Supporting Information

Sequential structural transitions with distinct dielectric responses in a layered perovskite organic-inorganic hybrid material: \([\text{C}_4\text{H}_9\text{N}]_2[\text{PbBr}_4]\)^†

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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 at 293, and 373 K

<table>
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<tr>
<th></th>
<th>293 K</th>
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<th>373 K</th>
<th></th>
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<tr>
<td></td>
<td>Pb1-Br1</td>
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<td>Pb1-Br1</td>
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<td>Pb1-Br2</td>
<td>3.018(9)</td>
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<td>Pb1-Br2</td>
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<td>Br2-Pb1-Br2</td>
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<td>Br2-Pb1-Br1</td>
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<td>Br2-Pb1-Br1</td>
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<td>Br2-Pb1-Br1</td>
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Br2\textsuperscript{v}-Pb1-Br1  & 90.00(7) & Br2-Pb1-Br1  & 90.00(7) \\
Br1\textsuperscript{vi}-Pb1-Br1  & 89.97(7) & Br1\textsuperscript{vii}-Pb1-Br1  & 90.03(7) \\
Br2\textsuperscript{v}-Pb1-Br1\textsuperscript{v}  & 90.00(7) & Br2-Pb1-Br1\textsuperscript{v}  & 90.00(7) \\
Br1\textsuperscript{vi}-Pb1-Br1\textsuperscript{v}  & 90.03(7) & Br1\textsuperscript{vii}-Pb1-Br1\textsuperscript{v}  & 89.97(7) \\
Br1-Pb1-Br1\textsuperscript{v}  & 180.00(14) & Pb1\textsuperscript{viii}-Br1-Pb1  & 153.16(6) \\

\textsuperscript{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\textsuperscript{b}

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<tr>
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<th>D–H···A</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
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<tr>
<td>373 K</td>
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</tr>
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<td>3.48(3)</td>
<td>146.6</td>
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<td>N1-H1D···Br1\textsuperscript{iv}</td>
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<td>3.44(3)</td>
<td>110.5</td>
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<td>N1-H1E···Br1\textsuperscript{vi}</td>
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<td>N1-H1F···Br1\textsuperscript{vi}</td>
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\textsuperscript{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