Electronic Supplementary Information

An Organic Plastic Ferroelectric with High Curie Point.

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Experimental details. (-)-Camphanic acid was purchased from Leyan company (https://www.leyan.com) and purified by recrystallization prior to the measurements.

Single-crystal diffraction. The variable temperature single crystal X-ray diffraction (XRD) data was carried out by using a Rigaku Oxford diffractometer with MoKa radiation (λ = 0.71073 Å). The test sample should be a high-quality single crystal that has just been precipitated. The direct method was used to solve the crystal structure at various temperatures, and the SHELXTL-2014 program package was used to correct it by the full-matrix least-squares method. For all non-hydrogen atoms, their anisotropy is refined. All hydrogen atoms are generated geometrically and at the same time in proper positions.

PXRD. Variable-temperature powder X-ray diffraction measurements were performed on a Rigaku D/MAX 2000 PC X-ray diffractometer. The measurement condition is in a 2θ range of 5°–50°, the step size is 0.02°, and the corresponding PXRD pattern is obtained.

Differential scanning calorimetry (DSC) The DSC measurement is performed by using a PerkinElmer Diamond DSC instrument. Added the power sample to an alumina crucible and cover it. Then the powder sample was studied in by heating and cooling with a rate of 20 K min^{-1} at nitrogen atmosphere.

Second Harmonic Generation (SHG). The SHG measurements was carried on the FLS 920, Edinburgh Instruments and the laser of Vibrant 355 II, OPOTEK (wavelength 1064 nm, pulse Nd:YAG).

PFM measurements. The ferroelectric domain structures were performed on a commercial atomic force microscope system (MFP-3D, Asylum Research). Conductive Pt/Ir-coated silicon probes (EFM-50, Nanoworld) were used for domain imaging and polarization switching studies. Resonant-enhanced PFM mode was used to enhance the signal, with the ac voltage frequency of about 330-380 kHz. The as-grown thin films of *R*- or *S*-DMIO on ITO-coated glass, was used for the PFM measurements. Specifically, 20 μL of ethanol solution of *R*- or *S*-DMIO (20 mg per 200 ul) was dripped onto a 1 cm × 1 cm ITO glass sheet, and the solvent was volatilized at room temperature to grow a smooth crystal film.

Thermogravimetric analysis (TGA). The TGA measurement was performed by using a PerkinElmer TGA 8000.

Polarization-Electric Field (*P-E*) Hysteresis Loops. *P-E* hysteresis loops measurements were recorded using the double-wave method at 298 K. The double-wave method was carried out with a homemade system, including a high voltage amplifier (Trek 623B), waveform generator (Agilent 33521A), and low-current electrometer (Keithley 6514). The measuring frequency was 0.033 Hz.

Table. S1 Crystal data and structure refinements for (-)-Camphanic acid at various temperature.

(*S*)-(-)Camphanic acid		
Temperature	100K	373K
Formula	$C_{10}H_{14}O_4$	$C_{10}H_{14}O_4$
weight	198.21	198.21
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	6.29835(9)	6.3879(2)
b (Å)	10.64131(14)	10.8484(3)
c (Å)	7.53892(11)	7.6137(3)
α (°)	90	90
β (°)	103.5036(14)	103.203(3)
γ (°)	90	90
Volume /Å^3	491.311(12)	513.67(3)
Z	2	2
Density/g cm^{-3}	1.340	1.281
R_1	0.0217	0.0544
wR_2	0.0587	0.2892
GOF	1.09	1.416

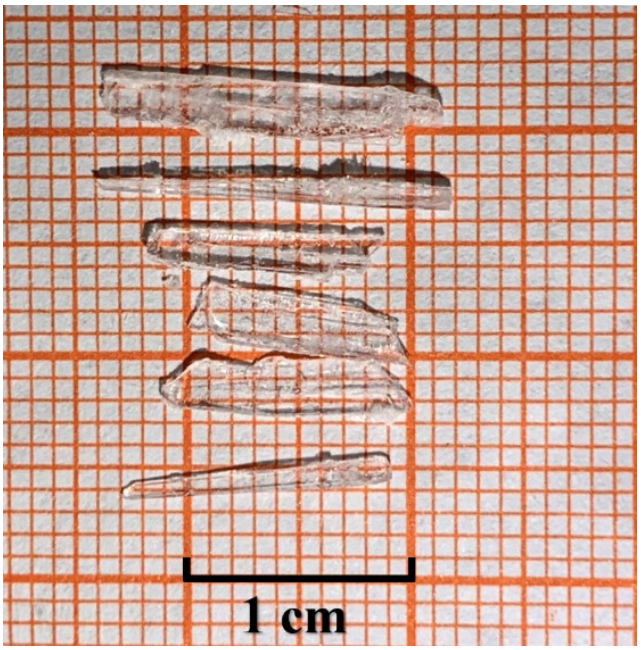

Figure S1. Crystal picture of (-)-Camphanic acid.

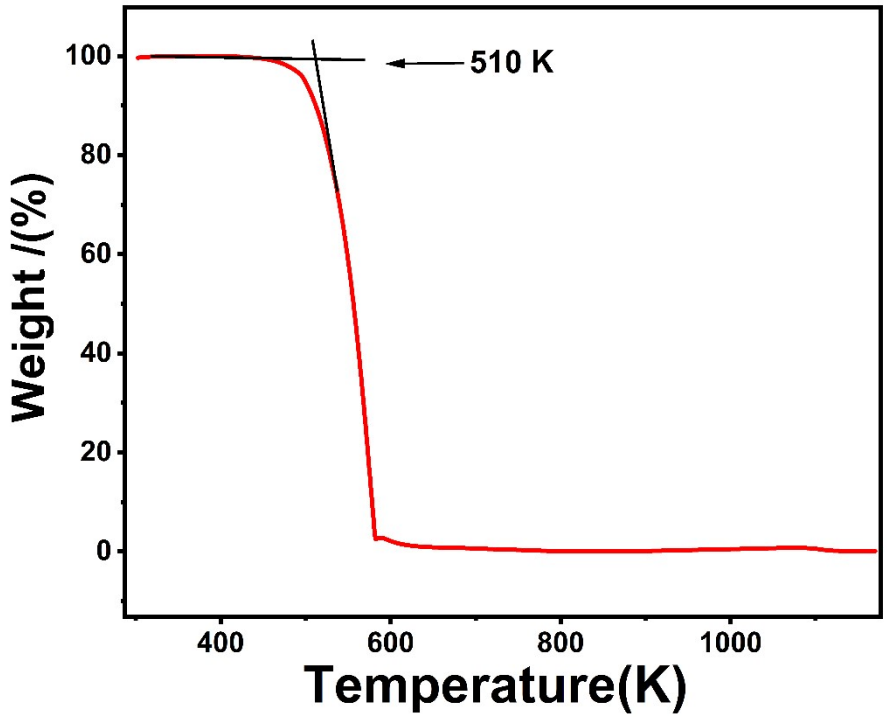

Figure S2. TGA plot of (-)-Camphanic acid.

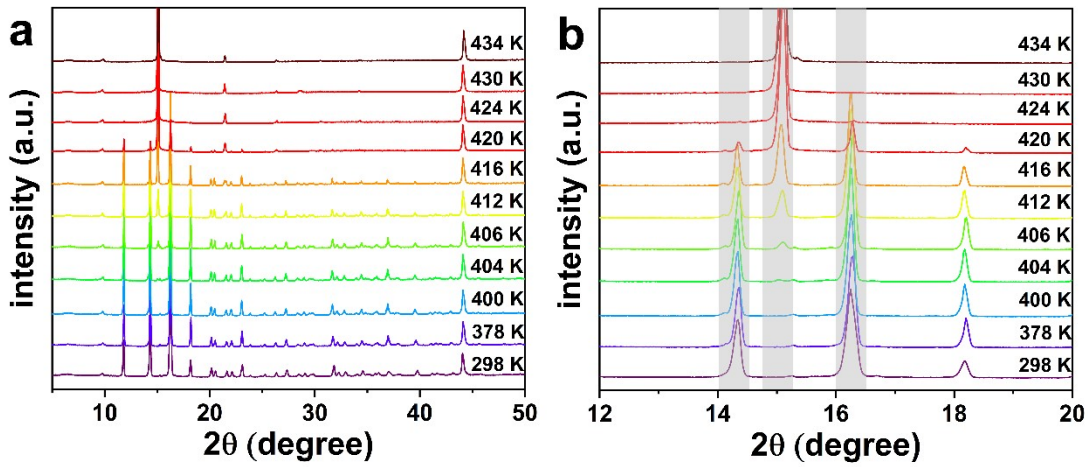

Figure S3. (a) Measured powder X-ray diffraction patterns of (-)-Camphanic acid at various temperature. (b) zoom in (a) between 12 and 20 degrees. The shaded area indicates the characteristic peaks.

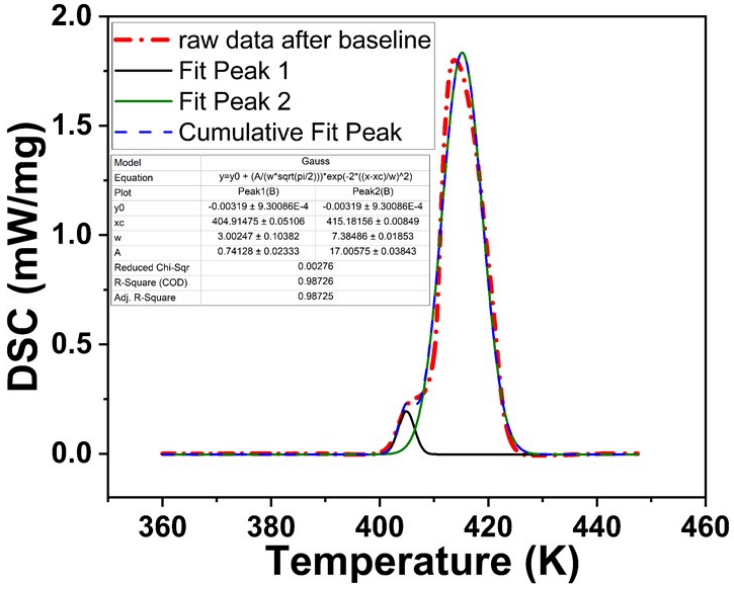

Figure S4. The endothermic peak upon heating. It splits into two parts through Gauss Fit. The integration area of the Fit peak 2 is taken as the entropy changes for the plastic phase transition.

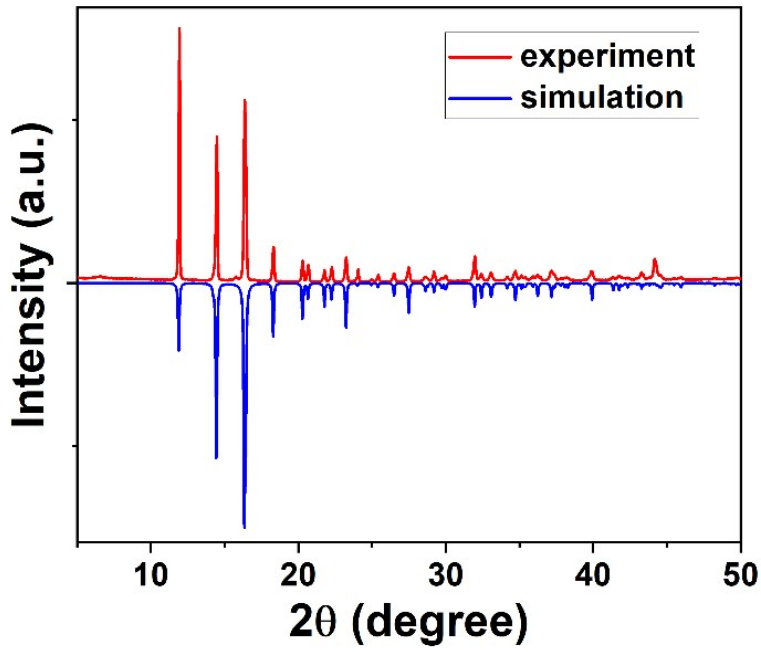

Figure S5. Measured and simulated powder X-ray diffraction patterns of (-)-Camphanic acid.

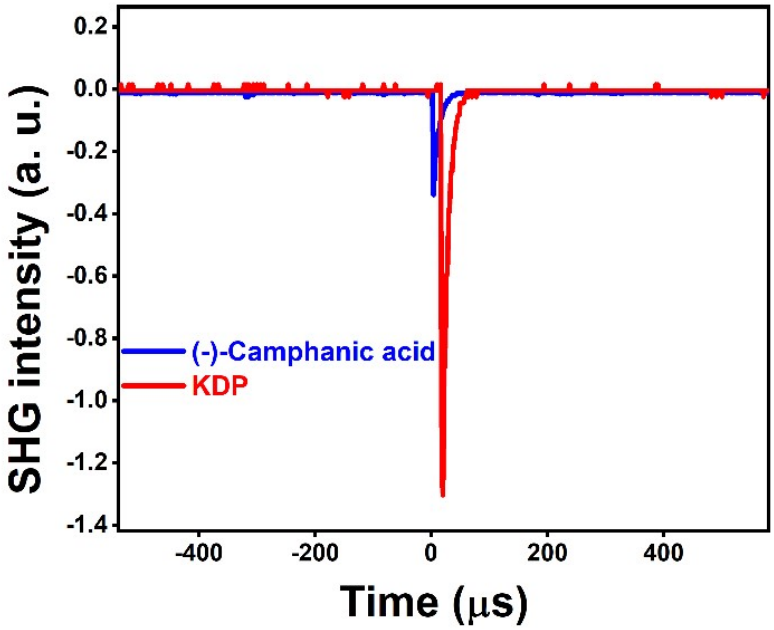

Figure S6. Oscilloscope traces of the SHG signals of (-)-Camphanic acid and KDP at room temperature.

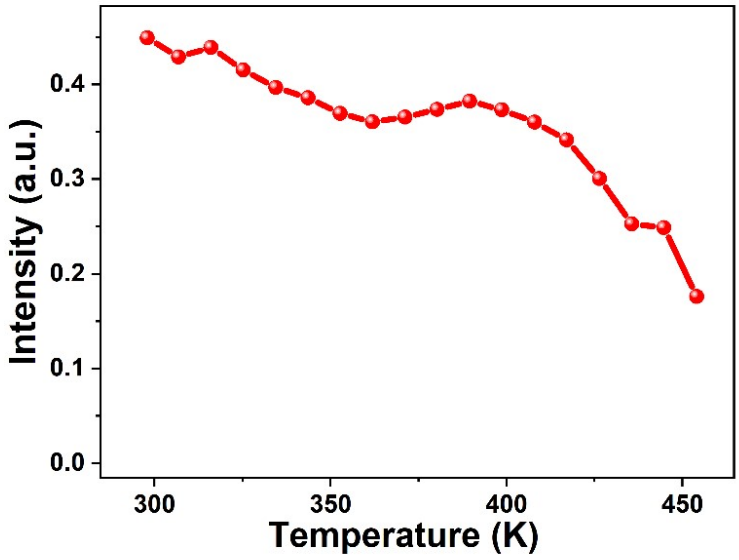

Figure S7. Temperature dependent SHG measurement of (-)-Camphanic acid.

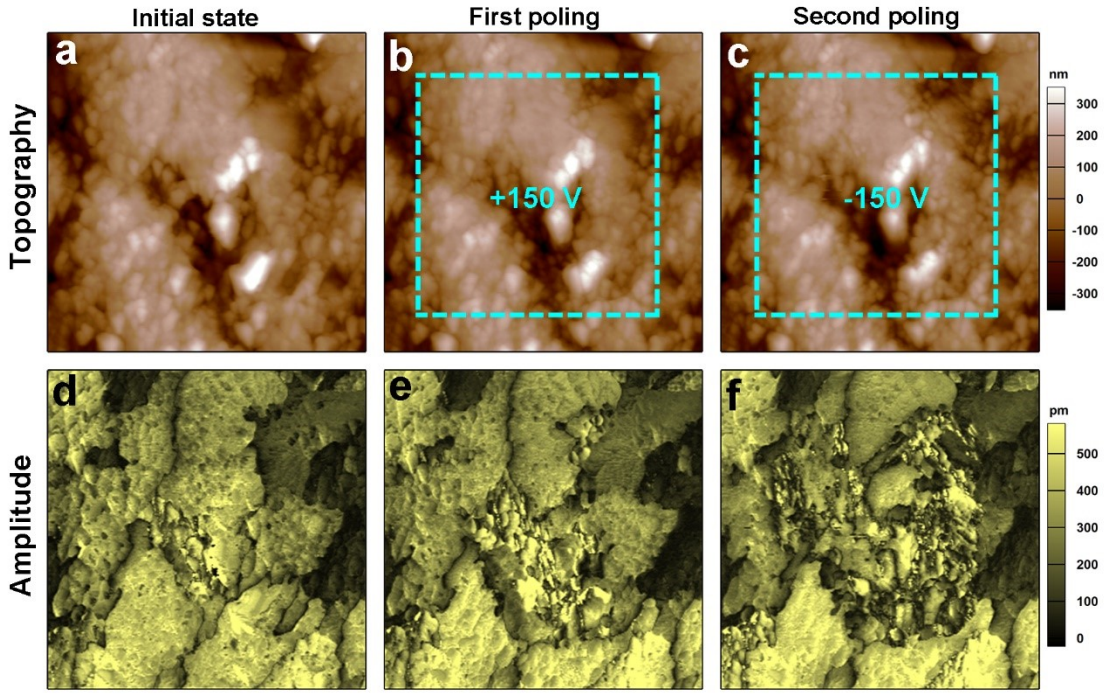

Figure S8. Detailed PFM information for the domain switching measurements. (a-c) Topographic and (d-f) amplitude images of the initial state (a, d), after poling the blue box region with tip voltage of +150 V (b, e) and after poling the same region with tip voltage of -150 V (c, f).