

## Supporting Information

### Fast Rotating Dipoles Array Inducing Large Dielectric Response in a Ruddlesden–Popper Hybrid Perovskite Ferroelastic

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## Experimental

### Sample preparation.

Materials:  $\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$  ( $\geq 98\%$ , ShangHai Titan Scientific Co., Ltd), trans-2-fluorocyclopentan-1-amine hydrochloride ( $\text{C}_5\text{H}_{10}\text{FN} \cdot \text{HCl}$ ) [ $>97\%$ , PharmaBlock sciences (Nanjing), Inc]. All chemicals are commercially available and used directly without purification.

Synthesis of Compound:  $\text{C}_5\text{H}_{10}\text{FN} \cdot \text{HCl}$ ,  $\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$  were weighed at stoichiometry 2:1, respectively. Using deionized water as solvent, slowly evaporates on 308 K constant-temperature heating table. After about four days, a mixture containing precipitated crystals and mother liquor is obtained.

### General Measurements.

The Powder X-ray Diffraction (PXRD) were measured at a measurement angle of  $5^\circ$ – $50^\circ$  and a scan rate of  $5^\circ/\text{min}$  on Rigaku D/MAX 2000 PC X-ray diffractometer. And the X-ray wavelength is 0.15406 nm. Thermogravimetric (TG) was measured on a NETZSCH STA2500 instrument under a nitrogen atmosphere with a heating rate of 10 K/min. Differential scanning calorimetry (DSC) was measured on a DSC 214 Polyma instrument under nitrogen atmosphere with a heating/cooling rate of 15 K/min. The dielectric measurements of compounds **1** were carried out on Tonghui TH2828A impedance analyzer: the polycrystals of compounds **1** were compacted into tight sheets, and the two sides were coated with silver glue and tested in the temperature range of 320 K to 430 K, 500 Hz, 1 kHz, 5 kHz, 10 kHz, 100 kHz and 1 MHz of composite dielectric constant ( $\epsilon_r = \epsilon' - i\epsilon''$ ) changes with temperature (Figure S4). The ferroelastic domain observations were detected with an Olympus BX51TRF optical polarizing microscope. The temperature remained stable with an accuracy of 0.2 K by using an INSTRON HCC602 cooling/heating stage.

### Variable-temperature NMR Experiments

All of the  $^{13}\text{C}$  NMR experiments were performed on a Bruker AVANCE NEO 400 WB spectrometer operating at 100. MHz for  $^{13}\text{C}$ . For all the high-temp NMR experiments, a 7.0 mm double-resonance WVT probe was used. The spinning rate

was set to 3 kHz and the recycle delay was set to 2 s. Number of scans was set to 512. And 4 us pulse widths were used for  $^1\text{H}$  and  $^{13}\text{C}$  spins. For  $^1\text{H}$ - $^{13}\text{C}$  CP/MAS NMR experiments, the cross polarization time was set to 1 ms. The  $^{13}\text{C}$  chemical shift was calibrated using Adamantane ( $\delta = 38.5$  ppm, methylene signal).

### X-ray diffraction experiments.

Single-crystal X-ray diffraction studies were recorded on a Rigaku synergy diffractometer using the  $\omega$  scan technique with Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. All structures are solved using direct methods and refined using the full matrix least squares technique in the SHELX2016 package. At high-temperature phase, the space groups were chosen according to the Aizu principle. The organic cations were not modeled according to its chemical sense, because of the highly disordered form at high-temperature phase. Detailed crystallographic data are recorded in **Tables S1–S4**. CCDC number: 2265824-2265825 contains supplemental crystallographic data for this article. These data are freely available from the Cambridge Crystallographic Data Centre.

### The procedure of spontaneous strain calculation for compound 1.

Firstly, the strain tensors  $e_{11}$  and  $e_{22}$  were calculated according to the cell parameters at 323 K ( $a_f, b_f, c_f$ ) and 423 K ( $a_p, b_p, c_p$ ) by the following formula (1).

$$e_{11} = \frac{a_f}{\sqrt{2}a_p} - 1 \quad e_{22} = \frac{b_f}{\sqrt{2}b_p} - 1 \quad \#(1)$$

Then the spontaneous strain tensor  $\varepsilon$  is calculated by equation (2).

$$\varepsilon = \frac{e_{11} - e_{22}}{2} = \left| \frac{a_f - b_f}{2\sqrt{2}a_p} \right| \quad \#(2)$$

Further, the spontaneous strains of  $\varepsilon_s(S_1)$  and  $\varepsilon_s(S_2)$  of the two orientation states  $S_1$  and  $S_2$  in the ferroelastic phase are calculated by equations (3).

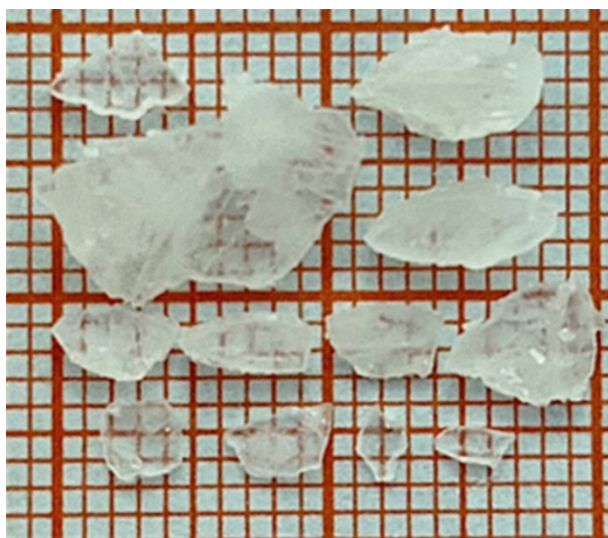
$$\varepsilon_s(S_1) = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & -\varepsilon & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \varepsilon_s(S_2) = \begin{bmatrix} -\varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \#(3)$$

For this hybrid molecular ferroelastic, the spontaneous strain in the paraelastic phase above  $T_c$  is zero and equal in the two orienting states of the ferroelastic phase.

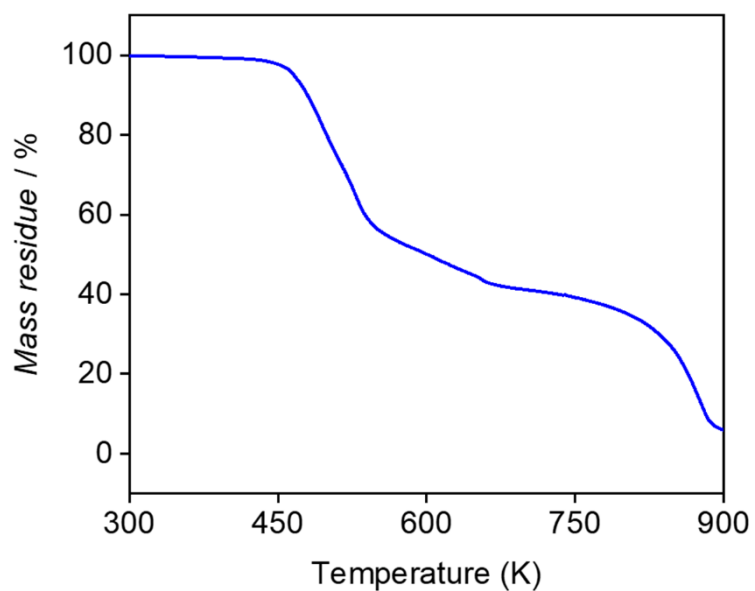
Therefore, the spontaneous strain ( $\varepsilon_s(S_1)$ ,  $\varepsilon_s(S_2)$ ) is given by equation (4).

$$\varepsilon_s(S_1) = \varepsilon_s(S_2) = \sqrt{\sum_{ij} \varepsilon_{Sij}^2} = \sqrt{2}\varepsilon \quad (4)$$

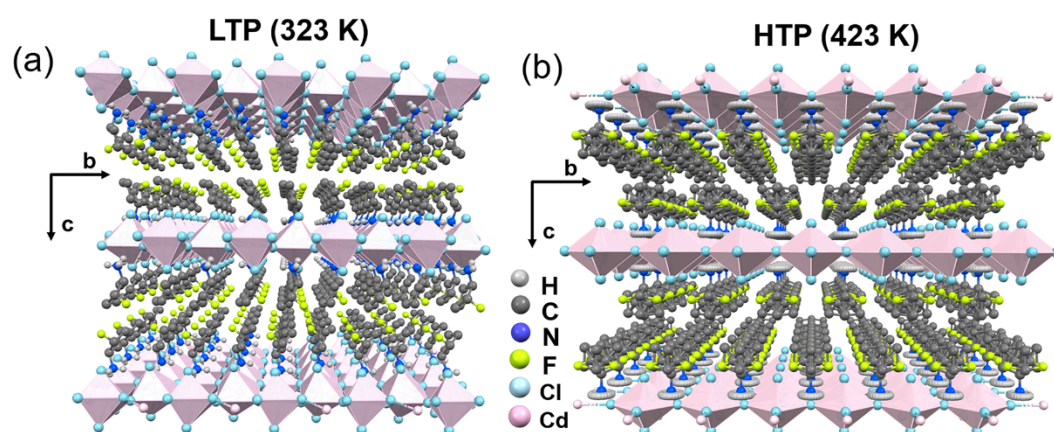
## Supplemental Figures



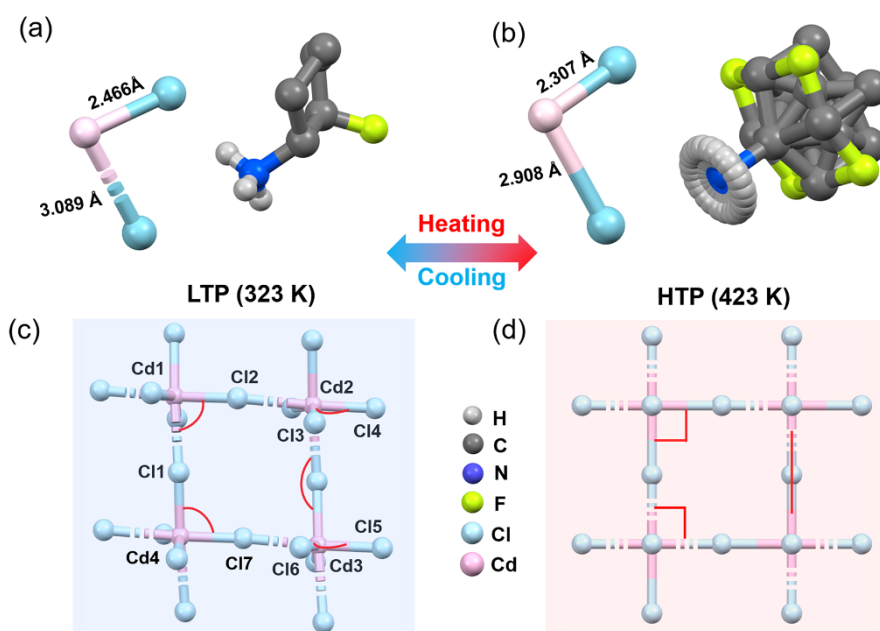
**Figure S1.** Colourless transparent crystal of compound **1**.



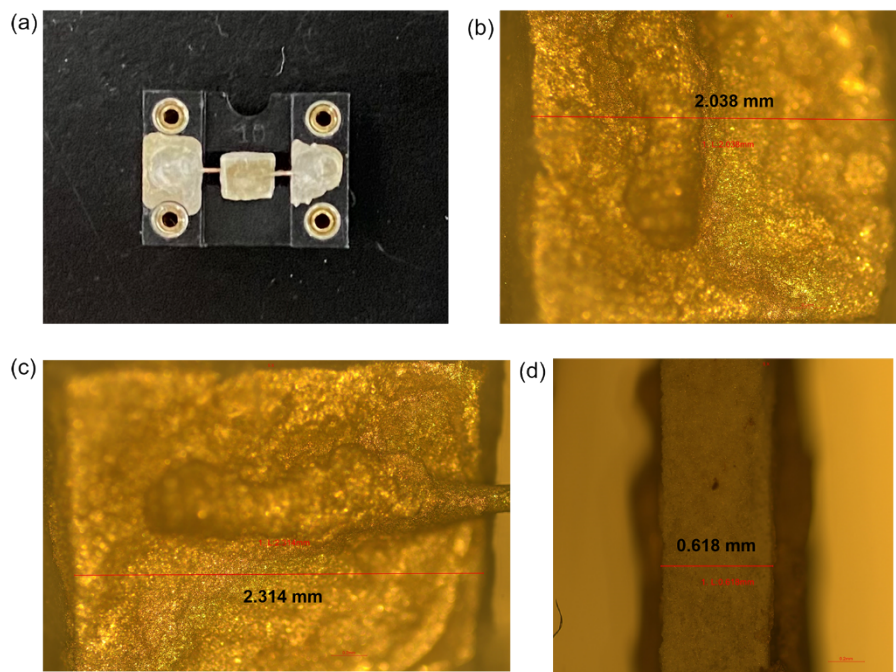
**Figure S2.** The thermogravimetric (TG) curve of compound **1**.



**Figure S3.** Comparison of crystal structures of **1**. (a) **1** in the LTP (ferroelastic phase). (b) **1** in the HTP (paraelastic phase) (Some of the hydrogen atoms have been omitted for clarity).



**Figure S4.** Minimum asymmetric unit for compound **1** LTP(a) and HTP(b), anion framework for LTP(c) and HTP(d) (Some of the hydrogen atoms have been omitted for clarity).



**Figure S5.** The polycrystalline solid electrodes (a) of compound **1** with silver paste and copper wires connected on either side. The area width (b), length (c) and electrode thickness (d) of the silver paste measured by polarizing microscope.

## Supplemental Tables

**Table S1.** Crystal Data and Structure Refinement Details for **1** at 293 K and 403 K.

<i>T</i> / K	323 K	423K
Formula weight	231.25	231.25
Empirical formula	C <sub>10</sub> H <sub>22</sub> F <sub>2</sub> N <sub>2</sub> CdCl <sub>4</sub>	C <sub>10</sub> H <sub>22</sub> F <sub>2</sub> N <sub>2</sub> CdCl <sub>4</sub>
Crystal system	orthorhombic	tetragonal
Space group	<i>Pbcn</i>	<i>I4/mmm</i>
<i>a</i> / Å	8.3356(4)	5.8052(10)
<i>b</i> / Å	7.5132(4)	5.8052(10)
<i>c</i> / Å	27.2065(12)	26.729(4)
$\alpha$ / °	90	90
$\beta$ / °	90	90
$\gamma$ / °	90	90
<i>V</i> / Å <sup>3</sup>	1703.86(14)	900.8(2)
<i>Z</i>	8	32
<i>D</i> <sub>calc</sub> / g·cm <sup>-3</sup>	1.803	1.458
$\mu$ / mm <sup>-1</sup>	1.916	1.797
<i>F</i> (000)	920.0	383.0
$2\theta$ range / °	5-732-62.046	6.096-59.546
Reflns collected	8469	2516
Independent reflns ( <i>R</i> <sub>int</sub> )	2136 (0.0318)	395(0.0415)
No. of parameters	88	42
<i>R</i> <sub>1</sub> <sup>[a]</sup> , <i>wR</i> <sub>2</sub> <sup>[b]</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0405, 0.0993	0.2144, 0.4887
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [all data]	0.0542, 0.1041	0.2886, 0.5206
GOF	1.119	1.743
$\Delta\rho$ <sup>[c]</sup> / e·Å <sup>-3</sup>	0.83, -0.82	1.51, -0.43
CCDC	2265825	2265824

[a]  $R_1 = \sum ||F_o| - |F_c|| / |F_o|$ ; [b]  $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2$ ]<sup>1/2</sup>; [c] maximum and minimum residual electron density.



**Table S2** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **1** at 323 K and 423 K.

<b>323K</b>			
Cd1–Cl2 <sup>i</sup>	2.4660 (10)	Cl2–Cd1–Cl1	98.79 (4)
Cd1–Cl2	2.4661 (10)	Cl2–Cd1–Cl1 <sup>ii</sup>	83.50 (4)
Cd1–Cl1 <sup>ii</sup>	3.0890 (12)	Cl2 <sup>i</sup> –Cd1–Cl1 <sup>i</sup>	98.79 (4)
Cd1–Cl1 <sup>i</sup>	2.5936 (12)	Cl2 <sup>i</sup> –Cd1–Cl1 <sup>iii</sup>	83.50 (4)
Cd1–Cl1	2.5935 (12)	Cl1 <sup>i</sup> –Cd1–Cl1 <sup>iii</sup>	83.041 (10)
Cd1–Cl1 <sup>iii</sup>	3.0890 (12)	Cl1–Cd1–Cl1 <sup>iii</sup>	176.81 (5)
Cl2 <sup>i</sup> –Cd1–Cl2	153.83 (6)	Cl1 <sup>i</sup> –Cd1–Cl1 <sup>ii</sup>	176.81 (5)
Cl2–Cd1–Cl1 <sup>i</sup>	98.89 (4)	Cl1 <sup>iii</sup> –Cd1–Cl1 <sup>ii</sup>	99.50 (5)
Cl2 <sup>i</sup> –Cd1–Cl1 <sup>ii</sup>	79.67 (4)	Cl1–Cd1–Cl1 <sup>i</sup>	94.48 (6)
Cl2 <sup>i</sup> –Cd1–Cl1	98.89 (4)	Cl1–Cd1–Cl1 <sup>ii</sup>	83.041 (9)
Cl2–Cd1–Cl1 <sup>iii</sup>	79.67 (4)		

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

<b>423K</b>			
Cd1–Cl1	2.9026 (5)	Cl1–Cd1–Cl1 <sup>i</sup>	90.0
Cd1–Cl1 <sup>i</sup>	2.9026 (5)	Cl2–Cd1–Cl1 <sup>ii</sup>	90.000 (1)
Cd1–Cl1 <sup>ii</sup>	2.9026 (5)	Cl2 <sup>iv</sup> –Cd1–Cl1 <sup>i</sup>	90.000 (1)
Cd1–Cl1 <sup>iii</sup>	2.9026 (5)	Cl2 <sup>iv</sup> –Cd1–Cl1 <sup>iii</sup>	90.000 (1)
Cd1–Cl2 <sup>iv</sup>	2.307 (15)	Cl2 <sup>iv</sup> –Cd1–Cl1 <sup>ii</sup>	90.000 (1)
Cd1–Cl2	2.307 (15)	Cl2–Cd1–Cl1 <sup>iii</sup>	90.000 (1)
Cl1–Cd1–Cl1 <sup>iii</sup>	90.0	Cl2–Cd1–Cl1	90.000 (1)
Cl1 <sup>ii</sup> –Cd1–Cl1 <sup>i</sup>	90.0	Cl2 <sup>iv</sup> –Cd1–Cl1	90.000 (1)
Cl1 <sup>iii</sup> –Cd1–Cl1 <sup>i</sup>	180.0	Cl2–Cd1–Cl1 <sup>i</sup>	90.000 (1)
Cl1–Cd1–Cl1 <sup>ii</sup>	180.0	Cl2–Cd1–Cl2 <sup>iv</sup>	180.0
Cl1 <sup>iii</sup> –Cd1–Cl1 <sup>ii</sup>	90.0	Cd1 <sup>xii</sup> –Cl1–Cd1	180.0

Symmetry codes: (i)  $-y+1, x, z$ ; (ii)  $x, y+1, z$ ; (iii)  $-y+2, x, z$ ; (iv)  $-x+2, -y+2, -z+1$ ; (v)  $y+1, x-1, z$ ; (vi)  $-x+3, y, z$ ; (vii)  $y+1, -x+2, z$ ; (viii)  $-y+2, -x+2, z$ ; (ix)  $x, -y+1, z$ ; (x)  $-x+3, -y+1, z$ ; (xi)  $-y+2, x-1, z$ ; (xii)  $x, y-1, z$ .

**Table S3.** Bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ] of the hydrogen bond at 323 K of **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1-H1A $\cdots$ C12	0.89	2.44	3.313 (4)	166
N1-H1B $\cdots$ C11 <sup>iv</sup>	0.89	2.50	3.362 (4)	162
N1-H1C $\cdots$ C12 <sup>v</sup>	0.89	2.45	3.290 (4)	158

Symmetry codes: (iv)  $x, y-1, z$ ; (v)  $-x+1/2, y-1/2, z$ .**Table S4.** Bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ] of the hydrogen bond at 423 K of **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1-H1A $\cdots$ C11 <sup>xi</sup>	0.89	2.91	3.68 (10)	145
N1-H1A $\cdots$ C12 <sup>xii</sup>	0.89	3.36	4.105 (2)	143
N1-H1B $\cdots$ C11	0.89	3.17	3.68 (10)	119
N1-H1B $\cdots$ C11 <sup>iii</sup>	0.89	3.02	3.68 (10)	133
N1-H1B $\cdots$ C12	0.89	3.29	4.105 (2)	153
N1-H1C $\cdots$ C11 <sup>xiii</sup>	0.89	2.86	3.68 (10)	155
N1-H1C $\cdots$ C12 <sup>xiii</sup>	0.89	3.50	4.105 (2)	128