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Supporting Information

Electronic Structures and Elastic Properties of a Family of Metal-free Perovskites

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Table S1 Crystal data and structure refinement for PIP-Cl, PIP-Br and PIP-I.

Compound	**PIP-Cl**	**PIP-Br**	**PIP-I**
Formula	$(C_4N_2H_{12})$ (NH_4Cl_3) H_2O	$(C_4N_2H_{12})$ (NH_4Br_3) H_2O	$(C_4N_2H_{12})$ (NH_4I_3) H_2O
M_w	230.56	363.94	504.91
T/K	120(10)	293(2)	293(2)
Crystal system		orthorhombic	
Space group		*Pbcm*	
a(Å)	6.4777(12)	6.7048(16)	7.0640(14)
b(Å)	12.8490(2)	13.3306(3)	14.0890(3)
c(Å)	12.7491(2)	13.1204(3)	13.6840(3)
V($Å^3$)	1061.14(3)	1172.68(5)	1361.9(5)
Z		4	
$\rho_{calcd.}$/(g cm^{-3})	1.443	2.061	2.463
μ/mm^{-1}	7.507	12.482	6.855
F(000)	488.0	704.0	920.0
GOF	1.176	1.143	1.087
R_1[a][$I > 2s(I)$]	0.027	0.020	0.056
wR_2[b](all data)	0.072	0.055	0.149

a. $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b.* $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Summary of the elastic properties of three compounds. All the elastic tensors are obtained from DFT calculations. The maximal and minimal values of Young's modulus (*E*), shear modulus (*G*), and Poisson's ratio (*v*) were determined by using the ELATE software. Anisotropy of *X* is denoted by $A_X = X_{max}/X_{min}$.

		PIP-Cl	**PIP-Br**	**PIP-I**
G_{ij} (GPa)	C_{11}	53.20	46.35	35.77
	C_{22}	59.11	53.28	41.99
	C_{33}	61.14	53.94	50.17
	C_{44}	7.51	7.85	7.22
	C_{55}	8.28	7.50	6.12
	C_{66}	12.65	10.47	8.21
	C_{12}	12.01	9.20	6.15
	C_{13}	17.79	16.41	12.01
	C_{23}	17.11	16.95	12.57
E (GPa)	E_{max}	*E*(010)=53.28	*E*(001)=49.49	*E*(001)=43.45
	E_{min}=*E*(111)	24.02	22.68	18.82
	A_E	2.2	2.2	2.3
G (GPa)	G_{max}=G(100)<011>	21.35	20.20	16.46
	G_{min}=*G*(100)<001>	7.51	7.50	6.12
	A_G	2.8	2.7	2.7
v	v_{max}=v<101,-101>	0.64	0.61	0.61
	v_{min}=v<101,010>	0.09	0.08	0.07
	A_v	6.92	7.62	8.54
Bulk modulus (GPa)		29.47	26.42	20.24

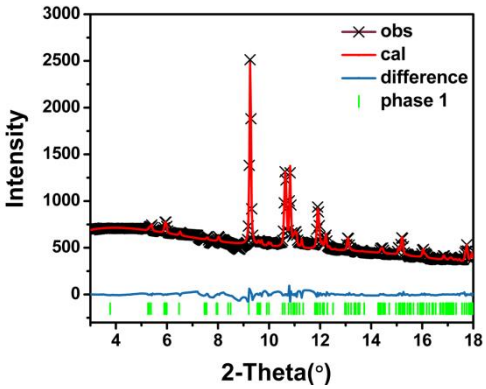

Fig. S1 The synchrotron X-ray diffraction patterns of material PIP-Br refined by Le-Bail whole profile fitting method. Red line: calculated profiles; Black cross: X-ray powder diffraction patterns at room temperature; Blue lines: The difference between experimental data and calculated profile. The green vertical markers indicate the allowed Bragg reflections.

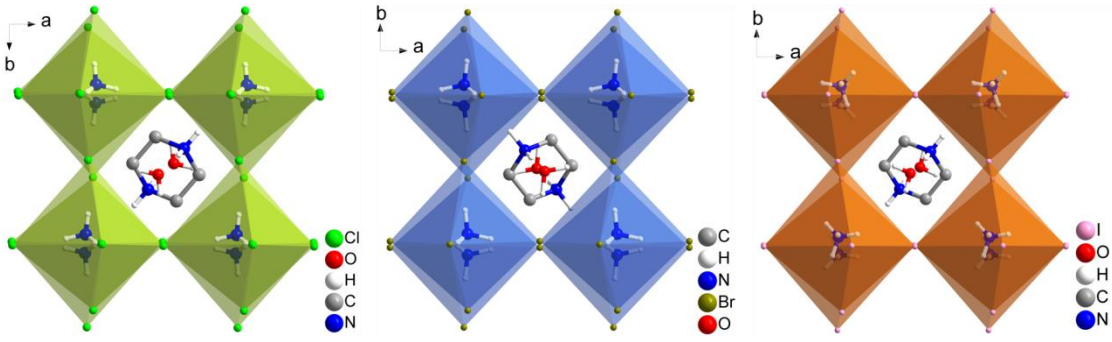

Fig. S2 The packing diagrams for PIP-Cl, PIP-Br and PIP-I.

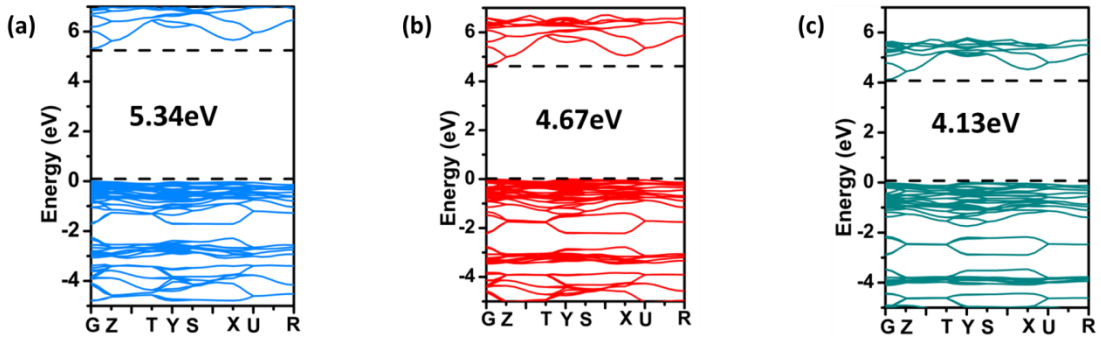

Fig. S3 DFT-calculated electronic band structures for PIP-Cl (a), PIP-Br (b) and PIP-I (c). The valence band maximum is set as zero.

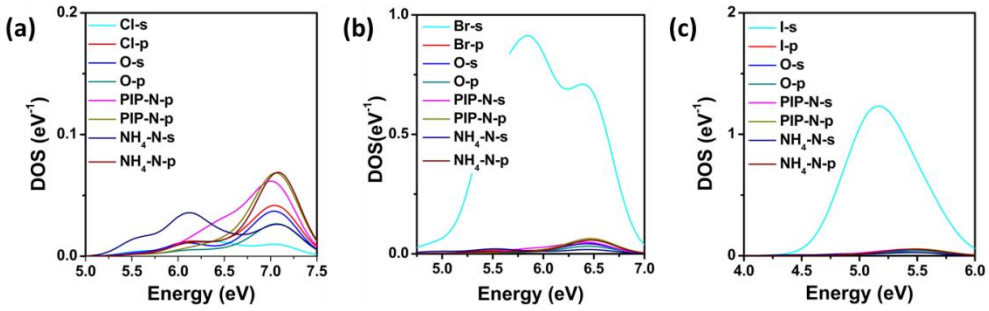

Fig. S4 The local enlarged plots of partial densities of states for PIP-Cl (a), PIP-Br (b) and PIP-I (c).

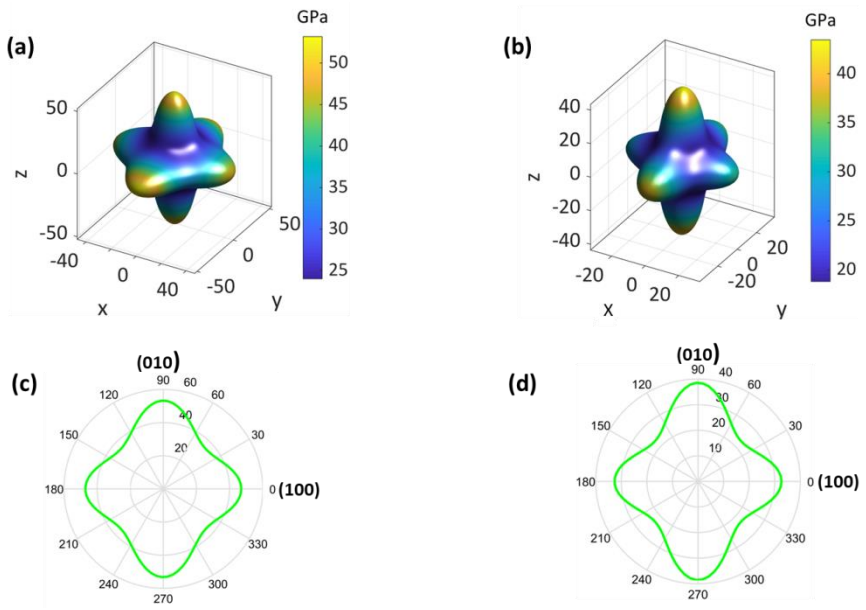

Fig.S5 Representative 3D and 2D plots of Young's modulus, herein (a) and (c) for PIP-Cl and (b) and (d) for PIP-I. In (a) and (b), the transparent outer layer and non-transparent inner layers represent the maximum and minimum values, respectively.

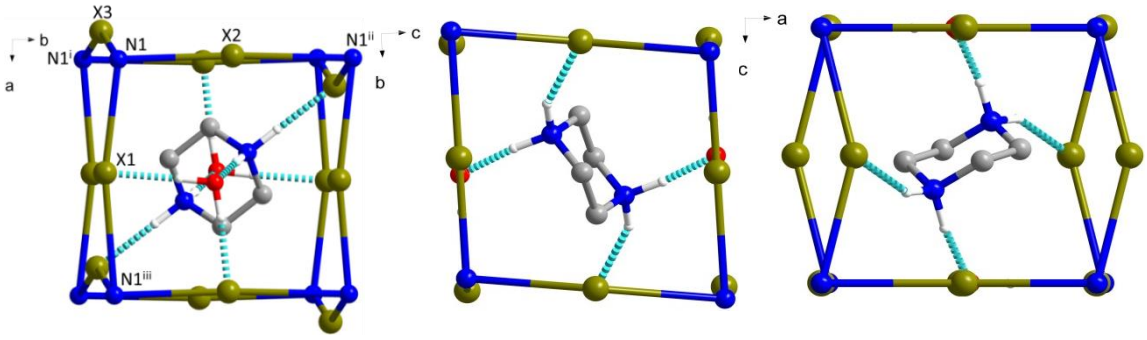

Fig. S6 Hydrogen bond plots of the simplified frameworks viewed along a, b, and c axes. Colour codes: N, blue; O, red; X, brown; C, gray; H, white. Symmetry codes: (i) X, 0.5-Y, -Z; (ii) -X, 0.5+Y, 0.5-Z; (iii) -X, -Y, 0.5+Z.

Table S3. The length of partial hydrogen bonds for PIP-Cl, PIP-Br and PIP-I. $d_{N\text{-}X}$ is denotes the distance between nitrogen atom of NH_4^+ and different halide anions. Xi is represents different halide anions, the details as shown in Fig. S6.

	$d_{N\text{-}X1}$(Å)	$d_{N\text{-}X2}$(Å)	$d_{N\text{-}X3}$(Å)
PIP-Cl	3.18	3.18	3.29
PIP-Br	3.50	3.26	3.43
PIP-I	3.51	3.54	3.50

Table S4 The angles of N1-X-N1 in different compounds considered here, the details as shown in Fig. S6.

	N1-X1-N1	N1-X2-N1	N1-X3-N1
PIP-Cl	163.3	175.8	155.9
PIP-Br	168.9	177.0	153.3
PIP-I	165.9	176.8	159.6

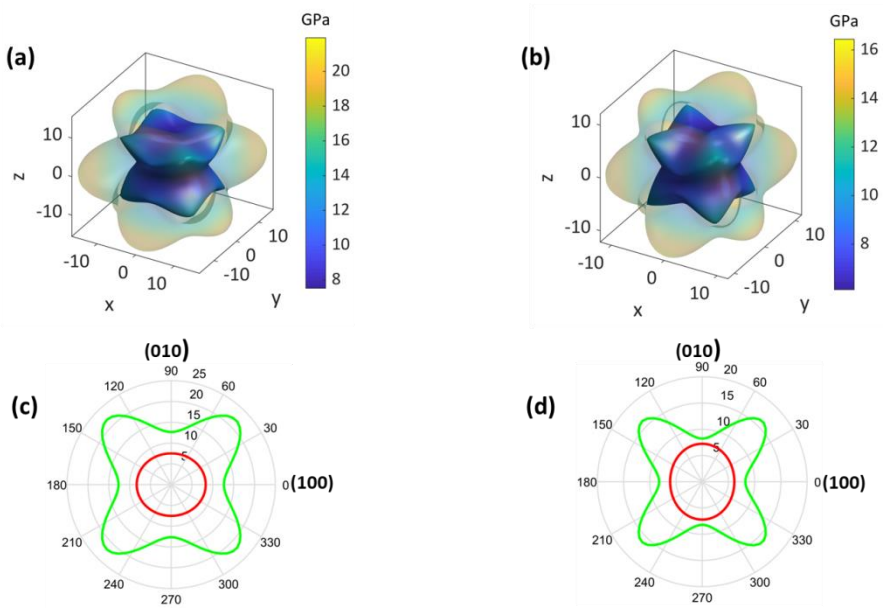

Fig. S7 3D and 2D representations of shear modulus for PIP-Cl (a, c) and PIP-I (b, d). In (a) and (b), the transparent outer layer and non-transparent inner layers represent the maximum and minimum values, respectively. In (c) and (d), the green outer and red inner lines mean the maximum and minimum values.

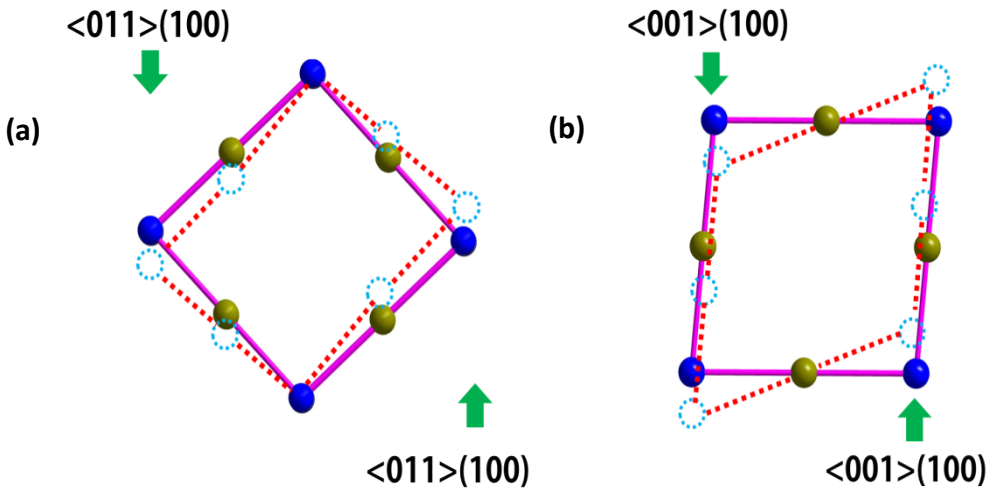

Fig. S8 Schematic diagrams of the (100) plane sheared along <011> (a) and <001> (b) directions. The solid and dashed lines represent the original edge and sheared edge, respectively. Similarly, solid and hollow spheres respective denote original atoms and sheared atoms. Green arrow is represents the direction of force exertion. Color codes: N, blue; X, dark yellow.

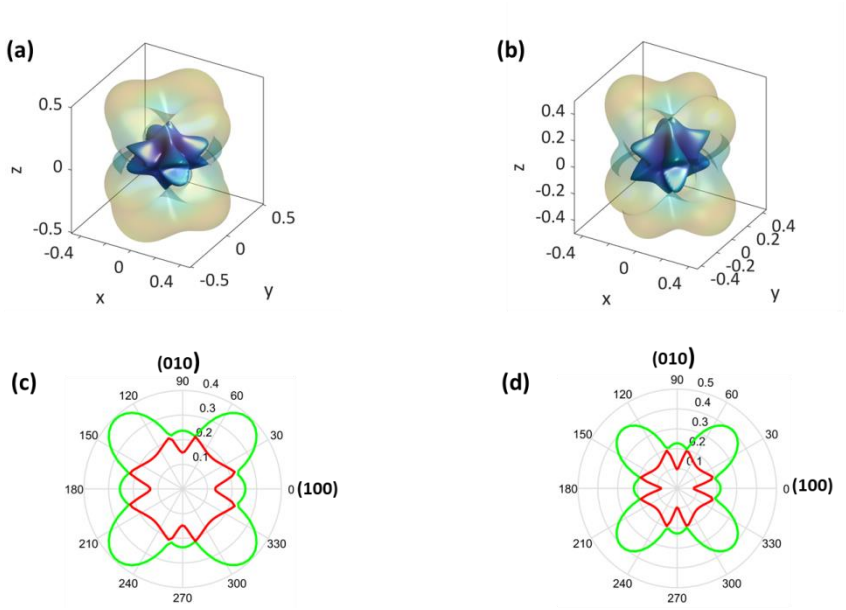

Fig. S9 3D and 2D representations of Poisson's ratios for PIP-Cl (a,c) and PIP-I (b,d). In (a) and (b), the transparent outer layer and non-transparent inner layers represent the maximum and minimum values, respectively. In (c) and (d), the blue outer and red inner lines mean the maximum and minimum values.

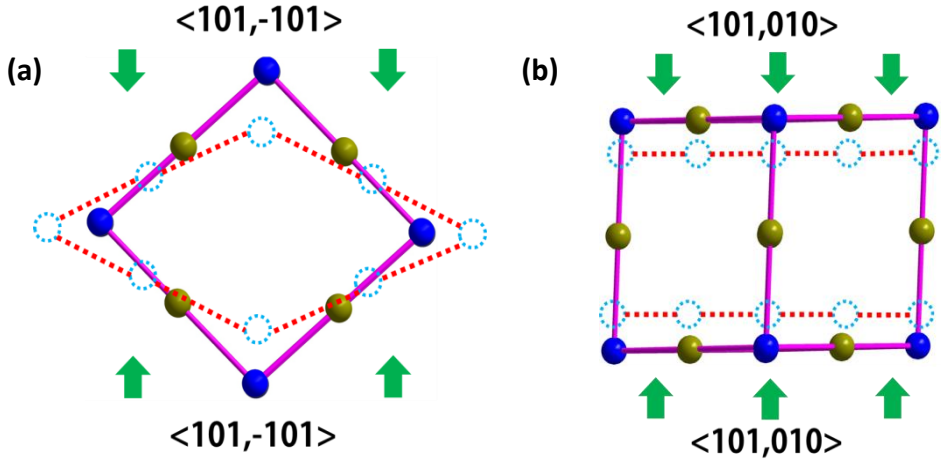

Fig. S10 Schematic diagrams of the Poisson's ratios present the transverse strain of <-101> (a) and <010> directions, when the stresses all exert along the <101> direction. The solid and dashed lines represent the original edge and deformation edge, respectively. Similarly, solid and hollow spheres respective denote original and deformation atoms. Color codes: N, blue; X, dark yellow.

Table S5 The elastic properties of three compounds compared with reported compounds.

	E(GPa)		*G*(GPa)		*v*		*K*(GPa)
	E_{max}	E_{min}	G_{max}	G_{min}	v_{max}	v_{min}	
PIP-Cl	53.3	27.1	21.6	9.1	0.58	0.10	29.6
PIP-Br	46.2	21.0	18.3	6.9	0.62	0.08	24.7
PIP-I	42.3	16.9	16.1	5.9	0.61	0.05	19.2
$CH_3NH_3PbBr_3$[1]	38.1	17.4	17.5	5.7	0.69	-0.12	26.9
$CH_3NH_3PbI_3$[1]	21.6	3.3	9.8	0.9	1.36	-0.64	18.1
MDABCO-NH_4-Cl_3[2]	19.0	7.5	6.5	2.7	0.60	0.05	10.7
MDABCO-NH_4-Br_3[2]	16.7	6.1	6.0	2.1	0.70	0.03	10.2
MDABCO-NH_4-I_3[2]	13.7	6.4	5.5	2.2	0.64	0.08	9.1
$CsAgBiCl_6$[3]	60.8	24.3	25.6	8.9	0.62	0.09	32.6
$CsAgBiBr_6$[3]	54.1	22.3	22.8	8.1	0.61	0.09	28.6
$CsAgBiI_6$[3]	40.6	20.0	17.3	7.5	0.53	0.09	20.6
$(CH_3NH_3)_2KGdCl_6$[4]	37.1	19.9	15.3	6.7	0.59	0.19	19.6
$(DABCOH_2)K(ClO_4)_3$[5]	36.6	31.6	14.6	12.3	0.32	0.20	24.5

Table S6 The evolution of the lattice parameters and unit cell volume of PIP-Br under selected pressure points.

P(GPa)	a(Å)	b(Å)	c(Å)	V(Å^3)
0	6.746	13.405	13.205	1194.5
0.205	6.699	13.336	13.141	1174.0
0.401	6.674	13.289	13.102	1162.1
0.670	6.639	13.225	13.048	1145.6
1.004	6.596	13.160	12.983	1126.9
1.545	6.567	13.104	12.931	1112.6
1.993	6.545	13.045	12.877	1099.4
2.664	6.488	12.923	12.768	1070.5
3.398	6.460	12.840	12.679	1051.6
4.114	6.437	12.781	12.619	1038.1
4.861	6.401	12.718	12.555	1022.1

Table S7 The evolution of selected distances and angles under 0, 1.99 and 4.86GPa, the details as shown in Fig. S6. Length unit is Å and angle unit is °.

	0GPa	1.99GPa	4.86GPa
Br1-N1	3.509	3.358	3.297
Br2-N1	3.441	3.277	3.184
Br3-N1	3.428	3.329	3.273
Br1-N1-Br2	92.5	94.9	95.4
Br1-N1-Br3	75.9	76.3	76.0
Br2-N1-Br3	82.1	81.2	77.9

Table S8 The evolution of N1-Br-N angle under 0, 1.99 and 4.86GPa, the details as shown in Fig. S6. Angle unit is °.

	0GPa	1.99GPa	4.86GPa
N1-Br1-N1	168.9	163.9	159.1
N1-Br2-N1	177.0	179.6	179.2
N1-Br3-N1	153.2	155.8	155.6

Notes and references

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