Correlated Proton Transfer and Ferroelectricity along Alternating Zwitterionic and Nonzwitterionic Anthranilic Acid Molecules

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Supporting Information

Experimental details

Electric Measurements. All the electric measurements were obtained from as-grown single crystals with painted gold or silver electrodes. The dielectric constant (Figure S1) was measured with an LCR meter (HP 4284A). The electric polarization (P)–electric field (E) hysteresis curves were collected on a ferroelectrics-evaluation system (Toyo Corporation, FCE-1) consisting of a current/charge–voltage converter (Toyo Corporation Model 6252), an arbitrary waveform generator (Biomation 2414B), an analog-to-digital converter (WaveBook 516), and a voltage amplifier (NF Corporation, HVA4321). The measurements were performed at room temperature with a high-voltage triangular wave field and various alternating frequencies. The crystals were immersed in silicon oil to prevent atmospheric discharge under a high electric field.

Thermal analysis. Differential scanning calorimetry (DSC) measurement was performed using a Hitachi DSC7000X instruments. The sample was encapsulated in an aluminum pan and heated at a rate of 4 or 8 K min^{-1}. The temperature was calibrated using the melting point of indium (429.8 K). The DSC charts of anthranilic acid (Form I) are shown in Figure S2.

Piezoresponse force microscopy. Before measurements, as-gown single crystal of anthranilic acid were dissolved the surface with ethanol to reduce its thickness less than 100 μm. The thickness of a single crystal for PFM measurement was estimated using a laser microscope (VK-X200; Keyence) with a wavelength of 408 nm. PFM measurements were performed using a commercially available scanning probe microscope (Asylum MFP-3D) in dual ac resonance tracking mode[1] with a Pt–Ir-coated Si tip (Nanosensors PPP-NCSTPt with a spring constant k ~ 7.4 N m^{-1}). The topography, phase shifts, and amplitude of the cantilever resonance were acquired simultaneously using an ac modulation voltage of about 0.5–1 V (point to point) at the shoulder of the contact resonance. Local poling was performed by applying the dc bias (± 200 V) at arbitrary positions.

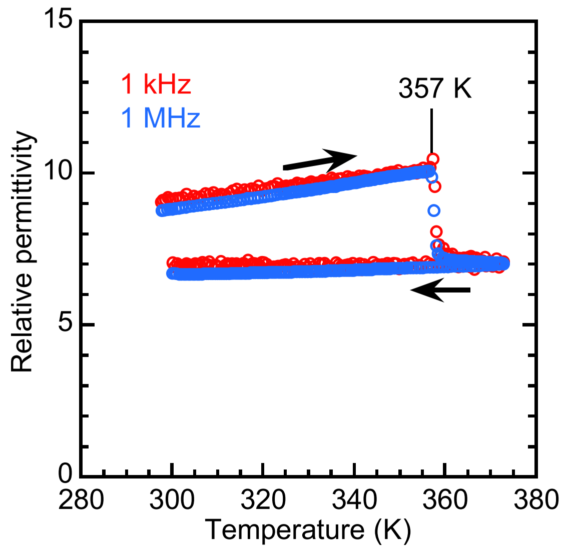

Figure S1. Temperature dependence of the relative permittivity ε_r for anthranilic acid I crystals measured with an ac field of various frequencies (1 kHz -1 MHz) of $E \| [100]$ configurations.

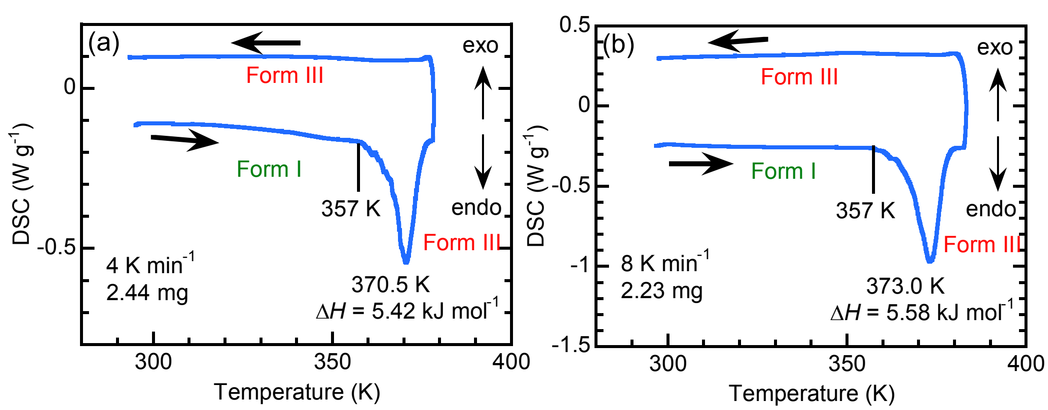

Figure S2. Differential scanning calorimetry (DSC) of anthranilic acid (Form I) powder at different sweep rate: (a) 4 K min^{-1} and (b) 8 K min^{-1}.

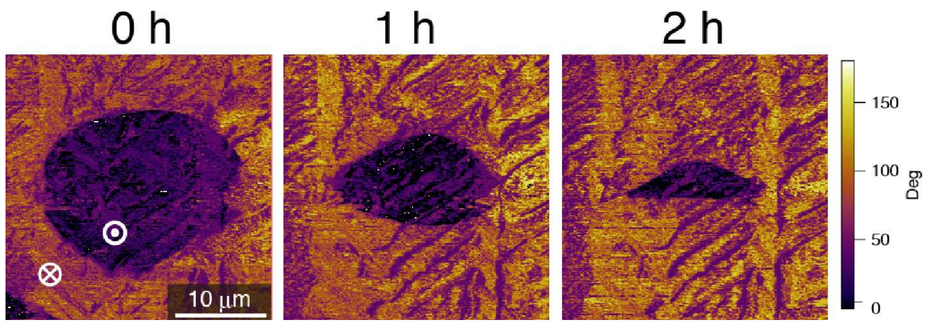

Figure S3. Time-lapse phase images after applying a poling voltage of −200 V for 100 s to the tip at the center on the surface of anthranilic acid single crystal.

REFERENCE

(1) Rodriguez, B. J.; Callahan, C.; Kalinin, S. V.; Proksch, R. Dual-frequency resonance-tracking atomic force microscopy. *Nanotechnology* **2007**, *18*, 475504.