Supplementary Information

for

Switchable Rashba Anisotropy in Layered Hybrid Organic-Inorganic Perovskite by Hybrid Improper Ferroelectricity

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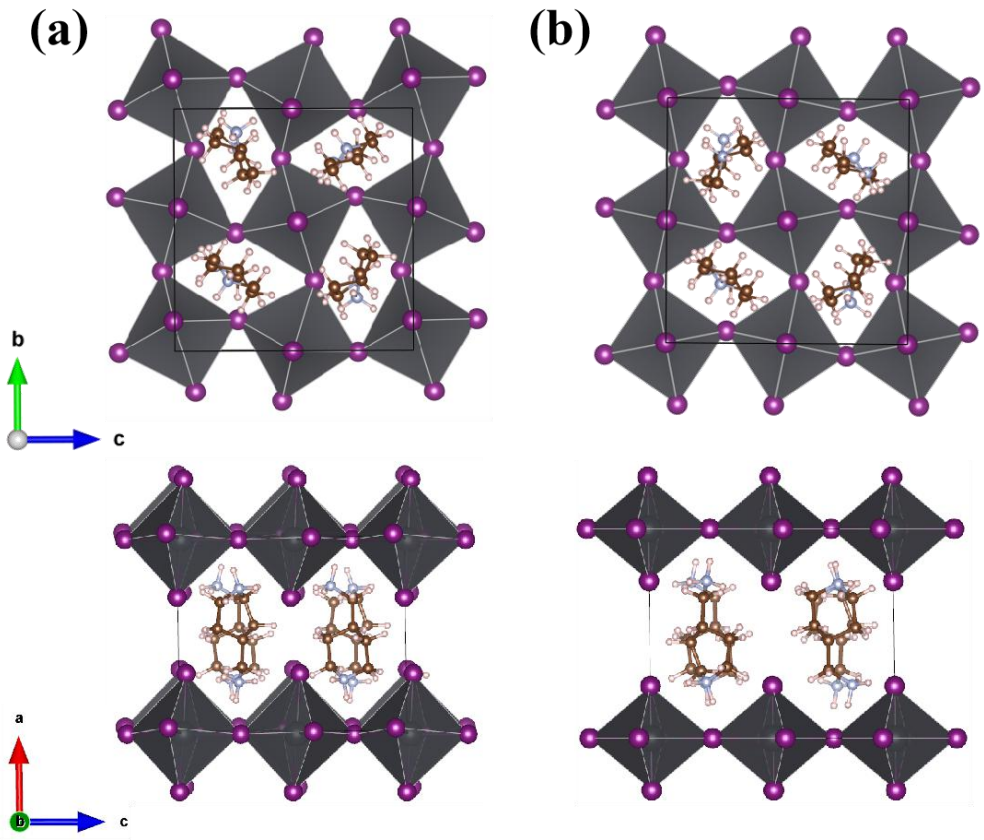
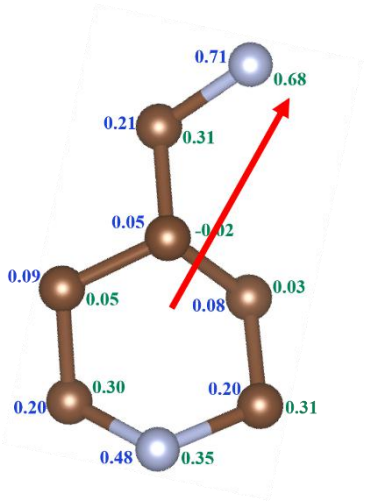
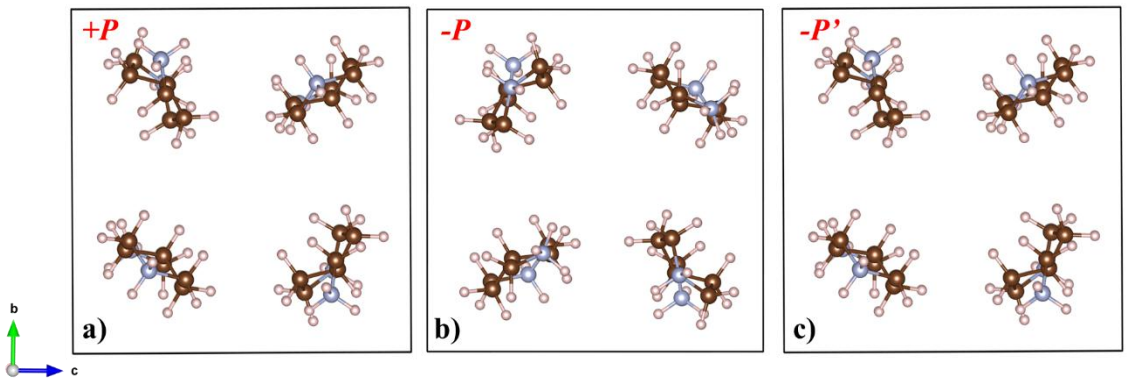


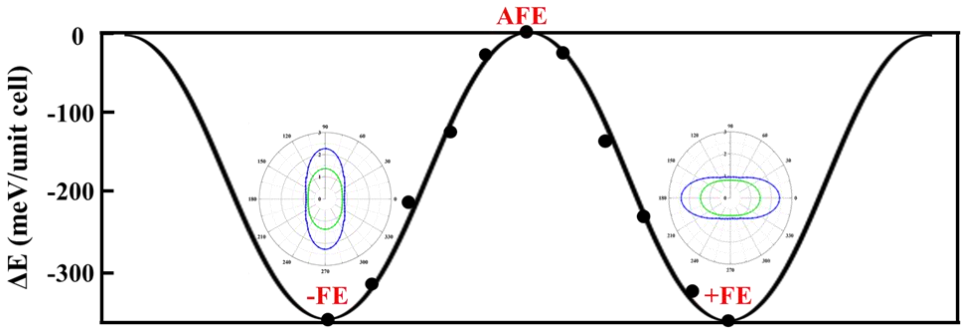
Supplementary Figure 1: **The 1×1×2 supercell of (AMP)PbI_4. (a)** the ferroelectric structure (FE); **(b)** the anti-ferroelectric structure (AFE). Purple Pb, gray I, brown C, blue N. The protons of the AMP cation were not shown for clarity here.



Supplementary Figure 2: **The Hirshfield (blue values) and Natural (green values) population analysis on the isolated AMP cation**, with purple Pb, gray I, brown C and blue N. The charges of hydrogen atoms (omitted) are summed into the heavy atoms. The red arrow indicates the direction of the dipole moment.



Supplementary Figure 3: **The orientations of four AMP molecules on *bc* plane of +*P* (a), -*P* (b) and -*P*' (c)**, in which the PbI_4^{2-} inorganic framework is ignore for clarity. Color code: brown C, blue N and pink H.



Supplementary Figure 4: The energy differences between +***P*** (+**FE**), -***P*** (-**FE**) and **AFE** states as a function of polarization parameter (λ), including the two Rashba anisotropy figures.

The space group, lattice constants and atomic Wyckoff positions for bulk (AMP)PbI_4.[1]

space group: *Pc*;

lattice constants*: a = 10.5315(2) Å, b = 12.5444(3) Å, c = 12.5572(3) Å, β = 89.99°

atomic coordinates:

Site	Occ.	x/a	y/b	z/c	m
C1	C1.00	0.8010	0.2160	0.5500	2
C2	C1.00	0.9390	0.1850	0.5400	2
C3	C1.00	1.0070	0.2700	0.4830	2
C4	C1.00	0.9590	0.2970	0.3790	2
C5	C1.00	0.8150	0.3220	0.3860	2
C6	C1.00	1.1470	0.2340	0.4830	2
C7	C1.00	1.1770	0.3290	-0.0240	2
C8	C1.00	1.0340	0.3570	-0.0300	2
C9	C1.00	0.9580	0.2540	-0.0180	2
C10	C1.00	0.9960	0.1750	-0.1060	2
C11	C1.00	1.1380	0.1490	-0.0950	2
C12	C1.00	0.8210	0.2890	-0.0450	2
H3	H1.00	1.0020	0.3342	0.5269	2
H9	H1.00	0.9646	0.2229	0.0531	2
H10A	H1.00	0.9796	0.2058	-0.1755	2
H10B	H1.00	0.9461	0.1101	-0.0998	2
H11A	H1.00	1.1475	0.0741	-0.0760	2
H11B	H1.00	1.1796	0.1597	-0.1629	2
H12A	H1.00	0.7984	0.3527	-0.0054	2
H12B	H1.00	0.8127	0.3040	-0.1207	2

H1A	H1.00	0.7271	0.1960	0.4138	2
H1B	H1.00	0.6739	0.2854	0.4684	2
H1C	H1.00	0.7528	0.1549	0.5745	2
H1D	H1.00	0.7927	0.2717	0.6032	2
H2A	H1.00	1.2972	0.2767	0.4127	2
H2B	H1.00	1.1847	0.2913	0.3473	2
H2C	H1.00	1.2118	0.3653	0.4333	2
H2D	H1.00	0.9752	0.1759	0.6108	2
H2E	H1.00	0.9464	0.1185	0.5021	2
H3A	H1.00	1.2847	0.2034	-0.0182	2
H3B	H1.00	1.1760	0.1928	0.0501	2
H4A	H1.00	0.9721	0.2374	0.3306	2
H4B	H1.00	1.0040	0.3580	0.3513	2
H4C	H1.00	0.6609	0.2132	-0.0271	2
H4D	H1.00	0.7651	0.1409	-0.0507	2
H4E	H1.00	0.7519	0.1858	0.0555	2
H5A	H1.00	0.8042	0.3946	0.4116	2
H5B	H1.00	0.7786	0.3189	0.3147	2
H6A	H1.00	1.1820	0.2402	0.5538	2
H6B	H1.00	1.1526	0.1601	0.4607	2
H7A	H1.00	1.2184	0.3552	-0.0877	2
H7B	H1.00	1.2136	0.3654	0.0365	2
H8A	H1.00	1.0124	0.4067	0.0263	2
H8B	H1.00	1.0156	0.3908	-0.0980	2
I1	I1.00	0.1764	0.0335	0.2366	2
I2	I1.00	0.7831	0.0349	0.2353	2
I3	I1.00	0.4789	-0.0577	-0.0402	2
I4	I1.00	0.4756	-0.2405	0.2686	2

I5	I1.00	0.4747	0.2614	0.1552	2
I6	I1.00	0.1808	0.5139	0.2147	2
I7	I1.00	0.7795	0.5152	0.2156	2
I8	I1.00	0.4791	0.5573	-0.0442	2
N1	N1.00	0.7470	0.2530	0.4520	2
N2	N1.00	1.2160	0.2980	0.4130	2
N3	N1.00	1.2010	0.2140	-0.0140	2
N4	N1.00	0.7420	0.1980	-0.0140	2
Pb1	Pb1.00	0.4811	0.0125	0.2160	2
Pb2	Pb1.00	0.4812	0.5114	0.2083	2

*Note that the *k*-point labelling in the main manuscript body correspond to the crystallographic setting with monoclinic axis along *c* rather than *b*.

References

1. Park, I. H. *et al.* Ferroelectricity and Rashba effect in a two-dimensional Dion-Jacobson hybrid organic-inorganic perovskite. *J. Am. Chem. Soc.* **141**, 15972-15976, doi:10.1021/jacs.9b07776 (2019).