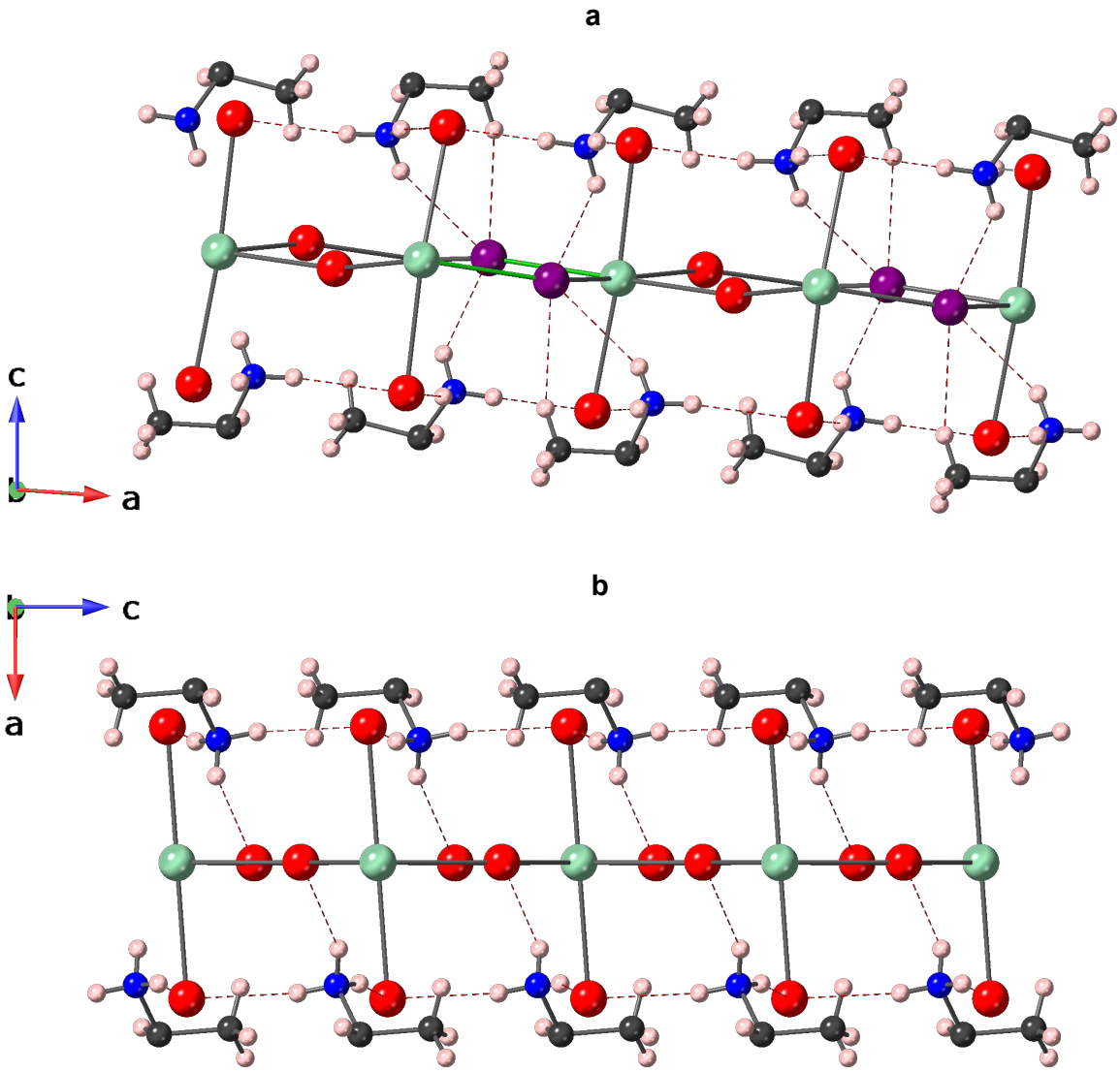
Supplementary Information

Organic-to-inorganic structural chirality transfer in a 2D hybrid perovskite and impact on Rashba-Dresselhaus spin-orbit coupling

Jana *et. al.*

Supplementary Figures



Supplementary Figure 1 | a,b, Hydrogen bonding interactions of axial and equatorial Br atoms with NEA^+ spacer cations in (**a**) R-NPB and (**b**) racemic-NPB. The dotted lines indicate the shortest H---Br contacts. Green, red/purple, black, blue and pink spheres denote Pb, Br, C, N and H atoms, respectively. See **Supplementary Table 2** for hydrogen bond distances and the main text for detailed discussion. Note that the hydrogen bonding interactions in S-NPB (not shown here) are analogous to those in R-NPB.

a S-NPB

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                    PLATON/ADDSYM for jmk157    P 21
ADDSYM Search on ALL NON-H Chemical Types [Max NonFit  0 Perc]
Criteria 0.30 Deg (Metric), 0.25 Ang (Rot), 0.25 Ang (Inv), 0.25 Ang (Transl)
Symm.  Input  Reduced  (Ang)       (Deg) Perc AvrDev.(Ang)          Input Cell
Elem Cell_Row Cell_Row   d  Typ Dot Angle Fit  MaxDev.            x     y     z
 2   [ 0 1 0] [ 1 0 0]  7.93  2  1     0  100       0  Through   1/2     0   1/2
  1                                                 0  Screw       0   1/2     0
  Reduced-to-Convent       Input-to-Reduced     T = Input-to-Convent:   a' = T a
(    0     1     0 )   (    0    -1     0 )   (    1     0     0 )     Det(T)
(   -1     0     0 ) X (    1     0     0 ) = (    0     1     0 )       =
(    0     0     1 )   (    0     0     1 )   (    0     0     1 )     1.000
Cell Lattice  a       b       c     Alpha   Beta  Gamma Volume CrystalSystem Laue
Input    mP  8.724   7.930  19.441  90.00  93.80  90.00   1342   monoclinic   2/m
Reduced  P   7.930   8.724  19.441  93.80  90.00  90.00   1342
Convent mP   8.724   7.930  19.441  90.00  93.80  90.00   1342   monoclinic   2/m
:: Origin Shifted to: 0.500, 0.000, 0.500 after Cell Transformation
:: SpaceGroup = P21         - No Obvious Spacegroup Change Needed/Suggested
```

b S-MBPI

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                    PLATON/ADDSYM for s-a-mepmapP 21 21 21
ADDSYM Search on ALL NON-H Chemical Types [Max NonFit  0 Perc]
Criteria 0.30 Deg (Metric), 0.25 Ang (Rot), 0.25 Ang (Inv), 0.25 Ang (Transl)
Symm.  Input  Reduced  (Ang)       (Deg) Perc AvrDev.(Ang)          Input Cell
Elem Cell_Row Cell_Row   d  Typ Dot Angle Fit  MaxDev.            x     y     z
 n * [ 1 0 0] [-1 0 0]  8.90  2  1  0.03  100   0.026  Through   1/2     0     0
                                    Pb1  -I4   0.079  Glide       0   1/2   1/2
 a * [ 0 1 0] [ 0 1 0]  9.31  2  1  0.03  100   0.026  Through     0   1/4     0
                                    Pb1  -I4   0.079  Glide     1/2     0     0
 m * [ 0 0 1] [ 0 0-1] 28.87  2  1  0.04  100   0.026  Through     0     0 0.001
                                    Pb1  -I4   0.079
-1 * ================================  100   0.026  at        1/4     0 0.251
                                    Pb1  -I4   0.079
  Reduced-to-Convent       Input-to-Reduced     T = Input-to-Convent:   a' = T a
(    1     0     0 )   (    1     0     0 )   (    1     0     0 )     Det(T)
(    0     0     1 ) X (    0     1     0 ) = (    0     0     1 )       =
(    0    -1     0 )   (    0     0     1 )   (    0    -1     0 )     1.000
Cell Lattice  a       b       c     Alpha   Beta  Gamma Volume CrystalSystem Laue
Input    oP  8.903   9.313  28.865  90.00  90.00  90.00   2393 orthorhombic   mmm
Reduced  P   8.903   9.313  28.865  89.97  89.98  89.99   2393
Convent oP   8.903  28.865   9.313  90.03  90.01  89.98   2393 orthorhombic   mmm
:: Origin Shifted to: 0.250, 0.251, 0.000 after Cell Transformation
Missed/Additional Symmetry : Suggested SPGR = Pnma       (No  62)
```
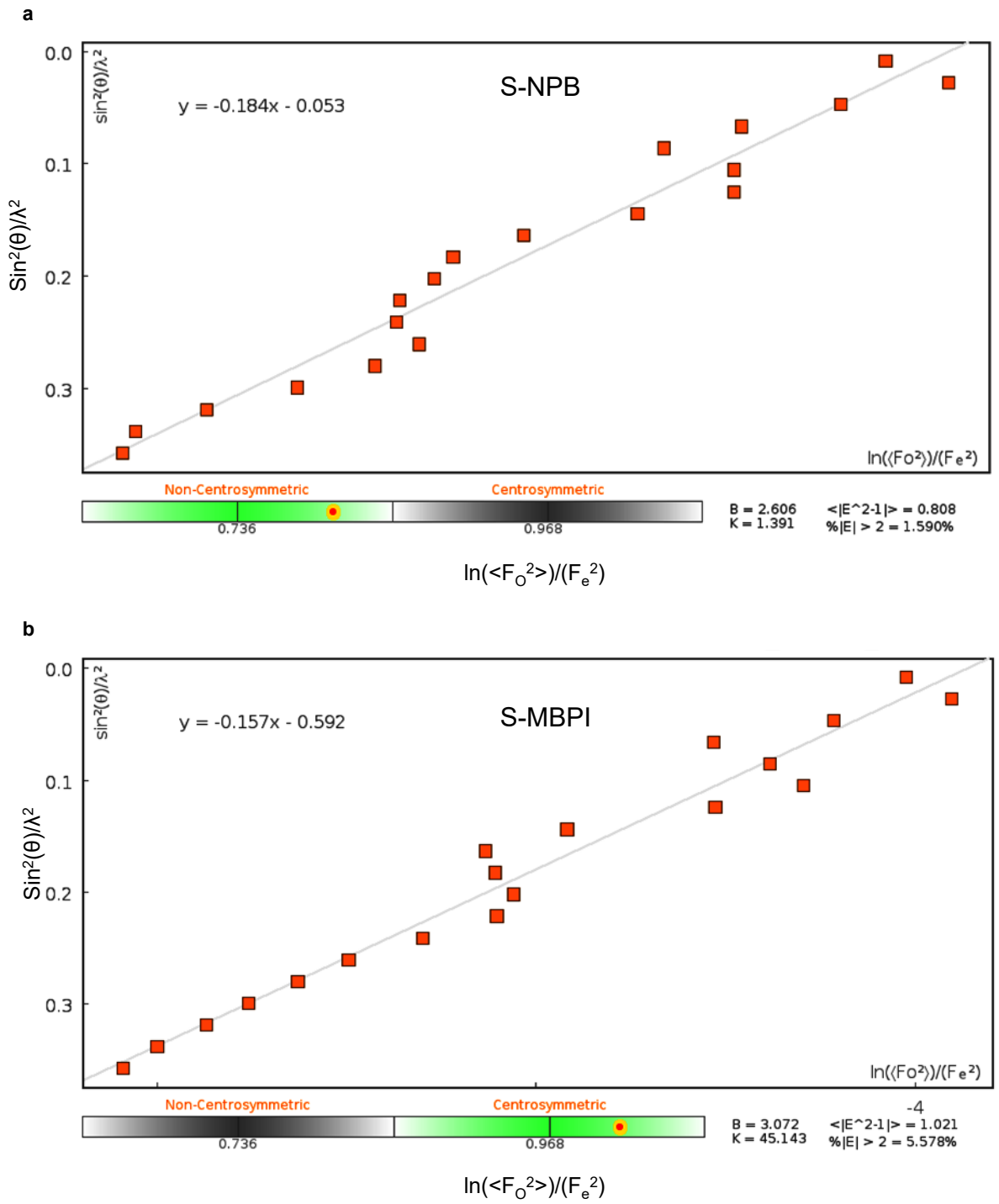
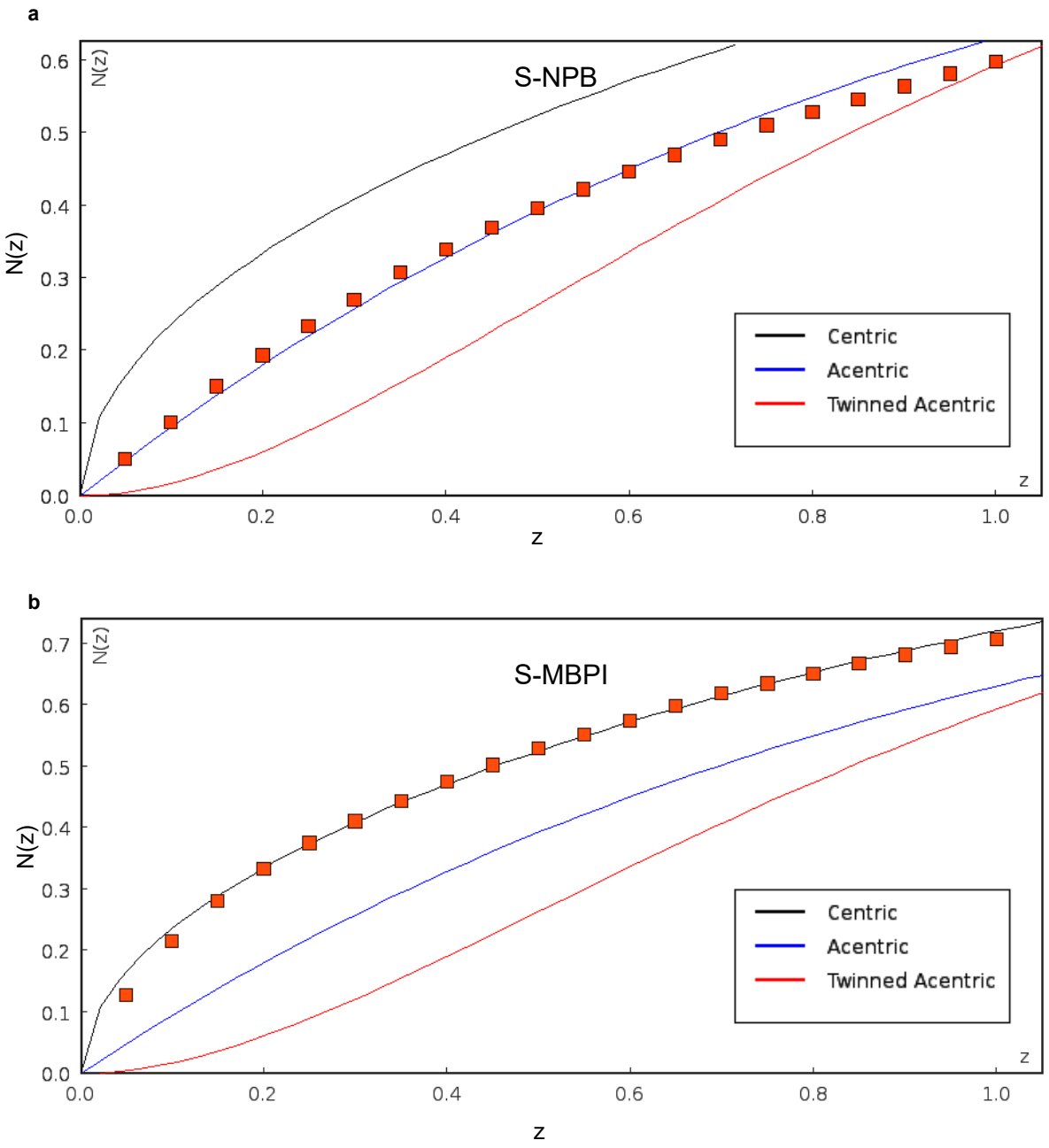
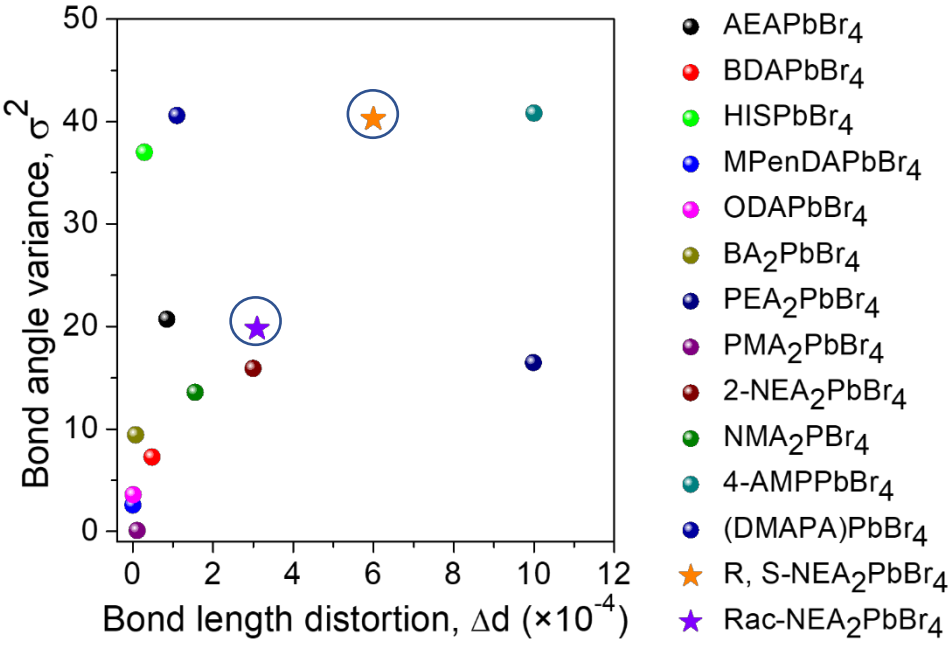

Supplementary Figure 2 | **a,b,** Post-refinement analysis for missing symmetry using PLATON's ADDSYM tool on isolated inorganic frameworks (i.e., without organic cations) in S-NPB (**a**) and S-MBPI (**b**). All the C, H, and N atoms were manually deleted from the fully refined structure using the CrystalMaker software. The remaining lead halide framework is exported into a CIF file for PLATON symmetry analysis. The analysis includes all Pb and Br/I atoms in the search (i.e., maximum allowed non-fitting atoms = 0 %). Default values of angle criterium (i.e., 0.3° for lattice metrical symmetry) and distance criterium (i.e., 0.25 Å for coinciding atoms for rotational, inversion and translational symmetry elements) were used in the symmetry search. For the lead bromide framework in S-NPB (**a**), there is no change from the original $P2_1$ space group, whereas for the lead iodide framework in S-MBPI (**b**), the PLATON analysis suggests an alternative centrosymmetric *Pnma* space group instead of the input $P2_12_12_1$ (see lowest line in (**b**)).



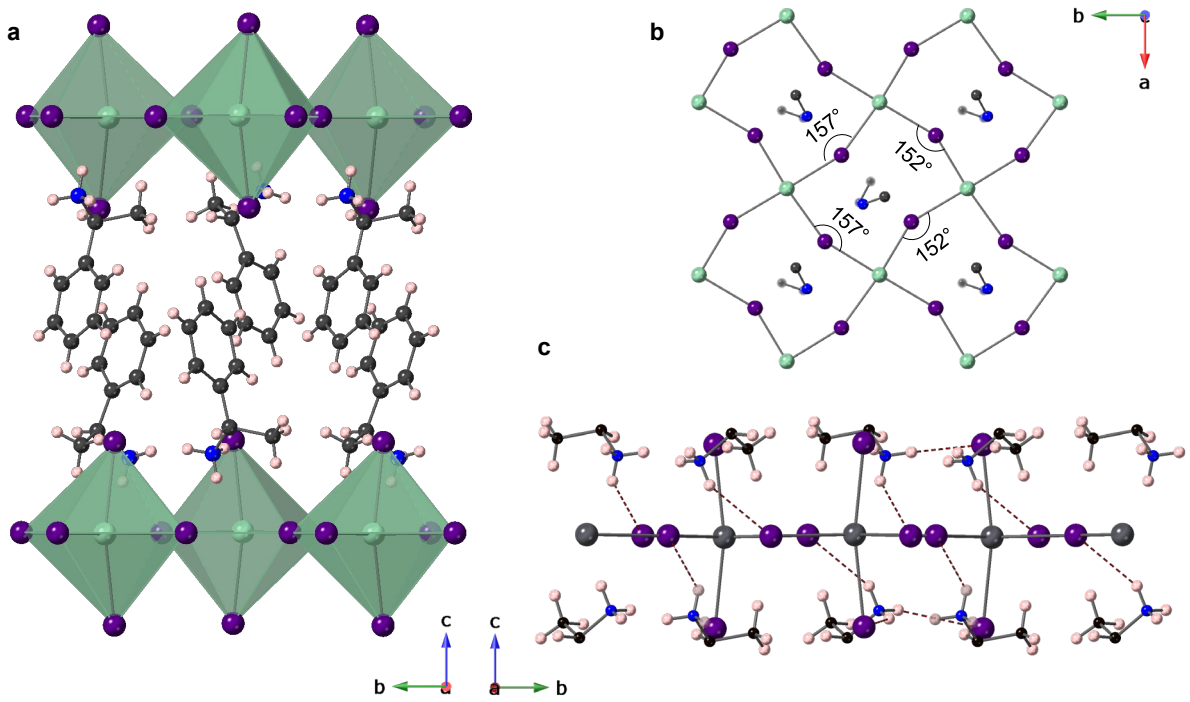
Supplementary Figure 3 | a, b, Wilson statistics obtained during the data reduction of 298 K single-crystal X-ray diffraction data for S-NPB (**a**) and S-MBPI (**b**). The statistics give $\langle E^2-1 \rangle$ values of 0.808 for S-NPB (i.e., corresponding to a noncentrosymmetric space group) and 1.021 for S-MBPI (i.e., corresponding to a centrosymmetric space group). Note that the inorganic framework comprising the heavy Pb and Br/I atoms scatters X-rays more strongly than the organic framework, and the Wilson statistics therefore preferentially reflect the inorganic framework symmetry. The Wilson statistics results for R-NPB vs. R-MBPI are analogous to the above.



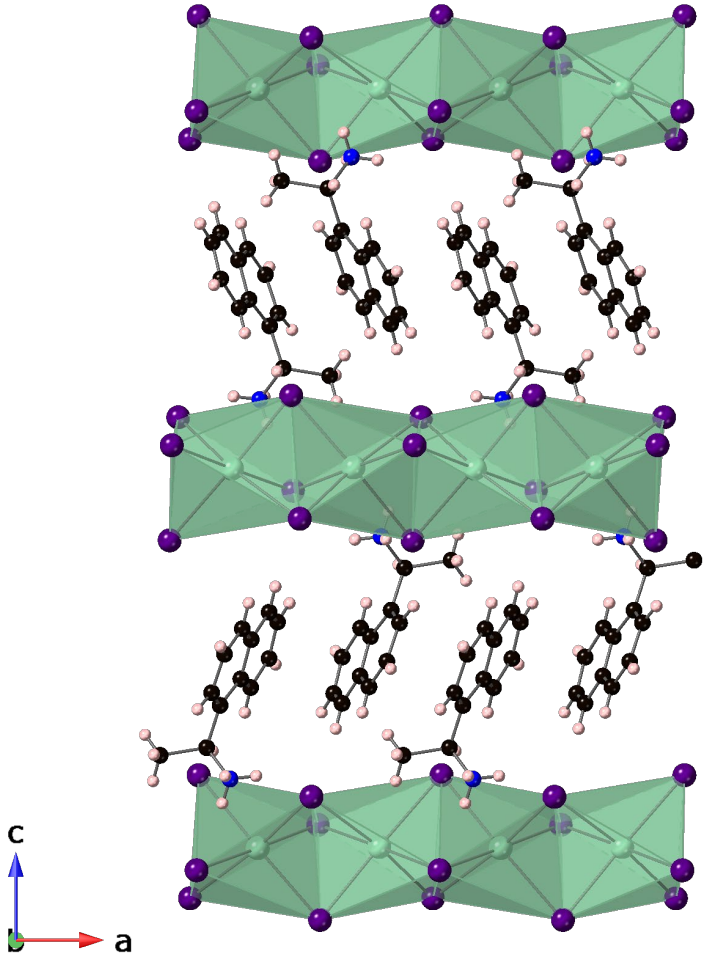
Supplementary Figure 4 | a,b, The cumulative intensity distribution of the 298 K single-crystal X-ray diffraction data for S-NPB (**a**) and S-MBPI (**b**). The X-ray reflections are fit to an acentric distribution in S-NPB and to a centric distribution in S-MBPI. Note that the inorganic framework comprising the heavy Pb and Br/I atoms scatters X-rays more strongly than the organic framework, and the cumulative intensity distribution therefore preferentially reflects the inorganic framework symmetry. The cumulative intensity distributions for R-NPB vs. R-MBPI are analogous to the above.



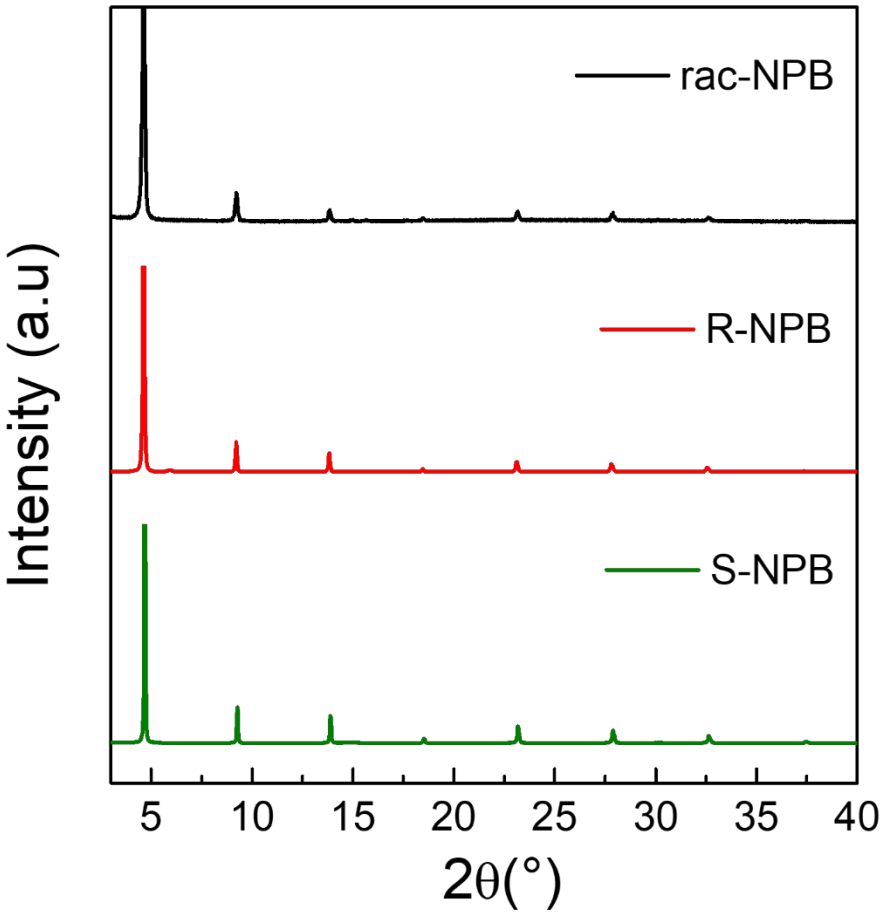
Supplementary Figure 5 | A plot of bond length distortion (Δd) vs. bond angle variance (σ^2), computed based on single-crystal X-ray structures of various 2D lead bromide based HOIPs reported in the literature including the racemic-, R- and S-NPB studied here. **AEA**: 3-(2-ammonioethyl)anilinium[1]; **BDA**: 1,4-butyldiammonium[1]; **HIS**: histammonium[1]; **MPenDA**: 2-methyl-1,5-pentanediammonium[1]; **ODA**: 1,8-diammoniooctane[1]; **BA**: n-butylammonium[1]; **PEA**: phenethylammonium[2]; **PMA**: phenylmethylammonium[3]; **2-NEA**: 2-(2-naphthyl)ethanammonium[3]; **NMA**: 1-(2-naphthyl)methanammonium[3]; **4-AMP**: 4-(aminomethyl)-piperidine[4]; **DMAPA**: 3-(dimethylamino)-1-propylamine[5]; **R/S/Rac-NEA**: R-/S-/rac- 1-(1-naphthyl)ethylammonium (this work).



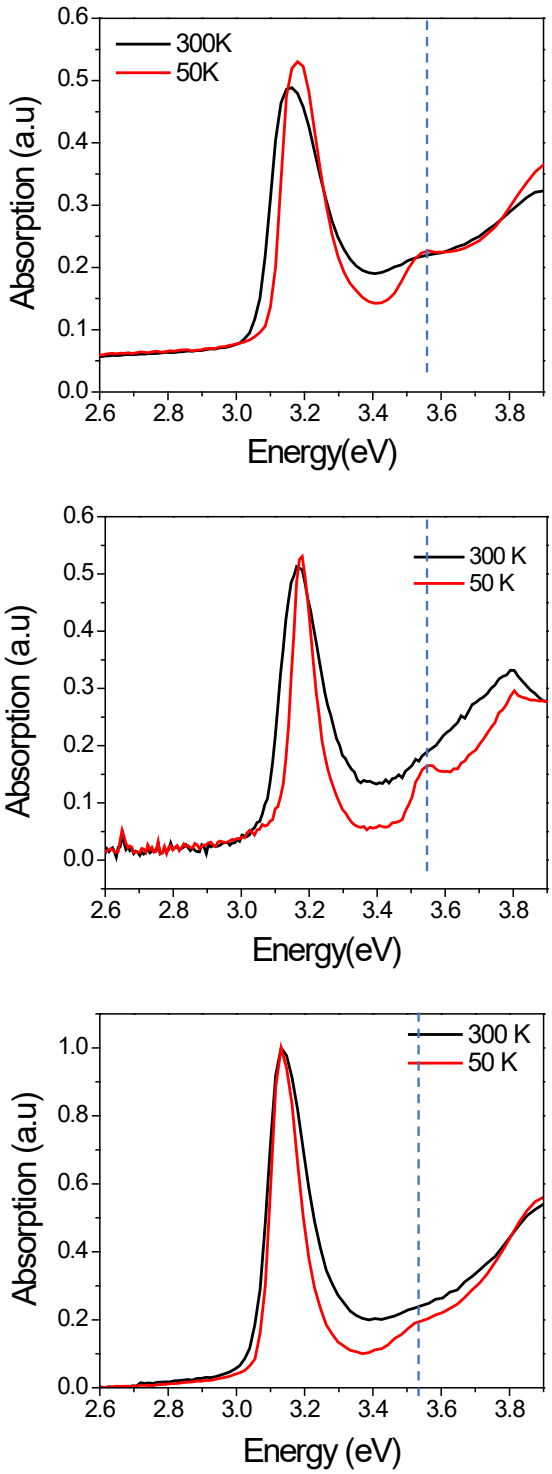
Supplementary Figure 6 | a, Schematic representation of single-crystal X-ray structure of S-MBPI at 298 K. **b**, In-plane view of a single perovskite $[PbI_4]^{2-}$ layer showing two equatorial Pb-I-Pb angles of 152° and 157°. Also shown are the organic terminal -CH-NH_3^+ groups represented as solid and shaded dumbbells for the upper and lower organic layers, respectively. **c**, Hydrogen bonding interactions of equatorial I atoms with -NH_3^+ groups, with alternating H…I contacts of 2.838 Å and 3.088 Å. Axial I atoms are omitted in (**b**) for clarity. Pb, I, C, N, H are denoted as green, purple, black, blue and pink spheres, respectively. Refer to **Supplementary Table 2** for complete list of hydrogen bonding parameters.



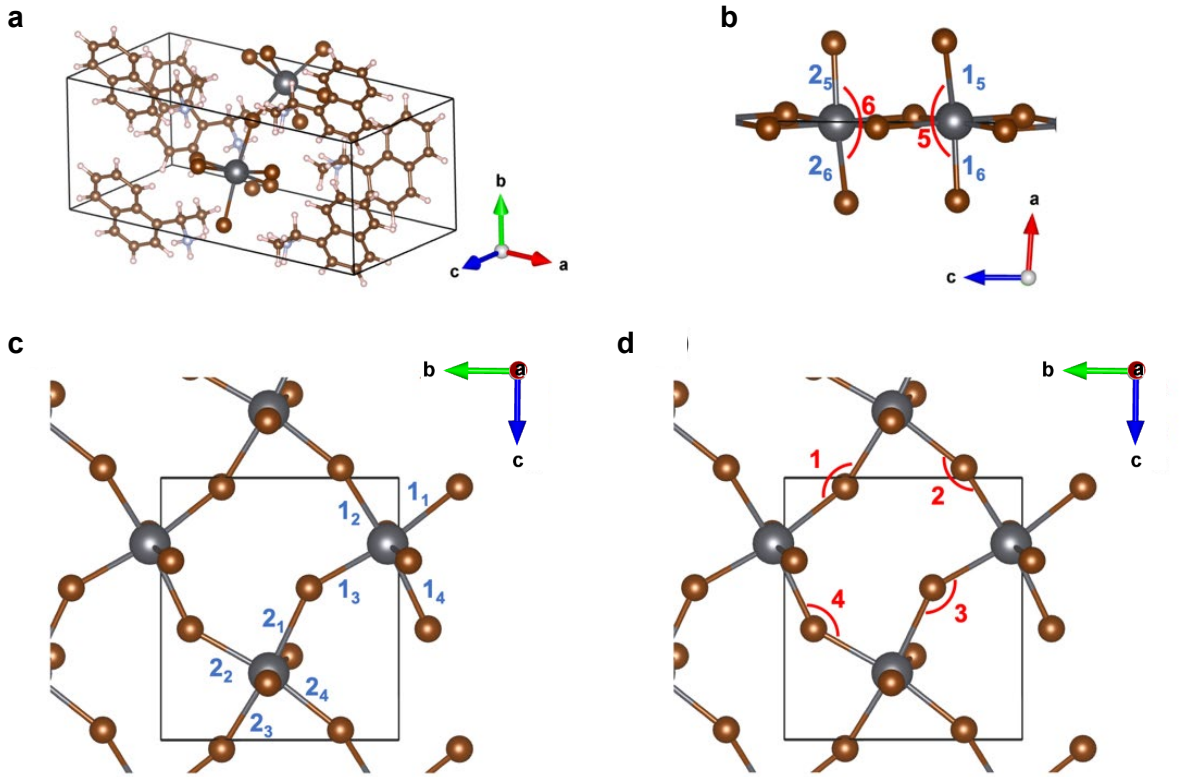
Supplementary Figure 7 | Schematic single-crystal X-ray structure of 1D S-$NEA_2Pb_2I_6$ at 298 K. 1D chains of face-sharing PbI_6 octahedra are separated by NEA^+ (1-(1-napthyl)ethylammonium) cations. Pb, I, C, N, H are denoted as green, purple, black, blue, and pink spheres, respectively.



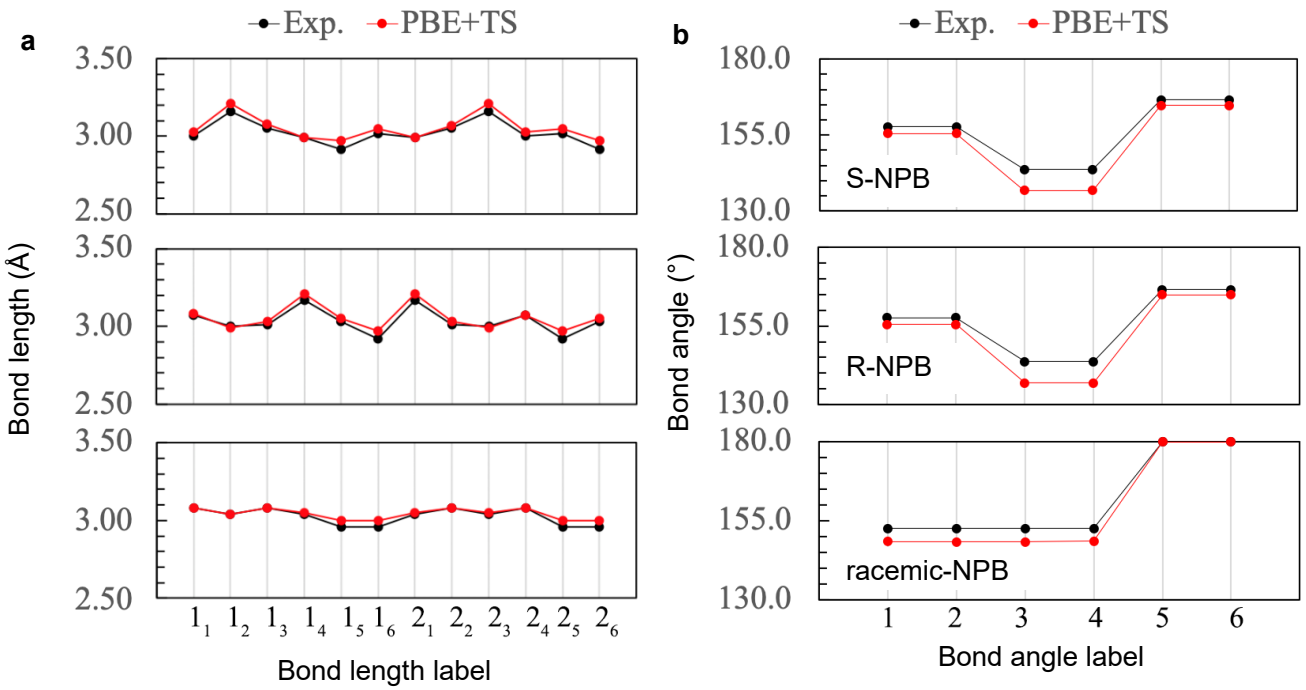
Supplementary Figure 8 | Powder X-ray diffraction patterns of spin-coated thin films of racemic-, R- and S-NPB.



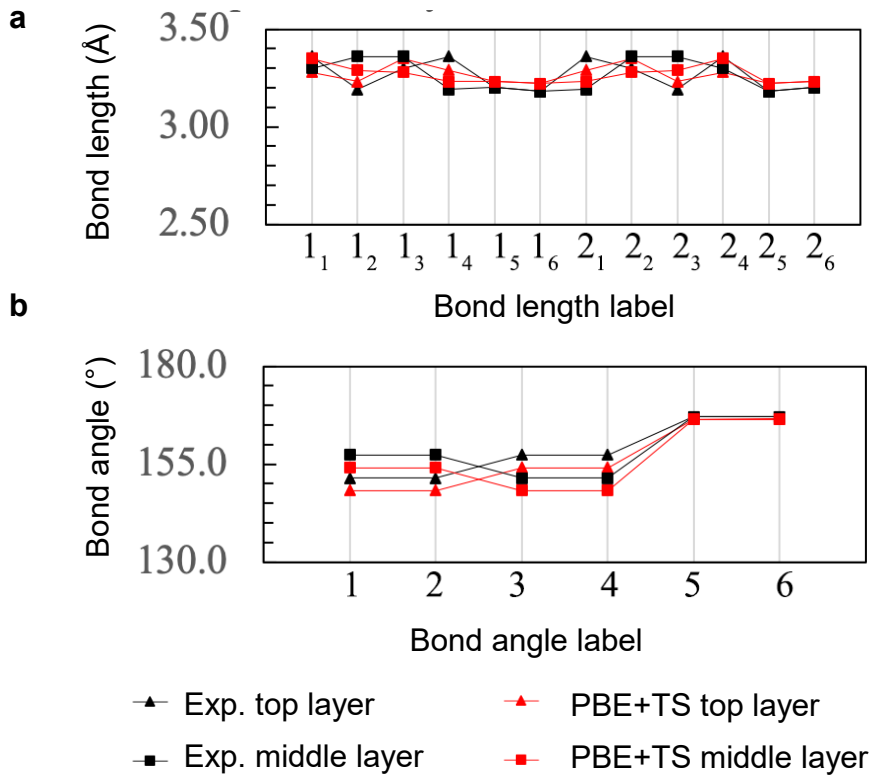
Supplementary Figure 9 | a-c, Thin-film linear absorption spectra of R-NPB (**a**), S-NPB (**b**) and racemic-NPB (**c**) at 300 K and 50 K. The dotted lines indicate the continuum band-edges, which are at 3.54(2) eV for the R- and S-NPB and 3.52(2) eV for the racemic-NPB. The band-edge energy is estimated from the photon energy of the maximum (indicated by the dashed lines) in the step-like feature preceding the excitonic band in the 50 K spectra.



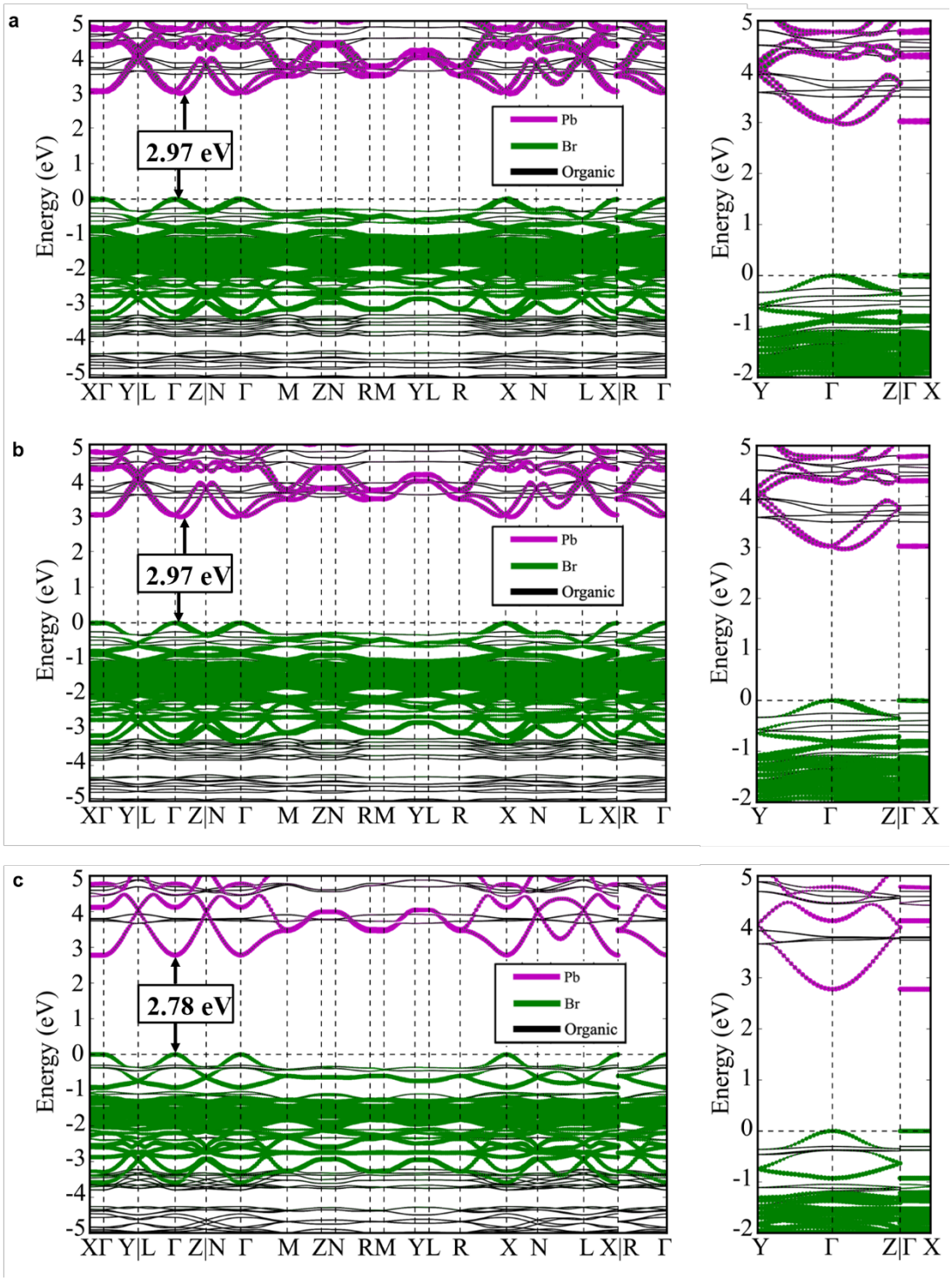
Supplementary Figure 10 | a-d, Illustration of the bond length and bond angle labels used in geometry comparison between experimental and relaxed structures. Relaxed S-NPB structure serves as the example here. **a**, DFT-PBE+TS relaxed S-NPB unit cell. **b**, Side view of the inorganic layer along *b*-axis. **c**,**d**, Top-views of the inorganic layer along *a*-axis. The labels of bond lengths are colored in blue and bond angles are colored in red.



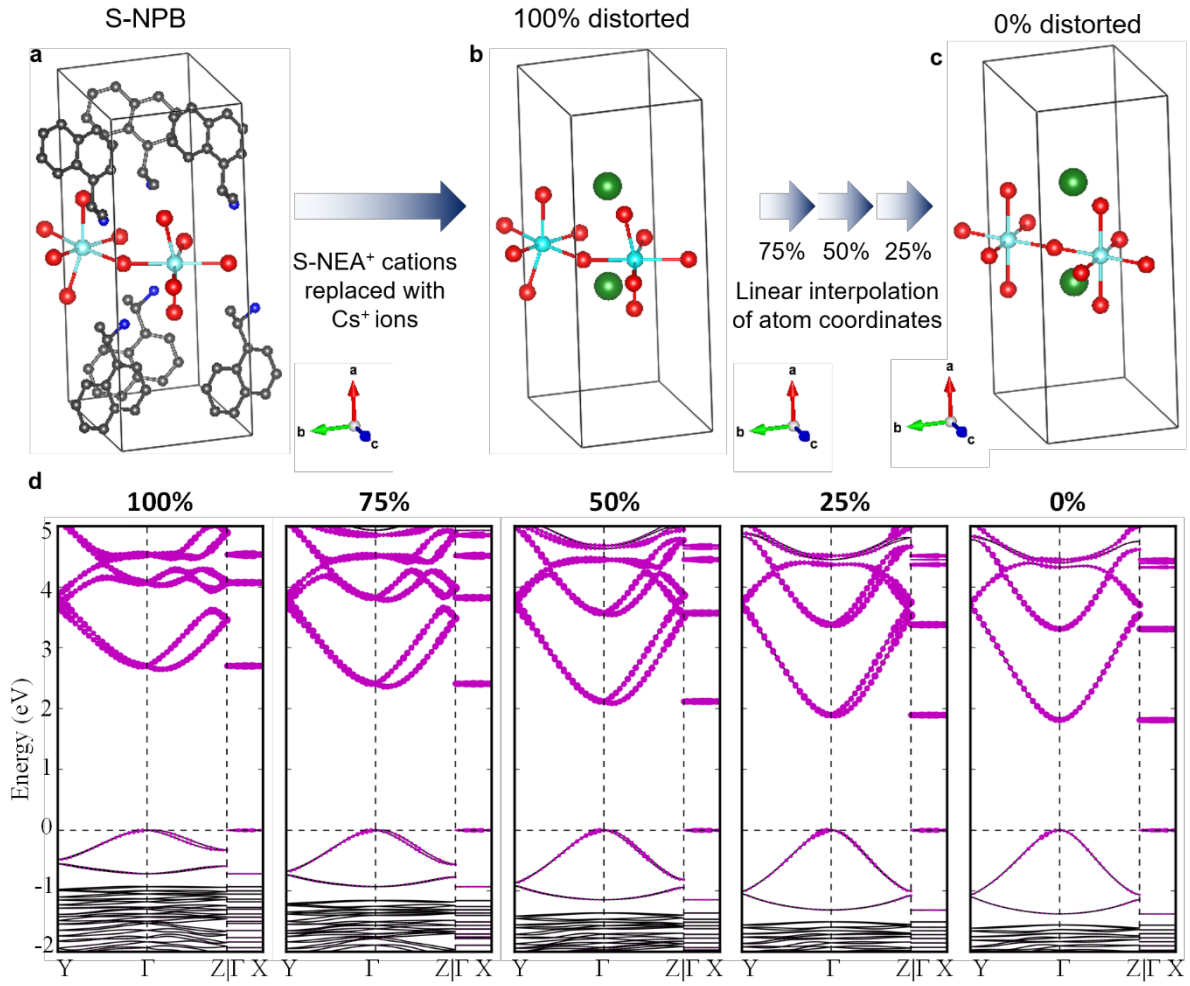
Supplementary Figure 11 | a, b, Comparison of (**a**) bond lengths and (**b**) bond angles between experimental (black data points) and DFT-PBE+TS relaxed (red data points) structures of R-, S-, and racemic-NPB. The label notations in (**a**) and (**b**) are the same as in **Supplementary Figure 10.** The agreement between theory and experiment is very good.



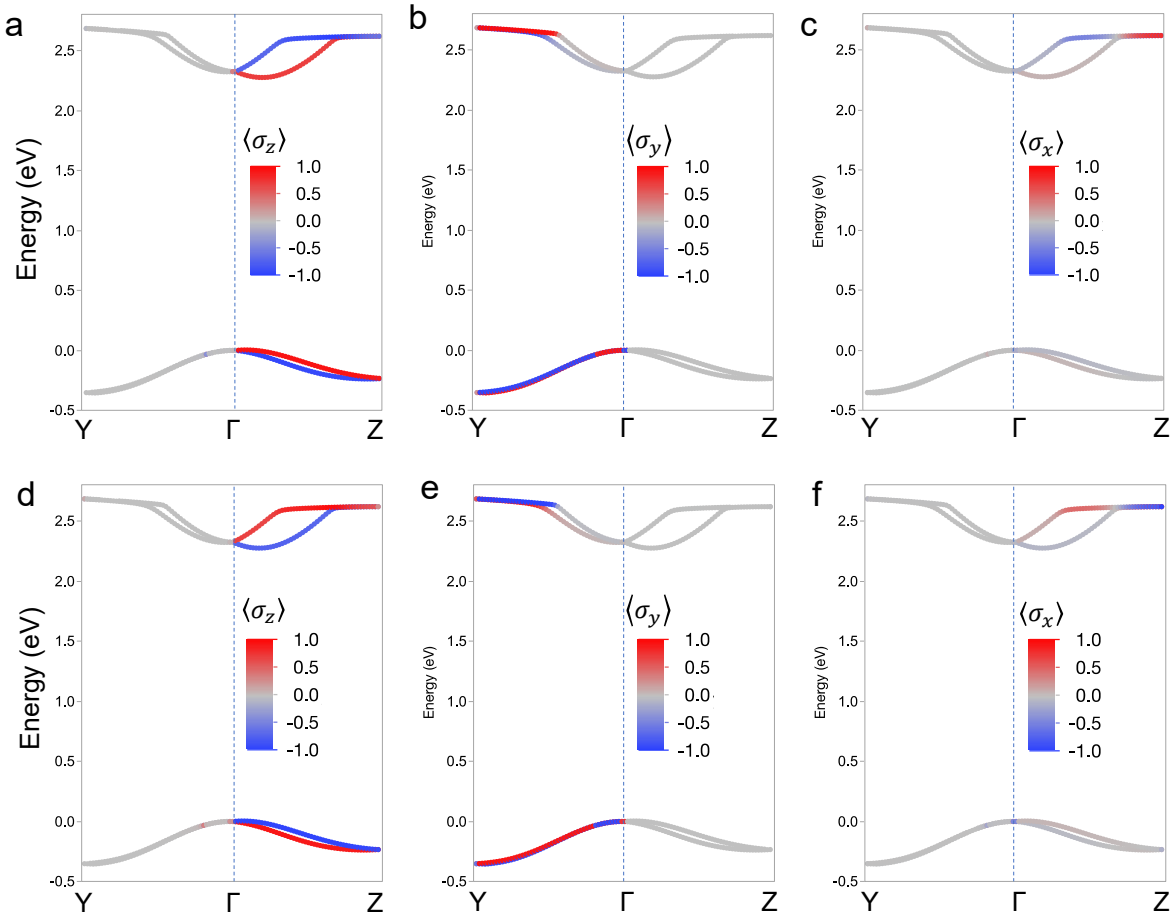
Supplementary Figure 12 | a, b, Geometry comparisons of (**a**) bond lengths and (**b**) bond angles in the perovskite layer between the experimental and DFT-PBE+TS relaxed structures of S-MBPI. The two inorganic layers in the unit cell of S-MBPI are labelled as 'top layer' and 'middle layer'. The label notations in (**a**) and (**b**) are the same as in **Supplementary Figure 10.** The agreement between theory and experiment is very good.



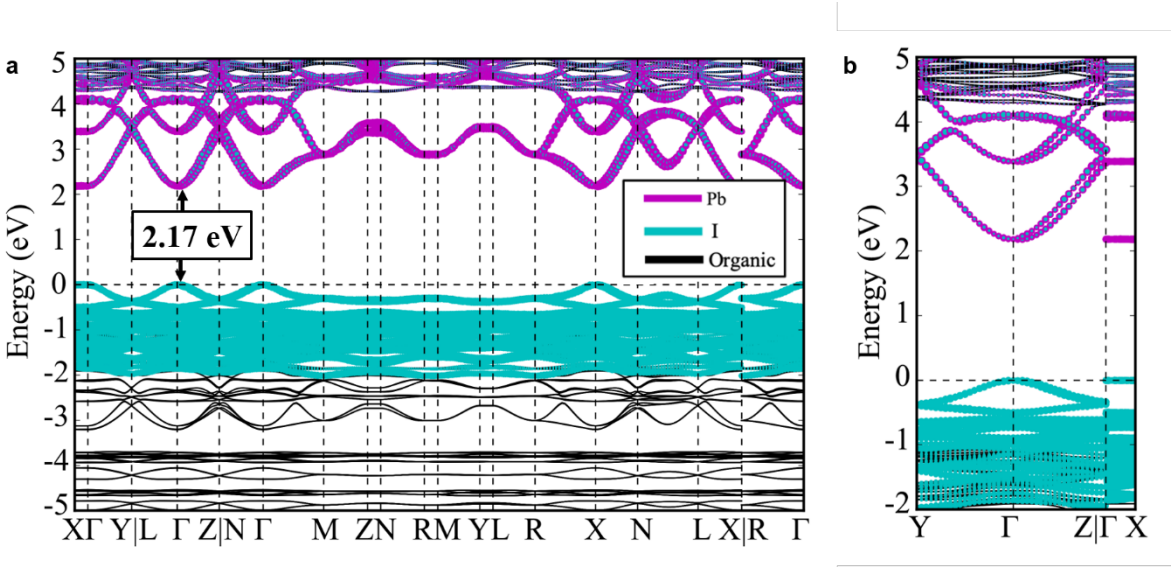
Supplementary Figure 13 | a-c, DFT+HSE06+SOC electronic band structures of (**a**) S-NPB, (**b**) R-NPB and (**c**) racemic-NPB for all the k-paths. The contributions of Pb (purple), Br (green) and organic-derived states (black) to the band structure are indicated. CB minima and VB maxima are pointed out by black arrows and the size of the band gap is shown for each structure.



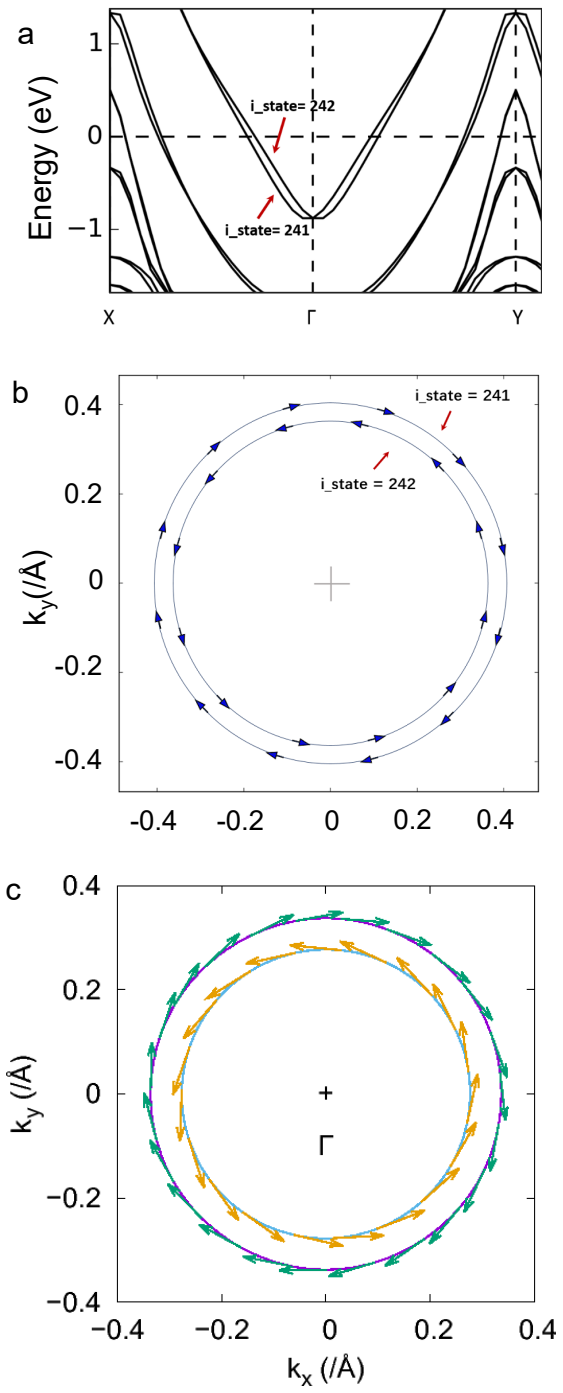
Supplementary Figure 14 | a, Original S-NPB relaxed structure. **b,** S-NEA$^+$ cations in (**a**) are replaced with Cs^+ ions maintaining the original octahedral distortions (denoted as 100%). **c**, An ideal structure where the octahedral distortions in (**b**) are artificially removed (denoted as 0%). By interpolation of the atomic coordinates between the ideal and the distorted structure, intermediate structures with gradually decreasing distortions (75%, 50%, 25%) are generated similarly. **d**, HSE06+SOC band structures calculated for the as-generated structures corresponding to 100%, 75%, 50%, 25%, and 0% octahedral distortions with respect to the original S-NPB structure. Note that the RD splitting along Γ-Z path gradually disappears upon going from 100% to 0% octahedral distortions. Cyan, red, black, blue, and green spheres denote Pb, Br, C, N, and Cs atoms, respectively.



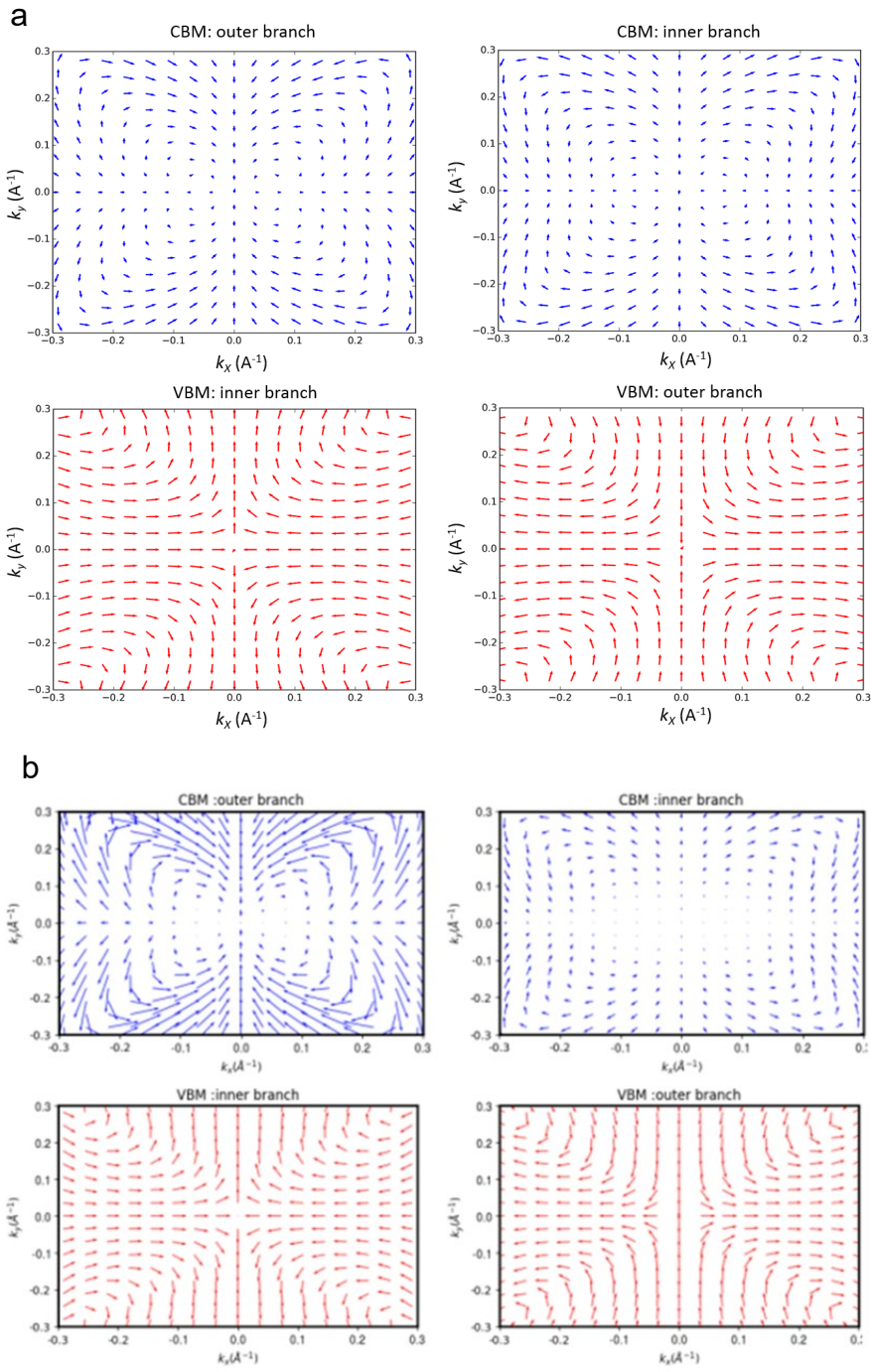
Supplementary Figure 15 | PBE+SOC band structures of (**a-c**) R-NPB and (**d-f**) S-NPB showing the spin polarization of frontier conduction and valence bands. The color bars give the magnitudes of $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$, and $\langle\sigma_z\rangle$, which are the expectation values of the Pauli spin matrices, σ_i (i=x,y,z). Here, x and y point along the two in-plane directions of the perovskite layer and z points along the layer-stacking direction. Note that along the spin splitting direction (i.e., the Γ-Z path), the dominant spin component is σ_z (**a, d**); the other two components are vanishingly small in line with a 1D RD picture, as previously noted for a related 2D HOIP, PMA_2PbCl_4.[6] Notably, owing to opposite structural chiralities of perovskite layers in R- and S-NPB, the spin polarization of conduction and valence spin subbands is opposite between R-NPB (**a**) and S-NPB (**d**), as clearly seen from the opposite signs of the respective σ_z components.



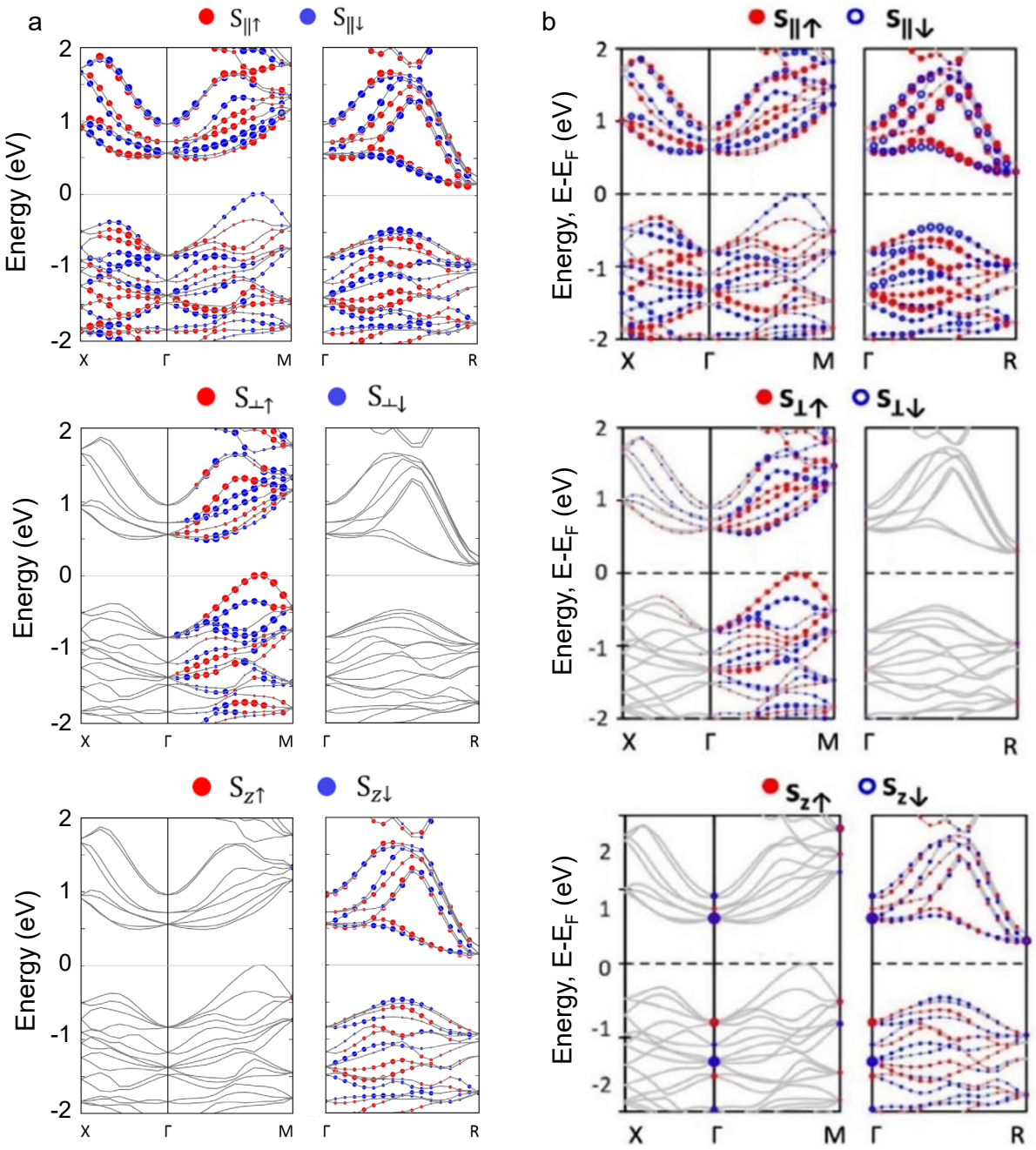
Supplementary Figure 16 | The DFT+HSE06+SOC (**a**) full band structure of S-MBPI and (**b**) selected extract along k-paths Y-Γ, Γ-Z and Γ-X showing a much lower RD splitting in this compound relative to R- and S-NPB. The contributions of Pb (purple), I (cyan) and of the organic component (black) to the band structure are indicated. CB minima and VB maxima are pointed out by black arrows and the size of the band gap is given.



Supplementary Figure 17 | a, Rashba splitting in the LDA band structure of the Au(111) surface. **b,** spin texture of the 241st and 242nd band at the Fermi surface, obtained from FHI-aims. **c,** spin texture of the 55th and 56th bands (corresponding to the 241st and 242nd bands in (**b**)) at the Fermi surface, reported using the OpenMX code (references 7-9).



Supplementary Figure 18 | a, The spin textures of the inner and outer branches of the valence (red) and conduction (blue) bands of (4-BrBzA)$_2$PbI$_4$. Arrow length denotes the magnitude of the spin polarizations in the k_x – k_y plane. **b,** The corresponding spin textures reported by reference 10. Both results were calculated using the PBE functional. Panel (**b**) is adapted from reference 10. © 2020, American Chemical Society.



Supplementary Figure 19 | a, The LDA spin textures of bulk IrBiSe, calculated using FHI-aims. $S_{\parallel}$ is the spin projection along the k-direction; $S_{\perp}$ is the spin projections perpendicular to the k-direction; S_z is the z component of the spin polarization, which is also along k_z-direction. The symbol sizes are proportional to the magnitude of the spin polarizations. **b,** The corresponding spin texture results in reference 11. Note that the net spin polarizations for all the degenerate bands at Γ point should be exactly zero. The visually red and blue dots at Γ in the right panel are simply leftovers due to the plotting style (each red/blue dot is overwritten by the blue/red dot of the other degenerate band, and their sum is zero). Panel (**b**) is adapted from reference 11.

Supplementary Tables

Supplementary Table 1 | Crystallographic and structural refinement data for R-, S- and racemic-NPB at 298 K

Empirical formula	R-$C_{24}H_{28}N_2PbBr_4$	S-$C_{24}H_{28}N_2PbBr_4$	Racemic-$C_{24}H_{28}N_2PbBr_4$
Formula weight	871.31	871.31	871.31
Temperature/K	298	298	298
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2₁*	*P2₁*	*P2₁/c*
a/Å	8.7569(2)	8.7537(2)	19.2528(9)
b/Å	7.9611(2)	7.9550(2)	8.0769(4)
c/Å	19.5188(6)	19.5038(5)	8.7280(5)
α/°	90	90	90
β/°	93.773(2)	93.806(2)	90.281(3)
γ/°	90	90	90
Volume/Å^3	1357.78(6)	1355.17(5)	1357.21(12)
Z	2	2	2
ρ_{calc}g/cm^3	2.131	2.135	2.132
μ/mm^{-1}	12.113	12.136	12.118
F(000)	816.0	816.0	816.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.182 to 61.868	4.186 to 52.728	5.47 to 53.128
Reflections collected	17623	18140	2783
Independent reflections	6685 [R_{int} = 0.0297, R_{sigma} = 0.0336]	5520 [R_{int} =0.0477, R_{sigma} = 0.0368]	2783 [R_{int} = 0.0436, R_{sigma} = 0.0395]
Data/restraints/parameters	6685/1/284	5520/1/236	2783/0/133
Goodness-of-fit on F^2	1.000	1.045	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0797	R_1 = 0.0472, wR_2 = 0.1167	R_1 = 0.0483, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0812	R_1 = 0.0563, wR_2 = 0.1248	R_1 = 0.0581, wR_2 = 0.1271
Largest diff. peak/hole / e Å^{-3}	1.62/-1.36	2.03/-2.13	3.64/-1.83
Flack parameter	-0.018(7)	-0.023(11)	

Supplementary Table 2 | Experimental hydrogen bonding parameters based on 298 K single crystal X-ray structures for various 2D HOIPs studied in this work. The subscripts 'eq' and 'ax' denote equatorial and axial, respectively.

Compound	H-bond	length (Å)	angle at H (°)
R-NPB	N-H---Br_{eq}	2.922	155.774
	N-H---Br_{eq}	2.865	139.996
	N-H---Br_{ax}	2.483	173.457
	N-H---Br_{ax}	2.587	172.108
	N-H---Br_{ax}	2.686	170.925
	N-H---Br_{ax}	2.493	157.262
	C-H---Br_{eq}	2.829	160.034
S-NPB	N-H---Br_{eq}	2.809	146.426
	N-H---Br_{eq}	2.935	150.543
	N-H---Br_{ax}	2.659	176.230
	N-H---Br_{ax}	2.587	176.575
	N-H---Br_{ax}	2.506	151.769
	N-H---Br_{ax}	2.465	174.464
	C-H---Br_{eq}	2.822	159.294
Racemic-NPB	N-H---Br_{eq}	2.597	155.541
	N-H---Br_{ax}	2.468	152.393
	N-H---Br_{ax}	2.659	157.790
S-MBPI	N-H---Br_{eq}	3.088	132.054
	N-H---Br_{eq}	2.838	151.015
	N-H---Br_{ax}	2.850	159.008
	N-H---Br_{ax}	2.641	155.389
	N-H---Br_{ax}	2.776	137.539
	N-H---Br_{ax}	3.010	148.490

Supplementary Table 3 | Global space group, inorganic layer symmetry, and computed distortion parameters based on single-crystal structures of racemic-/R-/S-NPB and R-/S-MBPI.

Compound	*Space group*	*Inorganic symmetry (PLATON)*	σ^2 *(deg^2)*	Δd *(10^{-4})*	*Axial Br-Pb-Br bond angle*	*Equatorial Pb-Br-Pb bond angle(s)*
Racemic-NPB	$P2_1/c$	$P2_1/c$ (centro)	19.8	3.1	180°	153°
R/S-NPB	$P2_1$	$P2_1$ (chiral)	40.26	6	166°	143°, 157°
R/S-MBPI	$P2_12_12_1$	*Pnma* (centro)	20.08	5.6	167°	151°, 157°

Supplementary Table 4 | Crystallographic and structural refinement data for S-MBPI at 100, 200 and 298 K

Empirical formula	S-$C_{16}H_{24}N_2PbI_4$	S-$C_{16}H_{24}N_2PbI_4$	S-$C_{16}H_{24}N_2PbI_4$
Formula weight	959.16	959.16	959.16
Temperature/K	100	200	298
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	28.6004(6)	8.8697(2)	8.9034(2)
b/Å	9.2078(2)	28.7060(8)	28.8647(7)
c/Å	8.8408(2)	9.2496(3)	9.3127(2)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/$Å^3$	2328.19(9)	2355.07(11)	2393.31(9)
Z	4	4	4
$\rho_{calc}g/cm^3$	2.736	2.705	2.662
μ/mm^{-1}	12.552	12.409	12.210
F(000)	1712.0	1712.0	1712.0
Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.648 to 52.74	4.626 to 52.736	4.596 to 52.734
Reflections collected	17922	12303	14448
Independent reflections	4725 [$R_{int} = 0.0251$, $R_{sigma} = 0.0194$]	4701 [$R_{int} = 0.0199$, $R_{sigma} = 0.0226$]	5731 [$R_{int} = 0.0237$, $R_{sigma} = 0.0255$]
Data/restraints/parameters	4725/0/212	4701/0/212	5731/0/212
Goodness-of-fit on F^2	1.123	1.004	1.040
Final R indexes [I>=2σ (I)]	$R_1 = 0.0191$, $wR_2 = 0.0460$	$R_1 = 0.0194$, $wR_2 = 0.0446$	$R_1 = 0.0313$, $wR_2 = 0.0722$
Final R indexes [all data]	$R_1 = 0.0203$, $wR_2 = 0.0465$	$R_1 = 0.0228$, $wR_2 = 0.0455$	$R_1 = 0.0391$, $wR_2 = 0.0747$
Largest diff. peak/hole / e $Å^{-3}$	1.41/-0.98	1.54/-0.58	0.93/-1.48
Flack parameter	0.024(4)	0.009(6)	0.024(8)

Supplementary Table 5 | Crystallographic and structural refinement data for S-$NEA_2Pb_2I_6$ (S-NPI) at 298 K

Empirical formula	S-$C_{24}H_{28}N_2Pb_2I_6$
Formula weight	1520.26
Temperature/K	298
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.1000(3)
b/Å	8.4632(3)
c/Å	25.3124(9)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1735.21(11)
Z	2
$\rho_{calc}g/cm^3$	2.910
μ/mm^{-1}	15.043
F(000)	1336.0
Crystal size/mm^3	0.159 × 0.075 × 0.046
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.28 to 52.766
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-31 \leq l \leq 30$
Reflections collected	12321
Independent reflections	3503 [R_{int} = 0.0240, R_{sigma} = 0.0367]
Data/restraints/parameters	3503/0/157
Goodness-of-fit on F^2	1.145
Final R indexes [I>=2σ (I)]	R_1 = 0.0228, wR_2 = 0.0504
Final R indexes [all data]	R_1 = 0.0264, wR_2 = 0.0586
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.92
Flack parameter	0.014(9)

Supplementary Table 6 | Comparison of lattice parameters and unit cell volumes between experimental and relaxed structures of S-, R-, and racemic-NPB, as well as S-MBPI. The experimental axes were reordered to fit the convention chosen for the theoretical axes.

Compound		*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å^3)
	Exp.	19.5	7.96	8.75	90.0	93.8	90.0	1355
S-NPB	PBE+TS	19.27	7.79	8.76	90.0	95.3	90.0	1309
	Deviation	-1.19%	-2.18%	0.11%		1.5		-3.5%
	Exp.	19.52	7.96	8.76	90.0	93.77	90.0	1358
R-NPB	PBE+TS	19.27	7.79	8.76	90.0	95.4	90.0	1309
	Deviation	-1.29%	-2.18%	0%		1.63		-3.7%
	Exp.	19.25	8.08	8.73	90.0	90.3	90.0	1357
Racemic-NPB	PBE+TS	19.28	7.90	8.75	90.0	92.0	90.0	1332
	Deviation	0.15%	-2.22%	0.24%		1.7		-1.89%
	Exp.	28.87	8.90	9.31	90.0	90.0	90.0	2393
S-MBPI	PBE+TS	28.83	8.81	9.19	90.0	90.0	90.0	2333
	Deviation	-0.13%	-1.07%	-1.36%				-2.54%

Supplementary Table 7 | Input geometry.in file of Au(111) surface corresponding to Supplementary Figure 17a,b.

```
lattice_vector     2.8830859661        0.0000000000        0.0000000000
lattice_vector    -1.4415431023        2.4968258944        0.0000000000
lattice_vector     0.0000000000        0.0000000000       50.0000000000

atom_frac      0.333333353     0.666666693     0.423725433    Au
atom_frac      0.666666687     0.333333347     0.470806046    Au
atom_frac      0.000000000     0.000000000     0.517886658    Au
atom_frac      0.333333353     0.666666693     0.564967270    H
```

Supplementary Table 8 | Input geometry.in file of $(4\text{-BrBzA})_2PbI_4$ corresponding to Supplementary Figure 18a.

```
lattice_vector     8.6328001022        0.0000000000        0.0000000000
lattice_vector     0.0000000000        8.9483003616        0.0000000000
lattice_vector    -1.5433467726        0.0000000000       15.8576739839
atom       0.578614831       8.447016716      15.850378990  Pb
atom       6.510838032       3.972866535       0.007294530  Pb
atom       1.930478096       8.089262962       3.201981544  I
atom       5.158975124       3.615113258      12.655692101  I
atom       0.656904459       8.734704971      12.715792656  I
atom       6.432549000       4.260554314       3.141880751  I
atom       3.833200932       2.201371431       0.105770685  I
atom       3.256252050       6.675521374      15.751902580  I
atom       8.122714996       1.229228020       0.229460537  I
atom      -1.033261418       5.703378201      15.628212929  I
atom       7.528899670       0.197757438       9.337791443  Br
atom      -0.439445734       4.671907425       6.519882202  Br
atom       5.186055183       3.527420044       8.733613968  Br
atom       1.903397918       8.001569748       7.124059677  Br
atom       6.997970581       7.758176327       2.694218636  N
atom       0.091482878       3.284026146      13.163455009  N
atom       2.780409336       4.662064552       2.476968765  N
atom       4.309043884       0.187914550      13.380704880  N
atom       6.366302490       8.831972122       4.838176250  C
atom       0.723150730       4.357821941      11.019497871  C
atom       5.758203030       7.937142849       5.764264584  C
atom       1.331250310       3.462992191      10.093409538  C
atom       6.082551003       8.026625633       7.132781982  C
atom       1.006902456       3.552475452       8.724891663  C
atom       7.001899719       0.044741500       7.532394886  C
```

atom	0.087553978	4.518891811	8.325278282	C
atom	7.532611847	0.948519826	6.603135109	C
atom	-0.443159044	5.422669888	9.254539490	C
atom	7.231693745	0.832191944	5.259990215	C
atom	-0.142240405	5.306342125	10.597683907	C
atom	6.027477264	8.742489815	3.352312326	C
atom	1.061975956	4.268339157	12.505360603	C
atom	2.847216606	3.677751541	4.717658043	C
atom	4.242236137	8.151902199	11.140015602	C
atom	3.408299208	2.451834202	5.161673069	C
atom	3.681154251	6.925984383	10.696001053	C
atom	4.132862091	2.380247831	6.320868969	C
atom	2.956591129	6.854398251	9.536805153	C
atom	4.292793274	3.597216845	7.072522640	C
atom	2.796660185	8.071367264	8.785151482	C
atom	3.721534252	4.724702358	6.644365311	C
atom	3.367919207	0.250552386	9.213308334	C
atom	2.998206377	4.832082272	5.472483158	C
atom	4.091246605	0.357931674	10.385190964	C
atom	2.075497150	3.758285999	3.422086000	C
atom	5.013956070	8.232436180	12.435587883	C
atom	7.850749969	8.056405067	2.804857969	H
atom	-0.761296391	3.582255363	13.052815437	H
atom	6.810063362	7.700755119	1.805491328	H
atom	0.279389977	3.226604939	14.052182198	H
atom	6.907192707	6.941661835	3.079306602	H
atom	0.182260633	2.467511892	12.778367043	H
atom	5.134750843	7.290198326	5.461350918	H
atom	1.954702497	2.816048145	10.396322250	H
atom	5.681096554	7.442471027	7.765248775	H

atom	1.408356905	2.968321085	8.092424393	H
atom	-0.522267103	1.642997503	6.897818089	H
atom	7.611721039	6.117147923	8.959855080	H
atom	7.643675804	1.410833716	4.629869938	H
atom	-0.554222107	5.884984016	11.227804184	H
atom	6.114563942	0.685171306	2.930640697	H
atom	0.974889278	5.159321308	12.927033424	H
atom	5.098641396	8.428072929	3.233791828	H
atom	1.990811706	3.953922749	12.623882294	H
atom	2.809207439	5.499258518	2.821666956	H
atom	4.280246258	1.025107741	13.036005974	H
atom	2.340891123	4.670001507	1.680929184	H
atom	4.748561859	0.195852026	14.176744461	H
atom	3.631511927	4.356023788	2.347252846	H
atom	3.457942009	8.830173492	13.510420799	H
atom	3.286421299	1.664240718	4.641620159	H
atom	3.803031921	6.138391018	11.216053009	H
atom	4.504052162	1.560583591	6.620975018	H
atom	2.585401297	6.034733295	9.236698151	H
atom	3.804540157	5.498775482	7.183209419	H
atom	3.284913063	1.024625659	8.674464226	H
atom	2.632024765	5.658269882	5.194799423	H
atom	4.457428932	1.184119582	10.662873268	H
atom	1.995134354	2.851376057	3.027721643	H
atom	5.094319344	7.325526237	12.829952240	H
atom	1.162436366	4.099842548	3.594649315	H
atom	5.927017212	8.573992729	12.263024330	H

Supplementary Table 9 | Input geometry.in file of IrBiSe corresponding to Supplementary Figure 19a.

lattice_vector	6.2899999619	0.0000000000	0.0000000000
lattice_vector	0.0000000000	6.2899999619	0.0000000000
lattice_vector	0.0000000000	0.0000000000	6.2899999619

atom	0.118063301	0.118063301	0.118063301	Ir
atom	3.026936531	6.171936989	3.263063192	Ir
atom	6.171936989	3.263063192	3.026936531	Ir
atom	3.263063192	3.026936531	6.171936989	Ir
atom	2.347805262	2.347805262	2.347805262	Bi
atom	0.797194660	3.942194462	5.492805481	Bi
atom	3.942194462	5.492805481	0.797194660	Bi
atom	5.492805481	0.797194660	3.942194462	Bi
atom	3.892377853	3.892377853	3.892377853	Se
atom	5.542622089	2.397622108	0.747377515	Se
atom	2.397622108	0.747377515	5.542622089	Se
atom	0.747377515	5.542622089	2.397622108	Se

Supplementary Table 10 | Input geometry.in file of racemic-NPB corresponding to Supplementary Figure 13c.

lattice_vector 19.28075432 0.11893738 -0.16084042

lattice_vector -0.04762409 7.89735002 -0.08918111

lattice_vector -0.23010841 0.09728093 8.74579059

atom 9.50419428 4.05496176 4.24359949 Pb

atom 9.64272421 0.05922138 -0.08488327 Pb

atom 9.59239632 5.39234681 1.47323567 Br

atom 9.53672969 1.45488956 2.65888312 Br

atom 9.41476145 2.71984904 7.01820401 Br

atom 9.47021079 6.65525434 5.83257514 Br

atom 6.52149394 3.81494085 4.06968567 Br

atom 12.58016831 7.75534441 0.00947094 Br

atom 12.48632053 4.29657061 4.42128484 Br

atom 6.42730750 0.35625700 8.48162335 Br

atom 4.40821563 3.85574320 0.73673337 C

atom 14.69102453 7.89780291 3.34024015 C

atom 14.59864031 4.25601932 7.75403740 C

atom 4.31568737 0.21403522 5.15070565 C

atom 3.27213868 4.72212750 0.63097143 C

atom 15.86383652 0.88311382 3.51494869 C

atom 15.73478673 3.38970660 7.85971080 C

atom 3.14284943 7.22878310 4.97583965 C

atom 4.23385780 2.57908024 1.23457073 C

atom 14.88127221 6.61224806 2.87196530 C

atom 14.77287811 5.53266184 7.25611800 C

atom 4.12543663 1.49962548 5.61889054 C

atom 5.07400758 1.89272073 1.30132753 H

atom 14.04976239 5.91407219 2.82147933 H

atom 13.93265113 6.21892457 7.18940671 H

atom 4.95696006 2.19777967 5.66950677 H
atom 1.98446113 4.21656116 1.01888294 C
atom 17.15762994 0.38495911 3.13798403 C
atom 17.02242507 3.89539564 7.47180502 C
atom 1.84904170 7.72697815 5.35264286 C
atom 3.34950118 6.06021372 0.15942559 C
atom 15.76999919 2.23045475 3.95622985 C
atom 15.65752930 2.05157234 8.33112315 C
atom 3.23667826 5.88147116 4.53446710 C
atom 4.07553436 6.58833605 8.61025571 H
atom 14.80863787 2.65595222 4.24171878 H
atom 14.93152366 1.52332794 -0.11980104 H
atom 4.19803853 5.45596306 4.24898397 H
atom 2.22209780 6.84795373 0.06472885 C
atom 16.88765343 3.03386745 4.03304352 C
atom 16.78500100 1.26392981 8.42579201 C
atom 2.11900498 5.07809480 4.45752960 C
atom 2.08350207 7.96206419 8.43283007 H
atom 16.78391800 4.05754612 4.38820256 H
atom 16.92370453 0.14975879 0.05755403 H
atom 2.22279026 4.05445458 4.10227835 H
atom 0.96162594 6.34505153 0.44907637 C
atom 18.15420940 2.53812406 3.65952878 C
atom 18.04544892 1.76699296 8.04158146 C
atom 0.85244331 5.57383558 4.83103157 C
atom 0.07472381 6.97108355 0.37343426 H
atom 19.03340407 3.17645550 3.72151180 H
atom 18.93241205 1.14105106 8.11725838 H
atom -0.02673061 4.93547241 4.76911257 H
atom 0.84960544 5.05808138 0.92218063 C

atom 18.28202067 1.24243108 3.21509361 C
atom 18.15736460 3.05399587 7.56854037 C
atom 0.72463688 6.86952198 5.27548435 C
atom -0.11894621 4.65666234 1.22201614 H
atom 19.25535225 0.84641859 2.92366112 H
atom 19.12588373 3.45550716 7.26872210 H
atom -0.24869610 7.26558062 5.56684509 H
atom 2.97223226 2.09707439 1.64173866 C
atom 16.14875086 6.13681925 2.47543173 C
atom 16.03443560 6.01474558 6.84883317 C
atom 2.85789546 1.97514289 6.01513426 C
atom 2.89361627 1.08912138 2.04767412 H
atom 16.23994851 5.12077600 2.09299281 H
atom 16.11296164 7.02266209 6.44278718 H
atom 2.76666540 2.99124572 6.39740843 H
atom 1.86211331 2.89485016 1.51484088 C
atom 17.24877542 6.95121645 2.58322148 C
atom 17.14463748 5.21709418 6.97578273 C
atom 1.75785786 1.16076890 5.90726162 C
atom 0.87325864 2.53353032 1.79238889 H
atom 18.24199545 6.59598916 2.31354079 H
atom 18.13345177 5.57851682 6.69821958 H
atom 0.76460345 1.51604804 6.17674417 H
atom 5.77081351 4.35602016 0.28984409 C
atom 13.36982639 0.49383717 3.86489262 C
atom 13.23610362 3.75568535 8.20109541 C
atom 5.63685274 7.61785135 4.62616400 C
atom 5.94884163 5.35583936 0.71205107 H
atom 13.17932371 1.48127496 3.41960631 H
atom 13.05804304 2.75588620 7.77886009 H

atom 5.82714028 6.63031256 5.07131195 H
atom 6.87044011 3.50288351 0.85491611 N
atom 12.23339224 7.51147803 3.23087935 N
atom 12.13632720 4.60881474 7.63631414 N
atom 6.77333869 0.59995804 5.26049998 N
atom 6.88892475 2.54699538 0.43810792 H
atom 12.22670874 6.56534939 3.66970500 H
atom 12.11767394 5.56450237 8.05352484 H
atom 6.77980976 1.54636746 4.82223558 H
atom 6.76590845 3.42426882 1.89735058 H
atom 12.33891923 7.40999883 2.19056758 H
atom 12.24080039 4.68790512 6.59395884 H
atom 6.66796502 0.70076682 6.30094731 H
atom 7.79427204 3.95342209 0.69878286 H
atom 11.30398632 7.95406965 3.37662839 H
atom 11.21253951 4.15792863 7.79212373 H
atom 7.70271023 0.15764655 5.11416317 H
atom 5.72020651 4.50563373 7.52061133 C
atom 13.18972535 0.57903782 5.37835962 C
atom 13.28689702 3.60594956 0.97035684 C
atom 5.81706760 7.53289175 3.11270077 C
atom 5.69411612 3.49268538 7.10508102 H
atom 13.18096198 7.47380861 5.72816328 H
atom 13.31297953 4.61886201 1.38597599 H
atom 5.82634397 0.63823621 2.76311055 H
atom 6.67944854 4.96563778 7.25176869 H
atom 12.22483214 1.03312764 5.63682828 H
atom 12.32768069 3.14589237 1.23922153 H
atom 6.78175276 7.07839196 2.85419779 H
atom 4.91578233 5.08363807 7.05492168 H

atom 13.98690064 1.17771954 5.83017990 H

atom 14.09135894 3.02791920 1.43593977 H

atom 5.01961974 6.93470662 2.66069117 H

Supplementary Table 11 | Input geometry.in file of R-NPB corresponding to Supplementary Figure 13b.

```
lattice_vector    -1.49555572    -0.00681572    19.20931905
lattice_vector    -0.03297736    -7.78884213    -0.00527112
lattice_vector     8.76195420    -0.03700259    -0.14106161
atom       5.05055629     3.41686722    19.05457723 Pb
atom       2.26202737     7.33591757     0.02111090 Pb
atom       6.72110530     3.41384287     2.81330377 Br
atom       0.59122119     7.32534769    16.26240531 Br
atom       3.57562082     4.60692884     0.13528501 Br
atom       3.71355208     0.69909699    18.93704058 Br
atom       8.45078011     5.81448294     0.17845392 Br
atom      -1.15116912     1.94779084    18.89523319 Br
atom       4.63889331     4.18574907    16.13461805 Br
atom       2.64683983     0.30827118     2.93703525 Br
atom       1.29117040     3.44014834     2.73660738 N
atom       6.02108489     7.30568918    16.33934104 N
atom       1.61655079     3.79071425     1.81768772 H
atom       5.69874718     7.65771389    17.25877065 H
atom       0.24297616     3.41194101     2.71866438 H
atom       7.06900180     7.26857252    16.35722182 H
atom       1.65659859     2.46418539     2.81739198 H
atom       5.64740582     6.33297286    16.25723482 H
atom       1.61814435     2.87942678    16.31843898 N
atom       5.68934041     6.76555143     2.75642261 N
atom       1.38207777     1.86464855    16.30230317 H
atom       5.91688413     5.74881239     2.77117340 H
atom       1.38205262     3.24990178    17.25991953 H
atom       5.92845444     7.13533124     1.81542350 H
```

atom 2.64759933 3.02659145 16.21256070 H
atom 4.66117532 6.92120779 2.86260580 H
atom 1.28640177 3.20243774 13.85047198 C
atom 6.02383117 7.08252123 5.22479560 C
atom 1.17329217 3.99925124 5.17957191 C
atom 6.11067828 0.07825180 13.89189404 C
atom 1.79821546 4.33315163 3.83755127 C
atom 5.48862185 0.41562881 15.23437349 C
atom 1.49471945 5.34530343 3.53361272 H
atom 5.80068452 1.42475243 15.53969449 H
atom 2.14927661 3.66809643 11.58215275 C
atom 5.16505735 7.55240233 7.49379556 C
atom 0.88370039 3.65473033 15.24411030 C
atom 6.43030110 7.53323952 3.83173778 C
atom 1.18772887 4.69277927 15.41195651 H
atom 6.10203688 0.78517284 3.65998916 H
atom 1.18306597 4.99343098 6.21143730 C
atom 6.10925152 1.07381927 12.86132993 C
atom -0.61128845 3.54303057 15.49747094 C
atom 7.92430196 7.40929978 3.57822421 C
atom -0.93593769 2.49633765 15.52290963 H
atom 8.24012996 6.35994323 3.55134144 H
atom -1.15396059 4.03353719 14.68589287 H
atom 8.43807444 0.10524491 4.38521521 H
atom -0.88990262 4.01315680 16.44782869 H
atom 8.17388947 0.08950634 2.62323956 H
atom 0.61126657 4.67373252 7.48866035 C
atom 6.67833187 0.75094479 11.58370702 C
atom 1.91703406 4.10700014 12.93414660 C
atom 5.36796745 0.20230333 6.13711262 C

atom 3.32008636 4.24367134 3.84540844 C
atom 3.96604924 0.33909067 15.22639574 C
atom 3.63690848 3.21684001 4.05328119 H
atom 3.67347070 7.10414083 15.02238606 H
atom 3.74166359 4.90183438 4.61166910 H
atom 3.55011814 1.00185862 14.46101196 H
atom 3.72119096 4.52541348 2.86575692 H
atom 3.56733256 0.62292242 16.20641754 H
atom 2.32715935 5.42164480 13.28010438 C
atom 4.96898638 1.52084550 5.79296873 C
atom 2.16843951 5.79366599 14.28918777 H
atom 5.13081511 1.89286818 4.78438043 H
atom 0.61957668 2.76203264 5.44282454 C
atom 6.68699395 6.62563093 13.63228925 C
atom 0.61466353 1.98823718 4.67827453 H
atom 6.68542402 5.85083259 14.39583454 H
atom 0.06616715 3.38443641 7.70910679 C
atom 7.24567623 7.24631134 11.36683244 C
atom -0.35437575 3.15632918 8.68869684 H
atom 7.66436027 7.01600564 10.38696360 H
atom 0.96279581 1.92538457 13.42458381 C
atom 6.33663231 5.80219855 5.64895135 C
atom 0.47967263 1.22438172 14.10636343 H
atom 6.81375457 5.09805250 4.96618419 H
atom 1.72685800 6.29137891 6.03324969 C
atom 5.57651506 2.37612569 13.04119898 C
atom 2.17840038 6.58196119 5.08638269 H
atom 5.12744293 2.66931523 13.98843962 H
atom 0.05322875 2.45291970 6.69929344 C
atom 7.25078881 6.31341211 12.37544309 C

atom	-0.39462216	1.47260580	6.85668488 H
atom	7.69044728	5.32959679	12.21679593 H
atom	3.11067799	5.82998525	11.02721965 C
atom	4.18905978	1.93276339	8.04644469 C
atom	3.54140002	6.50928325	10.29621868 H
atom	3.76415013	2.61469243	8.77840156 H
atom	1.79994411	2.34992985	11.20183618 C
atom	5.50321348	6.23081147	7.87231019 C
atom	1.98431297	2.03222865	10.17483090 H
atom	5.31618230	5.91331676	8.89889852 H
atom	2.73075036	4.56398058	10.65163588 C
atom	4.55828546	0.66308115	8.42028797 C
atom	2.86311599	4.23856579	9.62106761 H
atom	4.42323381	0.33742448	9.45042927 H
atom	1.68208235	7.22966118	7.03999360 C
atom	5.62934790	3.31532139	12.03569100 C
atom	2.07706927	0.42579138	6.86328715 H
atom	5.20981494	4.30370711	12.20842056 H
atom	0.56687731	5.66764991	8.49782612 C
atom	6.73116850	1.74575569	10.57582401 C
atom	0.12005742	5.40576976	9.45730984 H
atom	7.17572342	1.48133387	9.61598435 H
atom	1.08775837	6.92316340	8.28185511 C
atom	6.22103058	3.00538995	10.79342220 C
atom	1.05509020	7.67700754	9.06888815 H
atom	6.26009914	3.75995577	10.00737453 H
atom	2.92490204	6.25276768	12.35737105 C
atom	4.37834007	2.35575932	6.71685486 C
atom	3.24738527	7.24899833	12.65064706 H
atom	4.06427508	3.35507526	6.42495049 H

atom	1.23580838	1.49018140	12.11232673 C
atom	6.06001743	5.36754079	6.96062907 C
atom	0.97170660	0.47395802	11.83007424 H
atom	6.31550757	4.34873185	7.24148194 H

Supplementary Table 12 | Input geometry.in file of S-NPB corresponding to Supplementary Figure 13a.

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lattice_vector     8.76022728    -0.05995493     -0.22263015
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atom       5.98829082     4.22849770     9.49653022 Pb
atom       1.70258061     0.36940363    12.47230089 Br
atom       5.78608346     4.23592853     6.53016465 Br
atom       1.10624420     7.39071586     6.58963852 Br
atom       6.42557760     3.45928448    12.41264112 Br
atom       3.43526691     5.74185315     9.81905105 Br
atom       4.07386910     1.84319306     9.18340664 Br
atom       7.33296797     6.94308129     9.59941380 Br
atom       0.19309142     3.09795210     9.40260747 Br
atom       5.03200861     0.34333408    12.22331687 N
atom       2.45658563     4.25592292     6.77895308 N
atom       5.34445073    -0.00988284    11.30093523 H
atom       2.13908767     3.90708419     7.70128140 H
atom       5.40913843     1.31505001    12.30137611 H
atom       2.09290384     5.23275105     6.70082186 H
atom       3.98408315     0.38328051    12.21558358 H
atom       3.50495152     4.28141400     6.78686365 H
atom       0.68726629     4.81846245    12.42260609 N
atom       6.80924040     0.88264800     6.57986929 N
atom       0.91314068     4.44734249    11.47885961 H
atom       6.57843367     0.51459224     7.52362101 H
atom       0.92632956     5.83260533    12.43646584 H
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atom	7.83591682	0.72429009	6.46383867 H
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atom	1.93669952	3.36328652	5.68373058 C
atom	5.27536003	6.22335128	13.01671771 H
atom	2.24063640	2.35062753	5.98553029 H
atom	1.42992922	4.04093780	13.48955528 C
atom	6.05595191	0.11532695	5.51298806 C
atom	1.12091105	3.00387203	13.32488176 H
atom	6.40418578	6.86224350	5.67764392 H
atom	2.92265567	4.14779348	13.22114294 C
atom	4.56484014	0.24255557	5.78149925 C
atom	3.19018311	3.67630208	12.26827173 H
atom	4.34431109	7.56278830	6.73435749 H
atom	3.47193342	3.65602370	14.02746998 H
atom	4.06222253	7.54652910	4.97515777 H
atom	3.25033771	5.19344461	13.19179794 H
atom	4.25148767	1.29258907	5.81097289 H
atom	1.04265465	4.49451704	14.88713693 C
atom	6.44927394	0.56362637	4.11539615 C
atom	4.98541123	7.57150000	14.66692203 C
atom	2.54910175	3.69466070	4.33533790 C
atom	7.11591642	7.30421951	13.31146772 C
atom	0.41504449	3.45654897	5.69060639 C
atom	7.50418629	7.01889348	12.32768514 H
atom	0.02281268	3.17654266	6.67434443 H
atom	7.53753865	6.64067878	14.07304690 H
atom	-0.01555436	2.79884065	4.92898602 H
atom	7.39282846	0.53914908	13.51702978 H
atom	0.09880193	4.48399755	5.48501775 H

atom	4.99516638	6.57671527	15.69822610 C
atom	2.52581261	2.70005496	3.30407913 C
atom	0.20163116	4.03136896	17.16418731 C
atom	7.28407596	0.08931857	1.83836016 C
atom	0.41885423	3.59177915	15.80992015 C
atom	7.11409621	7.44065826	3.19254958 C
atom	1.37421989	5.77066347	15.30962006 C
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atom	5.66649962	2.55016817	4.37980470 H
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atom	3.11838002	5.70434423	4.82977645 H
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atom	7.51319260	6.12145556	3.53402688 C
atom	0.14904141	1.90569908	14.45766999 H
atom	7.36051298	5.75079074	4.54453837 H
atom	5.52238408	5.27281420	15.51367497 C
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atom	5.95995543	4.97750782	14.56170805 H
atom	1.53931974	1.11421503	4.44068721 H
atom	4.44103212	6.90226982	16.98174134 C
atom	3.08433822	3.01794456	2.02055080 C
atom	5.47868784	4.33483330	16.52076586 C
atom	2.01174579	0.46493423	2.48166478 C
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atom	1.63653614	7.26919298	2.65804863 H
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atom 7.12230969 1.72729226 0.43304802 H
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Supplementary Table 13 | Input geometry.in file of S-MBPI corresponding to Supplementary Figure 16.

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atom       3.48918573     4.66497955    14.37615526 Pb
atom       0.91395803     4.53042484    28.79326708 Pb
atom       3.73065964     2.94992950    28.80628490 I
atom       0.67250853     6.24575994    14.38963528 I
atom       5.07682068     7.53316930    14.44175324 I
atom       8.13582409     1.64280388     0.02537187 I
atom       2.59450395     7.40943394     0.00765125 I
atom       1.81007891     1.76709793    14.42302549 I
atom       6.21432680     2.82643768    14.40842563 I
atom       6.99749753     6.36903489    28.82418036 I
atom       5.47200934     8.91382496     3.23363892 I
atom       7.74048247     0.26929687    17.64940543 I
atom       3.33617560     4.32364180    11.18161780 I
atom       1.06712216     4.86463418    25.59841359 I
atom       5.51377854     8.92348237    25.65810670 I
atom       7.69829372     0.26358135    11.24460167 I
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atom       1.10998590     4.85453368     3.17385677 I
atom       8.46602159     9.06474630    21.60644866 C
atom       4.74685038     0.12031824     7.19463300 C
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atom 1.77417124 1.24805437 26.80080535 H
atom 2.63014592 7.94136639 12.38612662 H

atom	7.03382870	5.83820158	16.44498013 H
atom	6.17860212	3.34546093	2.03167592 H
atom	2.12603012	1.74552239	25.14145072 H
atom	2.27668123	7.44201025	10.72777124 H
atom	6.68144217	6.33677166	18.10381583 H
atom	6.53113995	2.84730578	3.69066695 H
atom	4.62284930	5.57650841	26.04641414 N
atom	8.58970243	3.61004807	11.63021058 N
atom	4.18539917	0.98232586	17.20006528 N
atom	0.21870477	8.20142333	2.78643485 N
atom	0.11480264	8.35344803	26.18796542 N
atom	4.28985898	0.83400967	11.77288115 N
atom	8.69352082	3.75875747	17.05802123 N
atom	4.51865052	5.42494699	2.64427730 N

Supplementary References

1 Smith, M. D., Jaffe, A., Dohner, E. R., Lindenberg, A. M. & Karunadasa, H. I. Structural origins of broadband emission from layered Pb–Br hybrid perovskites. *Chem. Sci.* **8**, 4497-4504 (2017).

2 Shibuya, K., Koshimizu, M., Nishikido, F., Saito, H. & Kishimoto, S. Poly[bis(phenethylammonium) [dibromidoplumbate(II)]-di-[mu]-bromido]]. *Acta Cryst.* **65**, m1323-m1324 (2009).

3 Du, K.-z. *et al.* Two-Dimensional Lead(II) Halide-Based Hybrid Perovskites Templated by Acene Alkylamines: Crystal Structures, Optical Properties, and Piezoelectricity. *Inorg. Chem.* **56**, 9291-9302 (2017).

4 Mao, L. *et al.* Structural Diversity in White-Light-Emitting Hybrid Lead Bromide Perovskites. *J. Am. Chem. Soc.* **140**, 13078-13088 (2018).

5 Mao, L., Wu, Y., Stoumpos, C. C., Wasielewski, M. R. & Kanatzidis, M. G. White-Light Emission and Structural Distortion in New Corrugated Two-Dimensional Lead Bromide Perovskites. *J. Am. Chem. Soc.* **139**, 5210-5215 (2017).

6 Kepenekian, M. *et al.* Rashba and Dresselhaus Effects in Hybrid Organic–Inorganic Perovskites: From Basics to Devices. *ACS Nano* **9**, 11557-11567 (2015).

7 FermiLoop: Calculation on a constant-energy level. *http://www.openmx-square.org/openmx_man3.9/node176.html* (2018).

8 Kotaka, H., Ishii, F. & Saito, M. Rashba Effect on the Structure of the Bi One-Bilayer Film: Fully Relativistic First-Principles Calculation. *Jpn. J. Appl. Phys.* **52**, 035204 (2013).

9 Ozaki, T. & Kino, H. Efficient projector expansion for the ab initio LCAO method. *Phys. Rev. B* **72**, 045121 (2005).

10 Schmitt, T. *et al.* Control of Crystal Symmetry Breaking with Halogen-Substituted Benzylammonium in Layered Hybrid Metal-Halide Perovskites. *J. Am. Chem. Soc.* **142**, 5060-5067 (2020).

11 Liu, Z. *et al.* A Giant Bulk-Type Dresselhaus Splitting with 3D Chiral Spin Texture in IrBiSe. *Phys. Status Solidi RRL* **14**, 1900684 (2020).