Electronic Supplementary Information (ESI) for

Bromocholine bromide is a molecular ferroelectric with moderate phase transition temperature

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Experiment section

Materials and physical measurements. All chemicals were commercially available and were used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, λ = 1.54056 Å). Thermogravimetric (TG) analysis was performed using a TA Q50 system with a heating rate of 10.0 °C/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) measurements were performed by heating/cooling the powder sample at a rate of 10 K/min on a TA DSC Q2000 instrument. The complex permittivity was measured using an Agilent Impedance Analyzer in a Mercury iTC cryogenic environment controller of Oxford Instrument for a powder pellet sample at a rate of 2 K/min. The SHG effect was measured using a XPL1064-200 Instruments. The pyroelectric current measurements were performed on the Keithley 6517B electrometer.

Crystal structure determination. Diffraction data for **BCB** were collected on a Rigaku XtaLAB P300DS single-crystal diffractometer by using graphite monochromated Mo Kα radiation. Absorption corrections were applied by using the multi-scan program *CrysAlisPro*. All the structures were solved by the direct method and refined by the full-matrix least-squares method on *F*2 with SHELXTL. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table S1. CCDC 1818992, 1818993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Summary of crystallographic data and structural refinements for **BCB** at 275 and 353 K.

Complex	**BCB**	
Formula	$C_5H_{13}Br_2N$	
Formula weight	246.98	
Temperature (K)	275(2)	353(2)
Phase	**α**	**β**
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/m$
a/Å	7.2735(3)	7.3865(6)
b/Å	8.5710(3)	8.6160(6)
c/Å	7.4768(3)	7.5120(6)
β/°	108.893(4)	109.395(9)
V/Å^3	441.00(3)	450.95(6)
Z	2	2
D_c/g cm^{-3}	1.860	1.819
R_{int}	0.0651	0.0299
R_1 [$I > 2\sigma(I)$]^a	0.0300	0.0296
wR_2 [$I > 2\sigma(I)$]^b	0.0779	0.0719
R_1 (all data)	0.0316	0.0374
wR_2 (all data)	0.0786	0.0748
GOF	1.074	1.087
Flack	0.07(2)	/

$^aR_1 = F_o - F_c/F_o$, $^bwR_2 = \{w[(F_o)^2 - (F_c)^2]^2/w[(F_o)^2]^2\}^{1/2}$

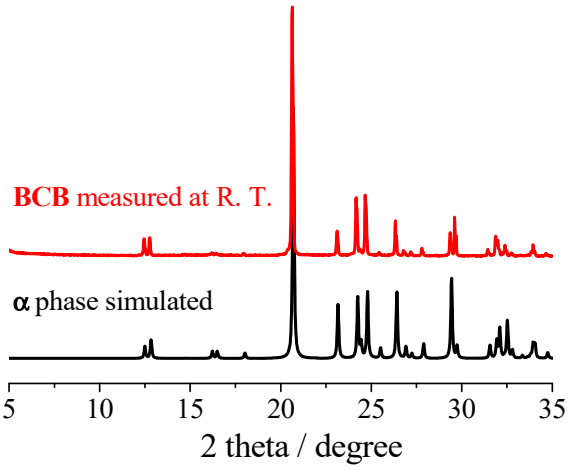

Fig. S1 The experimental PXRD pattern at room temperature compared to the simulated **α** phase.

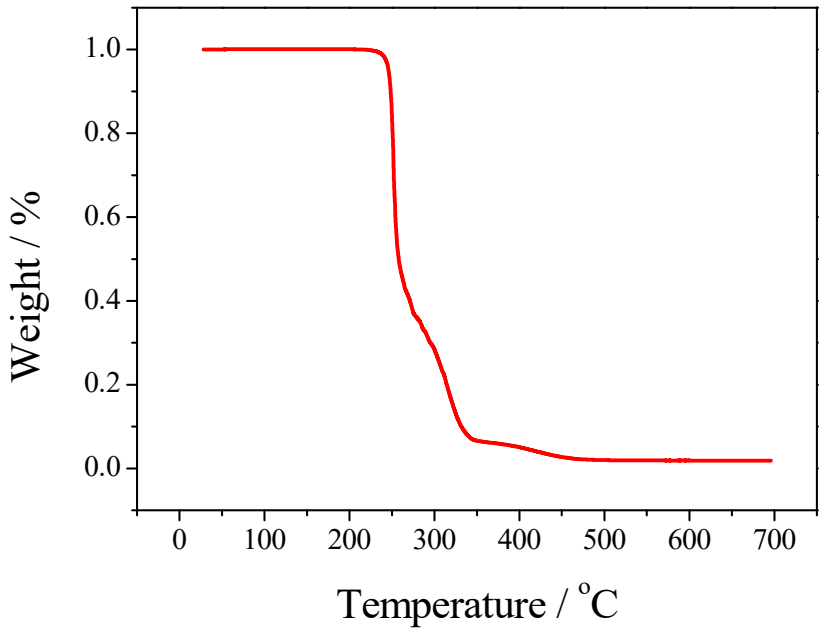

Fig. S2 TG curve of **BCB** under N_2 atmosphere.

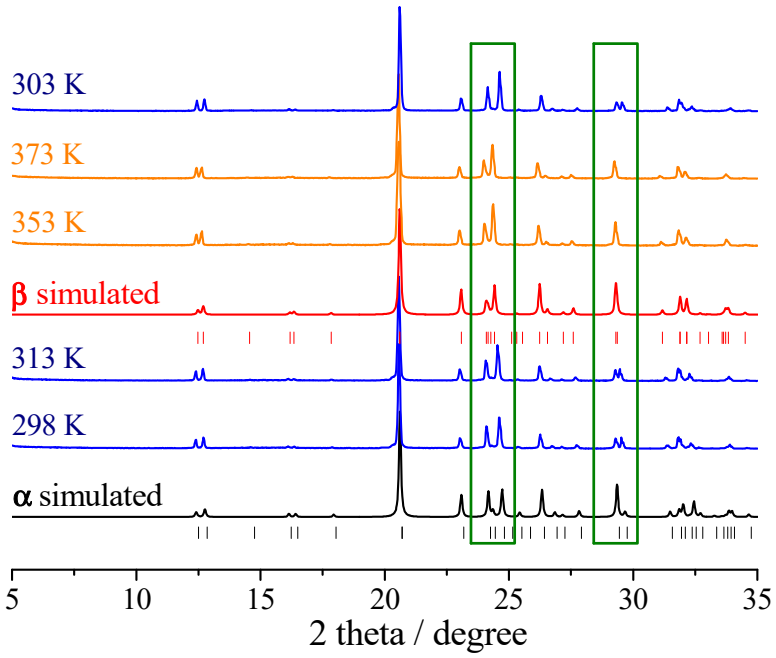

Fig. S3 The variable temperature powder X-ray diffraction patterns of **BCB**.

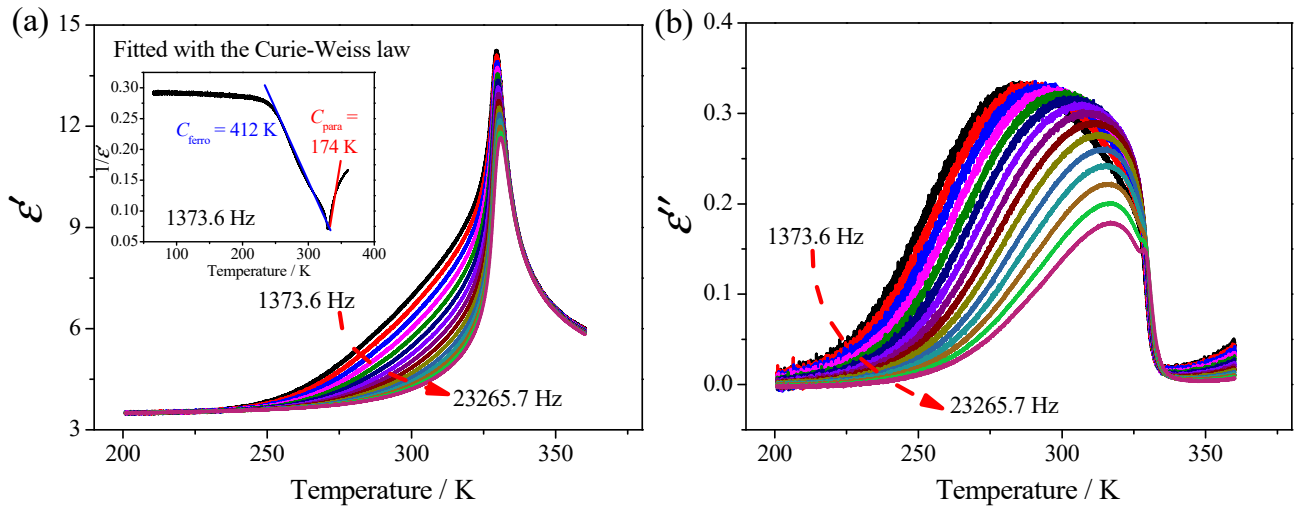

Fig. S4 (a) The real and (b) imaginary part of dielectric constant for **BCB** measured at different frequencies in a heating mode. Inset: Plot of $1/\varepsilon'$ *vs*. temperature (at 1373.6 Hz).

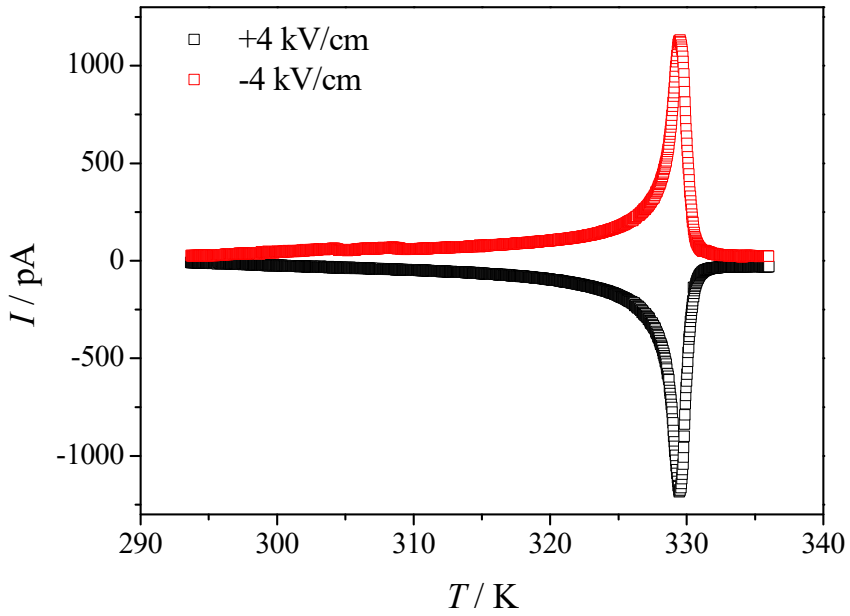

Fig. S5 The pyroelectric current was obtained from heating mode under zero electric field in the vicinity of the ferroelectric phase transition. Before measuring the pyroelectric current, the sample was cooled down from 340 K to 290 K with an applied electric field of about ±4 kV/cm and short cut the sample for enough time to release the remaining charge.

Table S2 Hydrogen bond distances (Å) and angles (°) of **BCB** at **α** phase.

D–H···A	D–H	H···A	D···A	∠D–H–A
C(1)–H(1B)···Br(2)^{i}	0.960	2.856	3.796	166.67
C(1)–H(1C)···Br(1)^{ii}	0.960	3.134	3.766	124.84
C(2)–H(2C)···Br(2)^{iii}	0.960	3.112	4.002	154.92
C(3)–H(3B)···Br(2)^{iv}	0.960	2.835	3.768	164.20
C(4)–H(4B)···Br(2)	0.970	3.030	3.956	160.20
C(5)–H(5A)···Br(2)^{i}	0.970	3.020	3.944	159.83
C(5)–H(5B)···Br(2)^{v}	0.970	2.885	3.853	175.18

Symmetry transformation: (i) –x+1, y+1/2, –z+1; (ii) x, y, z+1; (iii) x–1, y, z; (iv) –x+1, y–1/2, –z+1; (v) x–1, y, z–1.

Table S3 Hydrogen bond distances (Å) and angles (°) of **BCB** at **β** phase.

D–H…A	D–H	H···A	D···A	∠D–H–A
C(1)–H(1A)···Br(2)^{i}	0.960	2.990	3.913	161.74
C(1)–H(1B)···Br(2)^{ii}	0.960	2.925	3.875	170.52
C(2)–H(2A)···Br(2)^{iii}	0.960	3.111	4.017	158.01
C(2)–H(2B)···Br(2)	0.960	2.781	3.734	172.19
C(4)–H(4B)···Br(2) ^{iii}	0.970	3.044	3.968	159.69
C(5)–H(5A)···Br(2)^{iv}	0.970	2.937	3.905	176.18
C(5)–H(5B)···Br(2)	0.970	3.062	3.978	158.01

Symmetry transformation:(i) –x+1, –y+1, –z+1; (ii) x, y+1, z; (iii) –x, –y+1, –z+1; (iv) –x+1, –y+1, –z+2.

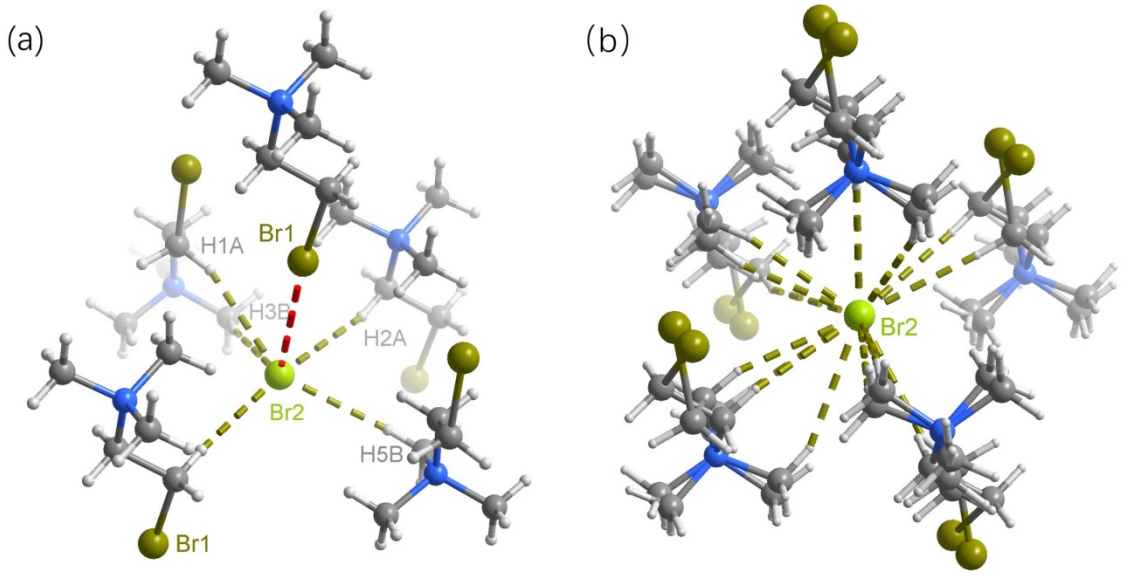

Fig.S6 C–H···Br interactions in the crystal structures of **BCB**: (a) **α** phase; (b) **β** phase.