Electronic Supplementary Information (ESI) for

Dielectric Phase Transition of an A_2BX_4-Type Perovskite with a Pentahedral to Octahedron Transformation

Siqian Chai,[a] Jianbo Xiong,[b] Yongshen Zheng,[b] Rongchao Shi,[b] Jialiang Xu*[a.b]

[1] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China

[2] School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

[a)]Author to whom correspondence should be addressed:

jialiang.xu@nankai.edu.cn

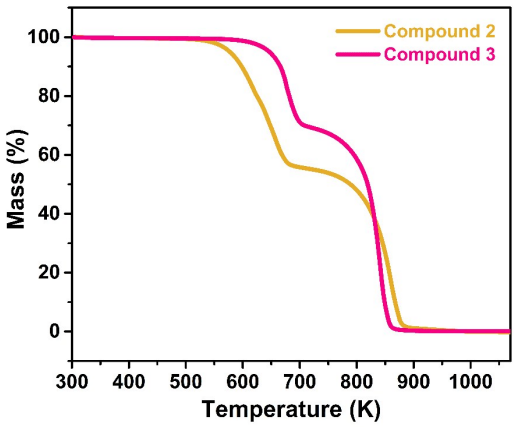

Fig. S1 TGA analyses of Compounds **2** (yellow line) and **3** (purple line).

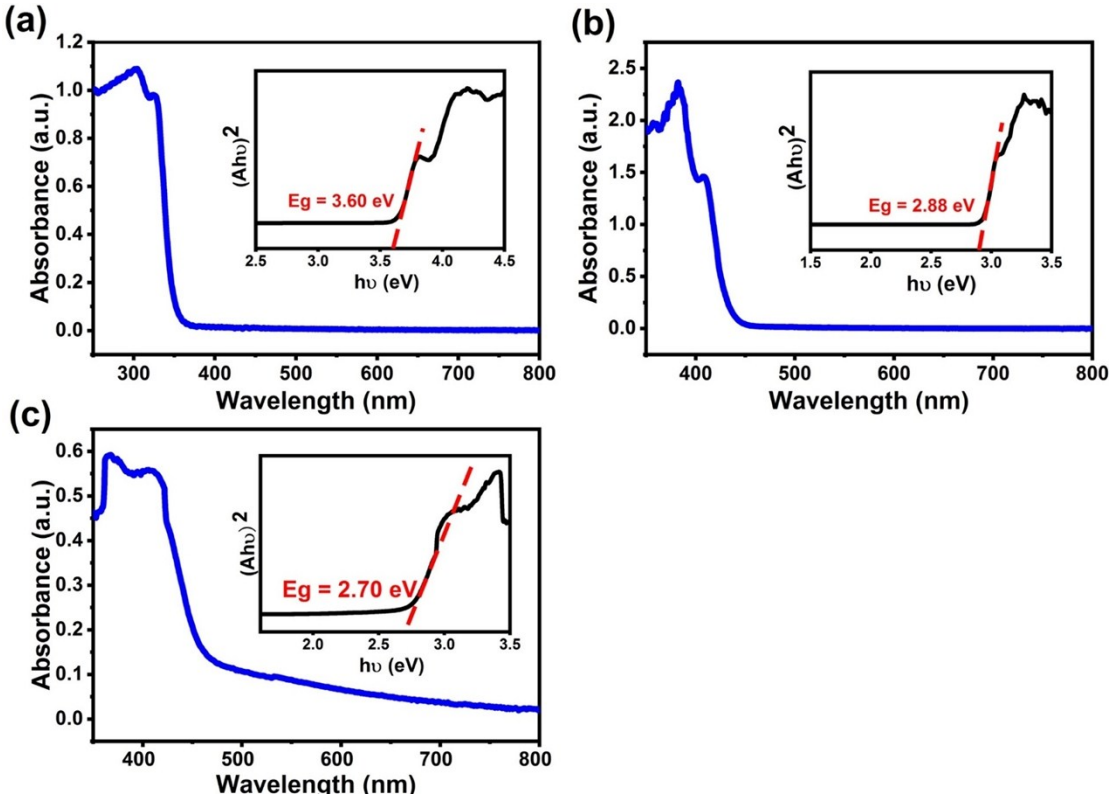

Fig. S2 UV-vis spectra of compounds **1** (a), **2** (b) and **3** (c). Insets: Calculated band gaps of **1** (a), **2** (b) and **3** (c).

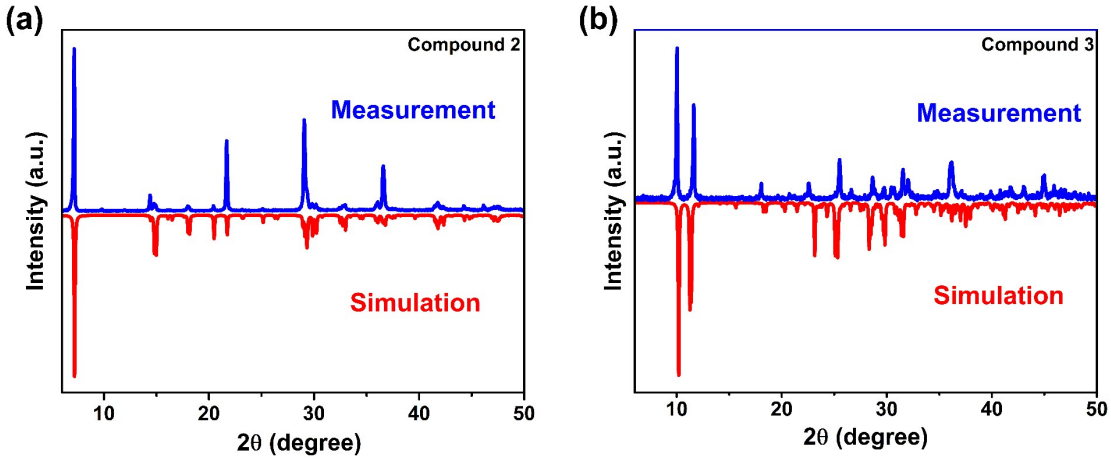

Fig. S3 Experimental and simulated powder X-ray diffraction patterns of compounds **2** (a) and **3** (b).

Table S1 Crystal data and structure refinements for **1**, **2** and **3**.

Empirical formula (CCDC number)	$[C_5H_{12}N]_2PbCl_4$ (1) (1962915)	$[C_5H_{12}N]_2PbCl_4$ (1) (1962913)	$[C_5H_{12}N]_2PbBr_4$ (2) (1962914)	$[C_5H_{12}N]PbI_3$ (3) (1962916)
Temperature	120 K	373 K	210 K	150 K
Formula weight	1042.60	521.30	699.14	674.05
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	Pnma	C2/c	Pnma	P21/c
a (Å)	22.4936(8)	25.0243(15)	12.15(5)	19.3160(19)
b (Å)	23.8631(10)	6.0344(3)	24.90(7)	8.2729(8)
c (Å)	6.1802(2)	11.7615(6)	6.200(10)	17.4841(17)
α (deg.)	90	90	90	90
β (deg.)	90	104.112(5)	90	116.121(3)
γ (deg.)	90	90	90	90
Volume ($Å^3$), Z	3317.3(2), 4	1722.46(17), 4	1875(9), 4	2508.6(4), 8
Calculated density (Mg/m^3)	2.088	2.010	2.476	3.569
F(000)	1984	992	1280	2320
Limiting indices	-31<=h<=30 -32<=k<=33 -8<=l<=8	-30<=h<=30 -7<=k<=7 -14<=l<=14	0<=h<=14 -28<=k<=28 0<=l<=7	-23<=h<=21 -9<=k<=10 -21<=l<=21
Collected reflections	31870	7651	1531	17269
Unique reflections	4528 [$R_{(int)}$ = 0.0519]	1690 [$R_{(int)}$ = 0.1733]	1531	4674 [$R_{(int)}$ = 0.0969]
Completeness	99.8%	99.9%	97.3%	98.2%
Data / restraints / parameters	4528/54/163	1690/276/137	1531/288/137	4674/144/182
GOF	1.031	1.026	1.071	1.038
R_1/wR_2 [$I>2\sigma(I)$]	0.0233/0.0560	0.0954/0.2400	0.1272/0.3062	0.1071/0.3232

Table S2 Hydrogen-Bond Geometry (Å, degree) for N–H···Cl interactions at 295 and 373 K in **1**.

	D–H···A	H···A [Å]	D···A [Å]	D–H···A [°]
295 K	N4–H4B···Cl6	2.91	3.34(8)	111.5
	N6–H6B···Cl1	2.99	3.37(9)	107.7
	N6–H6B···Cl3	2.89	3.40(8)	118.2
373 K	N1'–H1'2···Cl3	2.79	3.50(4)	138.0
	N1'–H1'2···Cl2	2.98	3.61(4)	130.1
	N1–H1B···Cl3	2.81	3.47(8)	131.8

Table S3 Selected bond lengths [Å] and angles [°] for **1** at 295 and 373 K.

295 K	Pb0A-Cl1	2.6763(11)	Pb1A-Cl5^{ii}	2.8657(8)
	Pb0A-Cl6^{i}	2.9095(10)	Pb1A-Cl5	2.8658(8)
	Pb0A-Cl3	2.7851(10)	Pb1A-Cl4	2.6289(11)
	Pb0A-Cl2	2.8814(8)	Pb1A-Cl6	2.8166(10)
	Pb0A-Cl2^{ii}	2.8815(8)	Pb1A-Cl3	2.9418(10)
	Cl1-Pb0A-Cl6^{i}	93.13(3)	Cl5^{ii}-Pb1A-Cl3	95.395(15)
	Cl1-Pb0A-Cl3	88.53(3)	Cl5-Pb1A-Cl3	95.396(15)
	Cl1-Pb0A-Cl2^{ii}	82.516(16)	Cl4-Pb1A-Cl5	86.717(16)
	Cl1-Pb0A-Cl2	82.517(16)	Cl4-Pb1A-Cl5^{ii}	86.717(16)
	Cl3-Pb0A-Cl6^{i}	178.34(3)	Cl4-Pb1A-Cl6	89.57(3)
	Cl3-Pb0A-Cl2	89.055(14)	Cl4-Pb1A-Cl3	88.68(3)
	Cl3-Pb0A-Cl2^{ii}	89.053(14)	Cl6-Pb1A-Cl5^{ii}	84.503(15)
	Cl2^{ii}-Pb0A-Cl6^{i}	91.163(14)	Cl6-Pb1A-Cl5	84.502(15)
	Cl2-Pb0A-Cl6^{i}	91.161(14)	Cl6-Pb1A-Cl3	178.25(3)
	Cl2-Pb0A-Cl2^{ii}	164.96(3)	Pb1A-Cl6-Pb0A	163.31(4)
	Cl5^{ii}-Pb1A-Cl5	167.23(3)	Pb0A-Cl3-Pb1A	167.76(4)
373 K	Pb1-Cl1	2.730(10)	Pb1-Cl2	2.95754(16)
	Pb1-Cl3^{iii}	2.851(7)	Pb1-Cl2^{iii}	2.95754(16)
	Pb1-Cl3	2.851(7)		
	Cl1-Pb1-Cl3^{iii}	84.73(15)	Cl1-Pb1-Cl2^{iii}	96.178(9)
	Cl1-Pb1-Cl3	84.73(15)	Cl3^{iii}-Pb1-Cl2^{iii}	90.22(17)
	Cl3^{iii}-Pb1-Cl3	169.5(3)	Cl3-Pb1-Cl2^{iii}	90.91(17)
	Cl1-Pb1-Cl2	96.178(9)	Cl2-Pb1-Cl2^{iii}	167.644(18)
	Cl3^{iii}-Pb1-Cl2	90.91(17)	Pb1^{v}-Cl2-Pb1	180.0
	Cl3-Pb1-Cl2	90.22(17)		

Symmetry code: (i) x-1/2,y,-z+1/2; (ii) x,-y+3/2,z; (iii) -x+1,y,-z+1/2; (v) -x+1,-y+1,-z.

Table S4 Hydrogen-Bond Geometry (Å, degree) for N–H···Br interactions in **2**.

D–H···A	H···A [Å]	D···A [Å]	D–H···A [°]
N1–H1C···Br3	2.72	3.41(8)	133.4
N1'–H2C···Br3	2.74	3.62(9)	165.8
N1'–H2D···Br3	2.97	3.72(8)	141.5

Table S5 Selected bond lengths [Å] and angles [°] for **2** at 210 K.

210 K	Pb1-Br2	2.958(7)	Pb1-Br3	3.051(10)
	Pb1-Br1	3.030(13)	Pb1-Br1^{ii}	3.072(13)
	Pb1-Br3^{i}	3.051(10)		
	Br2-Pb1-Br1	96.0(2)	Br2-Pb1-Br1^{ii}	94.8(2)
	Br2-Pb1-Br3^{i}	84.91(13)	Br1-Pb1-Br1^{ii}	169.16(8)
	Br1-Pb1-Br3^{i}	90.74(12)	Br3^{i}-Pb1-Br1^{ii}	90.21(12)
	Br2-Pb1-Br3	84.91(13)	Br3-Pb1-Br1^{ii}	90.22(12)
	Br1-Pb1-Br3	90.74(12)	Br1-Pb1-Br1^{iii}	179.2(3)
	Br3^{i}-Pb1-Br3	169.8(3)		

Symmetry code: (i) x,-y+1/2,z; (ii) x+1/2,y,-z+1/2; (iii) x-1/2,y,-z+1/2.

Table S6 Hydrogen-Bond Geometry (Å, degree) for N–H···I interactions in **3**.

D–H···A	H···A [Å]	D···A [Å]	D–H···A [°]
N2–H2C···I1	3.28	4.04(3)	142.3
N2–H2D···I3	3.27	3.95(3)	132.7
N1–H1B···I4	3.30	3.95(3)	130.3

Table S7 Selected bond lengths [Å] and angles [°] for **3** at 150 K.

150 K	Pb1-I4	3.063(3)	Pb2-I2	3.084(3)
	Pb1-I3	3.098(3)	Pb2-I5	3.157(3)
	Pb1-I1	3.183(2)	Pb2-I6	3.208(2)
	Pb1-I1^{i}	3.290(2)	Pb2-I5^{ii}	3.295(3)
	Pb1-I3^{i}	3.416(3)	Pb2-I6^{ii}	3.302(2)
	I4-Pb1-I3	86.48(7)	I5-Pb2-I6	85.93(7)
	I4-Pb1-I1	91.41(7)	I2-Pb2-I5^{ii}	87.47(7)
	I3-Pb1-I1	87.52(6)	I5-Pb2-I5^{ii}	176.64(8)
	I4-Pb1-I1^{i}	85.47(6)	I6-Pb2-I5^{ii}	96.20(6)
	I3-Pb1-I1^{i}	93.84(6)	I2-Pb2-I6^{ii}	85.88(7)
	I1-Pb1-I1^{i}	176.51(6)	I5-Pb2-I6^{ii}	95.54(6)
	I4-Pb1-I3^{i}	86.98(7)	I6-Pb2-I6^{ii}	177.54(8)
	I3-Pb1-I3^{i}	171.82(7)	I5^{ii}-Pb2-I6^{ii}	82.23(6)
	I1-Pb1-I3^{i}	97.57(6)	Pb1-I1- Pb1^{iii}	79.44(5)
	I1^{i}-Pb1-I3^{i}	80.73(6)	Pb1-I3- Pb1^{iii}	78.70(5)
	I2-Pb2-I5	89.86(7)	Pb2-I5- Pb2^{iv}	79.73(5)
	I2-Pb2-I6	92.16(7)	Pb2-I6- Pb2^{iv}	78.89(4)

Symmetry code: (i) -x+2,y-1/2,-z+3/2; (ii) -x+1,y+1/2,-z+3/2; (iii) -x+2,y+1/2,-z+3/2; (iv) -x+1,y-1/2,-z+3/2.