Electronic Supplementary Information

Unusually Symmetry Breaking from *1* to *2* in a High-Temperature Enantiomeric Ferroelectrics with Large Spontaneous Polarization

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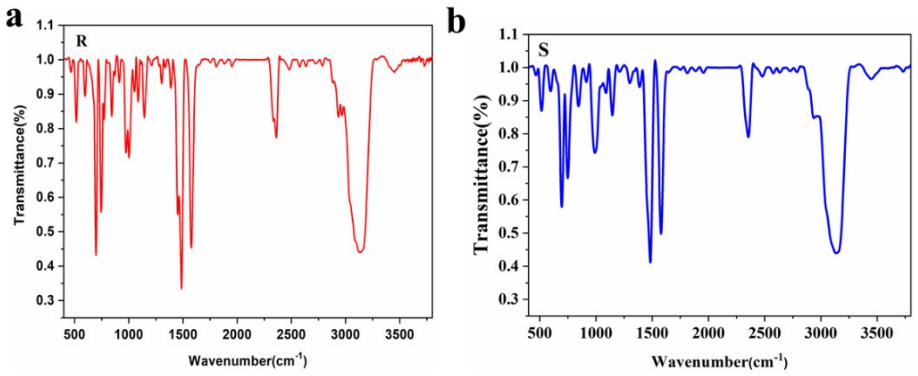

Fig. S1. Infrared spectrum of compound **1** (a) and **2** (b)

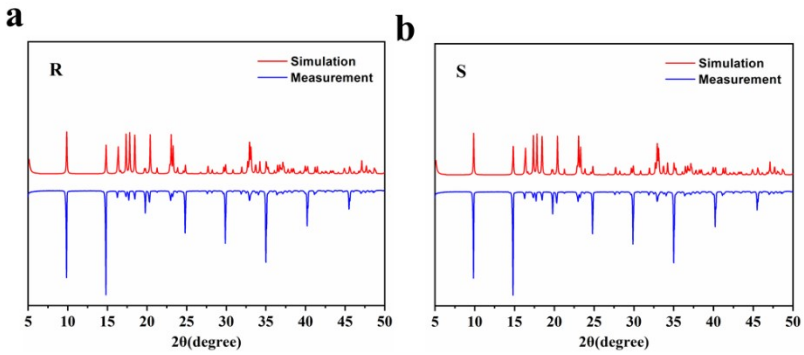

Fig. S2. The powder XRD of **1** (a) and **2** (b) with the simulated one in red and the measurement in blue.

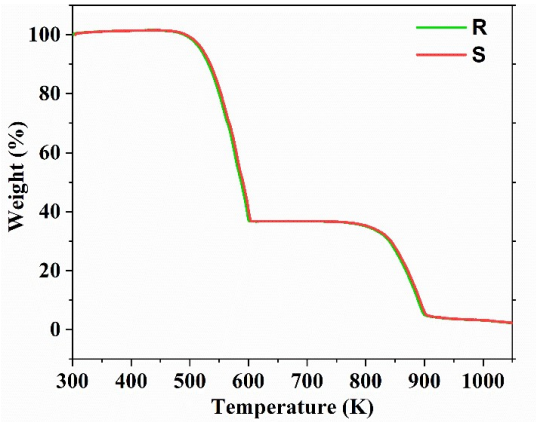

Fig. S3. Thermogravimetric analysis (TGA) curves of **1** and **2.**

Table S1. Crystal data and structure refinements for [(*R*)-*β*-MPA]$_2$CdCl$_4$ and [(*S*)-*β*-MPA]$_2$CdCl$_4$ at

various temperatures.

Compound	$[(R)$-β-MPA$]_2CdCl_4$		$[(S)$-β-MPA$]_2CdCl_4$	
Temperature	300 K	360 K	300 K	360 K
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2$	$P1$	$C2$	$P1$
a, b, c (Å)	35.8807(16)	7.7844(1)	35.910(7)	7.7817(1)
	5.4904(2)	7.8052(1)	5.4715(9)	7.7972(1)
	5.4314(2)	18.2463(2)	5.4511(10)	18.2458(3)
α, β, γ (°)	90	94.189(1)	90	94.151(1)
	94.076(1)	97.931(1)	94.108(5)	97.976(1)
	90	90.917(1)	90	90.842(1)
Volume /Å^3	1067.28(7)	1094.70(2)	1068.3(3)	1093.14(3)
Z	2	1	2	1
Density/g.cm^{-3}	1.639	1.598	1.637	1.597
R_1	0.0137(2348)	0.0327(9463)	0.0754(2374)	0.0400(9076)
wR_2	0.0338(2353)	0.0819(11780)	0.2003(2377)	0.1114(11847)
GOF	1.084	1.070	1.126	1.081

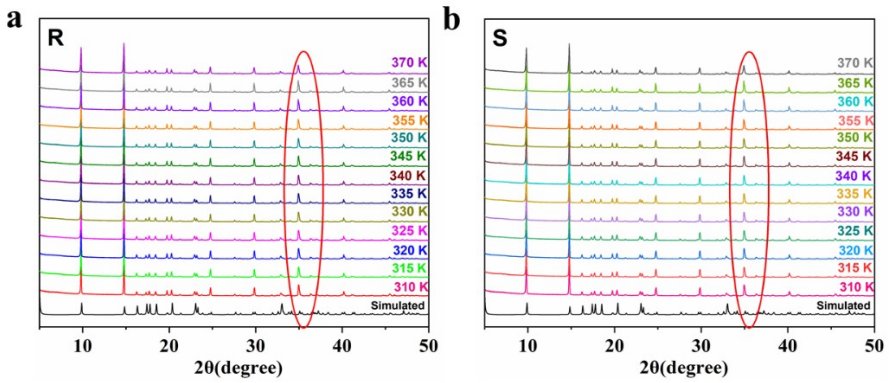

Fig. S4. Variable-temperature PXRD patterns of **1**(a) and **2**(b). The Ellipsoid box represents the slight change ranges of the diffraction peaks.

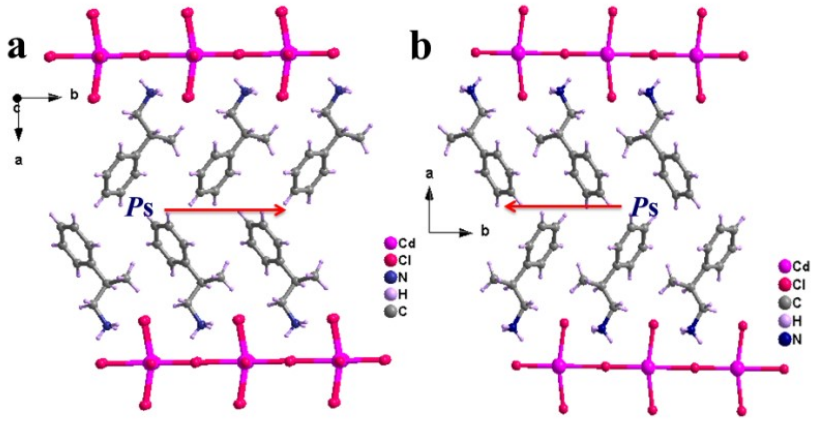

Fig. S5. Packing view of crystal structure of compounds **1**(a) and **2**(b), and the red arrow indicates the polarization direction.

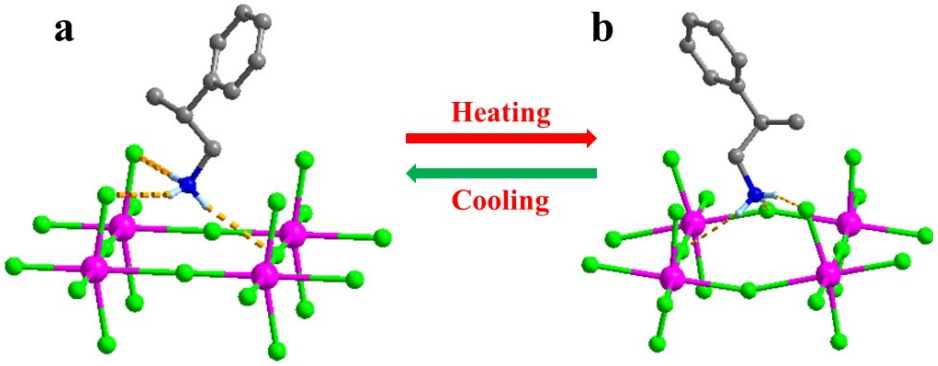

Fig. S6. Molecular structures of **1** at 300 K (a) and 360 K (b).

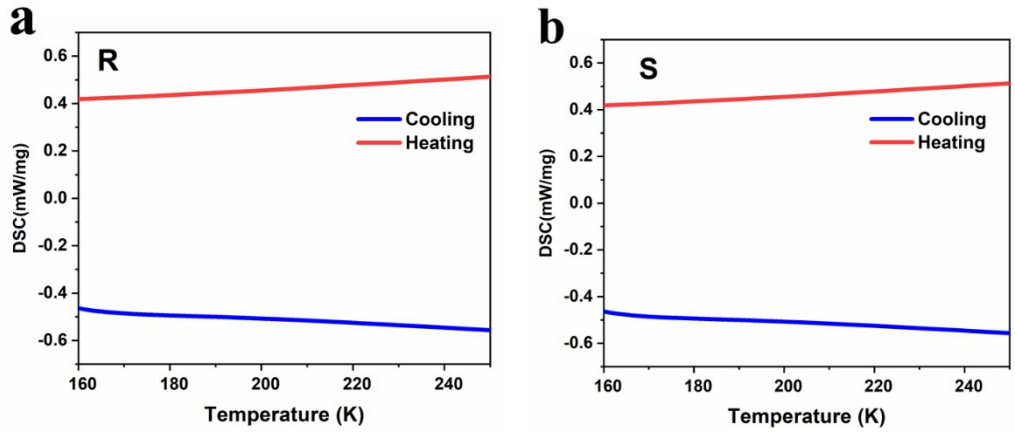

Fig. S7. DSC curves of compound **1** and **2** at 160-250K.

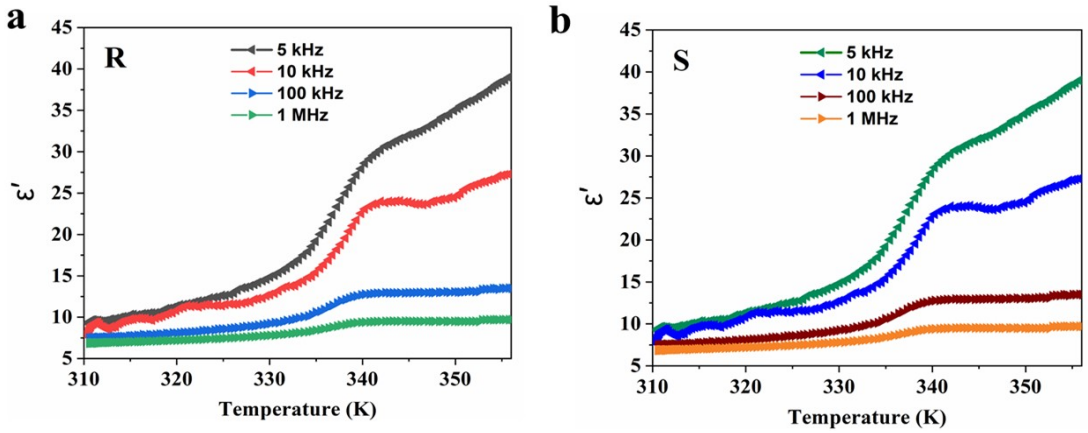

Fig. S8. The frequency dependence of the dielectric of compounds **1** (a) and 2 (b) during heating.

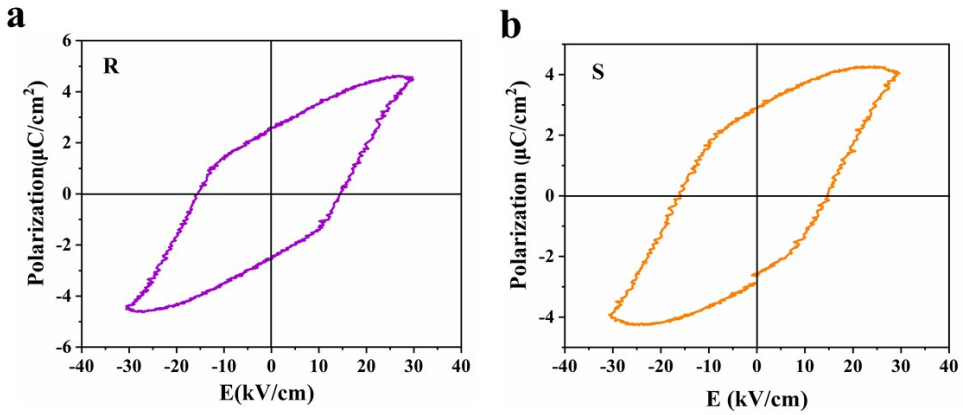

Fig. S9. Polarization hysteresis loops at 370 K of compounds **1** (a) and **2** (b).

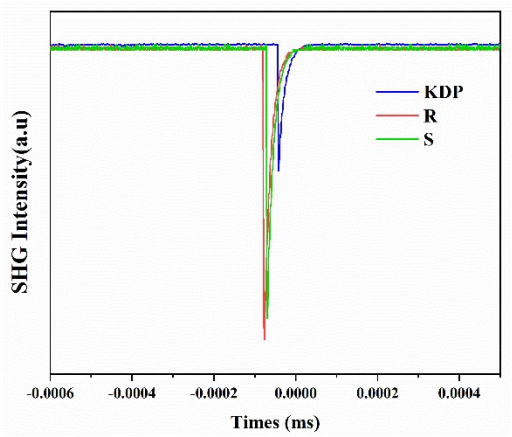

Fig. S10. SHG signal intensity of compounds 1, 2 and KDP at room temperature.

Table S2. Some related values of ferroelectric properties

	T_c (K)	P_s (μC·cm^{-2})
Compounds **1** and **2**	343	4.65/4.67
[(R)-N-(1-phenylethyl)ethane-1,2-diaminium]PbI_4[38]	378	0.15
(R)-3-quinuclidinol[39]	381	7
(S)-3-F-(pyrrolidinium)$CdCl_3$[13]	240	5.79
(R)-3-F-(pyrrolidinium)$CdCl_3$[13]	240	5.63
(S)-(N,N-dimethyl-3-fluoropyrrolidinium)iodide[40]	470	0.4
(R)-(N,N-dimethyl-3-fluoropyrrolidinium)iodide[40]	470	0.48

Table S3 Hydrogen bond geometry (Å, degree) for 1 at 300 K and 360 K

	D–H···A	H···A	D···A	∠D-H···A
300 K	N1-H1A···Cl1	2.73	3.562(9)	176
	N1-H1B···Cl2	2.66	3.510(9)	156
	N1-H1C···Cl2	2.57	3.466(9)	158
360 K	N3-H3A···C8	2.80	3.46(10)	131
	N3-H3B···Cl1	2.41	3.27(10)	165
	N3-H3C···Cl5	3.11	3.58(10)	113