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Electronic Supplementary Information

Unusual High-Temperature Host-Guest Inclusion Compound Ferroelectrics with Nonlinear Optical Switch and Large Spontaneous Polarization

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Experimental Section

Synthesis. 3-cyclopentene amine, Tetrafluoroboric acid / perchloric acid and 18-crown-6 were mixed in water and methanol solution (10 mL) at a molar ratio of 1:1:1, and then the mixed solution was slowly evaporated. Colorless bulk crystals were obtained after a few days (Figure S6). The melting point of compound **1** crystal is about 495 K, and the melting point of compound **2** crystal is about 425 K. The phase purity of the crystal was confirmed by infrared spectroscopy (Figure S1) and powder X-ray diffraction (Figure S2).

DSC and Thermogravimetric Analysis (TGA) Measurements. The PerkinElmer Diamond DSC instrument was used to study the thermal properties of **1** and **2** by differential scanning calorimetry (DSC). The DSC runs were recorded on cooling and heating the powdered sample at the rate of temperature changes of 10 K / min. On the TA-Instruments STD2960 system, thermogravimetric analysis (TGA) was performed at a rate of 10 K / min from 300 K to 1070 K in a nitrogen atmosphere.

X-Ray Single-Crystal Crystallography. The crystal structure of **1** and **2** were determined by X-ray single crystal diffraction at 100 K (**LTP**), 300 K (**RTP**). The data of *Lp* and absorption effect were corrected. Their crystal structures were solved by direct methods with the SHELXS-97 program. The crystal data and structure refinement for **LTP** and **RTP** are shown in Table S1.

Dielectric Constant Measurements. Using flake powder sample as electrode, the silver conductor was pasted tightly on both sides of the electrode for dielectric measurement. The dielectric constants of the compounds were measured by Agilent or TH2828a impedance analyzer in the frequency range of 500 Hz - 1 MHz. The heating and cooling rates were 10 K/min

Second Harmonic Generation (SHG) Measurements. The SHG responses experiments, an unexpanded laser beam with low divergence (pulsed Nd: YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used.

Ferroelectric Measurement. The ferroelectric properties of solid-state samples were measured from a single crystal sample in the form of a pellet using a standard RT 6000 ferroelectric tester (Radiant Technologies, Albuquerque, USA) at different temperatures while the sample was immersed in insulating oil, and the electric hysteresis loop was observed by Virtual Ground Mode (the measurement uses alternating current and the frequency is 10-60 Hz).

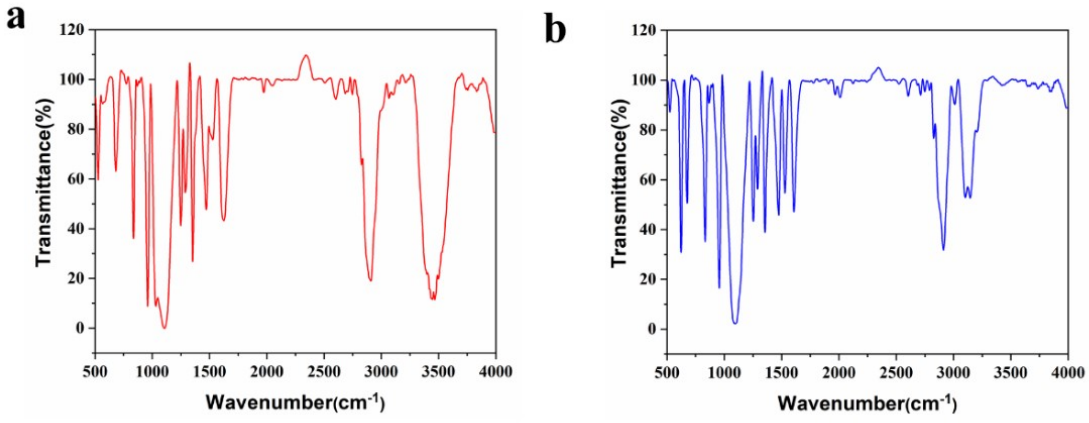

Fig. S1 Infrared spectrum of compounds **1** (a) and **2** (b).

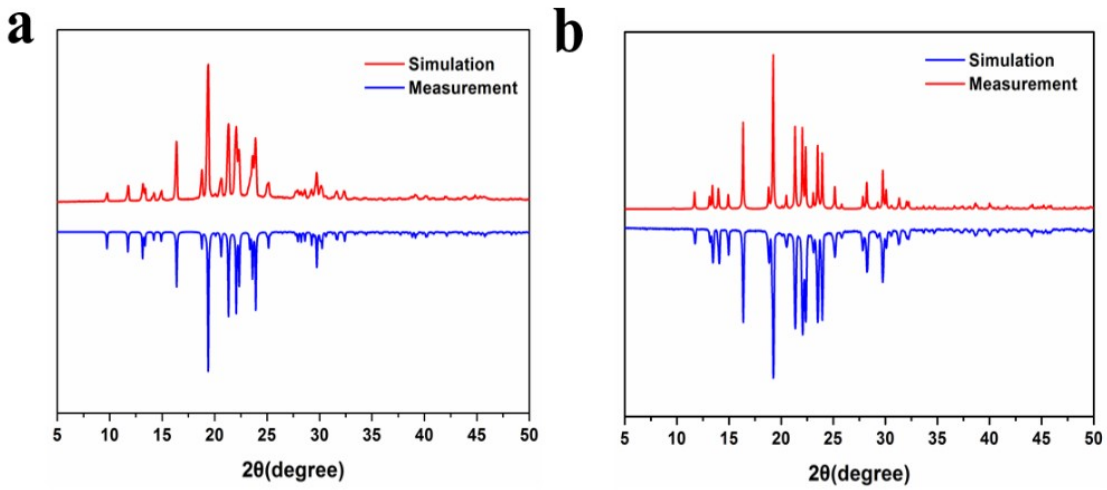

Fig. S2 The powder XRD of **1** (a) and **2** (b).

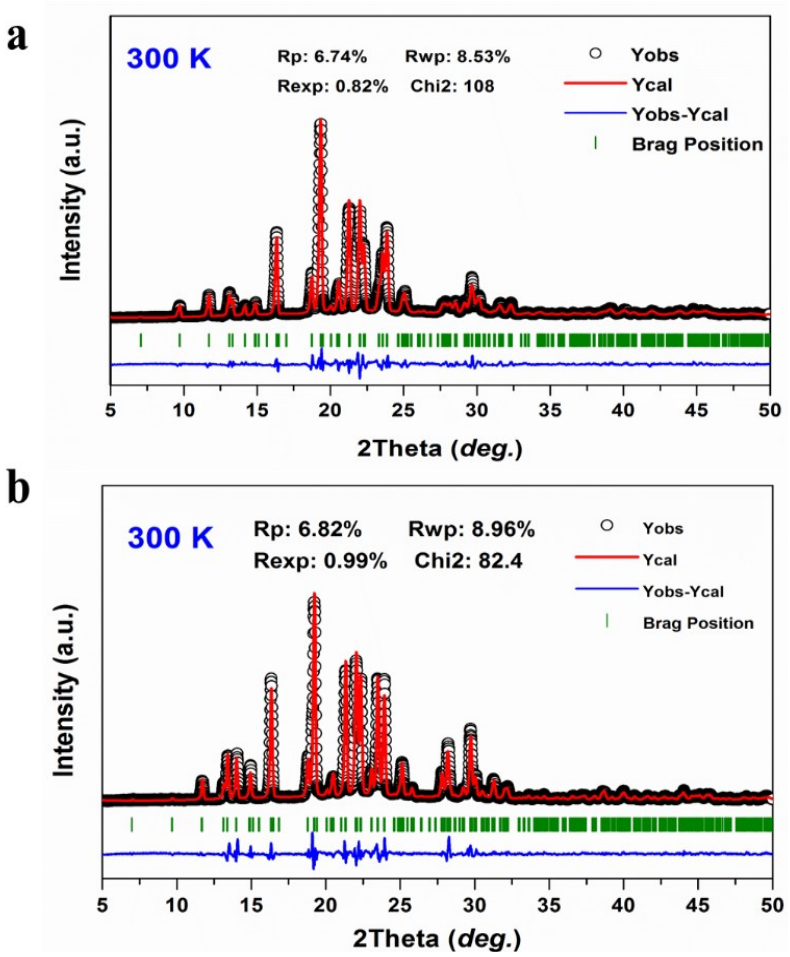

Fig. S3 Powder X-ray diffractograms of **1**(a) and **2**(b) collected in 300 K, refined by Rietveld method using the FULLPROF program.

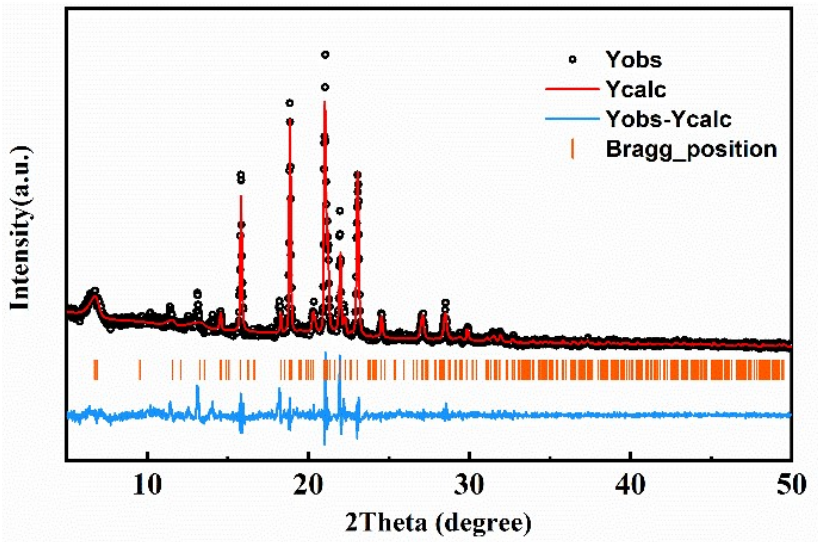

Fig. S4 Structural refinement results of PXRD data for compound **1** in 420 K (**HTP**). The indexing of PXRD data reveals a Monoclinic, and through the LeBail refinements, we obtained the *m* point group. The refined cell parameters are a = 14.685 Å, b = 13.542 Å, c = 9.860 Å, $\alpha = \gamma = 90°$, β= 115.335 and V = 1772.391 Å^3 (R_{wp} = 11.82 %, R_{exp} = 6.77 %). These results are highly consistent, confirming the phase purity of the compound and high accuracy of the simulation methods.

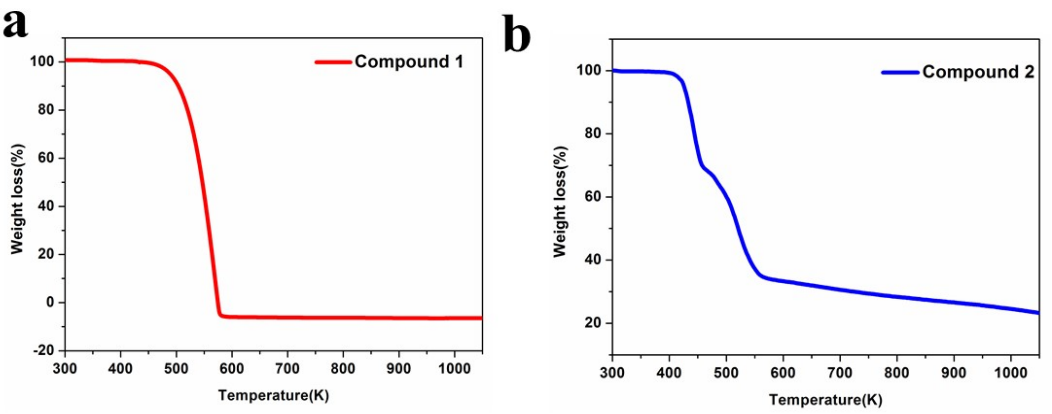

Fig. S5 TG curves for **1** (a) and **2** (b)**.**

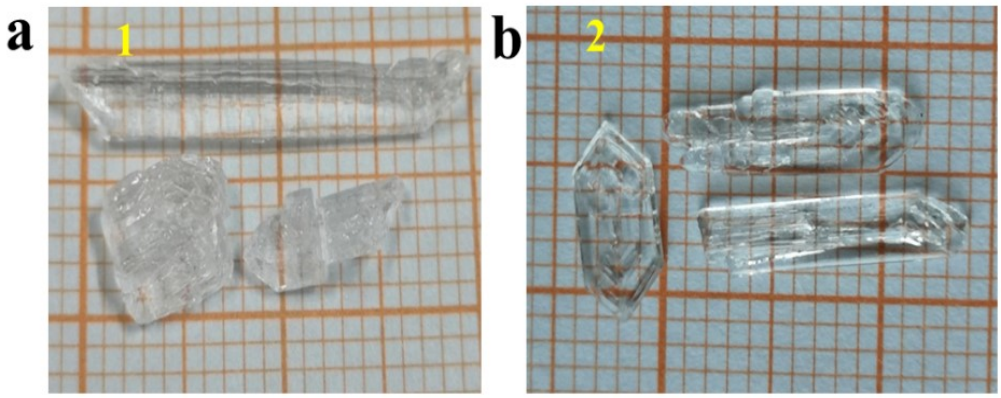

Fig. S6 Crystal morphology of compounds **1**(a) and **2** (b)

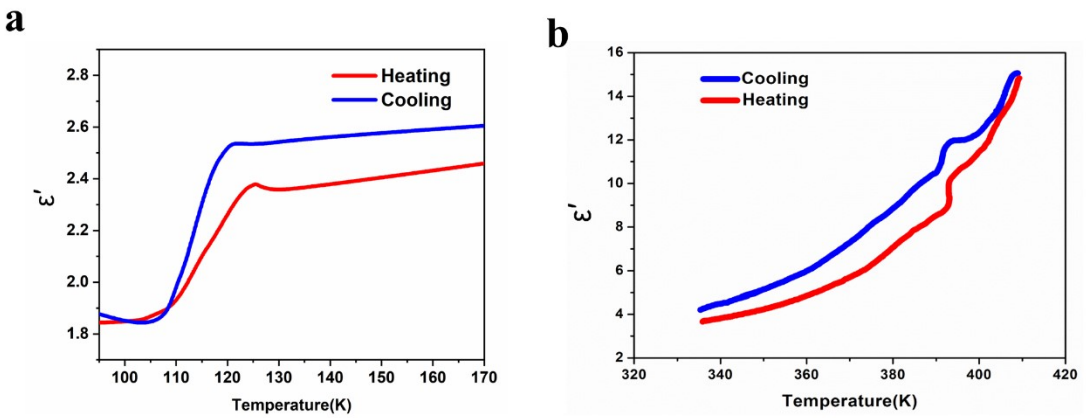

Fig. S7 Dielectric constant of compound **1**. (a) from 105 K to 170 K; (b) from 340 K to 410 K.

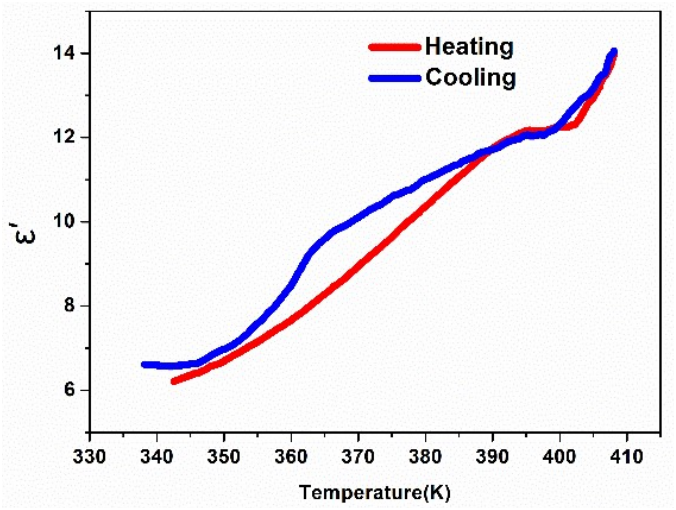

Fig. S8 Dielectric constant of compound **2**.

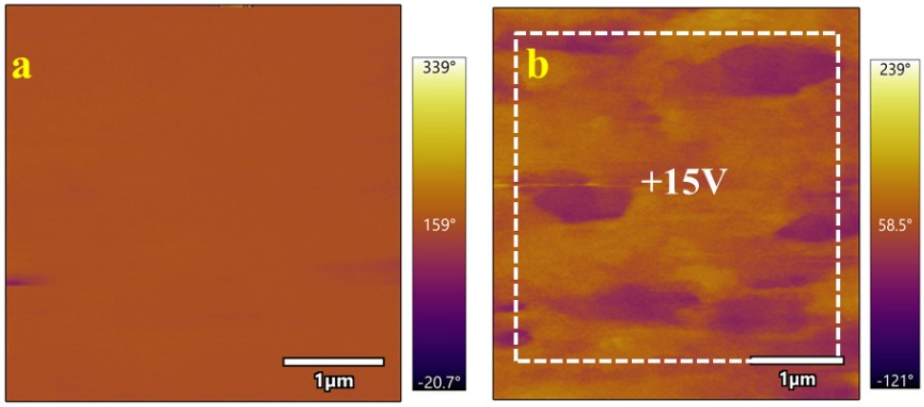

Fig. S9 Pristine PFM mapping for a region of 1 μm × 1 μm (a). Lateral PFM phase image after applying DC bias voltage +15 V in the white box (b).

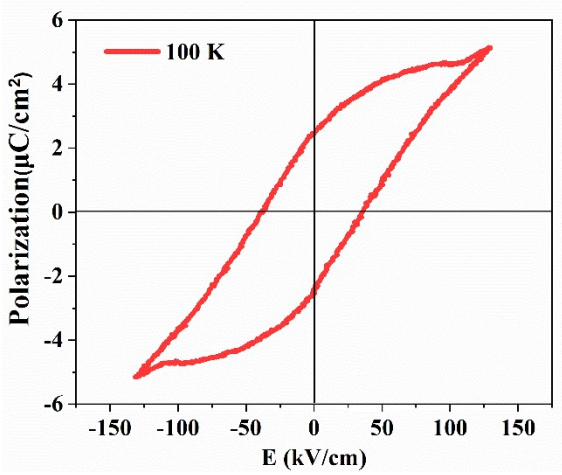

Fig. S10. Hysteresis loop of compound **1** at 100 K

Table.S1 Crystal data and refinement parameters for **1** and **2**

Compound	**1**		**2**
Temperature	100 K	300 K	300 K
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$
	13.4079(3)	13.2433(11)	13.2086(7)
a, b, c (Å)	12.3389(3)	12.4686(10)	12.6507(7)
	12.8405(3)	13.4680(9)	13.4674(7)
Volume / Å^3	2124.32(9)	2223.9(3)	2250.4(2)
Z	4	4	4
Density/g.cm^{-3}	1.361	1.294	1.319
R_1	0.0383	0.0787	0.0574
wR_2	0.0880	0.2464	0.1620

Table S2. Selected bond lengths (Å) for Compound **1** and **2**

	1			
	D–H···A	H···A	D···A	∠D-H···A
100 K	N1-H1A···O1i	2.060	2.925	163.79
	N1-H1B···O3i	2.107	2.960	160.15
	N1-H1C···O5i	2.081	2.930	159.25
	2			
300 K	N1-H1A···O1i	2.114	2.929	151.91
	N1-H1B···O3i	2.112	2.981	165.36
	N1-H1C···O5i	2.178	3.004	154.00

Table S3. Curie temperature and spontaneous polarization of ferroelectrics with various crown ether-based inclusion compound.

Compound	T_c (K)	P_s (μC / cm^2)	Ref
[Hcha-(18-crown-6)]$^+$[BF_4]$^-$	397	3.27	24
[Hcha-(18-crown-6)]$^+$[ClO_4]$^-$	390	3.78	24
[(DIPA)([18]crown-6)](ClO_4)	132	0.35	2
[(DIPA)([18]crown-6)][BF_4]	120	0.3	2
[(MeO−C_6H_4−NH_3)(18-crown-6)][TFSA]	415	2	14
[($C_7H_{10}NO$)([18]crown-6)][BF_4]	127	0.54	13
[H_3O(18-crown-6)]$^+$[$FeCl_4$]$^-$	365	2.18	36
[H_3O(18-crown-6)] [$GaCl_4$]	337	3.9	37
[(ATHTP)(18-crown-6)]BF_4	392	3.18	32