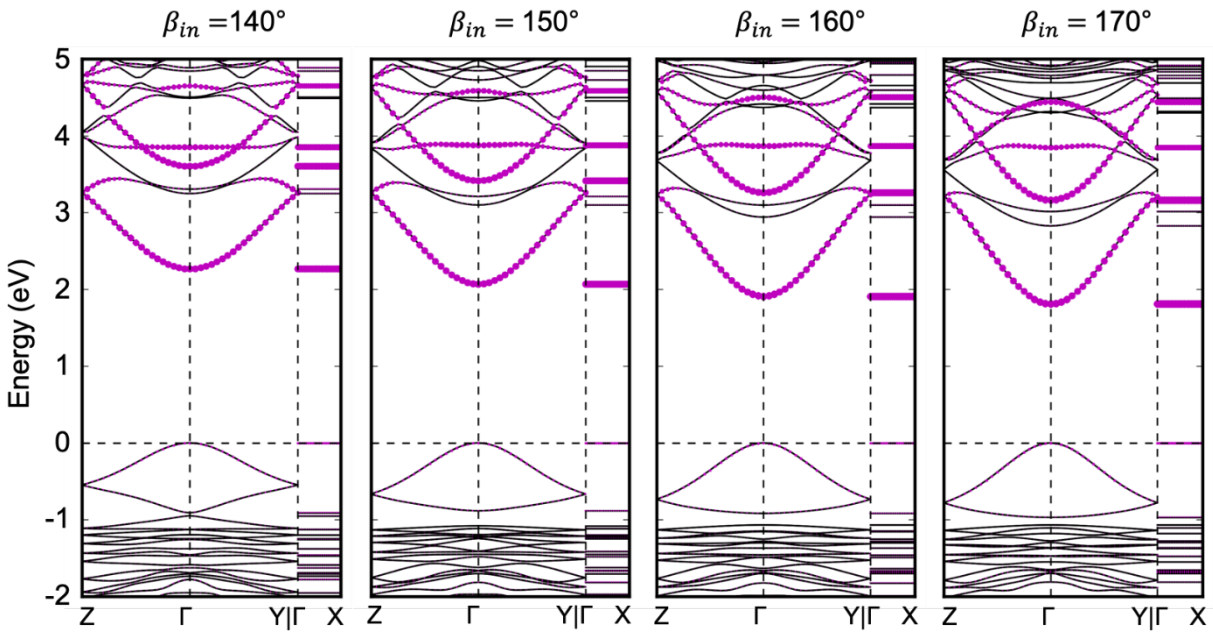
From the calculated DFT-PBE+SOC band structures, the constructed Cs_2PbBr_4 models involving only one β_{in} or β_{out} value in the $[PbBr_4]^{2-}$ layer lack band spin-splitting (Supplementary Figures 17 and 18). With decreasing β_{in} or β_{out}, the energy width of the doubly degenerate lowest conduction band, which is estimated as the energy difference between the Y and Γ points ($E_Y - E_\Gamma$), decreases significantly and the bandgap increases. This is consistent with earlier theoretical and experimental reports on bandgap correlations with β in 2D MHPs (Supplementary Figures 17 and 18).[3,4,30] Interoctahedral distortions leading to $\beta < 180°$ weaken the antibonding interactions between M- and X-derived orbitals at the band edges, leading to reduced band dispersions and increased bandgaps.[30] In contrast, Cs_2PbBr_4 models with disparate β_{in} or β_{out} values (i.e. $\Delta\beta_{in}$ or $\Delta\beta_{out} \neq 0$) in the $[PbBr_4]^{2-}$ layer exhibit spin-splitting mainly in the conduction bands (CBs) along one of the in-plane directions of the $[PbBr_4]^{2-}$ layer, i.e., $\Gamma - Y$ or $\Gamma - Z$ path in the reciprocal space (Supplementary Figures 19 and 20). The energy width of the singly degenerate lowest conduction subband along the $\Gamma - Y(Z)$ path ($E_{Y(Z)} - E_\Gamma$) is very similar for the corresponding models with the same values of pure $\Delta\beta_{in}$ and pure $\Delta\beta_{out}$ and decreases monotonically with increasing $\Delta\beta_{in}$ or $\Delta\beta_{out}$ (Fig. 6 in main text). Interestingly, the characteristic momentum offset ($\mathbf{k_0}$) increases more prominently with $\Delta\beta_{in}$ rather than $\Delta\beta_{out}$ (Fig. 6 in main text). As the CB spin-splitting magnitude ($\Delta E^{\pm}$) relates to both band dispersion and $\mathbf{k_0}$, $\Delta E^{\pm}$ increases steeply with $\Delta\beta_{in}$, but less significantly with $\Delta\beta_{out}$ (Fig. 6 in main text). This is an intrinsic difference between $\Delta\beta_{in}$ and $\Delta\beta_{out}$ and not, for example, related to the presence of formal local dipole moments (see Supplementary Tables 4-6 and Supplementary Figure 20). The above analysis decoupling the effects of $\Delta\beta_{in}$ and $\Delta\beta_{out}$ is noteworthy, as experimental MHPs exhibiting disparate β angles will not necessarily show strong spin-splitting if the disparity is dominantly due to the β_{out} component, whereas a dominant disparity due to the β_{in} component will yield a sizeable spin-splitting.



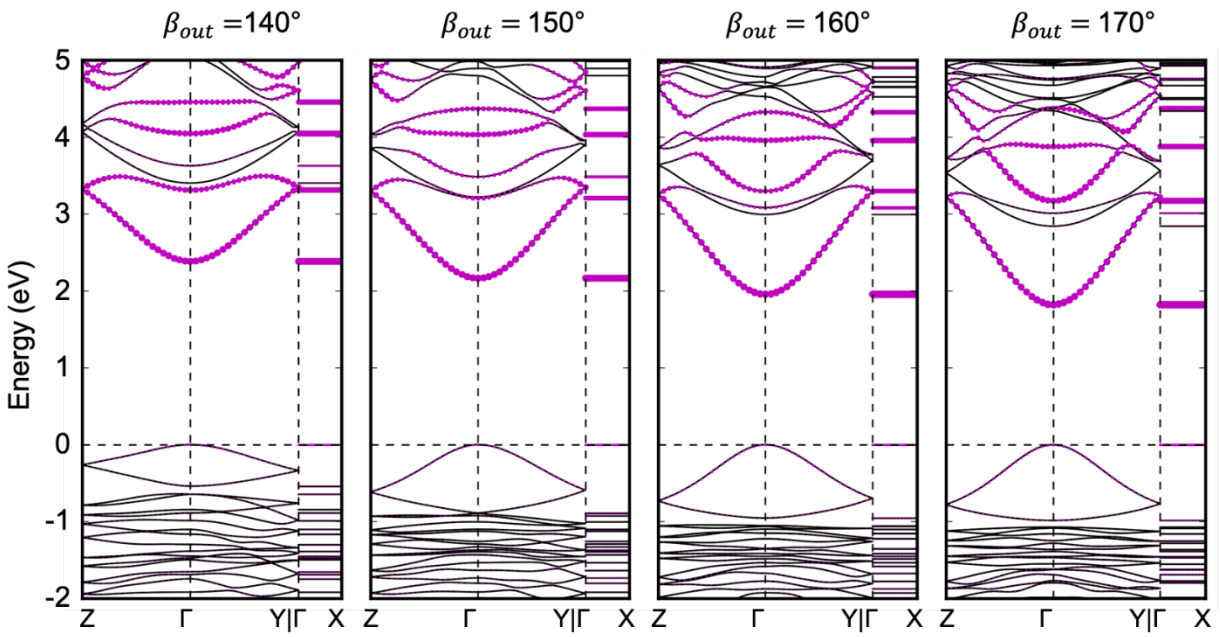
Supplementary Figure 15 | a,b, Series of $(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 models wherein the adjacent $PbBr_6$ octahedra are symmetrically tilted purely in-plane (**a**) and purely out-of-plane (**b**), giving rise to a zero disparity in the adjacent Pb-Br-Pb bond angles (i.e. $\Delta\beta_{in}$ or $\Delta\beta_{out} = 0$) across (**a**) and (**b**). Pb and Br atoms are denoted by orange and cyan spheres, respectively. Cs atoms have been omitted in the drawings for visual clarity but are included in computations based on the models.



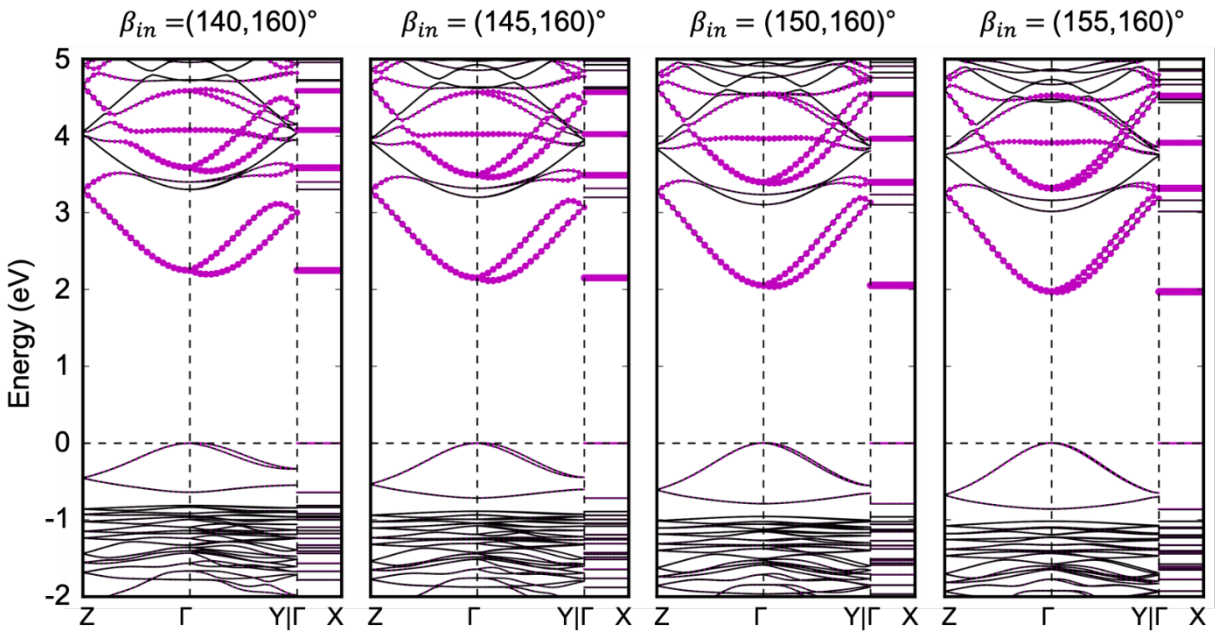
Supplementary Figure 16 | a-c, Series of $(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 models wherein the adjacent $PbBr_6$ octahedra are asymmetrically tilted purely in-plane (**a**) and purely out-of-plane (**b,c**), giving rise to an increasing Pb-Br-Pb bond angle disparity in the adjacent bond angles (i.e. $\Delta\beta_{in}$ or $\Delta\beta_{out}$) across (**a**) and (**b,c**). Note that the models in (**b**) are different from those in (**c**) in that the former do not exhibit a formal dipole on the Pb site whereas the latter do exhibit a formal dipole on the Pb site. For details, refer to **Supplementary Tables 5 and 6**. Pb and Br atoms are denoted by orange and cyan spheres, respectively. Cs atoms are omitted for visual clarity but are included in computations based on the models.



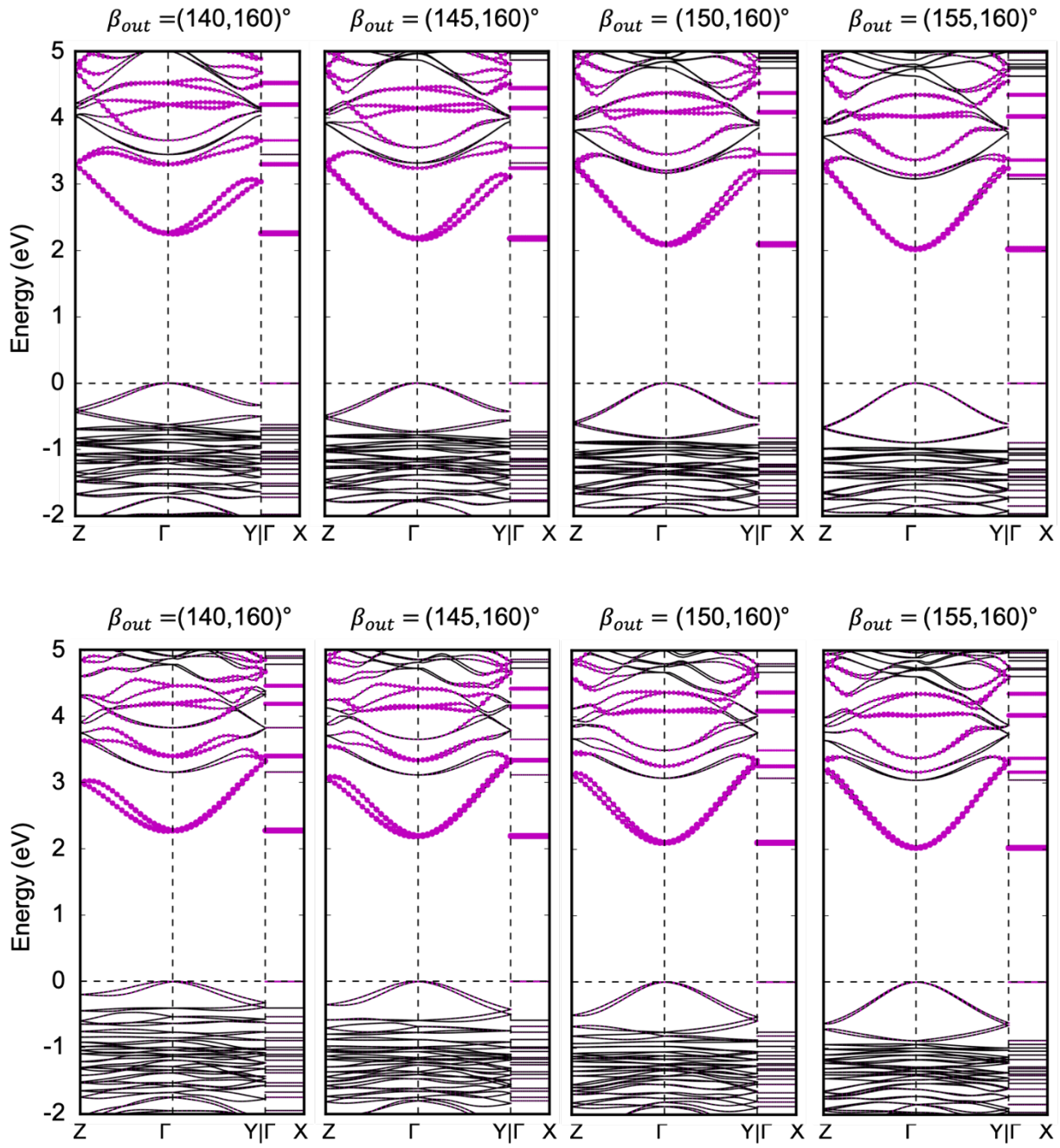
Supplementary Figure 17 | DFT-PBE+SOC band structures for the series of $(\sqrt{2} \times \sqrt{2}) - R45°$ Cs_2PbBr_4 models with purely in-plane symmetrical tilting of adjacent $PbBr_6$ octahedra.



Supplementary Figure 18 | DFT-PBE+SOC band structures for the series of $(\sqrt{2} \times \sqrt{2}) - R45°$ Cs_2PbBr_4 models with purely out-of-plane symmetrical tilting of adjacent $PbBr_6$ octahedra.



Supplementary Figure 19 | DFT-PBE+SOC band structures for the series of $(\sqrt{2} \times \sqrt{2}) - R45°$ Cs_2PbBr_4 models with purely in-plane asymmetrical tilting of adjacent $PbBr_6$ octahedra. Note that the conduction band splitting increases with $\Delta\beta_{in}$.



Supplementary Figure 20 | DFT-PBE+SOC band structures for the series of $(\sqrt{2} \times \sqrt{2}) - R45°$ Cs_2PbBr_4 models with purely out-of-plane asymmetrical tilting of adjacent $PbBr_6$ octahedra. Top and bottom rows correspond to models shown in **Supplementary Figure 16b** and **16c**, respectively. Note that the conduction band splitting increases with $\Delta\beta_{out}$, albeit not as significantly as in the case of $\Delta\beta_{in}$.

Supplementary Table 3 | List of space groups and point groups (as determined by PLATON) for the $(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 models constructed with pure $\Delta\beta_{in}$ (top block) and pure $\Delta\beta_{out}$ with (middle block) and without (bottom block) a resulting local formal dipole. For the qualitative analysis of local formal dipoles in representative models, refer to Supplementary Tables 4-6.

$(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 (β_{in}, β'_{in})	Space group	Point group
(140º, 160º)	P$mc2_1$	C_{2V}
(145º, 160º)	P$mc2_1$	C_{2V}
(150º, 160º)	P$mc2_1$	C_{2V}
(155º, 160º)	P$mc2_1$	C_{2V}

$(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 ($\beta_{out}, \beta'_{out}$)	Space group	Point group
(140º, 160º)	P$ma2$	C_{2V}
(145º, 160º)	P$ma2$	C_{2V}
(150º, 160º)	P$ma2$	C_{2V}
(155º, 160º)	P$ma2$	C_{2V}

$(\sqrt{2} \times \sqrt{2})$-R45° Cs_2PbBr_4 ($\beta_{out}, \beta'_{out}$)	Space group	Point group
(140º, 160º)	$P222_1$	D_2
(145º, 160º)	$P222_1$	D_2
(150º, 160º)	$P222_1$	D_2
(155º, 160º)	$P222_1$	D_2

Supplementary Table 4 | A qualitative analysis of formal local dipole moments in the representative Cs_2PbBr_4 model with $\Delta\beta_{in}$= 20º (see Fig. 6c in the main text). The coordinates of local dipole moment associated with a given Pb site (set as origin) are calculated from the coordinates of the surrounding six Br atoms using the general formula: $\sum q_{Br}\,(\vec{r}_{Br} - \vec{r}_{Pb})$ (here, q_{Br} is taken as -1 e where e is the elementary charge). The unit cell has a C_{2V} point group symmetry with lattice parameters a = 20Å (out-of-plane) and $b = c$ =8.3564Å (in-plane); see Supplementary Note 2 for details. Atomic positions in the table are given as fractional coordinates that must be multiplied by each lattice vector to obtain Cartesian coordinates.

Atom	**Fractional coordinates**			**Fractional coordinates with respect to Pb**		
	fa	*fb*	*fc*	*fa-fa(Pb)*	*fb-fb(Pb)*	*fc-fc(Pb)*
Pb	0.5	0.5	0.5	0	0	0
Br	0.5	0.159	0.341	0	-0.341	-0.159
Br	0.5	0.341	0.841	0	-0.159	0.341
Br	0.5	0.7941	0.7059	0	0.2941	0.2059
Br	0.5	0.7059	0.2059	0	0.2059	-0.2941
Br	0.35	0.5	0.5	-0.15	0	0
Br	0.65	0.5	0.5	0.15	0	0
local dipole about Pb				**0**	**0**	**-0.0938** x **8.3564 eÅ**
Pb	0.5	0	0	0	0	0
Br	0.5	0.159	0.341	0	0.159	0.341
Br	0.5	0.341	-0.159	0	0.341	-0.159
Br	0.5	-0.2059	-0.2941	0	-0.2059	-0.2941
Br	0.5	-0.2941	0.2059	0	-0.2941	0.2059
Br	0.35	0	0	-0.15	0	0
Br	0.65	0	0	0.15	0	0
local dipole about Pb				**0**	**0**	**-0.0938** x **8.3564 eÅ**

Supplementary Table 5 | A qualitative analysis of formal local dipole moments in the representative Cs_2PbBr_4 model with $\Delta\beta_{out}$= 20º (see Fig. 6d in the main text, as well as Supplementary Figure 16b). The coordinates of local dipole moment associated with a given Pb site (set as origin) are calculated from the coordinates of the surrounding six Br atoms using the general formula: $\sum q_{Br}\,(\vec{r}_{Br} - \vec{r}_{Pb})$ (here, q_{Br} is taken as -1 e where e is the elementary charge). The unit cell has D_2 point group symmetry with lattice parameters a = 20 Å (out-of-plane) and $b = c$ =8.3564 Å (in-plane); see Supplementary Note 2 for details. Atomic positions in the table are given as fractional coordinates that must be multiplied by each lattice vector to obtain Cartesian coordinates.

Atom	**Fractional coordinates**			**Fractional coordinates with respect to Pb**		
	fa	*fb*	*fc*	*fa-fa(Pb)*	*fb-fb(Pb)*	*fc-fc(Pb)*
Pb	0.5	0.5	0.5	0	0	0
Br	0.5538	0.25	0.75	0.0538	-0.25	0.25
Br	0.4462	0.25	0.25	-0.0538	-0.25	-0.25
Br	0.474	0.75	0.25	-0.026	0.25	-0.25
Br	0.526	0.75	0.75	0.026	0.25	0.25
Br	0.3597	0.5	0.6272	-0.1403	0	0.1272
Br	0.6403	0.5	0.3728	0.1403	0	-0.1272
local dipole about Pb				**0**	**0**	**0**
Pb	0.5	0	0	0	0	0
Br	0.474	-0.25	0.25	-0.026	-0.25	0.25
Br	0.526	-0.25	-0.25	0.026	-0.25	-0.25
Br	0.5538	0.25	-0.25	0.0538	0.25	-0.25
Br	0.4462	0.25	0.25	-0.0538	0.25	0.25
Br	0.3597	0	-0.1272	-0.1403	0	-0.1272
Br	0.6403	0	0.1272	0.1403	0	0.1272
local dipole about Pb				**0**	**0**	**0**

Supplementary Table 6 | A qualitative analysis of formal local dipole moments in the representative Cs_2PbBr_4 model exhibiting $\Delta\beta_{out}$= 20º as constructed in Supplementary Figure 16c. The local dipole moment associated with a given Pb site (set as the origin) is calculated from the coordinates of the surrounding six Br atoms using the general formula: $\sum q_{Br}\,(\vec{r}_{Br} - \vec{r}_{Pb})$ (q_{Br} is taken as -1 e, where e is the elementary charge). The unit cell has C_{2v} point group symmetry with lattice parameters a = 20Å (out-of-plane) and $b = c$ = 8.35637Å (in plane); see Supplementary Note 2 for details. Atomic positions in the table are given as fractional coordinates that must be multiplied by each lattice vector in order to obtain Cartesian coordinates.

Atom	**Fractional coordinates**			**Fractional coordinates with respect to Pb**		
	fa	*fb*	*fc*	*fa-fa(Pb)*	*fb-fb(Pb)*	*fc-fc(Pb)*
Pb	0.5	0.5	0.5	0	0	0
Br	0.44623	0.25	0.25	-0.05377	-0.25	-0.25
Br	0.52605	0.75	0.75	0.02605	0.25	0.25
Br	0.52605	0.25	0.75	0.02605	-0.25	0.25
Br	0.44623	0.75	0.25000	-0.05377	0.25000	-0.25000
Br	0.64026	0.50	0.37279	0.14026	0	-0.12721
Br	0.35974	0.50	0.62721	-0.14026	0	0.12721
local dipole about Pb				**0.0554x20** eÅ	**0**	**0**
Pb	0.5	0	0	0	0	0
Br	0.44623	0.25	0.25	-0.05377	0.25	0.25
Br	0.52605	-0.25	-0.25	0.02605	-0.25	-0.25
Br	0.52605	0.25	-0.25	0.02605	0.25	-0.25
Br	0.44623	-0.25	0.25	-0.05377	-0.25	0.25
Br	0.64026	0.00000	0.12721	0.14026	0	0.12721
Br	0.35974	0.00000	-0.12721	-0.14026	0	-0.12721
local dipole about Pb				**0.0554x20** eÅ	**0**	**0**

Supplementary Note 3: Analysis of spin-dependent Hamiltonian associated with bulk inversion asymmetry

In this section, we use symmetry theory to analyse the spin-dependent Hamiltonian associated with bulk inversion asymmetry (BIA) in MHPs. The dispersion of the lowest conduction bands and the highest valence bands associated with the metal halide framework can be written as:

$$H(\mathbf{k}) = H_0(\mathbf{k}) + H_{BIA}(\mathbf{k}), \tag{1}$$

where, for example, within an isotropic parabolic band approximation the in-plane dispersion of the conduction and valence bands are given respectively by $H_0(\mathbf{k}) = \pm\frac{\hbar^2\mathbf{k}^2}{2m}$. The angular momentum-dependent Hamiltonian associated with BIA can be written to linear order in wave vector **k** and the angular momentum **J** in general form as:

$$H_{BIA}(\mathbf{k}) = \sum_{i,j} \alpha_{ij} J_i k_j, \tag{2}$$

where α_{ij} are phenomenological spin splitting coefficients specific to a given band, J_i are Pauli operators representing the components of the carrier angular momentum, k_j are the components of the carrier wave vector, and the summation is taken over components i, j running over x, y, z. We define coordinates as in the main text (Fig. 3a), i.e. x, y, z are taken respectively along the crystallographic a, b and c directions, where a is the stacking direction and c coincides with a 2-fold rotation or screw axis.

Neumann's principle requires that the BIA Hamiltonian in equation 2 must be invariant under the operations of the crystal point group. We therefore consider the action of rotations and mirror reflections on the terms in equation 2. The 2D MHPs considered in this study have orthorhombic, monoclinic or lower point symmetries (see Table 1 in the main text). We note that wavevector **k** (a polar vector) and angular momentum **J** (an axial vector) transform in the same manner under rotation. Designating the operator for *n*-fold rotation about an axis u as C_n^u, the polar vector components k_i and axial vector components J_i must transform under 2-fold rotations as,

$$\begin{aligned} C_2^i\, k_i \rightarrow\ k_i; \qquad & C_2^i\, k_j \rightarrow\ -k_j\ (j \neq i); \\ C_2^i\, J_i \rightarrow\ J_i; \qquad & C_2^i\, J_j \rightarrow\ -J_j (j \neq i). \end{aligned} \tag{3}$$

Mirror reflections act in opposite fashion on the polar and axial vectors. We denote the operator for mirror reflection as M_u, where u is the direction perpendicular to the mirror plane. We have,

$$M_i\, k_i \rightarrow\ -\ k_i; \qquad M_i\, k_j \rightarrow\ +k_j\,(j \neq i); \tag{4}$$

$$M_i\ J_i \rightarrow\ +\ J_i; \qquad M_i\ J_j \rightarrow\ -J_j(j \neq i)\,.$$

Using these relations, we can directly establish which terms are permitted in Hamiltonian H_{BIA} for any point group. These results are tabulated for point groups D_2, C_2, and C_{2v}, which are particularly relevant to this study, in Supplementary Table 7.

Supplementary Table 7 | Angular-momentum-dependent BIA Hamiltonian for point groups relevant to 2D MHPs under study (see Table 1 in the main text). The C_n point groups are designated as C_n^u, where u is the axis of the n-fold rotation. BIA Hamiltonians are given for dispersion in 2D within the plane of the metal halide sheets.

Point group	Principal axis	Notes	BIA Hamiltonian, (2D; **k** in y-z plane)
D_2	-	Inversion asymmetry cannot be described as a vector	$\alpha_{yy}\, J_y\, k_y + \alpha_{zz}\, J_z\, k_z$
C_{2v}^z	Z (C_2 axis)	$D_{2\mathrm{h}}$ with inversion asymmetry $\hat{n} = \hat{z}$	$\alpha_{xy}\, J_x\, k_y$
C_2^z	Z (C_2 axis)	C_{2h}^z with inversion asymmetry $\hat{n} = \hat{z}$	$\alpha_{yy}\, J_y\, k_y$ + $\alpha_{zz}\, J_z\, k_z\ +\ \alpha_{xy}\, J_x\, k_y$

Supplementary Note 4: Analysis of spin dependent splitting and spin polarization for [S-4-NO_2-MBA]$_2$$PbBr_4$·$H_2O$

In this section, we analyse the spin-splitting and spin polarization for the specific compound, [S-4-NO_2-MBA]$_2$$PbBr_4$·$H_2O$ (Fig. 4) to illustrate the compatibility of the analysis presented in the main text with global symmetry considerations. This compound has a C_2 point group symmetry and exhibits a dominant out-of-plane spin polarization $\langle\sigma_x\rangle$ component aligned along the stacking a-direction, and relatively much smaller in-plane $\langle\sigma_z\rangle$ and $\langle\sigma_y\rangle$ components for the inorganic-derived frontier conduction band with substantial spin-splitting (see Fig. 4).

The dispersion of the lowest (highest) conduction (valence) bands associated with the metal halide framework can be written according to equation 1 with the angular-momentum-dependent BIA Hamiltonian given by equation 2. Referring to Supplementary Table 7 for the specific case of C_2 point symmetry with the 2-fold axis pointing along the z-direction (denoted as C_2^z), the only symmetry-allowed terms associated with the in-plane wavevector components k_y and k_z are:

$$H_{BIA}(k_y, k_z) = \alpha_{yy} J_y k_y + \alpha_{zz} J_z k_z + \alpha_{xy} J_x k_y \quad (5)$$

This can be represented in terms of an effective Zeeman Hamiltonian involving the effective k-dependent magnetic field,

$$\mathbf{B_{eff}} = \frac{1}{\mu_b}\{\alpha_{xy} k_y \hat{x} + \alpha_{yy} k_y \hat{y} + \alpha_{zz} k_z \hat{z}\}, \quad (6)$$

where μ_b is the Bohr magneton. With this expression, spin-splitting can be conceptually understood as resulting from an effective Zeeman splitting under $\mathbf{B_{eff}}$. We can thus understand the qualitative features of the k-dependent spin polarizations $\langle\sigma_x\rangle$, $\langle\sigma_z\rangle$, and $\langle\sigma_y\rangle$ shown in Fig. 4a as follows. Spin-splitting along the $\Gamma - Y$ path (k_y direction) is associated with the terms $\alpha_{xy} k_y \hat{x}$ and $\alpha_{yy} k_y \hat{y}$, which can only result in $\langle\sigma_x\rangle$ and $\langle\sigma_y\rangle$ components, respectively. Spin-splitting along the $\Gamma - Z$ path (k_z direction) results from the term $\alpha_{zz} k_z \hat{z}$, which can only produce $\langle\sigma_z\rangle$ component as shown in Fig. 4a.

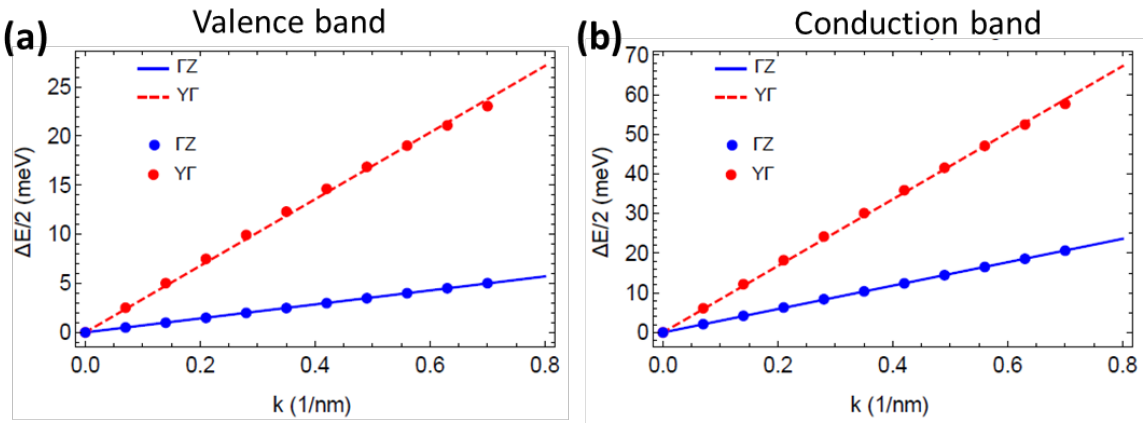
We can quantitatively understand the relative magnitudes of the spin polarizations in the out-of-plane versus in-plane directions of the metal halide framework in Fig. 4a. For the BIA Hamiltonian in equation 5, the eigenstates near Γ are found by diagonalizing the matrix,

$$\tilde{H}_{BIA}(k_y, k_z) = \begin{pmatrix} \alpha_{xy} k_y & \alpha_{yy} k_y - i\alpha_{zz} k_z \\ \alpha_{yy} k_y + i\,\alpha_{zz} k_z & -\alpha_{xy} k_y \end{pmatrix}. \quad (7)$$

The eigenvalues are,

$$E_{BIA}{}^{\pm} = \pm\sqrt{\alpha_{xy}^2 k_y^2 + \alpha_{yy}^2 k_y^2 + \alpha_{zz}^2 k_z^2} \tag{8}$$

Along the $\Gamma - Y$ and $\Gamma - Z$ paths, this leads to spin-dependent splitting $\Delta E^{\pm} = 2\alpha_{eff}\, k$; along the $\Gamma - Y$ path, $k_z = 0$ so that $\alpha_{eff} = \sqrt{\alpha_{xy}^2 + \alpha_{yy}^2}$, while along the $\Gamma - Z$ path, $k_y = 0$ so that $\alpha_{eff} = \alpha_{zz}$. Linear spin-dependent splitting of both the conduction and valence bands is observed in the DFT calculations (Supplementary Figure 21). A linear fit to the splitting yields the effective splitting parameters α_{eff} given in Supplementary Table 8. Note that the individual terms α_{xy} and α_{yy} cannot be determined based on the splitting, ΔE, alone, but can be determined in conjunction with analysis of the spin polarization (see next section). The effective masses in Supplementary Table 8 were determined by quadratic fit to the average of the two spin-split sub-bands whose energies are given by equation 1 in the main text.



Supplementary Figure 21 | **a,b,** Spin-splitting calculated using DFT in [S-4-NO_2-MBA]$_2PbBr_4 \cdot H_2O$. Linear-in-k splitting $\Delta E/2 = (E^+ - E^-)/2$ along different paths near the Γ-point calculated in DFT for the inorganic-derived uppermost valence bands, (**a**), and the lowest conduction bands, (**b**). The slopes are listed in Supplementary Table 8.

Diagonalization of the matrix in equation 7 yields Bloch function eigenvectors, ψ_+, ψ_-, in a basis of the zone-center Bloch functions, $u^{c,v}_{1\,\pm\frac{1}{2}}$, for the given valence (v) or conduction (c) band as,

$$\psi_+^{v,c} = \frac{1}{\sqrt{N}}\left(A u^{c,v}_{1\,\frac{1}{2},\frac{1}{2}} + B\, u^{c,v}_{1\,\frac{1}{2}^-,\frac{1}{2}}\right); \quad \psi_-^{v,c} = \frac{1}{\sqrt{N}}\left(-B^* u^{c,v}_{1\,\frac{1}{2},\frac{1}{2}} + A\, u^{c,v}_{1\,\frac{1}{2}^-,\frac{1}{2}}\right). \tag{9}$$

Here, the terms A and B, and the normalization factor, N, are given by the following expressions, with distinct coefficients $\alpha_{i,j}$ for the conduction and valence bands:

$$A = A(k_y, k_z) = \alpha_{xy} k_y + \sqrt{\alpha_{xy}^2 k_y^2 + \alpha_{yy}^2 k_y^2 + \alpha_{zz}^2 k_z^2} \tag{10}$$

$$B = B(k_y, k_z) = (\alpha_{yy} k_y + i\, \alpha_{zz} k_z) \tag{11}$$

$$N = N(k_y, k_z) = |A(k_y, k_z)|^2 + |B(k_y, k_z)|^2 \tag{12}$$

With these expressions, we calculate the spin polarization along a given direction i as a function of the in-plane wavevector components for the valence or conduction bands as follows:

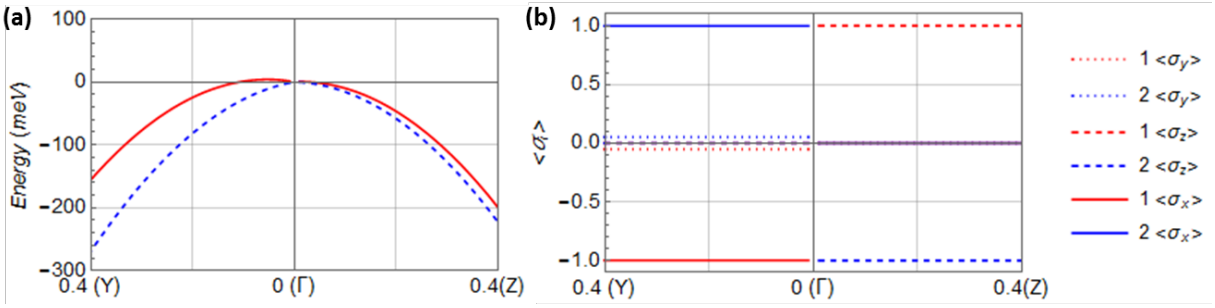
$$\langle \sigma_i \rangle_+^{v,c} = \frac{\langle \psi_+^{v,c} | \sigma_i | \psi_+^{v,c} \rangle}{\langle \psi_+^{v,c} | \psi_+^{v,c} \rangle}; \quad \langle \sigma_i \rangle_-^{v,c} = \frac{\langle \psi_-^{v,c} | \sigma_i | \psi_-^{v,c} \rangle}{\langle \psi_-^{v,c} | \psi_-^{v,c} \rangle}. \tag{13}$$

To analyse the magnitude of the spin polarization, the spin-dependent Bloch functions, $u_{\frac{1}{2},\pm\frac{1}{2}}^{c,v}$, must be specified for the conduction and valence bands.

Supplementary Table 8 | Valence and conduction band parameters near the Γ point for [S-4-NO_2-MBA]$_2PbBr_4 \cdot H_2O$. The effective spin-splitting coefficients α_{eff} were determined by linear fit to the k-dependent splitting $\Delta E = E^+ - E^-$ near Γ calculated using DFT (see Fig. 4 and Supplementary Figure 21) while the effective masses were obtained from a quadratic fit to the average $\bar{E} = (E_1 + E_2)/2$ near Γ. For each band and direction in k-space, the "Rashba energy" $E_R = \frac{{\alpha_{eff}}^2 m}{2\hbar^2}$ and the magnitude of "Rashba wave vector" $k_0 = \frac{m\alpha}{\hbar^2}$ are given. The parameter $\Delta E = 4E_R$ represents the splitting at k_0. Along the $Y - \Gamma$ path, $k_z = 0$ so that $\alpha_{eff} = \sqrt{\alpha_{xy}^2 + \alpha_{yy}^2}$, while along the $\Gamma - Z$ path, $k_y = 0$ so that $\alpha_{eff} = \alpha_{zz}$ (see equation 8).

Band/Direction	Effective mass	α_{eff} (eV.Å)	k_0 (1/nm)	E_R (meV)	$\Delta E = 4E_R$ (meV)
Valence band/ $\Gamma - Z$	0.392	α_{zz} =0.07	0.03	0.13	0.5
Valence band/ $Y - \Gamma$	0.497	$\sqrt{\alpha_{xy}^2 + \alpha_{yy}^2}$ =0.34	0.22	3.8	15
Conduction band/ $\Gamma - Z$	0.282	α_{zz} =0.292	0.11	1.6	6.5
Conduction band/ $Y - \Gamma$	0.312	$\sqrt{\alpha_{xy}^2 + \alpha_{yy}^2}$ =0.846	0.34	14.4	57.7

A) Spin polarization in the valence bands



Supplementary Figure 22 | a,b, Spin-splitting and spin polarization for the uppermost valence band in [S-4-NO_2-MBA]$_2PbBr_4 \cdot H_2O$ calculated using K.P theory. **a**, Energy versus wavevector along the in-plane $\Gamma - Y$ and $\Gamma - Z$ directions using the average in-plane effective mass from Supplementary Table 8. **b**, Spin polarization components $\langle \sigma_i \rangle$ for $i = x,y,z$. The labels 1 and 2 in the legend denote the upper (red line) and lower (blue line) valence sub-bands, respectively. The values of the individual spin-splitting coefficients were chosen to approximate the spin polarizations calculated in DFT, i.e. $\alpha_{xy} = -0.36$ eV.Å; $\alpha_{zz} = +0.07$ eV.Å; and $\alpha_{yy} = -0.01$ eV.Å, which is consistent with the α_{eff} values given in Supplementary Table 8.

For the MHPs of interest, the valence band Bloch functions near the Γ point can be represented in K.P theory as 2-fold degenerate $J = 1/2$ states with S orbital symmetry with respect to the transformation properties under the operations of the point group:[31,32]

$$u^{v}_{\frac{1}{2}'\frac{1}{2}} = S\uparrow, \quad u^{v}_{\frac{1}{2}',-\frac{1}{2}} = S\downarrow. \tag{14}$$

In this expression, the symbol S denotes an orbital function that is invariant under the operations of the point group while ↑ (↓) represent spin up (spin down) spin states with the quantization axis taken as the stacking direction $\hat{x}$. Using the Bloch functions in equation 9 and evaluating the spin polarization with equation 13, we find that the x, y, z components of the spin polarization in the valence band are proportional to the relevant components of the effective magnetic field:

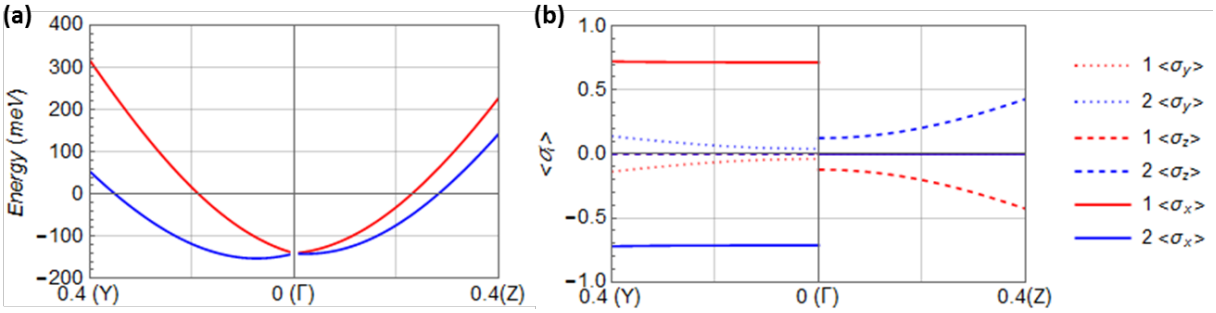
$$\langle \sigma_x \rangle^{v}_{\pm} = \pm \alpha_{xy} k_y \frac{2\,A(k_y,k_z)}{N(k_y,k_z)}; \tag{15}$$

$$\langle \sigma_y \rangle^{v}_{\pm} = \pm \alpha_{yy} k_y \frac{2\,A(k_y,k_z)}{N(k_y,k_z)}; \tag{16}$$

$$\langle \sigma_z \rangle_{\pm}^{v} = \pm \alpha_{zz} k_z \frac{2\,A(k_y, k_z)}{N(k_y, k_z)}. \tag{17}$$

With these expressions, we can understand why the dominant spin polarization along the $\Gamma - Y$ path has a magnitude near unity (see Fig. 4a). As described in the main text, for this direction, the dominant spin-splitting term is $\alpha_{xy} k_y$; in the limit that α_{yy} is negligible, $\langle \sigma_x \rangle_{\pm} \to \pm 1$. Along the $\Gamma - Z$ path, $k_y = 0$ leading to $\langle \sigma_z \rangle_{\pm} \to \pm 1$ (see Fig. 4a). In Supplementary Figure 22a, we show the spin-dependent valence band dispersion of [S-4-NO_2-MBA]$_2PbBr_4 \cdot H_2O$ calculated in a parabolic band approximation using the parameters in Supplementary Table 8. The corresponding spin polarization components are calculated using equations 15-17 (Supplementary Figure 22b), with specific spin splitting parameters chosen to match the results from DFT calculations in Fig. 4a, compatible with the effective parameters in Supplementary Table 8.

B) Spin polarization in the conduction bands



Supplementary Figure 23 | a,b, Spin-splitting and spin-polarization of the inorganic-derived lowest conduction band in [S-4-NO_2-MBA]$_2PbBr_4 \cdot H_2O$ calculated using K.P theory. **a,** Conduction band dispersion (near Γ) along the $\Gamma - Y$ and $\Gamma - Z$. **b,** Spin polarization components $\langle \sigma_i \rangle$ for i = *x,y,z*. The labels 1 and 2 in the legend denote the upper (red line) and lower (blue line) conduction sub-bands, respectively. The values of the individual spin-splitting coefficients were chosen to match the DFT-calculated spin polarizations near Γ, i.e., $\alpha_{xy} = -0.86$ eV-Å; $\alpha_{yy} = \alpha_{zz} = 0.29$ eV-Å. The use crystal field parameter $\sin\theta = 0.35$. Effective mass parameters are $m = 1/\gamma_1 = 0.30$; $\gamma_2 = 0.84$.

For the lowest conduction bands associated with the metal halide framework, we can perform calculations similar to those described in the last section for the valence bands. In this case, the

calculation is complicated by the fact that the Bloch functions at the Γ point have an odd parity corresponding to an overall P orbital symmetry. In 3D cubic perovskites, the band edge Bloch functions are represented by the 2-fold degenerate total angular momentum $J = 1/2$ states with P orbital symmetry, corresponding to orbital angular momentum $l = 1$:[32]

$$u^c_{\frac{1}{2},\frac{1}{2}} = \frac{-1}{\sqrt{3}}\{X\uparrow + (Y + i\,Z)\downarrow\}; \quad u^c_{\frac{1}{2},-\frac{1}{2}} = \frac{1}{\sqrt{3}}\{-(Y - i\,Z)\uparrow + X\downarrow\}. \tag{18}$$

Here, the quantization axis is taken along the stacking (x) direction as before, and the symbols X, Y, Z denote orbital functions that transform like *x, y, z* under rotations. For 2D MHPs however, the anisotropy between the stacking direction and the in-plane directions results in mixing of the $J = 1/2$ and $J = 3/2$ states.[33,34] Neglecting anisotropy in-plane, the result is that the Bloch functions at the Γ point are modified but can be represented as eigenstates of J_x: [33,34]

$$u^c_{1/2} = -\sin\theta\, X\uparrow - \cos\theta\,\frac{Y + iZ}{\sqrt{2}}\downarrow$$
$$u^c_{-1/2} = -\cos\theta\,\frac{Y - i\,Z}{\sqrt{2}}\uparrow + \sin\theta\, X\downarrow. \tag{19}$$

In these expressions, the phase angle θ is given by: [33,34]

$$\tan 2\theta = \frac{2\sqrt{2}\,\Delta_{SO}}{\Delta_{SO} - 3\delta}, \qquad \theta \leq \frac{\pi}{2}. \tag{20}$$

Here, Δ_{SO} is the spin-orbit split-off parameter separating the $J = 1/2$ and $J = 3/2$ conduction band states at Γ while δ is the crystal field reflecting the anisotropy between the stacking direction, x, and the $y - z$ plane. Using these expressions, we find that components of the spin polarization close to the Γ point are proportional to the corresponding components of the effective magnetic field as in the case of valence bands, but with the addition of a "g-factor", $\gamma_i(\theta)$, for each component, i:

$$\langle\sigma_x\rangle_{\pm} = \pm\alpha_{xy}k_y\,\frac{2\,A(k_y,k_z)}{N(k_y,k_z)}\,\gamma_x(\theta); \tag{21}$$

$$\langle\sigma_y\rangle_{\pm} = \pm\alpha_{yy}k_y\,\frac{2\,A(k_y,k_z)}{N(k_y,k_z)}\,\gamma_y(\theta); \tag{22}$$

$$\langle\sigma_z\rangle_{\pm} = \pm\alpha_{zz}k_z\,\frac{2\,A(k_y,k_z)}{N(k_y,k_z)}\,\gamma_z(\theta). \tag{23}$$

In these expressions, the new terms $\gamma_i(\theta)$ are given at the Γ point by,

$$\gamma_x(\theta) = -\cos 2\theta; \qquad \gamma_y(\theta) = \gamma_z(\theta) = -\sin^2\theta \tag{24}$$

The corresponding terms do not appear in equations 15-17 for the valence bands, for which the γ_i-factors are isotropic and equal to +1. The negative sign here is a consequence of the fact that, for the conduction band $P_{1/2}$ states, the spin and the angular momentum are anti-parallel. In fact, for cubic symmetry, all conduction band terms γ_i are equal with the values $\gamma_x = \gamma_y = \gamma_z = -1/3$. In 2D MHPs, the $\gamma_i(\theta)$ factors are highly anisotropic, being dependent on the crystal-field-dependent phase angle θ. For example, with a negative crystal field corresponding to $\sin\theta = 0.35$, $\gamma_y = \gamma_z = -0.12$, while $\gamma_x = -0.76$. The large asymmetry can be understood by examining the conduction band Bloch functions in the limit of large negative crystal field splitting $|\delta| \gg |\Delta_{so}|$. In this limit, $\theta \to 0$, leading to,

$$u^c_{\frac{1}{2}} \to -\frac{(Y + i\,Z)}{\sqrt{2}}\downarrow; \quad u^c_{-\frac{1}{2}} \to -\frac{(Y - i\,Z)}{\sqrt{2}}\uparrow \quad (\delta \gg \Delta_{so}). \tag{25}$$

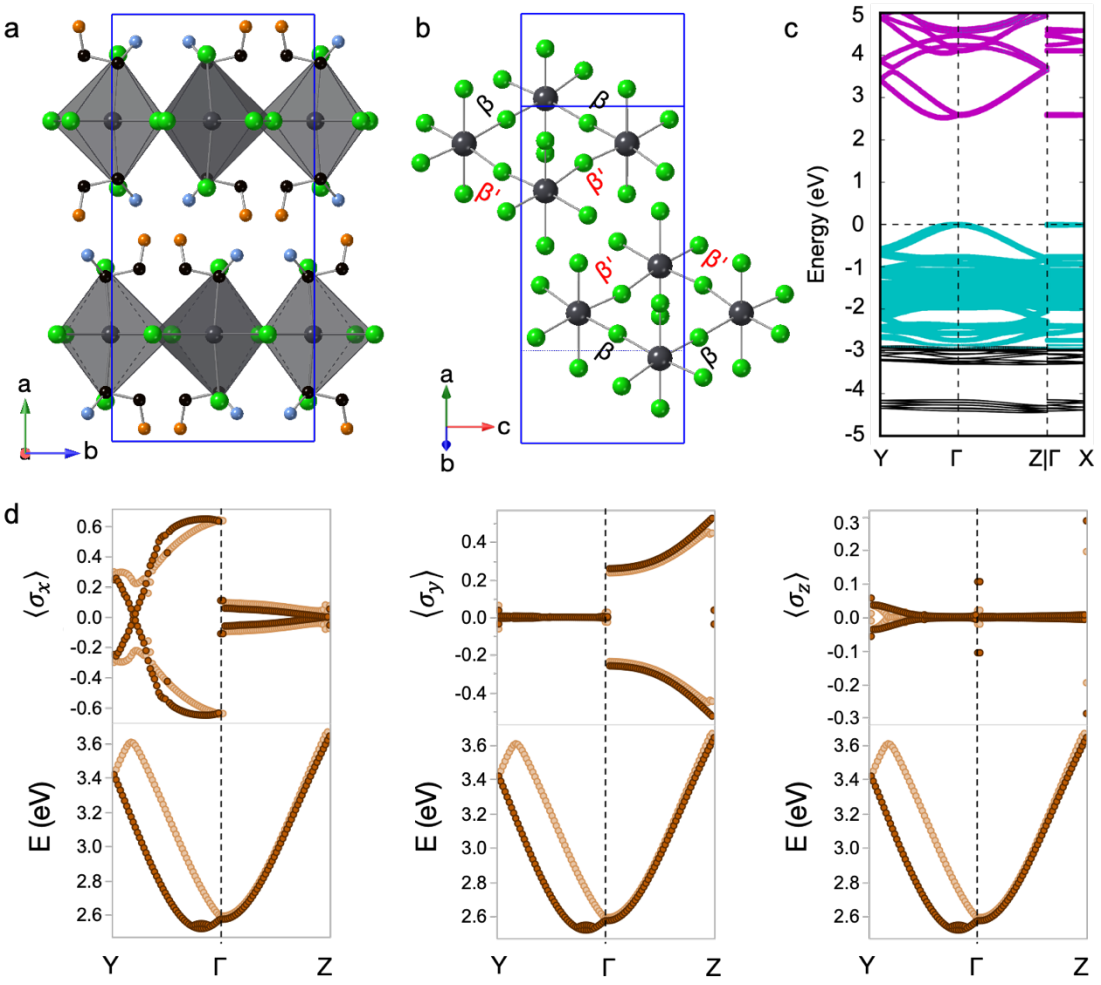
The corresponding γ-factors in this limit are $\gamma_x = -1$ and $\gamma_y = \gamma_z = 0$.

Away from the Γ point, the γ_i exhibit k-dependence which can be modelled within a 6-band K.P framework using an analogue of the Luttinger Hamiltonian[35] adapted for 2D MHPs and which will be described in detail in a later publication. In Supplementary Figure 23a, we show the spin-splitting of the lowest inorganic-derived conduction band in $[S\text{-}4\text{-}NO_2\text{-}MBA]_2PbBr_4{\cdot}H_2O$ as calculated using a 6-band K.P model using parameters compatible with the frontier band effective masses and the effective spin splitting coefficients determined by fitting to the DFT band structure near the Γ point (Supplementary Table 8). The crystal field is adjusted to yield $\sin\theta = 0.35$ in order to match the DFT-calculated spin polarization near Γ in the *x*-direction. For comparison, the crystal field parameter in other 2D lead bromide MHPs has been measured in the range $\sin\theta = 0.2 - 0.32$.[34,36] In Supplementary Figure 23b**,** the spin polarization components are shown along the $\Gamma - Y$ and $\Gamma - Z$ lines. These plots are in qualitative agreement with the results calculated near Γ using DFT in Fig. 4a. The σ_x spin polarization $\sim \pm 0.7$ in the $\Gamma - Y$ path near Γ is primarily determined by the effect of the crystal field, while the smaller in-plane spin polarization components reflect a combination of the smaller parameters α_{yy} and α_{zz} and smaller effective γ-factors for the in-plane directions.

One feature that is amiss in the model shown in Supplementary Figure 23 is the relative magnitude of the in-plane *y* and *z* spin polarization components at the Γ point. Additionally, away

from the Γ point, the K.P model reflected in Supplementary Figures 23 does not match the behaviour of DFT-calculated in-plane spin polarization along the $\Gamma - Y$ path (see Fig. 4a), which exhibits a sign change of the $\langle \sigma_y \rangle_{\pm}$ polarization away from Γ. These features can be qualitatively captured by extending the model to include anisotropy in the plane of the lead-halide sheets. Analysis of this situation will be published elsewhere.

Supplementary Note 5: Conduction band splitting and spin polarization for $(FC_2H_4NH_3)_2PbCl_4$ with a centrosymmetric P*nma* global space group.



Supplementary Figure 24 | **a**, Schematic crystal structure of $(FC_2H_4NH_3)_2PbCl_4$ that crystallizes in a centrosymmetric P*nma* global space group. The inversion center is between the two inorganic layers. **b**, View of isolated inorganic framework; the two inorganic layers are nominally noncentrosymmetric (P$mc2_1$ layer group) owing to widely disparate Pb-Cl-Pb bond angles of β = 165.9º and β' = 177.6º (i.e., $\Delta\beta$ = 11.7º). **c**, DFT-PBE+SOC band structure corresponding to relaxed atomic coordinates. **d**, k-dependent spin polarization components $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$ and $\langle\sigma_z\rangle$ (top panels) for the frontier CBs (bottom panels), shown along the in-plane $\Gamma - Y$ and $\Gamma - Z$ paths. $\langle\sigma_y\rangle$ and $\langle\sigma_z\rangle$ point along the two in-plane directions of the perovskite layer, while $\langle\sigma_x\rangle$ points along the out-of-plane stacking direction. Note that despite a significant CB splitting arising from a local inversion asymmetry of inorganic layers, the net spin polarization of both upper and lower 2-fold degenerate CBs is zero owing to the global inversion symmetry.

Supplementary Note 6: Input geometry files

Supplementary Table 9 | Input geometry.in file of Cs_2PbBr_4 model with a pure in-plane tilting distortion leading to disparate bond angles (β_{in}) of 140º and 160º (i.e., $\Delta\beta_{in} = 20°$).

```
lattice_vector     20.0000000000     0.0000000000     0.0000000000
lattice_vector      0.0000000000     8.3563995361     0.0000000000
lattice_vector      0.0000000000     0.0000000000     8.3563995361

atom      10.000000000   0.000000000     0.000000000 Pb
atom      10.000000000   4.178199768     4.178199768 Pb
atom      10.000000000   1.328731418     2.849468470 Br
atom      10.000011444   6.635663509     5.898935795 Br
atom      10.000000000   2.849468470     7.027667999 Br
atom      10.000000000   5.898935795     1.720736027 Br
atom      13.000000000   0.000000000     0.000000000 Br
atom       7.000000000   0.000000000     0.000000000 Br
atom      13.000000000   4.178199768     4.178199768 Br
atom       7.000000000   4.178199768     4.178199768 Br
atom       7.000000000   0.000000000     4.178199768 Cs
atom       7.000000000   4.178199768     0.000000000 Cs
atom      13.000000000   0.000000000     4.178199768 Cs
atom      13.000000000   4.178199768     0.000000000 Cs
```

Supplementary Table 10 | Input geometry.in file of Cs_2PbBr_4 model with a pure in-plane tilting distortion leading to disparate bond angles (β_{in}) of 145º and 160º (i.e., $\Delta\beta_{in} = 15°$).

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563995361      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563995361

atom      10.000000000   0.000000000   0.000000000 Pb
atom      10.000000000   4.178199768   4.178199768 Pb
atom      10.000000000   1.430410743   2.747789145 Br
atom      10.000011444   6.635663509   5.898935795 Br
atom      10.000000000   2.747789145   6.925988674 Br
atom      10.000000000   5.898935795   1.720736027 Br
atom      13.000000000   0.000000000   0.000000000 Br
atom       7.000000000   0.000000000   0.000000000 Br
atom      13.000000000   4.178199768   4.178199768 Br
atom       7.000000000   4.178199768   4.178199768 Br
atom       7.000000000   0.000000000   4.178199768 Cs
atom       7.000000000   4.178199768   0.000000000 Cs
atom      13.000000000   0.000000000   4.178199768 Cs
atom      13.000000000   4.178199768   0.000000000 Cs
```

Supplementary Table 11 | Input geometry.in file of Cs_2PbBr_4 model with a pure in-plane tilting distortion leading to disparate bond angles (β_{in}) of 150º and 160º (i.e., $\Delta\beta_{in} = 10°$).

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563995361      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563995361

atom      10.000000000   0.000000000      0.000000000 Pb
atom      10.000000000   4.178199768      4.178199768 Pb
atom      10.000000000   1.529328465      2.648871422 Br
atom      10.000011444   6.635663509      5.898935795 Br
atom      10.000000000   2.648871422      6.827071190 Br
atom      10.000000000   5.898935795      1.720736027 Br
atom      13.000000000   0.000000000      0.000000000 Br
atom       7.000000000   0.000000000      0.000000000 Br
atom      13.000000000   4.178199768      4.178199768 Br
atom       7.000000000   4.178199768      4.178199768 Br
atom       7.000000000   0.000000000      4.178199768 Cs
atom       7.000000000   4.178199768      0.000000000 Cs
atom      13.000000000   0.000000000      4.178199768 Cs
atom      13.000000000   4.178199768      0.000000000 Cs
```

Supplementary Table 12 | Input geometry.in file of Cs_2PbBr_4 model with a pure in-plane tilting distortion leading to disparate bond angles (β_{in}) of 155º and 160º (i.e., $\Delta\beta_{in} = 5°$).

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563995361      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563995361

atom      10.000000000   0.000000000      0.000000000 Pb
atom      10.000000000   4.178199768      4.178199768 Pb
atom      10.000000000   1.625958562      2.552241325 Br
atom      10.000011444   6.635663509      5.898935795 Br
atom      10.000000000   2.552241325      6.730441093 Br
atom      10.000000000   5.898935795      1.720736027 Br
atom      13.000000000   0.000000000      0.000000000 Br
atom       7.000000000   0.000000000      0.000000000 Br
atom      13.000000000   4.178199768      4.178199768 Br
atom       7.000000000   4.178199768      4.178199768 Br
atom       7.000000000   0.000000000      4.178199768 Cs
atom       7.000000000   4.178199768      0.000000000 Cs
atom      13.000000000   0.000000000      4.178199768 Cs
atom      13.000000000   4.178199768      0.000000000 Cs
```

Supplementary Table 13 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 140º and 160º (i.e., $\Delta\beta_{out} = 20°$) and no formal dipole on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000   0.000000000   0.000000000 Pb
atom      10.000000000   4.178184986   4.178184986 Pb
atom       8.924650192   2.089092493   2.089092493 Br
atom      10.520957947   6.267277718   6.267277718 Br
atom      11.075349808   2.089092493   6.267277718 Br
atom       9.479042053   6.267278194   2.089092016 Br
atom      12.805204391   0.000000000   1.062981606 Br
atom       7.194795132   0.000000000   7.293388367 Br
atom      12.805204391   4.178184986   3.115199327 Br
atom       7.194795132   4.178184986   5.241170406 Br
atom       7.000000000   0.000000000   4.178184986 Cs
atom       7.000000000   4.178184986   0.000000000 Cs
atom      13.000000000   0.000000000   4.178184986 Cs
atom      13.000000000   4.178184986   0.000000000 Cs
```

Supplementary Table 14 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 145º and 160º (i.e., $\Delta\beta_{out} = 15°$) and no formal dipole on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000   0.000000000   0.000000000 Pb
atom      10.000000000   4.178184986   4.178184986 Pb
atom       9.068450928   2.089092493   2.089092493 Br
atom      10.520958900   6.267277718   6.267277718 Br
atom      10.931550980   2.089092493   6.267277718 Br
atom       9.479043007   6.267666340   2.089092493 Br
atom      12.834528923   0.000000000   0.981287003 Br
atom       7.165473938   0.000000000   7.375082970 Br
atom      12.839260101   4.178184986   3.210602999 Br
atom       7.160741806   4.178184986   5.145766735 Br
atom       7.000000000   0.000000000   4.178184986 Cs
atom       7.000000000   4.178184986   0.000000000 Cs
atom      13.000000000   0.000000000   4.178184986 Cs
atom      13.000000000   4.178184986   0.000000000 Cs
```

Supplementary Table 15 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 150º and 160º (i.e., $\Delta\beta_{out} = 10°$) and no formal dipole on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563709259      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563709259

atom      10.000000000   0.000000000   0.000000000 Pb
atom      10.000000000   4.178185463   4.178185463 Pb
atom       9.208440781   2.089092731   2.089092731 Br
atom      10.521054268   6.267278194   6.267278194 Br
atom      10.791751862   2.089092731   6.267278194 Br
atom       9.479139328   6.267278194   2.089092731 Br
atom      12.855998993   0.000000000   0.918272316 Br
atom       7.144000053   0.000000000   7.438098431 Br
atom      12.855998993   4.178185463   3.259913206 Br
atom       7.144000053   4.178185463   5.096457958 Br
atom       7.000000000   0.000000000   4.178185463 Cs
atom       7.000000000   4.178185463   0.000000000 Cs
atom      13.000000000   0.000000000   4.178185463 Cs
atom      13.000000000   4.178185463   0.000000000 Cs
```

Supplementary Table 16 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 155º and 160º (i.e., $\Delta\beta_{out} = 5°$) and no formal dipole on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000   0.000000000    0.000000000 Pb
atom      10.000000000   4.178184986    4.178184986 Pb
atom       9.345004082   2.089092493    2.089092493 Br
atom      10.520958900   6.267277718    6.267277718 Br
atom      10.654997826   2.089092493    6.267277718 Br
atom       9.479043007   6.267277718    2.089092493 Br
atom      12.887493134   0.000000000    0.812237084 Br
atom       7.112507820   0.000000000    7.544132233 Br
atom      12.887493134   4.178184986    3.365947247 Br
atom       7.112507820   4.178184986    4.990421772 Br
atom       7.000000000   0.000000000    4.178184986 Cs
atom       7.000000000   4.178184986    0.000000000 Cs
atom      13.000000000   0.000000000    4.178184986 Cs
atom      13.000000000   4.178184986    0.000000000 Cs
```

Supplementary Table 17 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 140º and 160º (i.e., $\Delta\beta_{out} = 20°$) and formal dipole along the stacking direction on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000    0.000000000     0.000000000 Pb
atom      10.000000000    4.178184986     4.178184986 Pb
atom       8.924650192    2.089092493     2.089092493 Br
atom      10.520957947    6.267277718     6.267277718 Br
atom      10.520957947    2.089092493     6.267277718 Br
atom       8.924650192    6.267278194     2.089092016 Br
atom      12.805204391    0.000000000     1.062981606 Br
atom       7.194795132    0.000000000     7.293388367 Br
atom      12.805204391    4.178184986     3.115199327 Br
atom       7.194795132    4.178184986     5.241170406 Br
atom       7.000000000    0.000000000     4.178184986 Cs
atom       7.000000000    4.178184986     0.000000000 Cs
atom      13.000000000    0.000000000     4.178184986 Cs
atom      13.000000000    4.178184986     0.000000000 Cs
```

Supplementary Table 18 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 145º and 160º (i.e., $\Delta\beta_{out} = 15°$) and formal dipole along the stacking direction on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000    0.000000000     0.000000000 Pb
atom      10.000000000    4.178184986     4.178184986 Pb
atom       9.068450928    2.089092493     2.089092493 Br
atom      10.520958900    6.267277718     6.267277718 Br
atom      10.520956990    2.089092493     6.267277718 Br
atom       9.068449020    6.267666340     2.089092493 Br
atom      12.834528923    0.000000000     0.981287003 Br
atom       7.165473938    0.000000000     7.375082970 Br
atom      12.839260101    4.178184986     3.210602999 Br
atom       7.160741806    4.178184986     5.145766735 Br
atom       7.000000000    0.000000000     4.178184986 Cs
atom       7.000000000    4.178184986     0.000000000 Cs
atom      13.000000000    0.000000000     4.178184986 Cs
atom      13.000000000    4.178184986     0.000000000 Cs
```

Supplementary Table 19 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 150º and 160º (i.e., $\Delta\beta_{out} = 10°$) and formal dipole along the stacking direction on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563709259      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563709259

atom      10.000000000    0.000000000     0.000000000 Pb
atom      10.000000000    4.178185463     4.178185463 Pb
atom       9.208440781    2.089092731     2.089092731 Br
atom      10.521054268    6.267278194     6.267278194 Br
atom      10.520860670    2.089092731     6.267278194 Br
atom       9.208248138    6.267278194     2.089092731 Br
atom      12.855998993    0.000000000     0.918272316 Br
atom       7.144000053    0.000000000     7.438098431 Br
atom      12.855998993    4.178185463     3.259913206 Br
atom       7.144000053    4.178185463     5.096457958 Br
atom       7.000000000    0.000000000     4.178185463 Cs
atom       7.000000000    4.178185463     0.000000000 Cs
atom      13.000000000    0.000000000     4.178185463 Cs
atom      13.000000000    4.178185463     0.000000000 Cs
```

Supplementary Table 20 | Input geometry.in file of Cs_2PbBr_4 model with a pure out-of-plane tilting distortion leading to disparate bond angles (β_{out}) of 155º and 160º (i.e., $\Delta\beta_{out} = 5°$) and formal dipole along the stacking direction on Pb site.

```
lattice_vector      20.0000000000      0.0000000000      0.0000000000
lattice_vector       0.0000000000      8.3563699722      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.3563699722

atom      10.000000000    0.000000000     0.000000000 Pb
atom      10.000000000    4.178184986     4.178184986 Pb
atom       9.345004082    2.089092493     2.089092493 Br
atom      10.520958900    6.267277718     6.267277718 Br
atom      10.520956990    2.089092493     6.267277718 Br
atom       9.345002174    6.267277718     2.089092493 Br
atom      12.887493134    0.000000000     0.812237084 Br
atom       7.112507820    0.000000000     7.544132233 Br
atom      12.887493134    4.178184986     3.365947247 Br
atom       7.112507820    4.178184986     4.990421772 Br
atom       7.000000000    0.000000000     4.178184986 Cs
atom       7.000000000    4.178184986     0.000000000 Cs
atom      13.000000000    0.000000000     4.178184986 Cs
atom      13.000000000    4.178184986     0.000000000 Cs
```

Supplementary Table 21 | Input geometry.in file of [S-MHA]$_2$PbI$_4$ *experimental* structure

```
lattice_vector     33.7103996277     0.0000000000     0.0000000000
lattice_vector      0.0000000000     8.9499998093     0.0000000000
lattice_vector      0.0000000000     0.0000000000     8.9561996460

atom     8.514234543     2.238932133     3.436672688 Pb
atom    25.369434357     2.236067772     5.519526958 Pb
atom     8.340965271     6.711068153     7.914772511 Pb
atom    25.196165085     6.713931561     1.041427016 Pb
atom     8.441083908     4.998127460     5.175877571 I
atom    25.296283722     8.426872253     3.780322313 I
atom     8.414115906     3.951872587     0.697777033 I
atom    25.269315720     0.523127317     8.258421898 I
atom    11.709307671     2.374434948     3.155716896 I
atom    28.564506531     2.100564957     5.800482750 I
atom     5.145892620     6.575564384     7.633816719 I
atom    22.001092911     6.849435329     1.322382927 I
atom     8.385125160     8.443071365     1.746727347 I
atom    25.240325928     4.981928349     7.209472179 I
atom     8.470074654     0.506928265     6.224827290 I
atom    25.325273514     3.968071699     2.731372356 I
atom     5.347481251     2.120881557     3.714225531 I
atom    22.202680588     2.354118347     5.241974354 I
atom    11.507719040     6.829118252     8.192325592 I
atom    28.362918854     6.595881462     0.763874412 I
atom    11.057011604     5.932059765     2.747762203 N
atom    27.912210464     7.492939949     6.208437443 N
atom     5.798188210     3.017939806     7.225862026 N
atom    22.653388977     1.457060575     1.730337739 N
atom     5.747622490     7.598549843     4.075070858 N
atom    22.602821350     5.826449871     4.881128788 N
atom    11.107577324     1.351450205     8.553170204 N
atom    27.962778091     3.123549700     0.403029144 N
atom    10.219914436     6.190455437     2.901907444 H
atom    27.075113297     7.234544277     6.054292202 H
atom     6.635285378     2.759544373     7.380007267 H
atom    23.490486145     1.715455532     1.576192379 H
atom    11.207595825     5.154520035     3.154095650 H
atom    28.062795639     8.270479202     5.802103996 H
atom     5.647603512     3.795479774     7.632195473 H
atom    22.502803802     0.679520130     1.324004173 H
atom    11.182548523     5.837933064     1.871684432 H
atom    28.037748337     7.587066650     7.084515095 H
atom     5.672651768     3.112066984     6.349784374 H
atom    22.527851105     1.362932444     2.606415272 H
```

atom 4.968507767 7.740944386 2.149075985 H
atom 21.823707581 5.684055328 6.807123661 H
atom 11.886692047 1.209055424 6.627175808 H
atom 28.741891861 3.265944481 2.329023838 H
atom 5.299780369 7.632505894 4.842823029 H
atom 22.154979706 5.792493820 4.113376617 H
atom 11.555418968 1.317493796 0.364723027 H
atom 28.410619736 3.157505512 8.591476440 H
atom 6.091401100 8.399924278 3.895892859 H
atom 22.946599960 5.025075436 5.060306549 H
atom 10.763798714 0.550075710 8.373992920 H
atom 27.618999481 3.924924135 0.582206845 H
atom 6.406561375 7.002712727 4.142367363 H
atom 23.261760712 6.422286987 4.813832283 H
atom 10.448638916 1.947287321 8.620467186 H
atom 27.303838730 2.527712584 0.335732251 H
atom 5.955717087 5.615453243 2.362359047 H
atom 22.810916901 7.809546471 6.593840599 H
atom 10.899482727 3.334546566 6.840458870 H
atom 27.754682541 1.140453339 2.115740776 H
atom 4.501989365 5.525568485 1.782525539 H
atom 21.357189178 7.899431229 7.173674107 H
atom 12.353210449 3.424431086 6.260625362 H
atom 29.208410263 1.050569296 2.695574284 H
atom 4.768504620 5.177100182 3.287560940 H
atom 21.623704910 8.247899055 5.668638706 H
atom 12.086695671 3.772899389 7.765660763 H
atom 28.941894531 0.702100515 1.190538883 H
atom 11.746051788 7.800864220 2.878907919 H
atom 28.601251602 5.624135494 6.077291965 H
atom 5.109148502 1.149135470 7.357007504 H
atom 21.964347839 3.325864077 1.599191904 H
atom 11.104609489 7.562266827 5.023442268 H
atom 27.959810257 5.862732887 3.932757139 H
atom 5.750590324 1.387732983 0.545342624 H
atom 22.605789185 3.087266922 8.410857201 H
atom 12.646623611 7.320589542 5.169823170 H
atom 29.501823425 6.104410172 3.786376476 H
atom 4.208575726 1.629410267 0.691723406 H
atom 21.063776016 2.845589638 8.264475822 H
atom 11.662585258 6.100955486 5.127549648 H
atom 28.517784119 7.324044228 3.828649998 H
atom 5.192614555 2.849044323 0.649450362 H
atom 22.047815323 1.625955582 8.306749344 H
atom 13.647183418 5.663309097 3.230662584 H
atom 30.502382278 7.761690617 5.725537300 H

atom 3.208016396 3.286690712 7.708762169 H
atom 20.063217163 1.188309073 1.247437239 H
atom 13.407267570 6.341307640 1.845165253 H
atom 30.262466431 7.083692074 7.111034393 H
atom 3.447932482 2.608692169 6.323265076 H
atom 20.303133011 1.866307855 2.632934570 H
atom 14.769200325 7.461829662 4.025650978 H
atom 31.624401093 5.963170052 4.930548668 H
atom 2.085999250 1.488170028 8.503750801 H
atom 18.941198349 2.986829996 0.452449083 H
atom 14.284849167 8.369503021 2.842644215 H
atom 31.140048981 5.055496693 6.113555431 H
atom 2.570350170 0.580496848 7.320744038 H
atom 19.425550461 3.894503117 1.635455608 H
atom 3.158867121 6.891705513 4.153052330 H
atom 20.014066696 6.533294201 4.803147316 H
atom 13.696332932 2.058294296 8.631152153 H
atom 30.551532745 2.416705608 0.325047612 H
atom 3.434988737 8.412319183 3.868612528 H
atom 20.290187836 5.012680054 5.087586880 H
atom 13.420210838 0.537680149 8.346712112 H
atom 30.275411606 3.937319756 0.609487236 H
atom 2.464028358 6.639888287 1.930204034 H
atom 19.319227219 6.785111427 7.025995731 H
atom 14.391171455 2.310111523 6.408303738 H
atom 31.246372223 2.164888382 2.547895670 H
atom 2.659380198 8.181714058 1.717897892 H
atom 19.514579773 5.243286133 7.238301754 H
atom 14.195819855 0.768285990 6.195997715 H
atom 31.051019669 3.706713915 2.760201931 H
atom 32.032394409 8.549925804 3.058586836 H
atom 15.177196503 4.875073433 5.897612572 H
atom 18.533203125 0.400073767 7.536686897 H
atom 1.678003550 4.074926376 1.419512987 H
atom 31.689493179 7.098083973 2.576725245 H
atom 14.834293365 6.326915741 6.379474163 H
atom 18.876106262 1.851916075 7.054825306 H
atom 2.020906210 2.623083830 1.901374459 H
atom 31.571105957 8.302968979 1.580814242 H
atom 14.715906143 5.122031212 7.375385284 H
atom 18.994493484 0.647031248 6.058914185 H
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Supplementary Table 22 | Input geometry.in file of $[S\text{-}MHA]_2PbI_4$ *relaxed* structure

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Supplementary Table 23 | Input geometry.in file of $[R\text{-}4\text{-}Cl\text{-}MBA]_2PbI_4$ *experimental* structure

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atom	14.828577042	7.905230522	2.625993013	C
atom	13.983818054	4.051214695	1.043258190	C
atom	13.336494446	7.766558170	6.343202591	C
atom	3.029476881	4.182368755	8.932587624	C
atom	9.907295227	9.879553795	4.551935673	C
atom	2.959889412	8.231128693	6.243233204	C
atom	9.090047836	3.790691137	8.955087662	C
atom	9.822964668	5.702673912	8.801062584	H
atom	2.816490889	3.636889935	1.859575748	H
atom	1.415406585	6.581123829	0.319922447	H
atom	2.826751232	1.312528729	6.549297333	H
atom	9.793704987	1.512081623	6.506409168	H
atom	11.060163498	2.895600557	1.603946090	H
atom	15.385080338	9.471977234	1.518361092	H
atom	1.205479383	8.366841316	3.979180813	H
atom	11.527773857	7.482556820	5.545361996	H
atom	15.171949387	10.978178978	4.260599136	H
atom	14.050427437	10.394389153	8.019656181	H
atom	14.291021347	5.931713104	9.363131523	H
atom	0.900200784	2.445525646	6.529560566	H
atom	11.891165733	1.977434397	7.458921909	H
atom	14.624491692	6.306509972	3.784251213	H
atom	14.891366005	5.043858528	6.837665558	H
atom	12.047007561	6.384294510	8.961830139	H
atom	13.299839020	2.357843399	1.854180574	H
atom	0.707557142	3.485585213	2.730767727	H
atom	13.708123207	6.969356060	6.040124893	H
atom	3.407044411	0.659868002	3.931550503	H
atom	4.465775490	0.835983694	4.911517143	H
atom	3.617699862	1.958939433	4.548225880	H
atom	3.384016037	6.301141262	1.541311264	H
atom	4.471859932	5.341635227	1.450823426	H
atom	3.718941212	5.472107887	2.687070847	H
atom	8.262153625	8.759543419	6.186106205	H
atom	9.117040634	8.411655426	7.308787346	H
atom	9.310333252	7.766414165	6.020941257	H
atom	2.487536430	3.448588848	8.634564400	H
atom	3.957075834	3.947489023	8.856361389	H
atom	2.849439383	4.954220295	8.390272141	H
atom	10.581952095	1.585939050	4.272080421	H
atom	9.038311005	1.332493782	4.374899387	H
atom	10.009328842	9.054402351	4.065430641	H
atom	2.368445635	7.995385647	6.962151051	H
atom	3.869233608	8.169031143	6.543702126	H
atom	2.825569630	7.621520042	5.509962559	H
atom	8.285068512	5.307963371	1.571021676	H

atom	9.297240257	6.340587616	1.717533946 H
atom	9.477260590	5.050038338	2.361217499 H
atom	9.476662636	3.503717899	8.122301102 H
atom	8.171834946	4.033699036	8.810888290 H
atom	9.136493683	3.075797081	9.591566086 H
atom	3.641198158	1.079410434	4.680861950 N
atom	3.667090654	5.497622013	1.798779368 N
atom	9.086812019	8.525960922	6.426781178 N
atom	9.158017159	5.464378834	1.641682863 N

Supplementary Table 24 | Input geometry.in file of [R-4-Cl-MBA]$_2$PbI$_4$ *relaxed* structure

```
lattice_vector     16.11377573     2.20892986     1.03548801
lattice_vector     -0.13789862     8.80471966    -0.02135525
lattice_vector      0.08343573     0.06814966     9.01450975

atom         0.009402570     8.778249741     0.004470721   Pb
atom        16.094482422     6.348917007     5.724276543   Pb
atom        16.133068085     3.576680183     7.396850109   I
atom         3.188407421     8.845372200     8.793029785   I
atom        16.097749710     7.955562592     8.551532745   I
atom         0.061980218     2.724033356     1.699029207   I
atom        12.908586502     2.287695408     1.132809520   I
atom         0.031266760     7.269839287     2.940779924   I
atom         3.163183928     4.554043770     4.839527607   I
atom        12.898142815     6.081489086     5.936013699   I
atom         9.489064217     2.967112303     8.396280289   Cl
atom         6.643370152     3.085846901     3.644300938   Cl
atom         6.752621174     7.620211124     0.720984876   Cl
atom         9.400296211     7.467508793     6.078805447   Cl
atom         2.726526022     3.634151697     8.140599251   N
atom        13.354749680     2.654462814     4.574980259   N
atom        13.285193443     5.709723473     9.462243080   N
atom         2.742007732     7.976603985     5.307196140   N
atom         2.900397062     2.667635441     8.491484642   H
atom         2.785728931     3.621407509     7.093244553   H
atom         1.754505157     3.892442942     8.383969307   H
atom        13.222191811     3.568910122     5.059195518   H
atom        13.290668488     2.802701712     3.539217472   H
atom        14.317650795     2.316410542     4.767773628   H
atom        12.930866241     6.072994232     8.551904678   H
atom        13.221272469     4.662211418     9.426271439   H
atom        14.288291931     5.961548805     9.504900932   H
atom         2.930415154     8.411932945     6.237332821   H
atom         2.787934542     6.935156345     5.421890736   H
atom         1.771374226     8.210488319     5.031823635   H
atom         2.348729134     5.411528587     1.157737851   H
atom         4.068523407     5.754540920     1.421545863   H
atom         3.433145761     4.132450581     1.759386420   H
atom         3.545785427     5.542203903     8.014233589   H
atom         4.883628845     2.385795593     0.742606044   H
atom         7.230393410     1.701139688     0.612712860   H
atom         8.114748955     5.183637142     7.187771320   H
atom         5.720536709     5.823460102     7.224174976   H
atom        12.326442719     2.228780270     7.067606926   H
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atom	13.499801636	9.745870590	6.707902431	H
atom	11.762713432	9.376205444	6.775801182	H
atom	12.640327454	9.515060425	4.409985065	H
atom	10.965150833	3.903362751	5.641025543	H
atom	8.650474548	4.470858097	5.086805344	H
atom	8.236339569	9.602252007	2.884556770	H
atom	10.588443756	9.037166595	3.399158478	H
atom	14.324728966	7.058570862	2.516187906	H
atom	12.808235168	7.601377487	3.236273289	H
atom	13.301570892	8.223995209	1.642845869	H
atom	12.567664146	5.322139740	2.373938322	H
atom	11.519276619	8.439001083	9.425106049	H
atom	9.169606209	9.020473480	9.059531212	H
atom	7.944552898	5.246823311	1.832782269	H
atom	10.325187683	4.659838200	2.217733383	H
atom	2.386409044	1.050472260	3.342778444	H
atom	4.103179932	1.249486446	2.942635298	H
atom	3.510658741	1.731654167	4.540103436	H
atom	3.529497147	7.674898148	3.408524036	H
atom	5.156662464	1.042536259	6.119852543	H
atom	7.465886593	9.463056564	6.871379375	H
atom	7.819441319	6.165654182	4.127040863	H
atom	5.480620861	6.505149841	3.409633160	H
atom	3.359891415	4.991203785	1.081163645	C
atom	3.703233719	4.668117046	8.661173820	C
atom	5.124866009	4.180929184	8.496247292	C
atom	5.569756985	3.033905745	9.163164139	C
atom	6.900026321	2.636315346	9.098617554	C
atom	7.805260181	3.415748358	8.382869720	C
atom	7.389688492	4.561812878	7.707207680	C
atom	6.045101643	4.926545620	7.752222061	C
atom	12.497939110	10.129245758	6.472062111	C
atom	12.347954750	1.599413872	4.982720852	C
atom	10.951562881	2.011739254	4.570693970	C
atom	10.390740395	3.208917618	5.026499748	C
atom	9.079184532	3.545582533	4.714775085	C
atom	8.308941841	2.671728849	3.953152657	C
atom	8.847266197	1.480385542	3.470083714	C
atom	10.170533180	9.970083237	3.776533365	C
atom	13.290126801	7.338782310	2.288324118	C
atom	12.539875031	6.170489311	1.675755739	C
atom	11.095779419	6.482845783	1.351301908	C
atom	10.751023293	7.730486393	9.736193657	C
atom	9.419629097	8.073358536	9.532047272	C
atom	8.419784546	7.154829979	0.939814210	C
atom	8.734775543	5.934414387	1.535633445	C

atom	10.075695992	5.608236313	1.740983844	C
atom	3.405390739	0.985213041	3.744925737	C
atom	3.720656395	8.387134552	4.223610878	C
atom	5.138319016	8.189115524	4.714997292	C
atom	5.716578960	9.018863678	5.687007427	C
atom	7.024324417	8.812005997	6.120466232	C
atom	7.763774395	7.770444870	5.561984062	C
atom	7.220318794	6.951593399	4.576953411	C
atom	5.908293724	7.159972191	4.167059898	C

Supplementary Table 25 | Input geometry.in file of [S-4-NH_3-MBA] PbI_4 *experimental* structure

```
lattice_vector      23.0755004883    0.0000000000    0.0000000000
lattice_vector       0.0000000000    8.4849004745    0.0000000000
lattice_vector       0.0000000000    0.0000000000    9.0443000793

atom         5.641036987     6.341614723     7.775113106    Pb
atom        17.178787231     6.385735989     1.269186735    Pb
atom         5.896713734     2.143285990     3.252962828    Pb
atom        17.434463501     2.099164724     5.791337013    Pb
atom         5.218062878     3.684398413     6.083376884    I
atom        16.755813599     0.558051884     2.960922956    I
atom         6.319686890     4.800502300     1.561227560    I
atom        17.857437134     7.926848412     7.483073235    I
atom         5.209986210     7.988279343     5.060557365    I
atom        16.747737885     4.739071369     3.983742714    I
atom         6.327763557     0.496620983     0.538407385    I
atom        17.865512848     3.745829344     8.505892754    I
atom         8.659312248     6.169540882     7.042706013    I
atom        20.197061539     6.557809830     2.001594305    I
atom         2.878437996     2.315359831     2.520555735    I
atom        14.416188240     1.927089930     6.523744106    I
atom         2.488231182     6.523021698     8.581321716    I
atom        14.025980949     6.204329014     0.462977886    I
atom         9.049519539     1.961878777     4.059172153    I
atom        20.587268829     2.280571461     4.985127926    I
atom         8.600238800     6.843072414     3.641235113    N
atom        20.137989044     5.884278297     5.403064728    N
atom         2.937510967     1.641828060     8.163385391    N
atom        14.475261688     2.600621700     0.880914927    N
atom        14.581409454     6.733617306     6.036165714    N
atom         3.043660164     5.993733406     3.008134127    N
atom        20.031841278     1.751283288     1.514015913    N
atom         8.494091034     2.491167545     7.530284405    N
atom         8.507937431     6.487096310     4.451812267    H
atom        20.045688629     6.240254402     4.592487335    H
atom         3.029813290     1.997803926     8.973962784    H
atom        14.567563057     2.244645834     0.070337571    H
atom         7.858500004     6.701654434     3.169457197    H
atom        19.396251678     6.025696278     5.874842644    H
atom         3.679250240     1.783246040     7.691607475    H
atom        15.217000008     2.459204674     1.352692842    H
atom         8.741207123     7.718612194     3.716149330    H
atom        20.278957367     5.008738518     5.328150749    H
atom         2.796542883     0.766288340     8.238299370    H
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atom	14.334293365	3.476161957	0.806000829	H
atom	14.461600304	6.389172554	6.848226547	H
atom	2.923851252	6.338178158	2.196073532	H
atom	20.151651382	2.095727682	2.326076508	H
atom	8.613900185	2.146722555	6.718223572	H
atom	14.798871994	7.593434334	6.107778549	H
atom	3.261122942	5.133916378	2.936521530	H
atom	19.814378738	0.891465962	1.585628629	H
atom	8.276628494	3.350984335	7.458671570	H
atom	15.235991478	6.295303822	5.621945858	H
atom	3.698241234	6.432046890	3.422354221	H
atom	19.377260208	2.189596653	1.099795818	H
atom	7.839509010	2.052853107	7.944504261	H
atom	9.587224007	5.243829727	2.843500853	H
atom	21.124975204	7.483520985	6.200799465	H
atom	1.950525880	3.241070986	7.365650654	H
atom	13.488275528	1.001379371	1.678649187	H
atom	13.531427383	8.348378181	4.310685158	H
atom	1.993677258	4.378972054	4.733614922	H
atom	21.081823349	0.136521846	8.832835197	H
atom	9.544073105	4.105928898	0.211464733	H
atom	9.098484993	6.571326256	1.046362281	H
atom	20.636236191	6.156024456	7.997938156	H
atom	2.439265013	1.913574100	5.568511963	H
atom	13.977015495	2.328875780	3.475787878	H
atom	10.660396576	6.455846786	1.115116954	H
atom	22.198146820	6.271503925	7.929183006	H
atom	0.877353549	2.029053688	5.637267113	H
atom	12.415102959	2.213397264	3.407032967	H
atom	9.947363853	7.755860806	1.624184489	H
atom	21.485115051	4.971489906	7.420115948	H
atom	1.590386510	0.729039669	6.146334171	H
atom	13.128135681	3.513410568	2.897965670	H
atom	12.811264038	4.815664291	6.013636589	H
atom	1.273514152	7.911686420	3.030663490	H
atom	21.801986694	3.669235945	1.491486549	H
atom	10.264236450	0.573214233	7.552813530	H
atom	10.883790016	4.597899437	4.725221634	H
atom	22.421541214	8.129450798	4.319078445	H
atom	0.653959930	3.887000799	0.203072295	H
atom	12.191709518	0.355449885	8.841228485	H
atom	11.588239670	8.152029037	3.091197014	H
atom	0.050488442	4.575321198	5.953103065	H
atom	23.025011063	0.332871139	7.613347054	H
atom	11.487260818	3.909578562	1.430953026	H
atom	13.339947701	6.604646683	5.261973858	C

atom	1.802195787	6.122704029	3.782326460	C
atom	21.273303986	1.880253911	0.739823580	C
atom	9.735552788	2.362195730	8.304476738	C
atom	9.774782181	6.200765133	2.938493013	C
atom	21.312530518	6.526585579	6.105806828	C
atom	1.762968540	2.284135342	7.460643291	C
atom	13.300719261	1.958314300	1.583656907	C
atom	11.032397270	6.356887341	3.787752867	C
atom	22.570146561	6.370463371	5.256547451	C
atom	0.505353391	2.128013134	8.309903145	C
atom	12.043103218	2.114437103	0.734397173	C
atom	12.993813515	7.595683098	4.403669834	C
atom	1.456063628	5.131667614	4.640630722	C
atom	21.619436264	0.889217436	8.925819397	C
atom	10.081686974	3.353232861	0.118480317	C
atom	9.880928993	6.800647736	1.554715276	C
atom	21.418680191	5.926702976	7.489584446	C
atom	1.656820774	1.684252501	6.076865673	C
atom	13.194571495	2.558198214	2.967434883	C
atom	12.566917419	5.482942581	5.413013935	C
atom	1.029167533	7.244408131	3.631286383	C
atom	22.046333313	3.001957893	0.890863657	C
atom	10.508583069	1.240491986	8.153436661	C
atom	11.408527374	5.362457275	4.648770332	C
atom	22.946277618	7.364893436	4.395529747	C
atom	0.129222929	3.122443199	0.126619652	C
atom	11.666972160	1.120006561	8.917679787	C
atom	11.835424423	7.470954895	3.673794508	C
atom	0.297673851	5.256395817	5.370505333	C
atom	22.777826309	1.013945460	8.195944786	C
atom	11.240076065	3.228505373	0.848355412	C

Supplementary Table 26 | Input geometry.in file of [S-4-NH_3-MBA] PbI_4 *relaxed* structure

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lattice_vector     23.19104716    -0.00000072    -0.00001590
lattice_vector     -0.00005571     8.39915710    -0.00000210
lattice_vector     -0.00010385    -0.00000157     9.01922748

atom        5.649615765     6.295403957     7.712908268   Pb
atom       17.244342804     6.303306103     1.305963516   Pb
atom        5.946035862     2.103985071     3.203572035   Pb
atom       17.541519165     2.095874310     5.815821171   Pb
atom        5.225178242     3.595787764     6.025808334   I
atom       16.820230484     0.603798270     2.993297338   I
atom        6.370659351     4.803175449     1.516174078   I
atom       17.965848923     7.795292377     7.502520084   I
atom        5.157329082     7.832911491     4.903037071   I
atom       16.752399445     4.765656471     4.115601063   I
atom        6.438534260     0.566413462     0.393775523   I
atom       18.033638000     3.633129835     8.625314713   I
atom        8.706032753     6.099038124     6.944530010   I
atom       20.300764084     6.499668121     2.074479103   I
atom        2.890034199     2.300090790     2.434824228   I
atom       14.485362053     1.899395466     6.584043026   I
atom        2.482058764     6.496784210     8.512528419   I
atom       14.076493263     6.101798534     0.506255209   I
atom        9.114139557     1.902238965     4.003043175   I
atom       20.709365845     2.297091246     5.015983582   I
atom        8.622753143     6.766093731     3.552861214   N
atom       20.218225479     5.832478523     5.466007710   N
atom        2.972840548     1.632977724     8.062551498   N
atom       14.568317413     2.566492081     0.956416786   N
atom       14.570774078     6.713675976     6.086416245   N
atom        2.975256920     5.884909630     2.932621956   N
atom       20.215789795     1.685256124     1.576689005   N
atom        8.620262146     2.514089823     7.442177296   N
atom        8.533645630     6.434957027     4.545525551   H
atom       20.129001617     6.163613796     4.473344803   H
atom        3.062060356     1.964126229     0.035974421   H
atom       14.657411575     2.235360146     8.982967377   H
atom        7.759588242     6.494475842     3.039859533   H
atom       19.355108261     6.104155064     5.979069233   H
atom        3.835952044     1.904627681     7.549478531   H
atom       15.431490898     2.294850349     1.469401956   H
atom        8.685597420     7.809414387     3.595930099   H
atom       20.281019211     4.789151669     5.422971725   H
atom        2.910045385     0.589645565     8.105599403   H
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atom	8.374240875	3.525448561	7.342318535	H
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atom	13.600350380	0.899813592	1.732200384	H
atom	13.666730881	0.052035764	4.307972431	H
atom	2.071202278	4.147366047	4.711016655	H
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atom	9.048230171	6.566802502	0.877223432	H
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atom	12.371460915	2.241318226	3.555710316	H
atom	9.995160103	7.897577763	1.543450952	H
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atom	13.195927620	3.698006630	2.965856075	H
atom	12.849674225	4.620830059	6.097355843	H
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atom	13.027189255	7.575900078	4.391970158	C
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atom	23.029962540	7.295923233	4.407880306	C
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atom	11.756608009	1.102915049	8.917675972	C
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Supplementary Table 27 | Input geometry.in file of $[S\text{-}MBA]_2PbI_4$ *experimental* structure

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lattice_vector       0.0000000000      8.9034404755      0.0000000000

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atom      14.393290520    3.549885750      4.726875305 Pb
atom      28.855567932    3.661950350      2.973764181 I
atom      14.423021317    0.809324205      6.364803791 I
atom      14.442070961    5.261183739      7.621466160 I
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atom      14.431969643    6.275395393      2.762020826 I
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Supplementary Table 28 | Input geometry.in file of $[S\text{-}MBA]_2PbI_4$ *relaxed* structure

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atom     28.80628490     3.73065964     2.94992950 I
atom     14.38963528     0.67250853     6.24575994 I
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atom 3.06255367 6.27232292 3.70742973 C
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atom 7.92721975 3.32840070 4.32198148 H
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atom 26.46430708 6.19331465 3.34690640 H
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atom 18.48346882 2.18350971 7.70115020 H
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atom 10.85522762 8.27795468 6.22421913 H
atom 17.97529127 3.87489901 7.55396641 H
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atom 17.86994779 0.23533050 5.63952736 H
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atom 25.97882228 0.57014055 7.43871610 H
atom 11.56517415 3.83279017 1.74814126 H
atom 17.26634500 8.23697032 2.84448824 H
atom 2.85287448 4.97465451 6.33945098 H
atom 26.08538885 7.88767584 8.23218651 H
atom 11.66971446 5.32478596 0.95601293 H
atom 17.16194304 0.92041095 3.63741436 H
atom 2.74587987 3.48349604 5.54624481 H
atom 27.17859911 0.29919538 8.58514948 H
atom 12.76396107 4.10897400 0.60119978 H
atom 16.06716508 8.51112952 3.99135273 H
atom 1.65346513 4.70169617 5.19295743 H
atom 25.72791172 2.69605275 0.17007806 H
atom 11.31270145 1.70794602 9.01847942 H
atom 17.51827870 6.11168716 4.76090773 H
atom 3.10468445 7.10073490 4.42310377 H
atom 26.80080535 1.77417124 1.24805437 H
atom 12.38612662 2.63014592 7.94136639 H
atom 16.44498013 7.03382870 5.83820158 H
atom 2.03167592 6.17860212 3.34546093 H
atom 25.14145072 2.12603012 1.74552239 H

atom	10.72777124	2.27668123	7.44201025 H
atom	18.10381583	6.68144217	6.33677166 H
atom	3.69066695	6.53113995	2.84730578 H
atom	26.04641414	4.62284930	5.57650841 N
atom	11.63021058	8.58970243	3.61004807 N
atom	17.20006528	4.18539917	0.98232586 N
atom	2.78643485	0.21870477	8.20142333 N
atom	26.18796542	0.11480264	8.35344803 N
atom	11.77288115	4.28985898	0.83400967 N
atom	17.05802123	8.69352082	3.75875747 N
atom	2.64427730	4.51865052	5.42494699 N

Supplementary Table 29 | Input geometry.in file of **[**S-4-NO_2-MBA]$_2$$PbBr_4$·$H_2O$ *experimental* structure

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lattice_vector      18.1396270419     -0.5412233354      0.0000000000
lattice_vector       0.0000000000      8.8284997940      0.0000000000
lattice_vector       0.0000000000      0.0000000000      8.0875997543

atom       8.975125313   6.479924202   6.762527466 Pb
atom       9.164502144   1.807352185   2.718727112 Pb
atom      11.918279648   6.246705055   6.678901672 Br
atom       6.221348286   2.040571213   2.635101557 Br
atom       9.004510880   3.882850409   0.231063172 Br
atom       9.135116577   4.404426098   4.274863243 Br
atom       5.955421448   6.405458450   7.144666195 Br
atom      12.184206009   1.881817937   3.100866318 Br
atom       9.129674911   7.910209179   1.202545047 Br
atom       9.009952545   0.377067357   5.246345043 Br
atom      14.294026375   7.458249092   3.694415331 C
atom       3.845601320   0.829027057   7.738215446 C
atom      13.766162872   2.967932224   7.251341820 C
atom       4.373464584   5.319344521   3.207542181 C
atom      14.312165260   3.659687519   0.238584250 C
atom       3.827461958   4.627588749   4.282383919 C
atom      15.605521202   4.164934158   0.155281648 C
atom       2.534105778   4.122342587   4.199081421 C
atom      16.349246979   3.978533506   7.083928585 C
atom       1.790380955   4.308743000   3.040128946 C
atom      15.803243637   3.287661076   6.009086609 C
atom       2.336383581   4.999615192   1.965286970 C
atom      14.509887695   2.782415152   6.093197823 C
atom       3.629739523   5.504861355   2.049398422 C
atom      16.213199615  -0.157091483   0.085728325 C
atom       1.926428080   8.444367409   4.129528046 C
atom      15.240915298   7.679843903   0.050142761 C
atom       2.898712397   0.607432544   4.093942642 C
atom      14.571562767   7.320189476   1.214757562 C
atom       3.568064213   0.967086732   5.258557320 C
atom      14.876308441   7.952928543   2.414148092 C
atom       3.263318777   0.334347636   6.457947731 C
atom      15.848592758   0.115993902   2.449733734 C
atom       2.291034460   8.171282768   6.493533611 C
atom      16.517944336   0.474765152   1.285928726 C
atom       1.621682525   7.812511444   5.329728603 C
atom      14.747517586   6.019798756   4.069680691 C
atom       3.392109871   2.267477751   0.025880758 C
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atom 12.363969803 2.451807499 7.383169651 C
atom 5.775657654 5.835468769 3.339369774 C
atom 12.302295685 0.952803135 7.396918774 C
atom 5.837331772 7.334473133 3.353118896 C
atom 14.562075615 8.067071915 4.414139271 H
atom 3.577551842 0.220204324 0.370340496 H
atom 12.452509880 7.185894489 4.410467148 H
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atom 12.526229858 6.851204872 2.998089552 H
atom 5.613398075 1.436071515 7.041889668 H
atom 12.482112885 8.243177414 3.413703203 H
atom 5.657514572 0.044098966 7.457502842 H
atom 13.814051628 3.784022331 1.013877988 H
atom 4.325575829 4.503253937 5.057677746 H
atom 15.970871925 4.627125263 0.873946071 H
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atom 16.301521301 3.162730217 5.234173298 H
atom 1.838106513 5.124546528 1.190374017 H
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atom 3.994945049 5.967666626 1.330273271 H
atom 15.036572456 7.256433964 7.335064888 H
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atom 10.651407242 2.778512955 6.435157776 H
atom 7.488220215 5.508763313 2.391357183 H
atom 11.739858627 2.542258024 5.501508713 H
atom 6.399768829 5.745018482 1.457708240 H
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atom 6.521503925 4.457695484 2.121207952 H
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atom 5.428229809 7.678824902 2.556580067 H
atom 11.384339333 0.671564996 7.432544231 H
atom 6.755287647 7.615711212 3.388744116 H

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atom      12.768392563   0.620523095    0.079371899 H
atom       5.371234894   7.666753769    4.123171806 H
atom      11.370282173   4.843750954    2.544552565 H
atom       6.769345760   3.443525791    6.588352680 H
atom      12.003154755   5.023412228    1.322646141 H
atom       6.136472702   3.263864279    5.366446018 H
atom      12.782995224   7.431822300    3.621627569 N
atom       5.356632233   0.855454266    7.665427208 N
atom      16.958738327   0.206470579    6.982833385 N
atom       1.180889964   8.080805779    2.939033508 N
atom      11.505965233   2.951498747    6.256567001 N
atom       6.633661747   5.335777760    2.212767124 N
atom      17.662555695   4.541452885    6.944013119 N
atom       0.477072448   3.745823860    2.900213480 N
atom      16.552410126  -0.265208125    5.930636883 O
atom       1.587216973   8.552484512    1.886836767 O
atom      17.898370743   0.995071173    7.098485947 O
atom       0.241257071   7.292205334    3.054686308 O
atom      11.778059959   5.402117252    2.049397469 O
atom       6.361567497   2.885159254    6.093197346 O
atom      17.976369858   5.375211239    7.731745243 O
atom       0.163256705   2.912065029    3.687945366 O
atom       0.206791475   4.815957069    6.089962959 O
atom      17.932836533   3.471319437    2.046162844 O
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Supplementary Table 30 | Input geometry.in file of **[**S-4-NO_2-MBA]$_2$$PbBr_4$·$H_2O$ *relaxed* structure

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lattice_vector      0.11036920     8.82895089    -0.00151199
lattice_vector     -0.00187737    -0.00203195     7.90995217

atom      9.02681485     6.50760946     6.52354186 Pb
atom      9.26293772     1.80042617     2.57072988 Pb
atom     12.03998365     6.18337337     6.57571043 Br
atom      6.25183970     2.12317676     2.62293676 Br
atom      8.93989668     3.72707136    -0.00205316 Br
atom      9.35030392     4.58501372     3.95063647 Br
atom      6.02604755     6.52696539     6.97288821 Br
atom     12.26287900     1.78150324     3.02173365 Br
atom      9.28005712     7.90013317     1.20576084 Br
atom      9.00976834     0.40892141     5.16198976 Br
atom     14.45001788     7.44678198     3.65690629 C
atom      3.84525862     0.86605661     7.61174030 C
atom     13.88449488     2.90530532     7.10723553 C
atom      4.40027918     5.40014347     3.15258504 C
atom     14.40408402     3.62012977     0.28454756 C
atom      3.88981877     4.68497245     4.24179903 C
atom     15.66676278     4.19259371     0.21565343 C
atom      2.62637850     4.11361433     4.18081921 C
atom     16.40554672     4.02644245     6.95963239 C
atom      1.87627104     4.28276049     3.02168692 C
atom     15.94580543     3.26821178     5.88383574 C
atom      2.32858045     5.04294418     1.94424956 C
atom     14.67487874     2.71187727     5.96407993 C
atom      3.60183918     5.59617871     2.01542249 C
atom     16.31999649    -0.10194977     0.08373900 C
atom      1.97596406     8.42444987     4.03182673 C
atom     15.46097099     7.73245210    -0.01035053 C
atom      2.84114587     0.58398627     3.94244651 C
atom     14.78277241     7.35309725     1.14023854 C
atom      3.51887125     0.95988003     5.09441156 C
atom     15.07245706     7.95218483     2.37293266 C
atom      3.22268705     0.36343655     6.32677367 C
atom     15.91478492     0.14815656     2.42977051 C
atom      2.37429543     8.17303056     6.37891205 C
atom     16.59836268     0.54122355     1.28564829 C
atom      1.69100395     7.78353674     5.23336494 C
atom     14.98573024     6.07047421     4.05268242 C
atom      3.31416987     2.24536059     0.09838488 C
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atom 3.61260022 0.15167671 0.49973468 H
atom 12.55413512 7.12146025 4.49147257 H
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atom 3.57003844 3.00473629 7.26058165 H
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atom 6.26286167 5.54112419 4.16241461 H
atom 10.62927854 2.76760836 6.27989895 H
atom 7.65446395 5.53788962 2.31823633 H
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atom 11.74754150 3.97690789 6.04655608 H
atom 6.53652514 4.32817788 2.08738188 H
atom 12.80352260 0.42690216 6.28718418 H
atom 5.47786665 7.87812355 2.32534740 H
atom 11.33922114 0.52369253 7.29193816 H
atom 6.94593571 7.78273053 3.32477767 H

atom 12.93957654 0.46372129 0.14627448 H
atom 5.35029700 7.84585660 4.09492727 H
atom 11.13955836 5.13077542 2.39856264 H
atom 7.15455263 3.18041549 6.35639294 H
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atom 6.57610417 2.64413573 5.00448593 H
atom 12.94634845 7.40432259 3.56740791 N
atom 5.34896658 0.90504084 7.52305775 N
atom 17.08612689 0.26240525 6.79644039 N
atom 1.20757991 8.06298174 2.83341369 N
atom 11.63241191 2.93805720 6.08614938 N
atom 6.65119652 5.36709552 2.12557530 N
atom 17.70074776 4.70338590 6.85262308 N
atom 0.57751942 3.61073636 2.92632924 N
atom 16.74142821 -0.23529071 5.71533375 O
atom 1.55722851 8.55850293 1.75268057 O
atom 18.03266865 1.03917590 6.92651558 O
atom 0.25593626 7.29246306 2.96175472 O
atom 11.97305577 5.41275010 1.96010844 O
atom 6.32190846 2.89761046 5.91665918 O
atom 17.97653855 5.56845162 7.68849687 O
atom 0.32291878 2.71982560 3.74142408 O
atom 0.25917856 4.90105266 5.91461879 O
atom 17.99459980 3.44425256 2.01999067 O

Supplementary Table 31 | Input geometry.in file of $[R\text{-}4\text{-}Cl\text{-}MBA]_2PbBr_4$ *experimental* structure

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lattice_vector       0.0000000000     7.9134998322      0.0000000000
lattice_vector       0.0000000000     0.0000000000      8.8065996170

atom       8.847106934    5.906240463      0.368380070   Pb
atom      26.635957718    5.964009285      8.438219070   Pb
atom       8.941744804    2.007259369      4.771679878   Pb
atom      26.730594635    1.949491024      4.034919739   Pb
atom       8.799432755    7.421042919      2.904944897   Br
atom      26.588283539    4.449206829      5.901654720   Br
atom       8.989417076    0.492457032      7.308244705   Br
atom      26.778268814    3.464293003      1.498354793   Br
atom       8.493820190    3.373920679      1.849738240   Br
atom      26.282670975    0.582829297      6.956861496   Br
atom       9.295030594    4.539579391      6.253037930   Br
atom      27.083881378    7.330670357      2.553561687   Br
atom       5.839724064    6.180047989      0.564062655   Br
atom      23.628574371    5.690201759      8.242536545   Br
atom      11.949127197    1.733452082      4.967362881   Br
atom      29.737977982    2.223298311      3.839237213   Br
atom      11.749535561    5.622146130      0.856529891   Br
atom      29.538387299    6.248103619      7.950069904   Br
atom       6.039315224    2.291353941      5.259829521   Br
atom      23.828165054    1.665395498      3.546769857   Br
atom      18.176649094    2.283044815      7.401066303   Cl
atom       0.387797683    1.673705101      1.405533314   Cl
atom      35.189903259    5.630455017      2.997766256   Cl
atom      17.401052475    6.239794731      5.808833122   Cl
atom      17.496402740    5.708798885      1.025968790   Cl
atom      35.285255432    6.161450863      7.780630589   Cl
atom       0.292448252    2.204700947      5.429268837   Cl
atom      18.081298828    1.752049088      3.377331018   Cl
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Supplementary Table 32 | Input geometry.in file of [R-4-Cl-MBA]$_2$PbBr$_4$ *relaxed* structure

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atom	16.23980534	5.60024343	1.50546737 C
atom	33.63211788	6.15222831	7.35675085 C
atom	1.15337625	2.23709860	5.93196776 C
atom	18.54498475	1.68083623	2.92649055 C

Supplementary Table 33 | Input geometry.in file of **[**S-2-Me-BuA]$_2$PbBr$_4$ *experimental* structure

```
lattice_vector     15.6508998871      0.0000000000      0.0000000000
lattice_vector      0.0000000000      8.2846002579      0.0000000000
lattice_vector     -1.5775239343      0.0000000000      8.0757655110

atom     7.418079853      2.346198797      2.018133879 Pb
atom     6.655295849      6.488499165      6.057631969 Pb
atom     7.780080318      4.916910172      0.496659607 Br
atom     6.293295383      0.774610281      7.579105854 Br
atom     7.108809471      8.065887451      3.548491240 Br
atom     6.964566708      3.923586607      4.527274609 Br
atom     4.508862019      2.607163668      1.325233221 Br
atom     9.564513206      6.749464035      6.750532627 Br
atom    10.320226669      2.125828266      2.728801250 Br
atom     3.753148317      6.268128872      5.346963882 Br
atom    10.027739525      6.851364613      1.897804856 N
atom     4.045636654      2.709064484      6.177960396 N
atom     4.882758141      5.832358360      2.140885592 N
atom     9.190617561      1.690058470      5.934880257 N
atom     9.945204735      7.617110252      2.340833426 H
atom     4.128170967      3.474810123      5.734932423 H
atom     9.221228600      6.557037830      1.659392118 H
atom     4.852147579      2.414737225      6.416373253 H
atom    10.520330429      6.983056068      1.166326284 H
atom     3.553045273      2.840756178      6.909439087 H
atom     4.720666409      6.057782650      2.985820532 H
atom     9.352709770      1.915482402      5.089944839 H
atom     5.760635376      5.823941231      1.997855663 H
atom     8.312741280      1.681641340      6.077909946 H
atom     4.550125599      5.019747257      1.982988000 H
atom     9.523250580      0.877446949      6.092777252 H
atom     3.191000223      5.554965019      0.099186555 H
atom    10.882375717      1.412665129      7.976578712 H
atom    11.788506508      7.173353672      3.791265249 H
atom     2.284870148      3.031053543      4.284500122 H
atom    10.819477081      5.035926819      2.256401300 H
atom     3.253899097      0.893626630      5.819364071 H
atom    10.120545387      5.665009499      3.519313574 H
atom     3.952830315      1.522709608      4.556452274 H
atom     4.061411381      7.638823986      1.718022227 H
atom    10.011963844      3.496523857      6.357743263 H
atom     4.851793289      7.036044598      0.507174253 H
atom     9.221582413      2.893744469      7.568591118 H
atom    13.142057419      7.771336079      2.374081373 H
atom     0.931317568      3.629036188      5.701684475 H
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atom 12.737717628 6.618558884 1.391632080 H
atom 1.335658193 2.476258755 6.684133053 H
atom 13.806630135 6.357867241 2.508348942 H
atom 0.266745895 2.215567350 5.567416668 H
atom 1.778174520 6.665474415 2.219688654 H
atom 12.295201302 2.523174524 5.856076717 H
atom 2.388965845 5.226605415 2.200944901 H
atom 11.684410095 1.084305048 5.874820709 H
atom 1.654438734 7.848142624 7.300087929 H
atom 12.418937683 3.705842495 0.775677323 H
atom 1.981193900 8.102927208 0.134396896 H
atom 12.092182159 3.960627079 7.941369057 H
atom 0.334157407 7.036864758 7.062862873 H
atom 13.739217758 2.894564629 1.012902856 H
atom 12.854879379 4.536945820 3.444903612 H
atom 1.218497157 0.394645244 4.630861759 H
atom 11.756744385 4.828753948 4.532095432 H
atom 2.316631556 0.686453760 3.543670416 H
atom 0.372311205 4.651745319 1.674332380 H
atom 13.701065063 0.509445012 6.401432991 H
atom 0.815555096 5.030235291 0.219038993 H
atom 13.257821083 0.887935042 7.856726646 H
atom 0.021961674 6.063838482 1.090510964 H
atom 14.051414490 1.921538591 6.985254765 H
atom 13.316196442 5.616163731 5.931746483 H
atom 0.757179022 1.473863602 2.144019127 H
atom 13.781694412 6.665209770 4.863847733 H
atom 0.291681498 2.522909164 3.211917877 H
atom 14.419481277 5.233307362 4.885894775 H
atom -0.346105605 1.091007352 3.189870834 H
atom 2.971123457 6.346004009 0.637985528 C
atom 11.102252007 2.203703642 7.437780380 C
atom 11.977429390 6.428850174 3.181851625 C
atom 2.095945835 2.286549568 4.893914223 C
atom 10.669686317 5.857212543 2.745760441 C
atom 3.403689384 1.714912176 5.330005169 C
atom 4.233243465 6.818226337 1.227516294 C
atom 9.840132713 2.675925970 6.848248959 C
atom 12.996106148 6.826510429 2.293517590 C
atom 1.077269316 2.684210539 5.782248020 C
atom 1.978867412 5.906919956 1.647456169 C
atom 12.094509125 1.764619827 6.428309441 C
atom 0.898983061 7.439570904 7.728507996 C
atom 13.174391747 3.297271013 0.347257942 C
atom 12.484778404 5.219297886 4.029807091 C
atom 1.588597536 1.076997995 4.045958519 C

```
atom     0.679110706         5.360136509         1.106379867 C
atom    13.394265175         1.217836380         6.969386101 C
atom    13.621069908         5.732943535         5.023126125 C
atom     0.452305764         1.590643287         3.052639484 C
```

Supplementary Table 34 | Input geometry.in file of **[**S-2-Me-BuA]$_2$PbBr$_4$ *relaxed* structure

```
lattice_vector    15.38113645    -0.00000098     0.01624944
lattice_vector    -0.00000081     8.19245362     0.00001693
lattice_vector    -1.45316754     0.00001704     8.02970794

atom      7.30120631     2.19810871     2.00814229 Pb
atom      6.62661503     6.29427417     6.03776402 Pb
atom      7.66084041     4.81226958     0.57344358 Br
atom      6.26704472     0.71597550     7.47254622 Br
atom      7.08160300     7.78038232     3.47743899 Br
atom      6.84632531     3.68406353     4.56855280 Br
atom      4.30791094     2.46827145     1.35272149 Br
atom      9.61990462     6.56439556     6.69318173 Br
atom     10.27282127     1.99088023     2.68381575 Br
atom      3.65498313     6.08704176     5.36208518 Br
atom     10.01744639     6.96641336     1.80081778 N
atom      3.91051795     2.87019335     6.24517683 N
atom      4.74920526     5.67248071     2.24813745 N
atom      9.17876171     1.57623787     5.79786908 N
atom     10.07752683     7.94981115     2.15844310 H
atom      3.85045133     3.85360350     5.88756083 H
atom      9.01873820     6.74637574     1.64805725 H
atom      4.90923093     2.65013963     6.39792539 H
atom     10.46990371     6.92912321     0.85596298 H
atom      3.45808566     2.83291138     7.19004350 H
atom      4.31401278     5.72069405     3.20010195 H
atom      9.61400060     1.62443389     4.84590979 H
atom      5.75581409     5.86565076     2.38033628 H
atom      8.17216045     1.76942447     5.66562950 H
atom      4.65000929     4.69227760     1.89235535 H
atom      9.27794744     0.59604073     6.15368290 H
atom      3.08907097     5.33667570     0.05792033 H
atom     10.83891972     1.24043884     7.98806670 H
atom     11.68978626     7.23692325     4.07315974 H
atom      2.23821716     3.14067629     3.97278640 H
atom     10.72341253     5.03054431     2.17636138 H
atom      3.20454314     0.93433719     5.86967301 H
atom      9.85523957     5.78256982     3.52594821 H
atom      4.07274375     1.68630989     4.52007886 H
atom      4.03457399     7.61370633     1.88616853 H
atom      9.89338057     3.51747462     6.15983174 H
atom      4.90921911     6.87456109     0.53455980 H
atom      9.01874743     2.77832000     7.51143253 H
atom     12.62431558     7.89351866     1.90668516 H
atom      1.30357381     3.79739809     6.13914606 H
```

atom 13.06324091 6.21540312 1.51529276 H
atom 0.86476820 2.11934525 6.53071900 H
atom 13.91341030 7.09548648 2.80055661 H
atom 0.01456354 2.99920569 5.24539797 H
atom 1.52613267 6.63398055 2.35507438 H
atom 12.40179448 2.53776556 5.69089551 H
atom 2.25614549 5.03741133 2.41429463 H
atom 11.67181507 0.94119329 5.63169683 H
atom 1.65855218 7.62057236 7.07616684 H
atom 12.26943069 3.52428124 0.96985824 H
atom 2.05465939 8.21760178 0.34778445 H
atom 11.87328982 4.12137331 7.69823352 H
atom 0.01383918 6.99611035 7.22411281 H
atom 13.91414892 2.89983149 0.82187592 H
atom 12.88886863 4.47777419 3.52536910 H
atom 1.03902178 0.38160964 4.52065483 H
atom 11.63315987 4.75558058 4.72446805 H
atom 2.29481737 0.65925723 3.32161824 H
atom -0.10546707 4.75544613 1.89124934 H
atom 14.03344741 0.65926711 6.15467966 H
atom 0.84085007 4.29044272 0.46376816 H
atom 13.08718060 0.19425952 7.58217471 H
atom -0.00958292 5.84476025 0.50223831 H
atom 13.93758523 1.74856613 7.54367388 H
atom 13.07615673 6.36323540 5.96172816 H
atom 0.85202464 2.26686057 2.08410517 H
atom 14.40117130 6.12021521 4.79881150 H
atom -0.47308024 2.02417504 3.24703882 H
atom 13.86435550 4.78425258 5.82299735 H
atom 0.06360289 0.68797692 2.22301858 H
atom 2.85108093 6.21435932 0.68594350 C
atom 11.07689102 2.11812535 7.36005273 C
atom 11.92388881 6.41528835 3.37338865 C
atom 2.00408832 2.31907457 4.67258832 C
atom 10.60489533 5.96246727 2.74513103 C
atom 3.32307879 1.86624052 5.30087595 C
atom 4.16116633 6.68438434 1.31463808 C
atom 9.76680495 2.58815079 6.73135698 C
atom 12.93157436 6.93093523 2.33880059 C
atom 0.99638900 2.83477093 5.70714537 C
atom 1.80833693 5.77263934 1.72739350 C
atom 12.11962898 1.67642398 6.31858526 C
atom 0.88553155 7.32754305 7.79792250 C
atom 13.04244461 3.23126729 0.24808581 C
atom 12.47495659 5.24063407 4.20654328 C
atom 1.45302597 1.14439735 3.83946376 C

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atom      0.56599085      5.13629682      1.11146322 C
atom     13.36200612      1.04009935      6.93447955 C
atom     13.51357648      5.65149834      5.24821657 C
atom      0.41449184      1.55526504      2.79770690 C
```

Supplementary Table 35 | Input geometry.in file of $[S\text{-}1\text{-}1\text{-}NEA]_2PbBr_4$ *experimental* structure

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lattice_vector     19.3984513056    -1.2900429452     0.0000000000
lattice_vector      0.0000000000     8.7239398956     0.0000000000
lattice_vector      0.0000000000     0.0000000000     7.9297099113

atom       9.641612053   1.510046244   0.295936763 Pb
atom       9.756838799   5.923850536   4.260791779 Pb
atom      12.553319931   1.652980328   0.329082936 Br
atom       6.845130920   5.780917168   4.293937683 Br
atom       6.730292320   1.139565945   7.533065796 Br
atom      12.668158531   6.294331074   3.568210840 Br
atom       9.955090523   3.384039164   5.833094597 Br
atom       9.443360329   4.049857616   1.868239641 Br
atom       9.896895409   7.383561134   6.883226395 Br
atom       9.501555443   0.050336108   2.918371201 Br
atom      12.413069725   5.002093315   0.352079123 N
atom       6.985381603   2.431803703   4.316934109 N
atom      12.457685471   0.614474058   4.868049145 N
atom       6.940765858   6.819422722   0.903194010 N
atom      11.635830879   5.282348633   0.020966154 H
atom       7.762619495   2.151548386   3.985821247 H
atom      12.524977684   5.335539341   1.169378519 H
atom       6.873472691   2.098357916   5.134232998 H
atom      12.415881157   4.113163471   0.390815735 H
atom       6.982569695   3.320733309   4.355670452 H
atom      11.653154373   0.851398170   4.567798138 H
atom       7.745296955   6.582499027   0.602943480 H
atom      12.541486740   0.865219116   5.717987061 H
atom       6.856964111   6.568677902   1.753131986 H
atom      12.547500610  -0.268595070   4.808750629 H
atom       6.850950241   7.702491760   0.843895674 H
atom      13.334262848   5.213638306   6.466440201 H
atom       6.064188480   2.220258713   2.501585484 H
atom      13.422060013   0.969273090   3.117462158 H
atom       5.976390839   6.464623928   7.082317352 H
atom      12.357297897   2.927244902   3.694483519 H
atom       7.041152954   4.506651878   7.659338474 H
atom      13.887176514   3.224275589   3.524605513 H
atom       5.511274338   4.209621429   7.489460468 H
atom      13.269335747   3.089986563   4.959121704 H
atom       6.129114628   4.343910217   0.994266570 H
atom      12.689961433   7.327785015   7.282922745 H
atom       6.708489418   0.106112249   3.318068266 H
atom      14.199840546   7.329068661   6.861213207 H
atom       5.198610306   0.104827777   2.896358252 H
```

atom 13.809408188 7.239424229 0.447124630 H
atom 5.589043140 0.194472909 4.411979675 H
atom 14.659137726 1.695068002 6.339025974 H
atom 4.739313602 5.738829136 2.374171019 H
atom 14.406143188 4.341986656 1.724664330 H
atom 4.992307663 3.091910362 5.689519405 H
atom 14.697604179 0.084051155 1.971944571 H
atom 4.700846672 7.349845886 5.936799526 H
atom 14.955508232 5.708095551 5.254931450 H
atom 4.442943096 1.725800872 1.290076613 H
atom 16.693937302 5.638426304 3.767666817 H
atom 2.704513073 1.795470357 7.732522011 H
atom 18.387210846 7.500414371 1.413336158 H
atom 1.011240959 -0.066517107 5.378190994 H
atom 16.451961517 3.457935095 2.306641817 H
atom 2.946489334 3.975961685 6.271496773 H
atom 18.174970627 3.469150066 0.855520546 H
atom 1.223479986 3.964746714 4.820375443 H
atom 16.797817230 1.268065333 7.116470814 H
atom 2.600634336 6.165831566 3.151615620 H
atom 19.007299423 -0.554931343 3.482546091 H
atom 0.391150624 7.988827705 7.447401047 H
atom 18.364183426 0.361758202 5.726788521 H
atom 1.034267426 7.072138786 1.761933804 H
atom 16.269054413 -0.912991583 0.667776763 H
atom 3.129396915 8.346887589 4.632631779 H
atom 19.059404373 3.981951714 6.518617630 H
atom 0.339045912 3.451945305 2.553763151 H
atom 18.768970490 4.810560226 4.417268276 H
atom 0.629480124 2.623336792 0.452413738 H
atom 13.536238670 5.469156742 7.390489578 C
atom 5.862212181 1.964740634 3.425634623 C
atom 13.518780708 1.283698797 4.040187359 C
atom 5.879670143 6.150197506 0.075332217 C
atom 13.231683731 2.766668558 4.060011387 C
atom 6.166767597 4.667228222 0.095156476 C
atom 14.892190933 0.941114247 4.499317169 C
atom 4.506259918 6.492782593 0.534462512 C
atom 14.861152649 4.851503372 7.793318748 C
atom 4.537297726 2.582393646 3.828464031 C
atom 13.561457634 6.979338169 7.485646248 C
atom 5.836993694 0.454558641 3.520791292 C
atom 15.916429520 4.845009804 6.836996078 C
atom 3.482021570 2.588887215 2.872141123 C
atom 17.171508789 0.131749138 4.083800316 C
atom 2.226941586 7.302147388 0.118945532 C

atom	15.844655037	0.331654549	3.619912624 C
atom	3.553796291	7.102242470	7.584767342 C
atom	15.276280403	1.289828420	5.774414539 C
atom	4.122170448	6.144068718	1.809559703 C
atom	15.093935013	4.340503693	1.098264813 C
atom	4.304515839	3.093393564	5.063119411 C
atom	15.551737785	-0.057146166	2.311510324 C
atom	3.846712828	7.491043091	6.276365280 C
atom	15.770940781	5.350205421	5.520664215 C
atom	3.627509832	2.083691835	1.555809140 C
atom	17.192848206	4.337014198	7.216035843 C
atom	2.205603361	3.096882820	3.251181126 C
atom	16.814577103	5.320057869	4.630950451 C
atom	2.583873510	2.113838673	0.666095555 C
atom	17.761220932	-0.823481798	1.974497914 C
atom	1.637229204	8.257378578	5.939352989 C
atom	16.333496094	3.814893484	1.459066629 C
atom	3.064954996	3.619003773	5.423921585 C
atom	17.351915359	3.818702221	0.594728291 C
atom	2.046536207	3.615194559	4.559583187 C
atom	16.570156097	1.052858353	6.240681648 C
atom	2.828294039	6.381038666	2.275826693 C
atom	18.127851486	-0.446562380	3.203602791 C
atom	1.270598888	7.880459309	7.168457508 C
atom	17.499343872	0.502524674	5.415991783 C
atom	1.899107814	6.931372643	1.451136947 C
atom	16.496442795	-0.634683728	1.530434132 C
atom	2.902008772	8.068580627	5.495289326 C
atom	18.230665207	4.327319622	6.272400379 C
atom	1.167786241	3.106577635	2.307545662 C
atom	18.059957504	4.818488121	5.019506454 C
atom	1.338493228	2.615408421	1.054651260 C

Supplementary Table 36 | Input geometry.in file of $[S\text{-}1\text{-}1\text{-}NEA]_2PbBr_4$ *relaxed* structure

```
lattice_vector    -19.22478634     1.30473266    -0.00799337
lattice_vector     -0.22263015     8.76022728    -0.05995493
lattice_vector     -0.00001155    -0.05336867    -7.78810274

atom       9.50593812     1.50003325     0.36546718 Pb
atom       9.49653022     5.98829082     4.22849770 Pb
atom      12.47230089     1.70258061     0.36940363 Br
atom       6.53016465     5.78608346     4.23592853 Br
atom       6.58963852     1.10624420     7.39071586 Br
atom      12.41264112     6.42557760     3.45928448 Br
atom       9.81905105     3.43526691     5.74185315 Br
atom       9.18340664     4.07386910     1.84319306 Br
atom       9.59941380     7.33296797     6.94308129 Br
atom       9.40260747     0.19309142     3.09795210 Br
atom      12.22331687     5.03200861     0.34333408 N
atom       6.77895308     2.45658563     4.25592292 N
atom      11.30093523     5.34445073    -0.00988284 H
atom       7.70128140     2.13908767     3.90708419 H
atom      12.30137611     5.40913843     1.31505001 H
atom       6.70082186     2.09290384     5.23275105 H
atom      12.21558358     3.98408315     0.38328051 H
atom       6.78686365     3.50495152     4.28141400 H
atom      12.42260609     0.68726629     4.81846245 N
atom       6.57986929     6.80924040     0.88264800 N
atom      11.47885961     0.91314068     4.44734249 H
atom       7.52362101     6.57843367     0.51459224 H
atom      12.43646584     0.92632956     5.83260533 H
atom       6.56603435     6.58401363     1.89994597 H
atom      12.53851040    -0.34147674     4.67411702 H
atom       6.46383867     7.83591682     0.72429009 H
atom      13.31848564     5.59312937     7.23176407 C
atom       5.68373058     1.93669952     3.36328652 C
atom      13.01671771     5.27536003     6.22335128 H
atom       5.98553029     2.24063640     2.35062753 H
atom      13.48955528     1.42992922     4.04093780 C
atom       5.51298806     6.05595191     0.11532695 C
atom      13.32488176     1.12091105     3.00387203 H
atom       5.67764392     6.40418578     6.86224350 H
atom      13.22114294     2.92265567     4.14779348 C
atom       5.78149925     4.56484014     0.24255557 C
atom      12.26827173     3.19018311     3.67630208 H
atom       6.73435749     4.34431109     7.56278830 H
atom      14.02746998     3.47193342     3.65602370 H
atom       4.97515777     4.06222253     7.54652910 H
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atom 5.81097289 4.25148767 1.29258907 H
atom 14.88713693 1.04265465 4.49451704 C
atom 4.11539615 6.44927394 0.56362637 C
atom 14.66692203 4.98541123 7.57150000 C
atom 4.33533790 2.54910175 3.69466070 C
atom 13.31146772 7.11591642 7.30421951 C
atom 5.69060639 0.41504449 3.45654897 C
atom 12.32768514 7.50418629 7.01889348 H
atom 6.67434443 0.02281268 3.17654266 H
atom 14.07304690 7.53753865 6.64067878 H
atom 4.92898602 -0.01555436 2.79884065 H
atom 13.51702978 7.39282846 0.53914908 H
atom 5.48501775 0.09880193 4.48399755 H
atom 15.69822610 4.99516638 6.57671527 C
atom 3.30407913 2.52581261 2.70005496 C
atom 17.16418731 0.20163116 4.03136896 C
atom 1.83836016 7.28407596 0.08931857 C
atom 15.80992015 0.41885423 3.59177915 C
atom 3.19254958 7.11409621 7.44065826 C
atom 15.30962006 1.37421989 5.77066347 C
atom 3.69300984 6.13506072 1.84419058 C
atom 14.62287814 1.85230515 6.47027908 H
atom 4.37980470 5.66649962 2.55016817 H
atom 14.93652668 4.39468229 1.02643953 C
atom 4.06568291 3.10339059 4.93023298 C
atom 14.17240825 4.39025741 1.80065729 H
atom 4.82977645 3.11838002 5.70434423 H
atom 15.46827344 0.00163517 2.27824309 C
atom 3.53402688 7.51319260 6.12145556 C
atom 14.45766999 0.14904141 1.90569908 H
atom 4.54453837 7.36051298 5.75079074 H
atom 15.51367497 5.52238408 5.27281420 C
atom 3.48870243 1.98086666 1.40347870 C
atom 14.56170805 5.95995543 4.97750782 H
atom 4.44068721 1.53931974 1.11421503 H
atom 16.98174134 4.44103212 6.90226982 C
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atom 2.48166478 2.01174579 0.46493423 C
atom 16.34443092 5.89377385 3.34521933 H
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atom 1.27327004 8.26945386 5.70528467 C
atom 18.46443617 -1.18505995 1.19396897 H
atom 0.53785392 8.68536895 5.02152443 H

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atom 2.80314559 3.65723306 5.23734144 C
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atom 17.20842975 3.85889282 0.40916957 C
atom 1.79379663 3.63073344 4.30560414 C
atom 18.19262358 3.45154459 0.64139410 H
atom 0.80959948 4.04122116 4.53221982 H
atom 16.62460799 1.11596913 6.20665378 C
atom 2.37808214 6.39929701 2.27676236 C
atom 16.90410319 1.38596125 7.22209735 H
atom 2.09866879 6.14312635 3.29580212 H
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atom 19.13246427 -0.49383920 3.46298149 H
atom -0.12989882 8.02535523 7.29991102 H
atom 17.54084733 0.55868015 5.34852084 C
atom 1.46181570 6.94502718 1.41125636 C
atom 18.56967211 0.38583866 5.66682407 H
atom 0.43304802 7.12230969 1.72729226 H
atom 16.39712249 -0.58884033 1.44872904 C
atom 2.60510660 8.09234339 5.28406867 C
atom 16.10720905 -0.91688469 0.45332341 H
atom 2.89487993 8.40662478 4.28419311 H
atom 17.99127130 4.39722299 5.90867968 C
atom 1.01107388 3.11458592 2.02379430 C
atom 18.95575892 3.96411666 6.17522146 H
atom 0.04657407 3.55128897 2.28433982 H
atom 17.76937198 4.90200716 4.64762409 C
atom 1.23303592 2.59263159 0.76975868 C
atom 18.55675819 4.87026043 3.89410491 H
atom 0.44569902 2.61408678 0.01582451 H

Supplementary Table 37 | Input geometry.in file of [4AMP]$PbBr_4$ *experimental* structure

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lattice_vector      0.0000000000       0.0000000000      7.8298997879

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atom    11.049101830      5.042886734      1.264763713 Pb
atom     6.695898533      5.192112923      5.179713726 Pb
atom     2.699192047      2.117519140      1.106364727 Br
atom    15.045808792      8.117480278      5.021314621 Br
atom    11.571692467      8.117480278      1.106364727 Br
atom     6.173308849      2.117519140      5.021314621 Br
atom     2.005362511      8.041639328      1.455578446 Br
atom    15.739638329      2.193360090      5.370528221 Br
atom    10.877862930      2.193360090      1.455578446 Br
atom     6.867137909      8.041639328      5.370528221 Br
atom     4.134407520      5.317798615      3.632290602 Br
atom    13.610592842      4.917201042      7.547240257 Br
atom    13.006908417      4.917201042      3.632290602 Br
atom     4.738092899      5.317798615      7.547240257 Br
atom    17.085950851      5.089865208      2.626931429 Br
atom     0.659049332      5.145133972      6.541881084 Br
atom     8.213450432      5.145133972      2.626931429 Br
atom     9.531550407      5.089865208      6.541881084 Br
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atom    15.654640198      2.423648119      0.931757748 N
atom    10.962861061      2.423648119      4.846708298 N
atom     6.782139301      7.811351776      0.931757748 N
atom     2.965189695      2.689757586      5.650838852 N
atom    14.779810905      7.545241833      1.735888362 N
atom    11.837690353      7.545241833      5.650838852 N
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atom     2.290879488      7.816469193      3.898507118 H
atom    15.454121590      2.418530226      7.813457012 H
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atom     6.581620693      7.816469193      7.813457012 H
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atom     6.835374355      6.887131691      1.222247601 H
atom     3.781459808      2.461517096      5.376791954 H
atom    13.963541031      7.773482323      1.461842179 H
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atom     5.091040611      2.461517096      1.461842179 H
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atom 5.976515770 2.548514366 2.611271858 H
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atom 13.773669243 10.068169594 1.732756853 H
atom 12.843832016 10.068169594 5.647706985 H
atom 4.901169300 0.166830122 1.732756853 H
atom 3.488667250 10.005735397 4.207787991 H
atom 14.256333351 0.229264215 0.292838305 H
atom 12.361167908 0.229264215 4.207787991 H
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atom 15.990019798 9.812294006 2.439796448 H
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atom 7.117519855 0.422706097 2.439796448 H
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atom 17.645629883 2.209736347 0.644400358 H
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atom 15.604953766 8.336406708 0.068120234 H
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atom 13.718660355 2.186195612 1.485332012 H
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atom 1.022112012 9.982194901 3.716070414 H
atom 16.722888947 0.252804339 7.631020069 H

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atom 7.850388527 9.982194901 7.631020069 H
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atom 8.881373405 10.118320465 4.854537964 H
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atom 14.479920387 0.276345104 1.237124085 C
atom 12.137580872 0.276345104 5.152073860 C
atom 5.607419968 9.958654404 1.237124085 C
atom 1.948401213 0.441128492 5.394801140 C
atom 15.796600342 9.793870926 1.479851127 C
atom 10.820900917 9.793870926 5.394801140 C
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atom 0.786103547 8.472532272 5.073775291 C
atom 16.958896637 1.762467146 1.158825159 C
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atom 8.086397171 8.472532272 1.158825159 C
atom 1.955499172 1.870958447 4.932837009 C
atom 15.789502144 8.364041328 1.017886877 C
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atom 14.563322067 1.743020535 1.667769074 C
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atom 0.862407029 9.927949905 4.674450397 C
atom 16.882593155 0.307049692 0.759500325 C
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Supplementary Table 38 | Input geometry.in file of [4AMP]$PbBr_4$ *relaxed* structure

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atom     15.68094935      5.13225687      5.09703283 Pb
atom     11.12286815      5.13209523      1.24844512 Pb
atom      6.74651865      5.27157940      5.09713172 Pb
atom      2.72479633      2.15958309      1.10850786 Br
atom     15.14442065      8.24452439      4.95698359 Br
atom     11.65935360      8.24455946      1.10853594 Br
atom      6.20976690      2.15966920      4.95698647 Br
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atom     15.85282647      2.22026205      5.27665740 Br
atom     10.95099645      2.22042183      1.42820904 Br
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atom      4.10891710      5.39690151      3.62714214 Br
atom     13.76053481      5.00742984      7.47559864 Br
atom     13.04341393      5.00737573      3.62709019 Br
atom      4.82597936      5.39684922      7.47554460 Br
atom     17.15455515      5.16460596      2.47626169 Br
atom      0.71477029      5.23967781      6.32476058 Br
atom      8.22009061      5.23971866      2.47616183 Br
atom      9.64926139      5.16458748      6.32465846 Br
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atom     15.81308484      2.43175413      0.94060668 N
atom     10.99067159      2.43176666      4.78915587 N
atom      6.87850978      7.97247931      0.94056956 N
atom      3.02783615      2.72670165      5.55354439 N
atom     14.84131870      7.67751378      1.70500171 N
atom     11.96240019      7.67752128      5.55357107 N
atom      5.90675978      2.72672871      1.70499797 N
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atom     15.90554921      3.40956245      1.28468017 H
atom     10.89823501      3.40957329      5.13324180 H
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atom     13.85332222      7.94113041      1.46510879 H
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atom      4.91876179      2.46314141      1.46507247 H
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atom 11.87138242 6.67697290 5.30655951 H
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atom 9.96598748 8.02982719 5.02740281 H
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atom 16.89753269 0.21776929 7.35745617 H

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atom	17.99528445	10.20100762	0.98331047 H
atom	8.80848452	10.20104292	4.83175511 H
atom	9.06069196	0.20322380	0.98323833 H
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atom	14.56522704	0.30222465	1.17900910 C
atom	12.23849949	0.30222144	5.02752173 C
atom	5.63068363	10.10202360	1.17900150 C
atom	1.99184197	0.45220810	5.30021943 C
atom	15.87734158	9.95199669	1.45172044 C
atom	10.92642265	9.95200826	5.30022440 C
atom	6.94276229	0.45224319	1.45169688 C
atom	0.75211664	8.67181560	5.02139298 C
atom	17.11707489	1.73238280	1.17284586 C
atom	9.68668116	1.73239948	5.02137297 C
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atom	2.00637637	1.90621845	4.83660446 C
atom	15.86279219	8.49799153	0.98809399 C
atom	10.94094721	8.49799555	4.83661989 C
atom	6.92822808	1.90625250	0.98808549 C
atom	3.21436742	8.64637713	5.45868230 C
atom	14.65483827	1.75783842	1.61016500 C
atom	12.14892612	1.75783472	5.45868960 C
atom	5.72028150	8.64640581	1.61014519 C
atom	0.83535915	10.12750896	4.60126665 C
atom	17.03382369	0.27667712	0.75276372 C
atom	9.76990888	0.27670590	4.60125036 C
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Supplementary Table 39 | Input geometry.in file of $[NMA]_2PbBr_4$ *experimental* structure

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atom    20.665700912      4.528653622      7.954989910 Br
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atom    17.658262253      5.988162041      2.493790627 Br
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atom    25.565538406      6.030986786      6.331883907 C
atom    36.431564331      1.990936637      6.331883907 C
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atom    36.431564331      6.089163303      2.290083170 C
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atom    26.161123276      1.296855927      1.334602237 C
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Supplementary Table 40 | Input geometry.in file of $[NMA]_2PbBr_4$ *relaxed* structure

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atom 15.05223807 3.85527455 3.56739543 H
atom 25.79704829 4.17164708 7.58068160 H
atom 35.47630445 0.16071258 7.58031681 H
atom 5.37301971 7.86662210 3.56745174 H
atom 35.47574430 7.86894752 3.56667465 H
atom 5.37352008 0.15821349 7.58163020 H
atom 17.75642657 5.25644525 5.90366836 N
atom 23.09269588 2.77079545 1.88954834 N
atom 17.75641910 2.77058796 1.88976243 N
atom 23.09265055 5.25638364 5.90334162 N
atom 38.18063353 1.24594278 5.90310185 N
atom 2.66866790 6.78144312 1.89024443 N
atom 38.18019894 6.78425165 1.88920526 N
atom 2.66906099 1.24284986 5.90413831 N

Supplementary Table 41 | Input geometry.in file of $[PMA]_2PbCl_4$ *experimental* structure

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lattice_vector      0.0000000000     7.8169999123     0.0000000000
lattice_vector      0.0000000000     0.0000000000     7.7369999886

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atom    16.817499161     5.951159954     3.888616323 Pb
atom     0.000000000     5.774339676     0.020116201 Pb
atom     0.000000000     2.042659998     3.888616323 Pb
atom    16.817499161     0.665226698     5.180695057 Cl
atom    16.817499161     7.151773453     1.312195301 Cl
atom     0.000000000     4.573726654     5.180695057 Cl
atom     0.000000000     3.243273258     1.312195301 Cl
atom    19.676137924     2.112935066     7.583807468 Cl
atom    13.958859444     5.704064369     3.715307236 Cl
atom    19.676137924     5.704064369     3.715307236 Cl
atom    13.958859444     2.112935066     7.583807468 Cl
atom     2.858639240     6.021435261     7.583807468 Cl
atom    30.776359558     1.795564890     3.715307236 Cl
atom     2.858639240     1.795564890     3.715307236 Cl
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atom    16.817499161     4.346251965     6.292502403 Cl
atom    16.817499161     3.470747948     2.424002171 Cl
atom     0.000000000     0.437751949     6.292502403 Cl
atom     0.000000000     7.379248142     2.424002171 Cl
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atom    13.511179924     6.146507263     7.441446304 C
atom    20.123819351     6.146507263     7.441446304 C
atom    13.511179924     1.670492887     3.572946548 C
atom     3.306319714     5.578992844     3.572946548 C
atom    30.328678131     2.238007069     7.441446304 C
atom     3.306319714     2.238007069     7.441446304 C
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atom    21.600395203     1.786184430     3.930396080 C
atom    12.034602165     6.030815601     0.061896127 C
atom    21.600395203     6.030815601     0.061896127 C
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atom     4.782896519     5.694684505     3.930396080 C
atom    28.852102280     2.122315407     0.061896127 C
atom     4.782896519     2.122315407     0.061896127 C
atom    28.852102280     5.694684505     3.930396080 C
atom    22.185646057     0.973216474     4.803129673 C
atom    11.449353218     6.843783379     0.934629738 C
atom    22.185646057     6.843783379     0.934629738 C
atom    11.449353218     0.973216474     4.803129673 C
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atom 5.368146420 2.935283422 0.934629738 C
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atom 23.541133881 6.736690521 1.245657086 C
atom 10.093863487 1.080309391 5.114157200 C
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atom 6.723633289 2.828190804 1.245657086 C
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atom 24.301286697 5.771290779 0.618959427 C
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atom 7.483789921 1.862791061 0.618959427 C
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atom 23.739582062 4.902822495 7.504890442 C
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atom 6.922084332 0.994322419 7.504890442 C
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atom 22.380729675 5.055253983 7.174520016 C
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atom 28.071767807 1.146753788 7.174520016 C
atom 5.563229561 1.146753788 7.174520016 C
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atom 19.992643356 5.918250561 6.507590294 H
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atom 30.459854126 2.009750605 6.507590294 H
atom 3.175141573 2.009750605 6.507590294 H
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atom 13.810530663 7.058751106 7.575296402 H

atom 19.824468613 7.058751106 7.575296402 H
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atom 3.006970644 3.150250912 7.575296402 H
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atom 18.475704193 5.305397511 0.352033824 H
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atom 1.658203959 1.396897912 0.352033824 H
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atom 19.609203339 4.395498753 0.417798162 H
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atom 21.681119919 7.501974583 1.352427006 H
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atom 4.863617897 4.223525047 5.220927238 H
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atom 4.863617897 3.593474865 1.352427006 H
atom 28.771377563 4.223525047 5.220927238 H
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atom 23.927936554 7.311240196 1.862295985 H
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atom 7.110439777 3.402740002 1.862295985 H
atom 26.524560928 4.414259911 5.730795860 H

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atom 25.212795258 5.721261978 0.792269289 H
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atom 9.394253731 4.211017609 7.134287834 H
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atom 7.423244953 7.514482021 3.265787840 H
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atom 7.423244953 0.302518010 7.134287834 H
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atom 11.637709618 4.500247002 6.533896446 H
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atom 28.455209732 0.591746986 6.533896446 H
atom 5.179791451 0.591746986 6.533896446 H
atom 28.455209732 7.225252628 2.665396452 H
atom 19.340124130 2.584300041 4.424016476 N
atom 14.294875145 5.232699394 0.555516541 N
atom 19.340124130 5.232699394 0.555516541 N
atom 14.294875145 2.584300041 4.424016476 N
atom 2.522626400 6.492800236 4.424016476 N
atom 31.112373352 1.324199796 0.555516541 N
atom 2.522626400 1.324199796 0.555516541 N
atom 31.112373352 6.492800236 4.424016476 N

Supplementary Table 42 | Input geometry.in file of $[PMA]_2PbCl_4$ *relaxed* structure

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lattice_vector    -0.00561572    -0.07587350     7.60582442

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atom     16.64297545     1.77241332     6.79037032 Pb
atom     -0.00323312     2.01863699     2.96938559 Pb
atom     -0.00771034     5.63789967     6.80884448 Pb
atom     19.55231128     5.68978911     2.88306979 Cl
atom     13.73115547     1.99169678     6.64416719 Cl
atom     19.55390405     1.99615800     6.64973573 Cl
atom     13.72934378     5.68428244     2.87800035 Cl
atom      2.90760154     1.80236047     2.82344460 Cl
atom     30.37499183     5.87483199     6.69360607 Cl
atom      2.90274603     5.86038249     6.66751575 Cl
atom     30.37964383     1.81703931     2.84945293 Cl
atom     16.64529819     0.69824026     4.14863602 Cl
atom     -0.00204246     3.14524560     0.34931951 Cl
atom     -0.00559344     4.56295812     4.16774908 Cl
atom     16.64205083     4.32802008     5.41121559 Cl
atom     -0.00450454     0.44119749     5.35155008 Cl
atom     19.21934991     5.07166024     7.36316823 N
atom     14.06333681     2.59548400     3.53012227 N
atom     19.22392778     2.59997128     3.53527716 N
atom     14.06006000     5.06729306     7.35848951 N
atom      2.57088477     1.18333390     7.30367590 N
atom     30.71022754     6.48010558     3.57981581 N
atom      2.57130087     6.46512133     3.55332270 N
atom     30.70995020     1.19816847     7.32998938 N
atom     18.22359914     5.24636031     7.14132520 H
atom     15.05955087     2.42538712     3.30678232 H
atom     18.22845910     2.42881952     3.30933830 H
atom     15.05609771     5.24302462     7.13871262 H
atom      1.57506954     1.35785858     7.08210349 H
atom     31.70610033     6.30991649     3.35512078 H
atom      1.57580886     6.29419892     3.32751771 H
atom     31.70581934     1.37383971     7.10954072 H
atom     13.92919674     2.39849311     4.55040609 H
atom     19.35624444     2.40297241     4.55581517 H
atom     30.57676067     6.28268885     4.60007262 H
atom      2.70375804     6.26785273     4.57374169 H
atom     19.40777560     4.05902573     7.16977684 H
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atom     19.41102811     3.61658166     3.36259891 H
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atom 30.52196395 7.49649068 3.40697452 H
atom 2.75902097 7.48163751 3.38064717 H
atom 30.52262461 0.18540598 7.13608965 H
atom 20.10074378 5.96614969 6.54067035 C
atom 13.18382493 1.71719381 2.68835601 C
atom 20.10663003 1.72325558 2.69522944 C
atom 13.17978222 5.96118075 6.53417011 C
atom 3.45169562 2.07845906 6.48124790 C
atom 29.82934494 5.60259722 2.73868013 C
atom 3.45372947 5.58819906 2.71320225 C
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atom 4.75826202 3.98184906 4.45162821 H
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atom 25.77643258 5.97364637 4.14423919 C
atom 7.50522756 5.96328138 4.12182253 C
atom 25.77610666 1.69414614 7.90477410 C
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atom 25.17786157 2.19230447 4.47665215 H
atom 24.75657433 6.07005195 4.51584398 H
atom 8.52474248 6.06070649 4.49411482 H
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atom 23.66428744 3.00077968 3.16199081 C
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atom 23.33682526 6.59596911 8.42320177 C
atom 25.17231968 5.46700422 8.31279063 H
atom 8.10307451 5.45808397 8.29072745 H
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atom 6.68790003 2.70979984 8.36302942 C
atom 8.52350793 1.58092014 8.25291961 H
atom 24.75622768 1.59050170 8.27437374 H
atom 26.59079453 2.72090447 8.38589321 C
atom 21.40226096 7.53998891 8.31023567 H
atom 11.87219154 7.53270390 8.30160884 H
atom 4.75321154 3.65349582 8.24975656 H
atom 28.52474579 3.66626630 8.27403115 H
atom 23.70395265 7.28450519 9.18306927 H
atom 9.56778366 7.27566784 9.16673931 H
atom 7.05499783 3.39894318 9.12237030 H
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atom 19.35163286 5.24790226 8.38753409 H
atom 13.92525271 5.24382288 8.38240877 H
atom 2.70366958 1.35961118 8.32790800 H
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Supplementary Table 43 | Input geometry.in file of $(FC_2H_4NH_3)_2PbCl_4$ *relaxed* structure

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lattice_vector       0.0000000000       8.7524995804       0.0000000000
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