Supporting Information

Sequential structural transitions with distinct dielectric responses in a layered perovskite organic-inorganic hybrid material: $[C_4H_9N]_2[PbBr_4]$†

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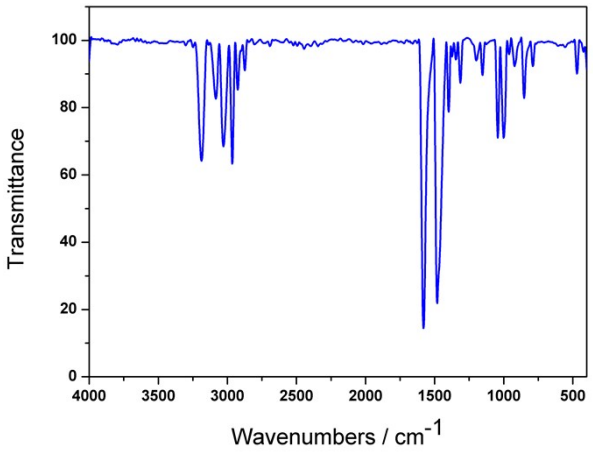

Fig. S1 Infrared (IR) spectra of solid **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature

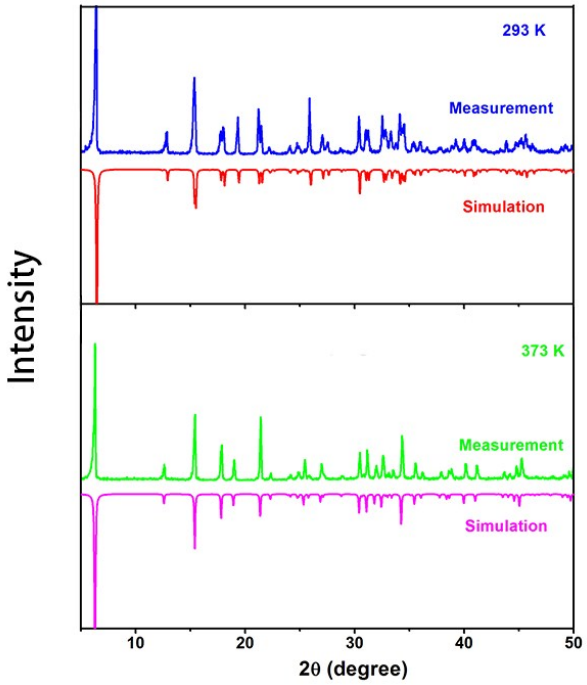

Fig. S2 Experimental powder diffraction (XRPD) patterns matching very well with the simulated ones in terms of the crystal structures for different phases

Table S1. Selected bond lengths [Å] and angles [°] for **1**[a] at 293, and 373 K

293 K	Pb1-Br1	3.018(9)	Pb1-Br2	2.990(14)
	Br2-Pb1-Br2^{i}	180.00(14)	Br2-Pb1-Br1^{ii}	89.30(4)
	Br2^{i}-Pb1-Br1^{ii}	90.70(4)	Br2-Pb1-Br1^{iii}	90.70(4)
	Br2^{i}-Pb1-Br1^{iii}	89.30(4)	Br1^{ii}-Pb1-Br1^{iii}	180.00(3)
	Br2-Pb1-Br1	85.99(3)	Br2^{i}-Pb1-Br1	94.01(3)
	Br1^{ii}-Pb1-Br1	90.66(16)	Br1^{iii}-Pb1-Br1	89.34(16)
	Br2-Pb1-Br1^{i}	94.01(3)	Br2^{i}-Pb1-Br1^{i}	85.99(3)
	Br1^{ii}-Pb1-Br1^{i}	89.34(16)	Br1^{iii}-Pb1-Br1^{i}	90.66(16)
	Br1-Pb1-Br1^{i}	180.00(2)	Pb1^{iv}-Br1-Pb1	153.22(3)
373 K	Pb1-Br1	3.021(2)	Pb1-Br2	2.983(4)
	Br2-Pb1-Br2^{v}	180.00(14)	Br2^{v}-Pb1-Br1^{vi}	90.00(7)
	Br2-Pb1-Br1^{vi}	90.00(7)	Br2^{v}-Pb1-Br1^{vii}	90.00(7)
	Br2-Pb1-Br1^{vii}	90.00(7)	Br1^{vi}-Pb1-Br1^{vii}	180.00(14)

Br2^{v}-Pb1-Br1	90.00(7)	Br2-Pb1-Br1	90.00(7)
Br1^{vi}-Pb1-Br1	89.97(7)	Br1^{vii}-Pb1-Br1	90.03(7)
Br2^{v}-Pb1-Br1^{v}	90.00(7)	Br2-Pb1-Br1^{v}	90.00(7)
Br1^{vi}-Pb1-Br1^{v}	90.03(7)	Br1^{vii}-Pb1-Br1^{v}	89.97(7)
Br1-Pb1-Br1^{v}	180.00(14)	Pb1^{viii}-Br1-Pb1	153.16(6)

[a] Symmetry codes: (i) -x,-y,-z (ii) -x,y-1/2,-z+1/2 (iii) x,-y+1/2,z-1/2 (iv) -x,y+1/2,-z+1/2 (v) -x,-y,-z (vi) -x,y-1/2,-z+1/2 (vii) x,-y+1/2,z-1/2 (viii) -x,y+1/2,-z+1/2

Table S2. Hydrogen-Bond Geometry (**Å**, deg) for N-H···Br interactions at 293, and 373 K in **1**[b]

	D–H···A	H···A	D···A	D–H···A
293 K	N1-H1D···Br1^{ii}	2.65	3.49(7)	157.9
	N1-H1E···Br1^{i}	2.69	3.45(7)	144.9
	N1-H1E···Br2^{iii}	2.93	3.44(6)	117.8
	N1-H1F···Br2^{ii}	3.00	3.43(8)	111.5
373 K	N1-H1D···Br1^{v}	2.69	3.48(3)	146.6
	N1-H1D···Br1^{iv}	3.03	3.44(3)	110.5
	N1-H1E···Br1	2.71	3.56(2)	157.9
	N1-H1F···Br1^{vi}	2.75	3.60(2)	158.7

[b] Symmetry codes: (i) -x,y+1/2,-z+1/2 (ii) x,-y+3/2,z+1/2 (iii) x,y+1,z (iv) x,y-1/2,-z-1/2 (v) -x+1,-y+1/2,z+1/2 (vi) x,y+1/2,-z-1/2