

## Electronic Supplementary Information

### Homochiral Anionic Modification toward the Chemical Design of Organic Enantiomeric Ferroelectrics

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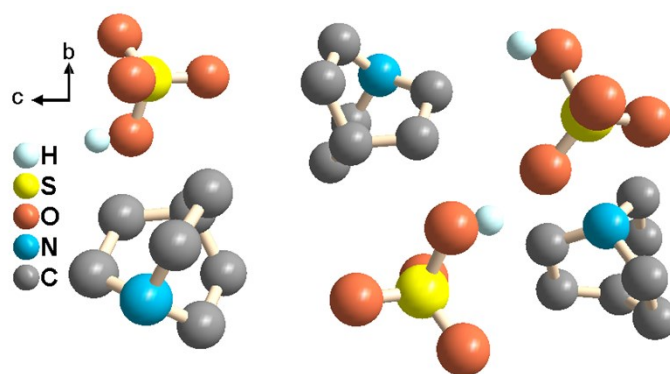
#### Experimental details

**Sample preparation.** Quinuclidine, H<sub>2</sub>SO<sub>4</sub> (98%), and *L*-, *D*- and *DL*-camphorsulfonate were commercially available. The crystalline samples of quinuclidine *L*-camphorsulfonate (*L*-HQCS), quinuclidine *D*-camphorsulfonate (*D*-HQCS), (*DL*)-camphorsulfonate (*DL*-HQCS) and quinuclidinium(HSO<sub>4</sub>) (HQHSO<sub>4</sub>) were obtained by slow evaporation of stoichiometric amounts of quinuclidine and *L*-camphorsulfonate, *D*-camphorsulfonate, *DL*-camphorsulfonate and H<sub>2</sub>SO<sub>4</sub>(98%) in ethanol at room temperature, respectively.

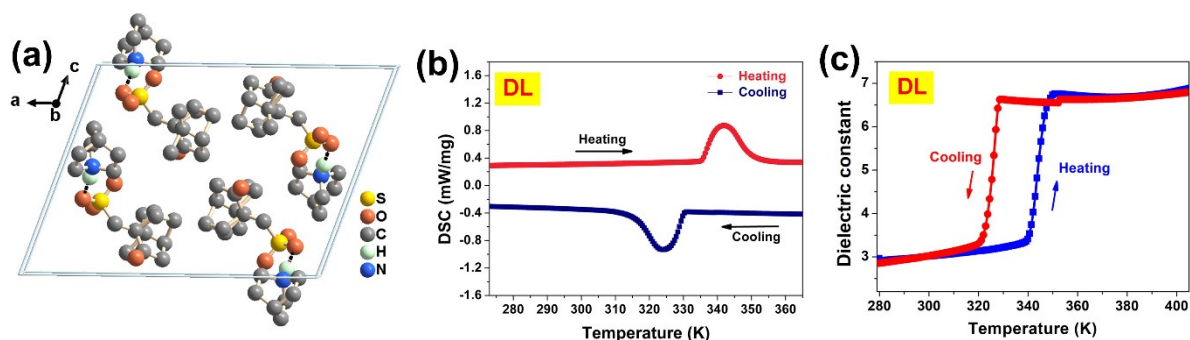
**Thin film preparation.** The precursor solutions of *L*-HQCS was prepared by dissolving 50 mg of the as-grown crystals in 1 mL ethanol. The precursor solution (10 μL) was dropped onto a clean indium tin oxide (ITO) coated conductive glass substrate (1.5 × 1.5 cm). Thin film of *L*-HQCS formed on the ITO-glass substrate after the solvent slowly evaporated on a hot plate of 40 ± 1 °C.

**Characterization methods.** Single-crystal X-ray diffraction data were performed using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$ ) on a Rigaku Saturn 924 diffractometer in the scan mode. We used the CrystalClear software package to process the data. The crystal structures were solved by using the SHELXLTL software package. The VCD and IR measurement was carried out by using Bruker PMA-50 instrument. Thermogravimetric analysis (TGA) used the TA Q50 system. Differential scanning calorimetry (DSC) measurements were carried out on a TA Q2000 instrument under a dinitrogen

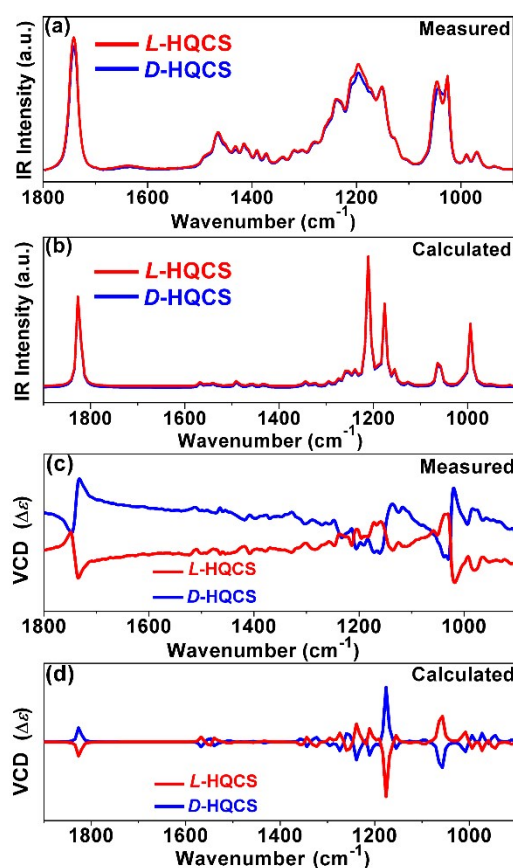
atmosphere in aluminum crucibles. The dielectric measurements were carried on a TH2828A impedance analyzer. Silver conduction paste deposited on the pressed-powder pellets surfaces was used as the electrodes. We used the Rigaku D/MAX 2000 PC X-ray diffraction instrument in the  $2\theta$  between  $5^\circ$  and  $50^\circ$  with a step size of  $0.02^\circ$  to record PXRD patterns. The SHG measurements were carried on an INSTEC Instrument (pulsed Nd: YAG laser with a wavelength of 1081 nm, 1.6MW peak power, 5 ns pulse duration). Nano-scale polarization imaging and local switching spectroscopy were carried out using a resonant-enhanced piezoresponse force microscopy (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 applied to enhance the signal.



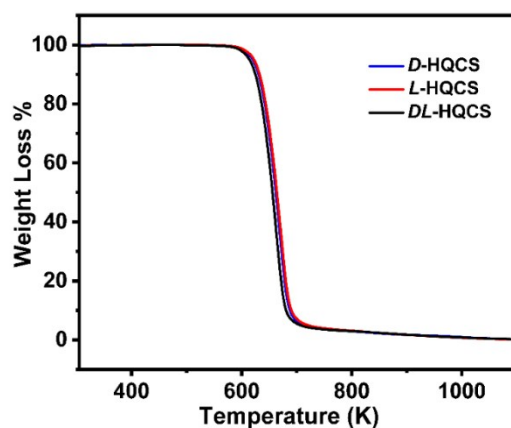
**Figure S1.** Packing views of the structure of HQHSO<sub>4</sub> along the *a*-axis at 293 K.



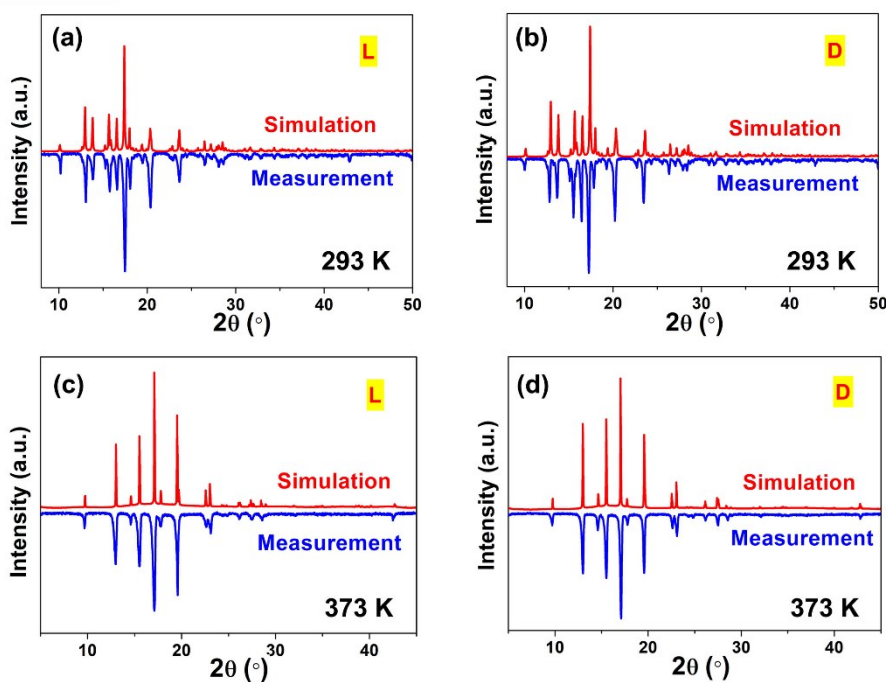
**Figure S2.** (a) Packing views of the structures of *DL*-HQCS. The dashed line denotes N–H···O hydrogen-bonding interactions. (b) DSC curves in a heating–cooling run of *DL*-HQCS. (c) Temperature dependent  $\epsilon'$  of *DL*-HQCS.



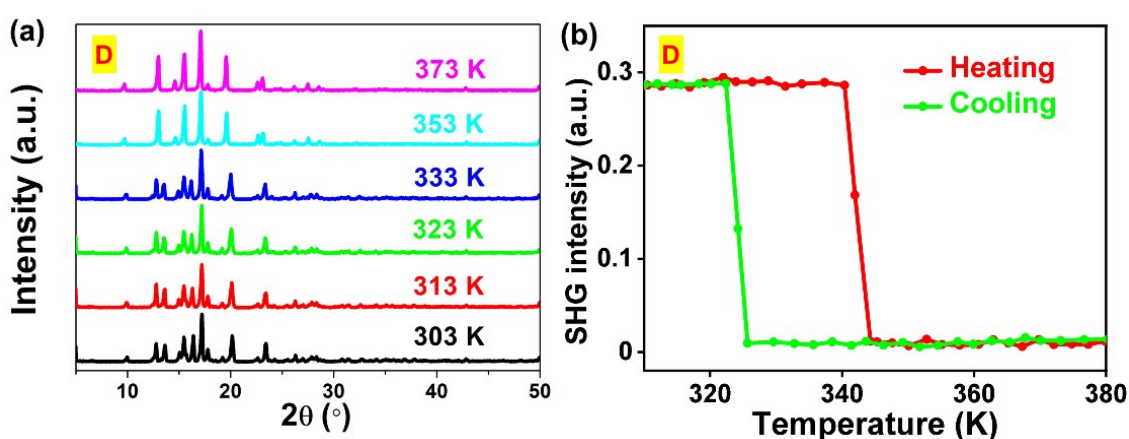
**Figure S3.** Measured and calculated (a, b) IR and (c, d) VCD spectra for *L*-HQCS and *D*-HQCS. It should be mentioned that the calculated IR and VCD spectra show a slight peak shift compared to the experimental ones. Such a mismatch can be attributed to the different molecular configuration under experiment and density-functional theory (DFT) calculation, because the calculated IR and VCD spectra are based on the geometry preoptimization under corresponding B3LYP/6–31G(d) level.



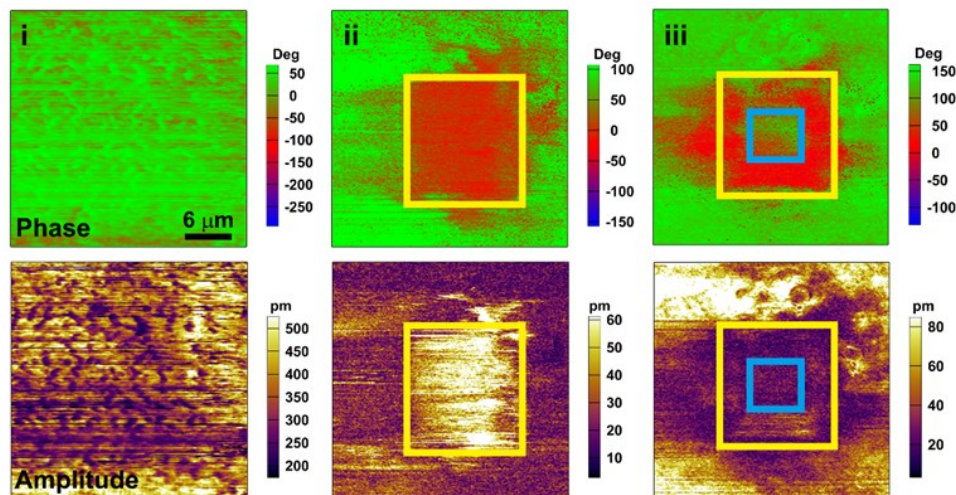
**Figure S4.** TGA curves of *L*-HQCS, *D*-HQCS and *DL*-HQCS.



**Figure S5.** Experimental PXRD patterns and simulated ones from crystal structure of (a) *L*-HQCS and (b) *D*-HQCS in RTP. Experimental PXRD patterns and Pawley refinement of PXRD data of (c) *L*-HQCS and (d) *D*-HQCS in HTP. Experimental PXRD patterns match with the simulated ones in both RTP and HTP. The Pawley refinements reveal tetragonal crystal lattices with cell parameters of  $a = b = 7.3248 \text{ \AA}$  and  $c = 18.1716 \text{ \AA}$  for *L*-HQCS, and  $a = b = 7.3538 \text{ \AA}$  and  $c = 18.1295 \text{ \AA}$  for *D*-HQCS at 373 K.



**Figure S6.** (a) Variable temperature PXRD patterns and (b) temperature-dependent second harmonic generation (SHG) intensity of *D*-HQCS.



**Figure S7.** Polarization switching behavior of *L*-HQCS measured on its thin film. PFM amplitude (top), and phase (bottom) images of the thin film. (i) Initial state. (ii) After the first switching with negative bias at  $-60$  V in the yellow line marked rectangle region. (iii) After the succeeding back-switching with positive bias at  $+60$  V in the blue line marked rectangle region. The green and red regions in phase images indicate the polarizations oriented upward and downward, respectively.

**Table S1.** Crystal data for *L*-HQCS, *D*-HQCS, *DL*-HQCS and HQHSO<sub>4</sub> at 293 K.

Compound	<i>L</i> -HQCS	<i>D</i> -HQCS	<i>DL</i> -HQCS	HQHSO <sub>4</sub>
Temperature	293 K			
Formula	[C <sub>7</sub> H <sub>14</sub> N][C <sub>10</sub> H <sub>15</sub> SO <sub>4</sub> ]	[C <sub>7</sub> H <sub>14</sub> N][C <sub>10</sub> H <sub>15</sub> SO <sub>4</sub> ]	[C <sub>7</sub> H <sub>14</sub> N][C <sub>10</sub> H <sub>15</sub> SO <sub>4</sub> ]	[C <sub>7</sub> H <sub>14</sub> N][HSO <sub>4</sub> ]
Formula weight	343.47	343.47	343.47	209.26
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.9958(6)	14.0095(2)	18.6138(3)	7.0131(7)
	7.4192(3)	7.4162(1)	7.3953(1)	7.1214(5)
	18.5276(8)	18.5511(2)	14.0162(2)	19.4770(17)
$\alpha$ , $\beta$ , $\gamma$ (°)	90	90	90	90.0
	109.796(5)	109.791(2)	109.918(2)	93.127(8)
	90	90	90	90.0
Volume / Å <sup>3</sup>	1810.17(14)	1813.56(5)	1813.98(5)	971.30(15)
<i>Z</i>	4	4	4	4
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0545	0.0581	0.1097	0.0545
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1799	0.1864	0.3322	0.1537
GOF	1.080	0.991	1.004	1.075