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Supporting Information

Heat-sensitive structural phase transitions of hybrid halide perovskite with double dielectric ON/OFF switches

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Table S1. Crystal data and structure refinements for **1** at 193 K, 293 K and 323 K

	193 K (LTP)	293 K (RTP)	323 K (HTP)
Empirical formula	$C_3H_{10}CdCl_3NO$	$C_3H_{10}CdCl_3NO$	$C_6H_{20}Cd_2Cl_6N_2O_2$
Formula weight	293.86	294.87	589.74
Temperature(K)	193 (2)	293 (2)	323(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pmcn*	*Pbcm*	*Pbcm*
a/ Å	9.737 (8)	9.3456 (19)	9.40 (3)
b/ Å	13.925 (12)	14.974 (3)	15.61 (4)
c/ Å	6.765 (6)	6.7563 (14)	6.871 (19)
Volume/(Å^3)	917.3 (14)	945.5 (3)	1008 (5)
Z	4	4	2
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
D_{calc} / g cm^{-3}	2.128	2.071	1.943
F(000)	564	568	568
GOF	1.350	1.089	1.135
$R_1[I > 2\sigma(I)]$	0.0899	0.0814	0.104
$wR_2[I > 2\sigma(I)]$	0.2589	0.2365	0.3238

Table S2 Selected bond lengths [Å] and angles [°] for **1** at 193 K, 293 K and 323 K

Temperature (K)				
193 K	Cd1—Cl1	2.599 (3)	Cd1—Cl2	2.666 (3)
	Cd1—Cl1^{i}	2.616 (3)	Cd1—Cl2^{iii}	2.666 (3)
	Cd1—Cl2^{ii}	2.648 (3)	Cl1—Cd1^{iv}	2.616 (3)
	Cd1—Cl2^{i}	2.648 (3)	Cl2—Cd1^{iv}	2.648 (3)
	Cl1—Cd1—Cl1^{i}	179.52 (10)	Cl2^{ii}—Cd1—Cl2	97.41 (11)
	Cl1—Cd1—Cl2^{i}	96.60 (9)	Cl1—Cd1—Cl2^{iii}	83.72 (8)
	Cl1^{i}—Cd1—Cl2^{i}	83.75 (8)	Cl1^{i}—Cd1—Cl2^{iii}	95.92 (9)
	Cl1—Cd1—Cl2^{ii}	96.60 (9)	Cl2^{i}—Cd1—Cl2^{iii}	97.41 (11)
	Cl1^{i}—Cd1—Cl2^{ii}	83.75 (8)	Cl2^{ii}—Cd1—Cl2^{iii}	179.50 (3)
	Cl2^{i}—Cd1—Cl2^{ii}	82.93 (12)	Cl2—Cd1—Cl2^{iii}	82.24 (12)
	Cl1—Cd1—Cl2	83.72 (8)	Cd1—Cl1—Cd1^{iv}	80.87 (10)
	Cl1^{i}—Cd1—Cl2	95.92 (9)	Cd1^{iv}—Cl2—Cd1	79.07 (9)
	Cl2^{i}—Cd1—Cl2	179.50 (3)		
293 K	Cd1—Cl2^{i}	2.6371 (17)	Cd1—Cl1^{ii}	2.6554 (17)
	Cd1—Cl2	2.6371 (17)	Cl1—Cd1^{iii}	2.6554 (17)
	Cd1—Cl3	2.6437 (17)	Cl2—Cd1^{iv}	2.6371 (17)
	Cd1—Cl3^{i}	2.6437 (17)	Cl3—Cd1^{iv}	2.6437 (17)
	Cd1—Cl1	2.6554 (17)		
	Cl2^{i}—Cd1—Cl2	178.39 (11)	Cl3^{i}—Cd1—Cl1	83.50 (6)
	Cl2^{i}—Cd1—Cl3	95.24 (6)	Cl2^{i}—Cd1—Cl1^{ii}	97.50 (6)
	Cl2—Cd1—Cl3	83.69 (6)	Cl2—Cd1—Cl1^{ii}	83.59 (6)
	Cl2^{i}—Cd1—Cl3^{i}	83.69 (6)	Cl3—Cd1—Cl1^{ii}	83.50 (6)
	Cl2—Cd1—Cl3^{i}	95.24 (6)	Cl3^{i}—Cd1—Cl1^{ii}	177.99 (7)
	Cl3—Cd1—Cl3^{i}	98.02 (8)	Cl1—Cd1—Cl1^{ii}	95.02 (8)
	Cl2^{i}—Cd1—Cl1	83.59 (6)	Cd1—Cl1—Cd1^{iii}	79.00 (6)
	Cl2—Cd1—Cl1	97.50 (6)	Cd1—Cl2—Cd1^{iv}	79.66 (6)
	Cl3—Cd1—Cl1	177.99 (7)	Cd1—Cl3—Cd1^{iv}	79.42 (6)
323 K	Cd1—Cl3	2.686 (19)	Cd1—Cl2	2.687 (18)
	Cd1—Cl3^{i}	2.686 (19)	Cl1—Cd1^{iii}	2.693 (17)

	Cd1—Cl1	2.693 (17)	Cl2—Cd1^{iii}	2.687 (18)
	Cd1—Cl1^{i}	2.693 (17)	Cl3—Cd1^{iii}	2.686 (19)
	Cd1—Cl2^{i}	2.687 (18)		
	Cl3—Cd1—Cl3^{i}	178.6 (12)	Cl1^{i}—Cd1—Cl2^{i}	84.5 (7)
	Cl3—Cd1—Cl1	83.6 (6)	Cl3—Cd1—Cl2	82.5 (7)
	Cl3^{i}—Cd1—Cl1	97.3 (6)	Cl3^{i}—Cd1—Cl2	96.5 (7)
	Cl3—Cd1—Cl1^{i}	97.3 (6)	Cl1—Cd1—Cl2	84.5 (7)
	Cl3^{i}—Cd1—Cl1^{i}	83.6 (6)	Cl1^{i}—Cd1—Cl2	179.9 (4)
	Cl1—Cd1—Cl1^{i}	95.5 (9)	Cl2^{i}—Cd1—Cl2	95.5 (11)
	Cl3—Cd1—Cl2^{i}	96.5 (7)	Cd1—Cl1—Cd1^{iii}	79.3 (6)
	Cl3^{i}—Cd1—Cl2^{i}	82.5 (7)	Cd1^{iii}—Cl2—Cd1	79.5 (6)
	Cl1—Cd1—Cl2^{i}	179.9 (4)	Cd1—Cl3—Cd1^{iii}	79.5 (7)

Symmetry codes:

193 K (i) −x+3/2, −y+1/2, z+1/2; (ii) x, −y+1/2, z+1/2; (iii) −x+3/2, y, z; (iv) −x+3/2, −y+1/2, z−1/2.

293 K (i) x, −y+3/2, z−1/2; (ii) x, −y+3/2, z+1/2; (iii) x, y, −z−1/2; (iv) x, y, −z+1/2.

323 K (i) x, −y+1/2, −z; (ii) x, y, −z−1/2; (iii) x, y, −z+1/2; (iv) x, y, −z+3/2.

Table S3 Hydrogen bonds under 293 K for **1**

D—H ··A	D—H	H ··A	D ··A	D—H ··A
O1—H3 ··Cl1^{v}	0.89 (2)	2.52 (3)	3.20 (3)	133 (4)

Table S4 Hydrogen bonds under 193 K for **1**

D—H ··*A*	*D*—H	H ··*A*	*D* ··*A*	*D*—H ··*A*
O1—H1F ··O1^{viii}	0.98	2.55	3.496 (7)	162

Symmetry codes: (viii) −x+1/2, −y+1/2, z+1/2.

Table S5 The distance of intermolecular O-O for **1** at 193 K, 293 K and 323 K

Temperature (K)	193 K	293 K	323 K
Intermolecular O-O distances (Å)	3.4965	3.7904	7.9601

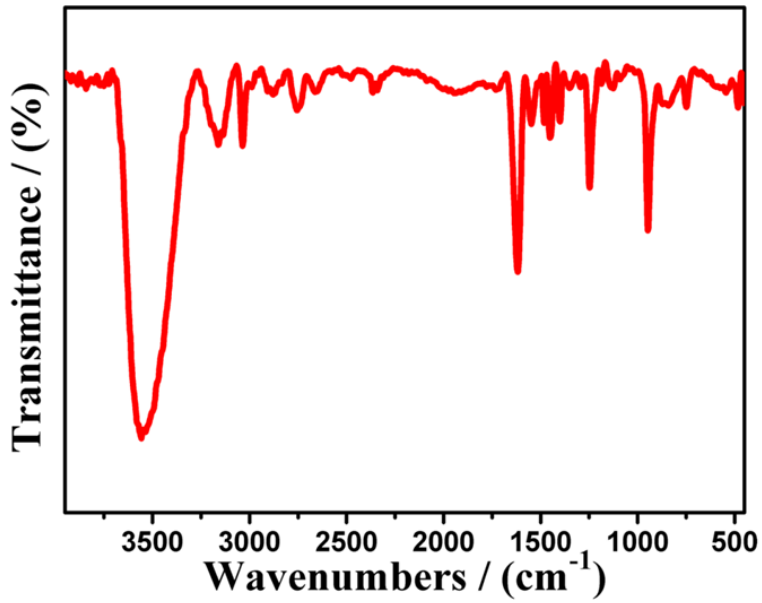

Fig. S1 The IR spectrum for compound **1**

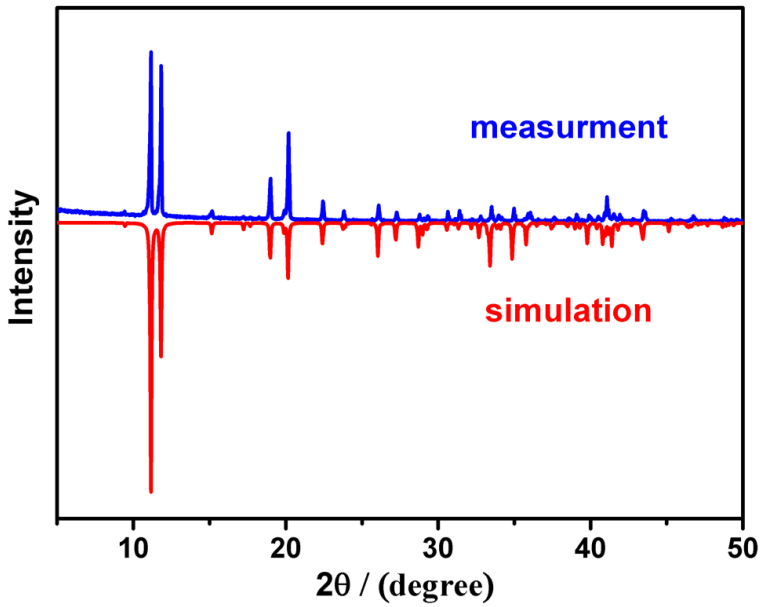

Fig. S2 The powder X-ray diffraction (PXRD) pattern for compound **1**

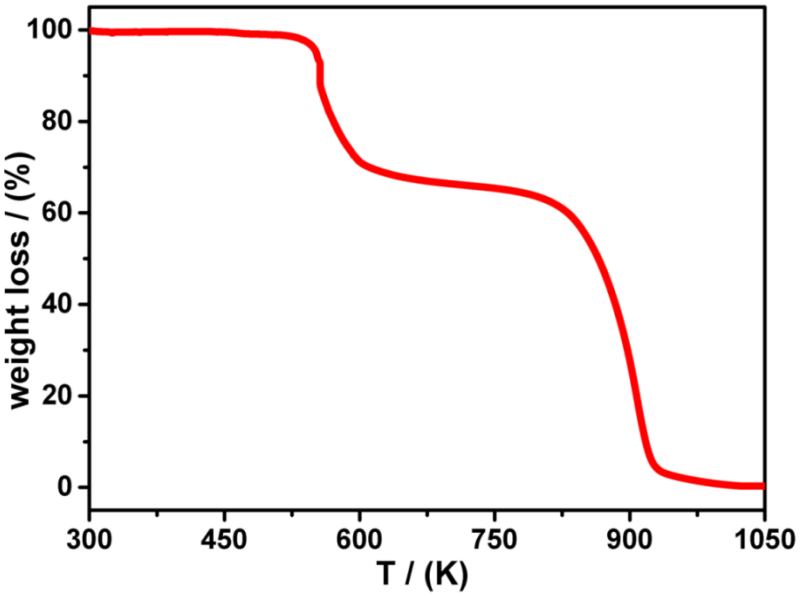

Fig. S3 TGA curves of crystalline sample **1**

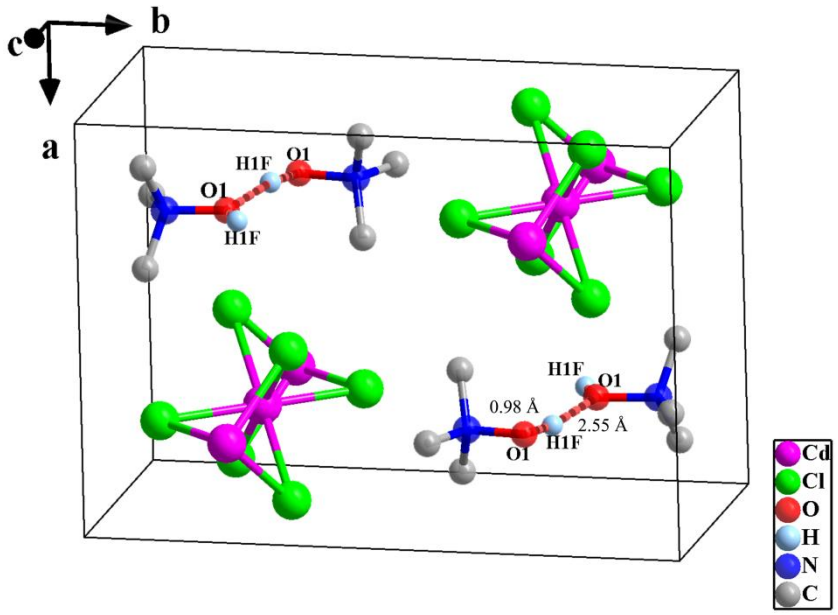

Fig. S4 The crystal structure of 193 K for **1**. The orange red dotted line is represented the hydrogen bonding between two organic cations (O1-H1F···O1).

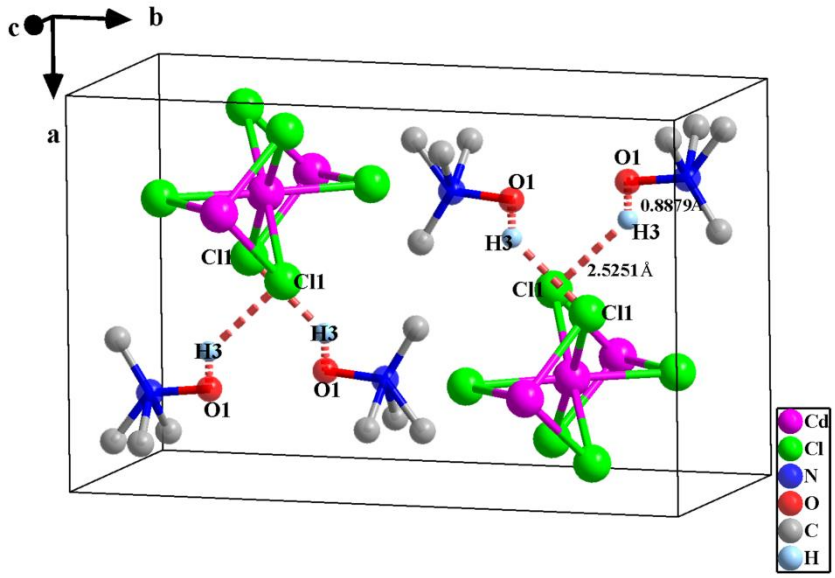

Fig. S5 The crystal structure of 293 K for **1**. The orange red dotted line is represented the hydrogen bonding between organic cations and inorganic framework (O1-H3 ··Cl1).

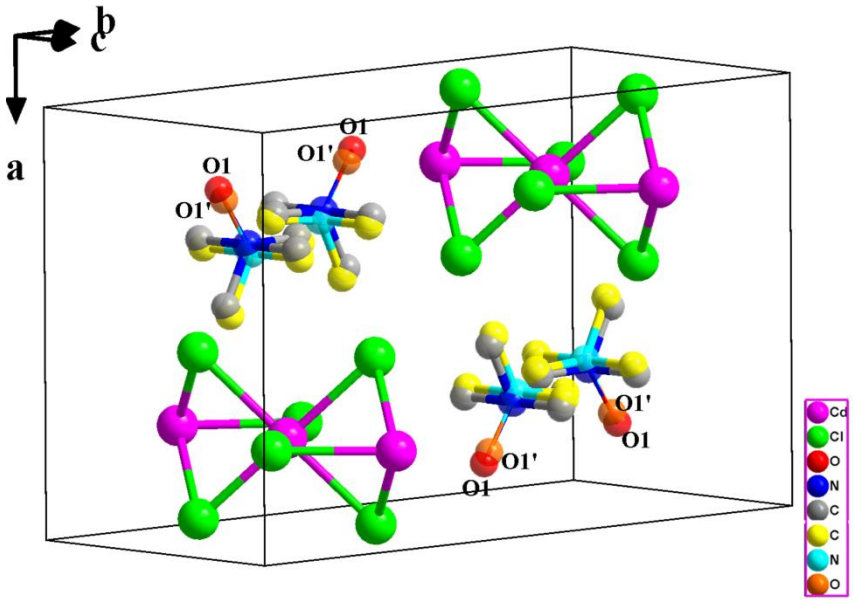

Fig. S6 The crystal structure of 323 K for **1**. There is no hydrogen bond between the organic cations and inorganic framework/the organic cations. So all H atoms were omitted for clarity.

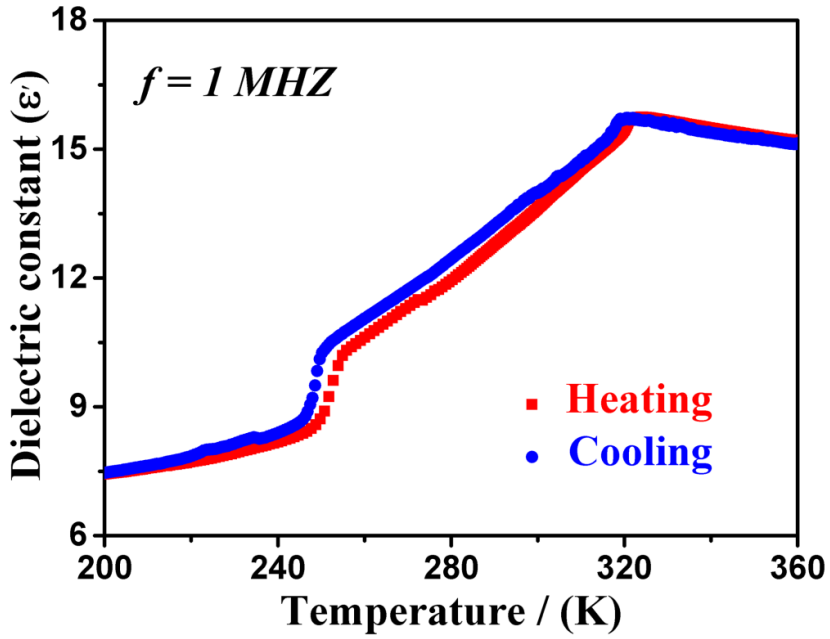

Fig. S7 The temperature-dependent real part (ε') of the dielectric permittivity of **1** measured on the polycrystalline sample at 1 MHz in heating and cooling.

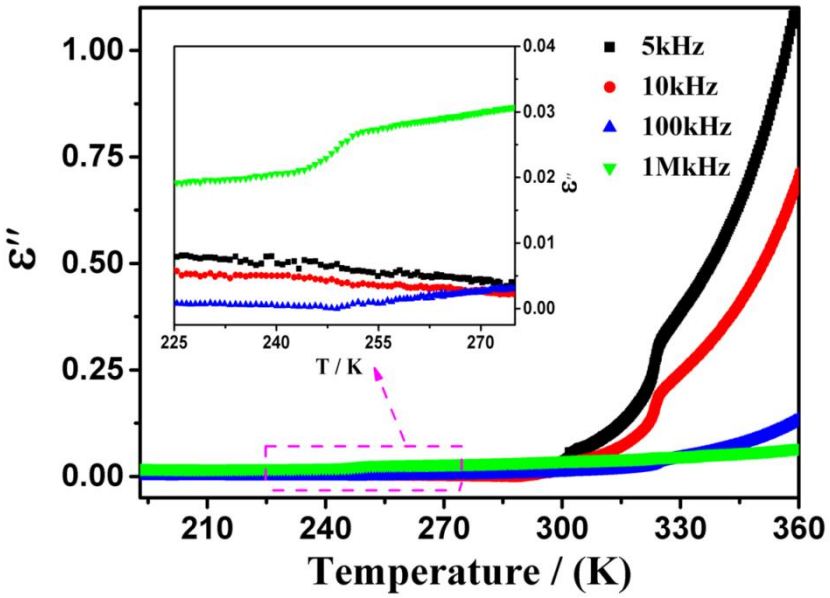

Fig. S8 Imaginary part of dielectric constant of powder sample **1** measured at selected frequencies 5 kHz to 1 MHz in a heating mode.

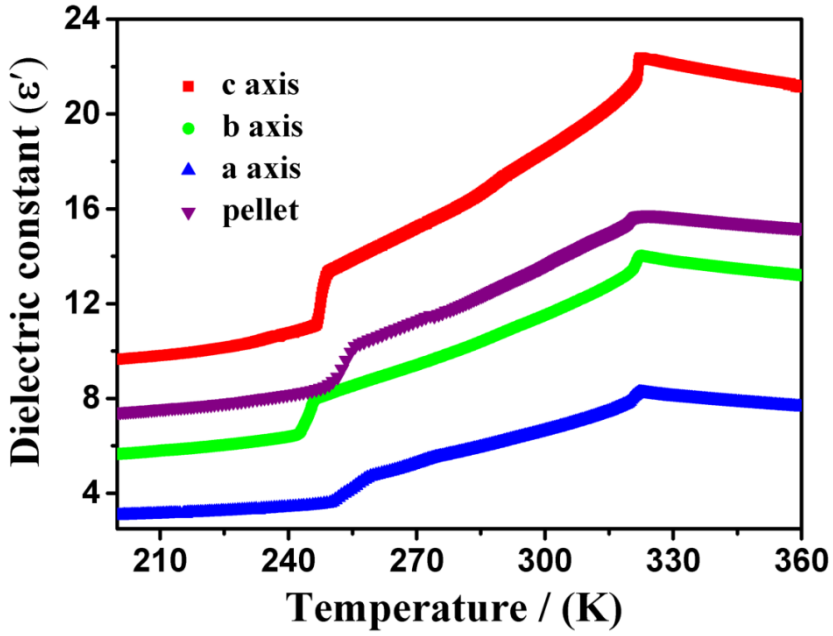

Fig. S9 The temperature-dependent real part of the complex dielectric constants of the crystal sample **1** along each of the different crystallographic directions of a-axis, b-axis, c-axis and polycrystalline at 1 MHz.

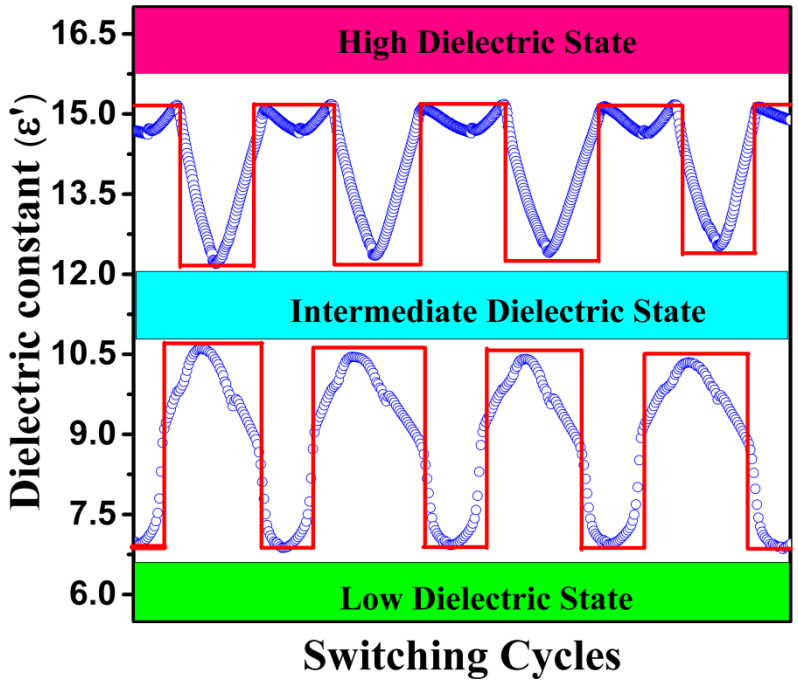

Fig. S10 The recoverable switching of dielectric effects of pressed-powder pellet for **1**. Of which, the blue line represents the actual measured dielectric constant with time gone, and the red line represents their fitting curves.

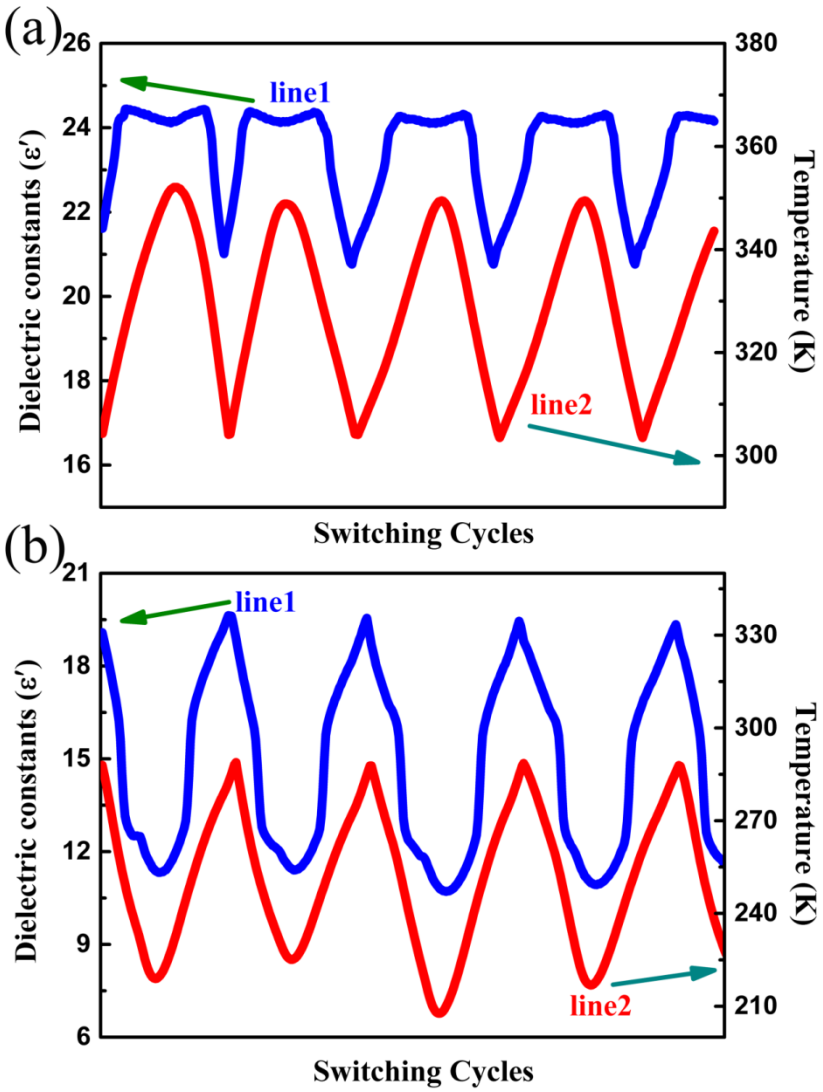

Fig. S11 (a) The recoverable switching of dielectric effects of single-crystal along the c-axis for **1** above room temperature (blue line 1). And the corresponding temperature curve is red line 2, indicating the relationship of dielectric switching curves and temperature profiles over time is matched the switches. (b) The recoverable switching of dielectric effects of single-crystal along the c-axis for **1** below room temperature (blue line 1). And the corresponding temperature curve is red line 2, indicating the relationship of dielectric switching curves and temperature curves over time is matched the switches.

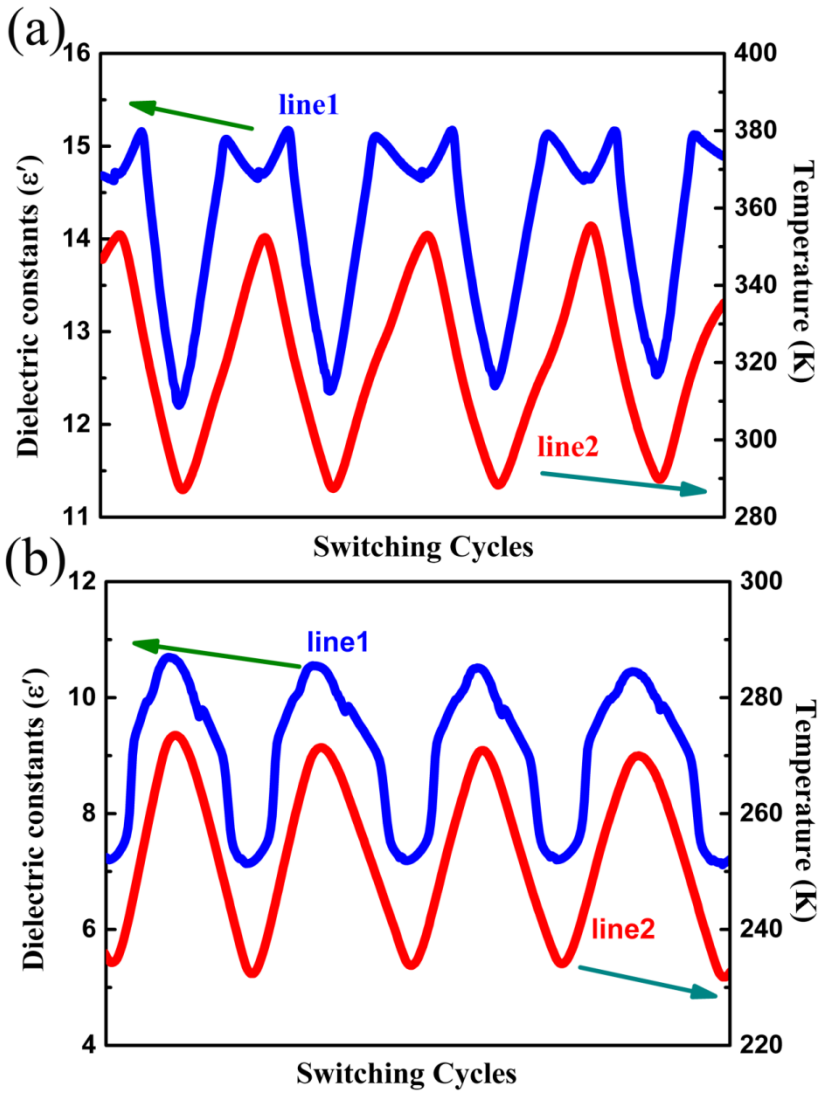

Fig. S12 (a) The recoverable switching of dielectric effects of pressed-powder pellet for **1** above room temperature (blue line 1). And the corresponding temperature curve is red line 2, indicating the relationship of dielectric switching curves and temperature curves over time is matched the switches. (b) The recoverable switching of dielectric effects of pressed-powder pellet for **1** below room temperature (blue line 1). And the corresponding temperature curve is red line 2, indicating the relationship of dielectric switching curves and temperature profiles over time is matched the switches.