Supporting information

[(CH₃)₃PCH₂OH][CdBr₃] Is a Perovskite-type Ferroelastic Compound Above Room Temperature

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Experimental section

Synthesis and crystal growth

All of the experimental reagents were used without any further purification. Preparation of hydroxymethyl-trimethyl-phosphonium bromide: Dehydrated diethyl ether (50 mL) was added into a dry flask under nitrogen at room temperature. Then, trimethylphosphine (4 mL, 40 mmol) and HBr (6 mL, 51 mmol) were added to this solution via syringe, respectively. The mixed solution was stirred for 4h at room temperature. The solvent was evaporated to yield the trimethylphosphine bromide as white solid. The solids were added into the aqueous solution with paraformaldehyde

at 100°C. The reaction mixture was stirred at 100°C for 3h. The reaction mixture was

cooled down to room temperature, the solvent was then evaporated to yield the hydroxymethyl-trimethyl-phosphonium bromide as white soild, in *ca*. 60% yield based on trimethylphosphine.^{S1}

Synthesis of 1: Hydroxymethyl-trimethyl-phosphonium bromide (0.02 mol) and equimolar amounts of concentrated HBr (0.02 mol) were added dropwise to an aqueous solution (50 mL), and then the mixed solution was added to an aqueous solution of $CdBr_2 \cdot 4H_2O$ (0.02 mol) with stirring at room temperature. Colorless prism-shaped crystals were easily obtained by slow evaporation of the mixed solution at room temperature after about a few weeks, in *ca.* 85% yield based on Cd (Fig. S1). The phase purity of crystal 1 was verified by the IR spectroscopy using on a Shimadzu model IR-60 spectrometer (Fig. S2). Besides, variable-temperature powder X-ray diffraction (PXRD) patterns match very well with the simulated patterns based on the crystal structures of 1 for different phases, confirming the phase purity of the as-grown crystals (Fig. S5).



Fig. S1 Single-crystal samples of 1



Fig. S2 IR spectrum of 1 measured on a KBr-diluted pellet at room temperature

Single crystal X-ray crystallography

Single-crystal X-ray diffraction data of **1** were collected at 293 K and 359 K on a Rigaku Saturn 724 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing and empirical absorption correction were performed using the Crystalclear software package (Rigaku, 2005). The crystal structures were solved by direct methods, and refined by full-matrix least-squares refinements based on F^2 by using the SHELXLTL software package (SHELX-97).

All non-H atoms were refined anisotropically using reflections with $I > 2\sigma(I)$. All hydrogen atoms were generated geometrically and refined using the 'riding' model

with U_{iso} = 1.2 U_{eq} (C and P). The asymmetric units and the packing views were drawn by using DIAMOND (Brandenburg and Putz, 2005). Some bond distances and angles were calculated by using DIAMOND, and other calculations were calculated out by using SHELXLTL. A summary of the crystallographic data and structure refinement details of 1 at 293K and 359 K were given in Table S1.

	293K	359K	
Chemical Formula	C ₄ H ₁₂ OPCdBr ₃		
Formula weight	459.24		
Crystal system	Orthorhombic	Hexagonal	
Space group	Pmcn	P63/mmc	
<i>a</i> , Å	10.127(2)	9.839(3)	
b, Å	15.938(3)	9.839(3)	
<i>c</i> , Å	6.9785(14)	6.934(4)	
α , deg	90.00	90.00	
β , deg	90.00	90.00	
γ, deg	90.00	120.00	
<i>V</i> , Å ³	1126.4(4)	581.3(4)	
Ζ	4	2	
	$-13 \le h \ge 12$	$-11 \le h \ge 10$	
Index ranges	$-20 \le l \ge 18$	$-11 \le l \ge 11$	
	$-9 \le k \ge 9$	$-8 \le k \ge 8$	
$D_{calcd}, g \cdot cm^{-3}$	2.708	2.555	
μ , cm ⁻¹	12.67	12.27	
refns measured	7327	3198	
independent reflns	1361	211	
reflns used	1120	184	
Goodness-of-fit on F ²	bodness-of-fit on F^2 1.119		
Final <i>R</i> indices $[I >$	$R_1 = 0.0569, wR_2 =$	$R_1 = 0.125, wR_2 = 0.314$	
2sigma(I)]	0.1901		

Table S1 Crystal data, data collection and reduction parameter of crystals of 1 at 293K and 359 K.

	-	-		
	Cd1—Br1	2.7818(12)	P1—C1	1.781(11)
	Cd1—Br2	2.7139(19)	P1—C2	1.780(14)
	Cd1—Br1 i	2.7873(12)	P1—C3	1.826(18)
	Cd1—Br1 ii	2.7873(12)	P1—C1 iii	1.781(11)
	Cd1—Br1iii	2.7819(12)	C1—01	1.32(2)
	Cd1—Br2iv	2.7413(19)		
	Br1—Cd1—Br1 i	96.33(4)	Br1 i —Cd1—Br2iv	96.32(4)
293 K	Br1—Cd1—Br1 ii	179.02(4)	Brl ii —Cd1— Brl iii	96.33(4)
	Br1—Cd1—Br1 iii	83.76(5)	Brl ii—Cdl—Br2iv	96.32(4)
	Br1—Cd1—Br2	94.45(4)	Br1iii—Cd1—Br2iv	84.66(4)
	Br1—Cd1—Br2iv	84.66(4)	C1—P1—C2	109.3(5)
	Br2—Cd1—Br1 i	84.56(4)	C1—P1—C3	108.5(6)
	Br2—Cd1—Br1 ii	84.56(4)	C1—P1—C1 iii	108.9(8)
	Br2—Cd1—Br1 iii	94.45(4)	C2—P1—C3	112.3(8)
	Br2—Cd1—Br2iv	178.81(6)	C2—P1—C1 iii	109.3(5)
	Br1 i —Cd1— Br1 ii	83.56(5)	C3—P1—C1 iii	108.5(6)
	Br1 i —Cd1— Br1 iii	179.02(4)	P1-C1-O1	110.0(11)
	Cd1—Br1	2.743(4)	Cd1—Br1ix	2.743(4)
	Cd1—Br1 v	2.743(4)	P1—C1	2.014(2)
	Cd1—Br1 vi	2.743(4)	P1—C2	2.066(5)
	Cd1—Br1vii	2.743(4)	C1—01	1.505(2)
	Cd1—Br1viii	2.743(4)		
359 K	Br1—Cd1—Br1 v	180.0(2)	Br1vi—Cd1—Br1vii	180.00(10)
	Br1—Cd1—Br1 vi	95.69(11)	Br1vi—Cd1—Br1viii	95.69(11)
	Br1—Cd1—Br1vii	84.31(11)	Br1vi—Cd1—Br1ix	84.31(11)
	Br1—Cd1—Br1viii	84.31(11)	Br1vii—Cd1—Br1viii	84.31(11)
	Br1—Cd1—Br1ix	95.69(11)	Brlvii—Cd1—Brlix	95.69(11)
	Br1 v —Cd1—Br1 vi	84.31(11)	Br1viii—Cd1—Br1ix	180.0(2)
	Br1 v —Cd1—Br1 vii	95.69(11)	C1—P1—C2	90.000(1)
	Br1 v —Cd1—Br1 viii	95.69(11)	O1—C1—P1	164.9(2)
	Brl v —Cd1—Brl ix	84.31(11)		

Table S2. The key bond distances and angles of 1 at 293 K and 359 K

Symmetry code:(i) x, -y+1/2, z+1/2;(ii) x+1/2, -y+1/2, -z+1/2;(iii) x, -y+1/2, z; (iv) -x+1/2, -y+1/2, z-1/2;(v) -x, -y, -z; (vi) y, -x+y, -z; (vii) -y, x-y, z; (vii) -x+y, -x, -z+1/2; (ix) x-y, x, z-1/2;

DSC Measurement

Differential scanning calorimetry experiments were carried out on a NETZSCH DSC 200F3 instrument by heating and cooling the crystalline samples (24.5mg) over the temperature range of 275–370 K under nitrogen at atmospheric pressure in aluminum crucibles with a rate of 10 K/min.

Dielectric Measurement

A powder-pressed pellet (0.69 mm thick and 8.96 mm² in area) and single-crystal samples deposited with silver conducting glue were used for dielectric studies. The complex dielectric permittivity ε ($\varepsilon = \varepsilon' - i\varepsilon''$) of **1** was measured on a Tonghui TH2828A in the temperature range of 300-350 K at 1 MHz, with an applied electric field of 1 V and a rate of 10 K/min.



Fig.S3. The DSC curves of 1 in two heating and cooling cycles.



Fig S4 Packing diagrams of 1 at (a) 293 K and (b) 359 K. Parallelogram void formed by four nearest-neighbour Cd atoms or four adjacent P atoms at (c) 293 K and (d) 359 K.



Fig. S5 Powder XRD patterns of 1 at different temperatures by grinding in the heating and cooling cycle.



Space group P63/mmc (No.194)

Space group Pmcn (No.62)

Fig. S6. Spatial symmetry operations change of **1** from the HTP (*P*63/*mmc*) to the RTP (*Pmcn*).



Fig S7. The possible twin boundaries of ferroelastic domains of 6/mmmFmmm.

References

S1. H. H. Karsch, *Chemische Berichte*, 1982, **115**, 823-827.