Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Competing Ferroelectric Polarization: Hydroxyl Flip-Flop versus Proton-Transfer Mechanisms

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Electronic Supplementary Information

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Preparation of deuterated CRCA and PhMDA crystals

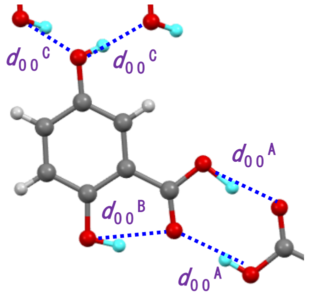
Deuterated croconic acid crystals were grown as orange elongated plates by slow evaporation of solution in deuterium oxide (D_2O 99.9%D, Aldrich) under a stream of inert gas. The deuterated phenylmalondialdehyde was recrystallized from D_2O and its transparent thick plates were obtained by temperature-gradient sublimation under reduced pressure.

Table S1. Crystal data and experimental details of DHBA and NPTL crystals.

	DHBA	DHBA-d_3	NPTL
Chemical formula	$C_7H_6O_4$	$C_7H_6O_4$	$C_{10}H_8O$
Formula wt.	154.12	154.12	144.17
Temperature (K)	296	296	295
a (Å)	4.9705(12)	4.9736(9)	32.026(14)
b (Å)	11.838(3)	11.826(3)	5.919(2)
c (Å)	11.248(3)	11.220(2)	8.120(3)
α (deg.)	90	90	90
β (deg.)	90.405(6)	90.477(5)	101.288(9)
γ (deg.)	90	90	90
V (Å^3)	661.8(3)	659.9(2)	1509.5(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Pc (#7)	Pc (#7)	Cc (#9)
ρ_{calc} (g cm^{-3})	1.547	1.551	1.269
Z	4	4	8
Dimensions (mm)	0.40×0.27×0.19	0.40×0.20×0.19	0.30×0.20×0.08
Radiation	MoKα (λ = 0.7108 Å)	MoKα (λ = 0.7108 Å)	MoKα (λ = 0.7108 Å)
$2\theta_{\mathrm{max}}$ (deg.)	55	55	55
R_{int}	0.019	0.019	0.036
Reflection used ($2\sigma(I) < I$) [a]	2684	2660	2958 (1713)
No. of variables	224	224	208 (102)
R [a]	0.046	0.044	0.049 (0.075)
R_w [a]	0.140	0.142	0.151 (0.207)
GOF [a]	1.04	1.14	1.07 (1.19)
$d_{\mathrm{OO}}{}^{\mathrm{A}}$ (COOH···O=)	2.678(4), 2.666(4)	2.690(4), 2.667(4)	
$d_{\mathrm{OO}}{}^{\mathrm{B}}$ (OH···O=)	2.628(4), 2.637(4)	2.629(4), 2.632(4)	
$d_{\mathrm{OO}}{}^{\mathrm{C}}$ (OH···OH)	2.730(5), 2.768(5)	2.732(5), 2.767(5)	2.744(6), 2.736(5)

a) The numbers in parenthesis represent the refinement results assuming the space group $C2/c$ (#15).

For definitions of hydrogen bonded O(H)···O distances, see this structure.



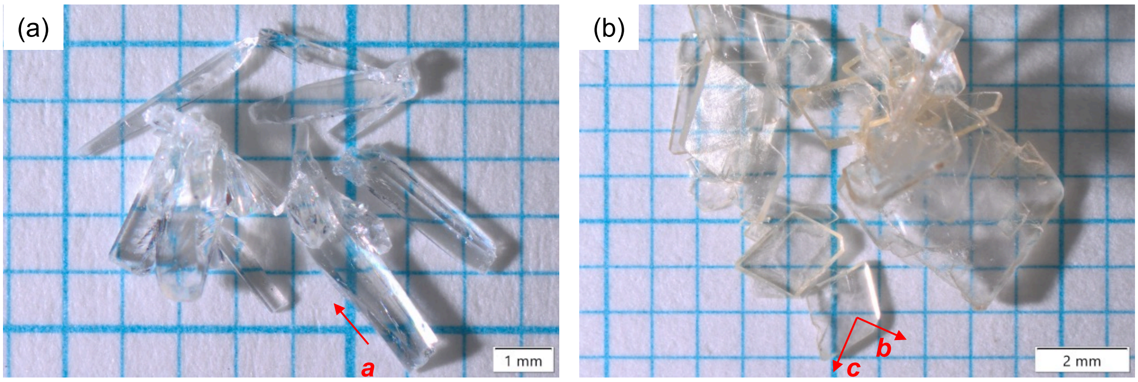


Figure S1. Photographs of single crystals of (a) DHBA and (b) NPTL. Red arrows represent the crystallographic directions.

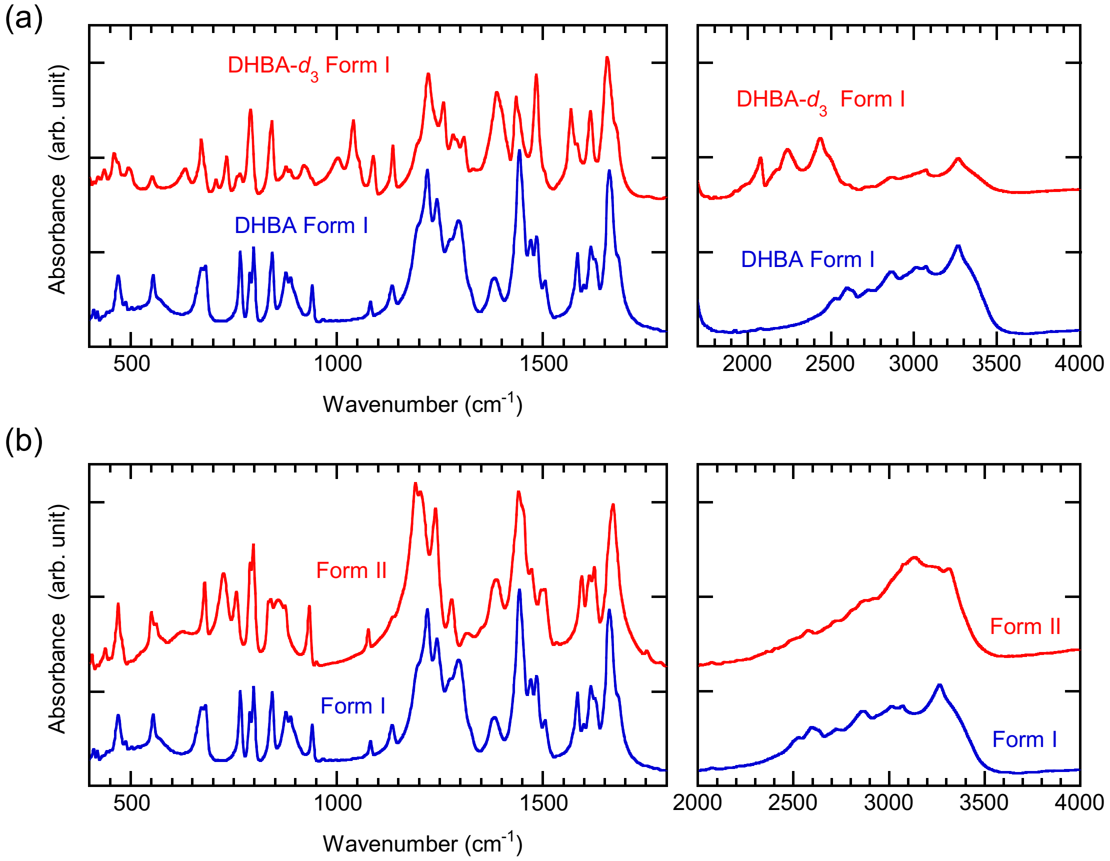
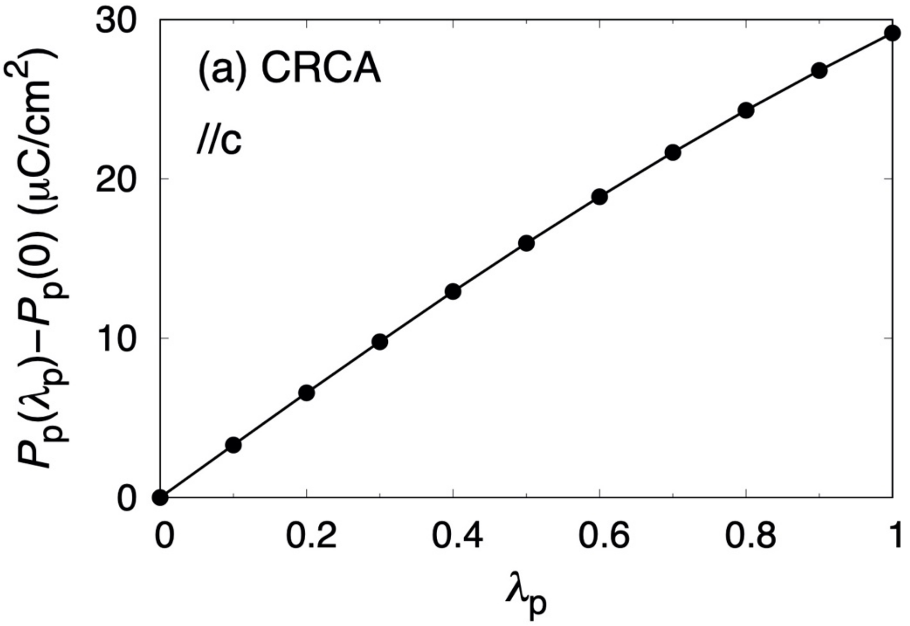


Figure S2. Infrared absorption spectra measured on KBr disks containing powdered specimens. (a) Form I crystals of DHBA (blue) and deuterated DHBA-d_3 (red). (b) DHBA crystals of Form I (blue) and Form II (red).



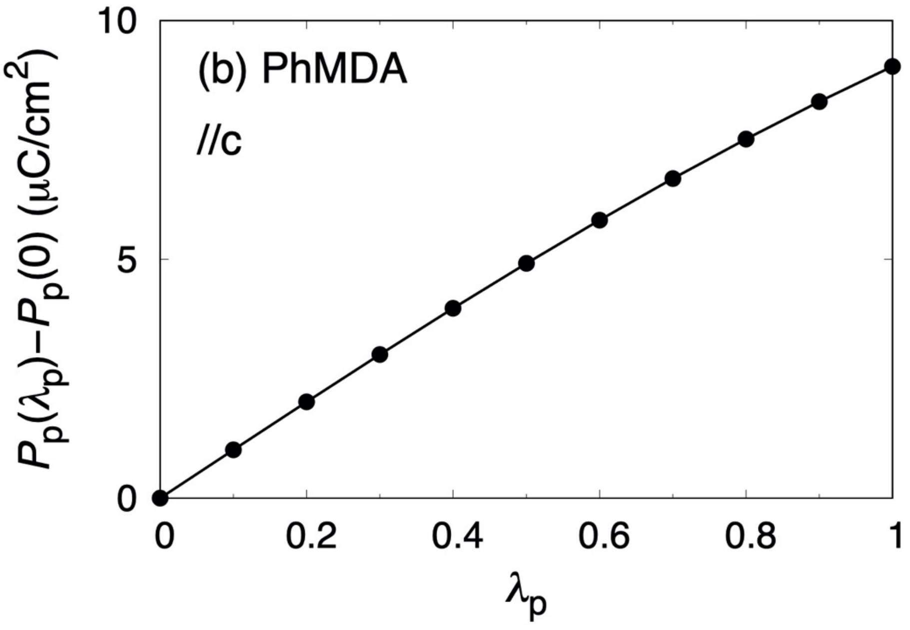


Figure S3. λ_p-P_p plot for test simulations of spontaneous polarization along the *c* crystal axis in (a) CRCA and (b) PhMDA. $\boldsymbol{P}_p(1) - \boldsymbol{P}_p(0) = (0.00, 0.00, 29.15)$ μC/cm^2 in CRCA and (0.00, 0.00, 9.04) μC/cm^2 in PhMDA along the *a*, *b*, *c* crystal axes. For the theoretical and experimental values in the previous works, see Ref. 19.

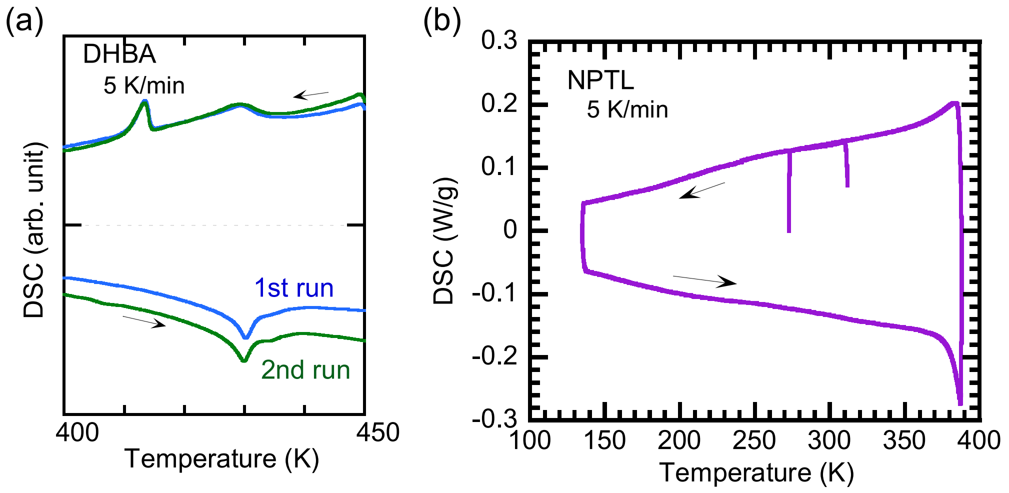


Figure S4. Differential scanning calorimetry (DSC) thermographs of (a) DHBA (first (blue) and second runs (green)) and (b) NPTL. Arrows indicate the directions of temperature changes at a rate of 5 K/min.

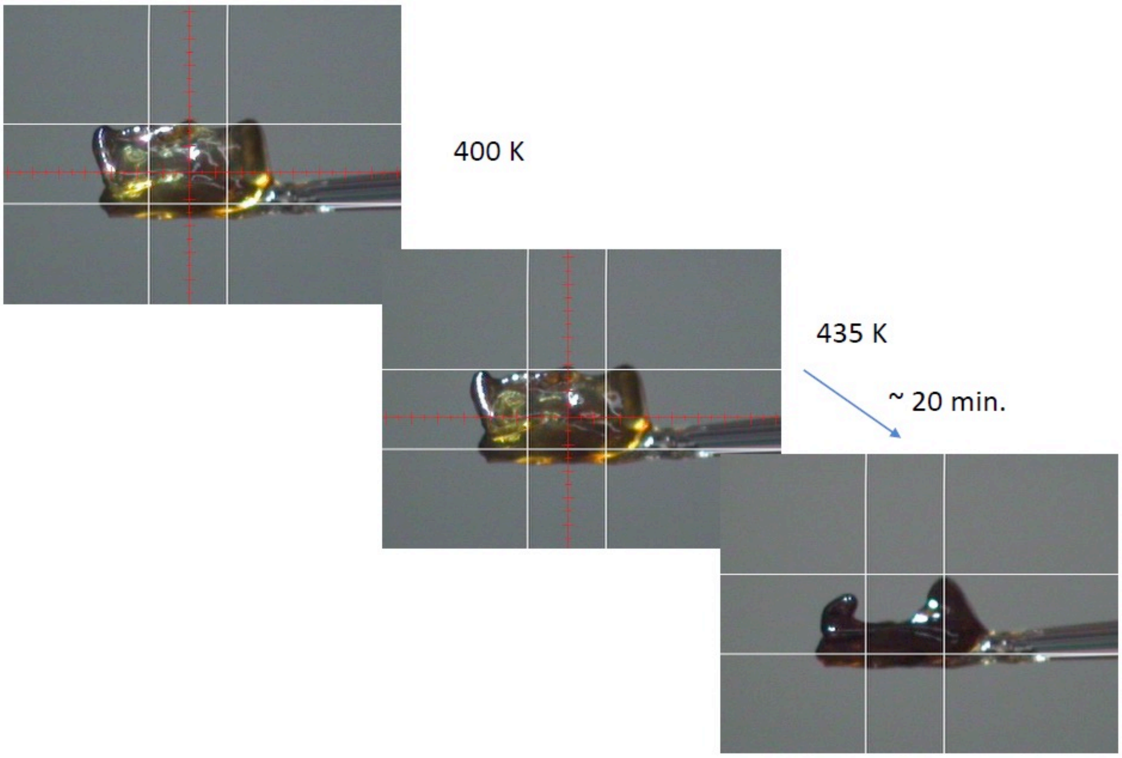


Figure S5. Time evolution of grease-coated DHBA single crystal at high temperatures. Attempts to collect the X-ray diffraction images and second harmonic generation (SHG) at high temperatures around the phase transition points were failed due to sublimation of the specimen.

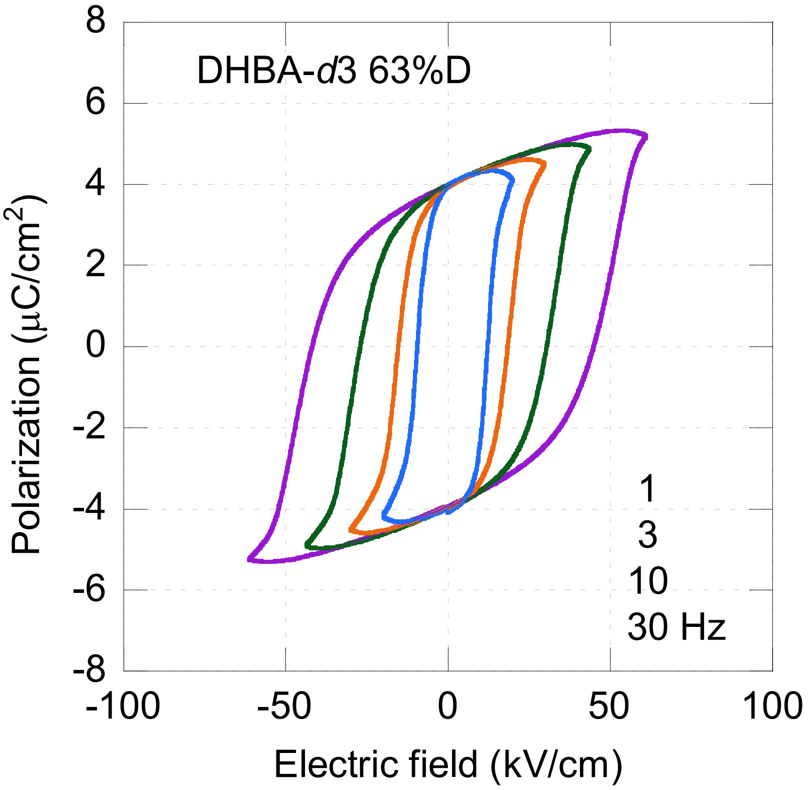


Figure S6. *P*-*E* hysteresis loops of DHBA-d_3 Form I with $E||a$ configuration at room temperature.

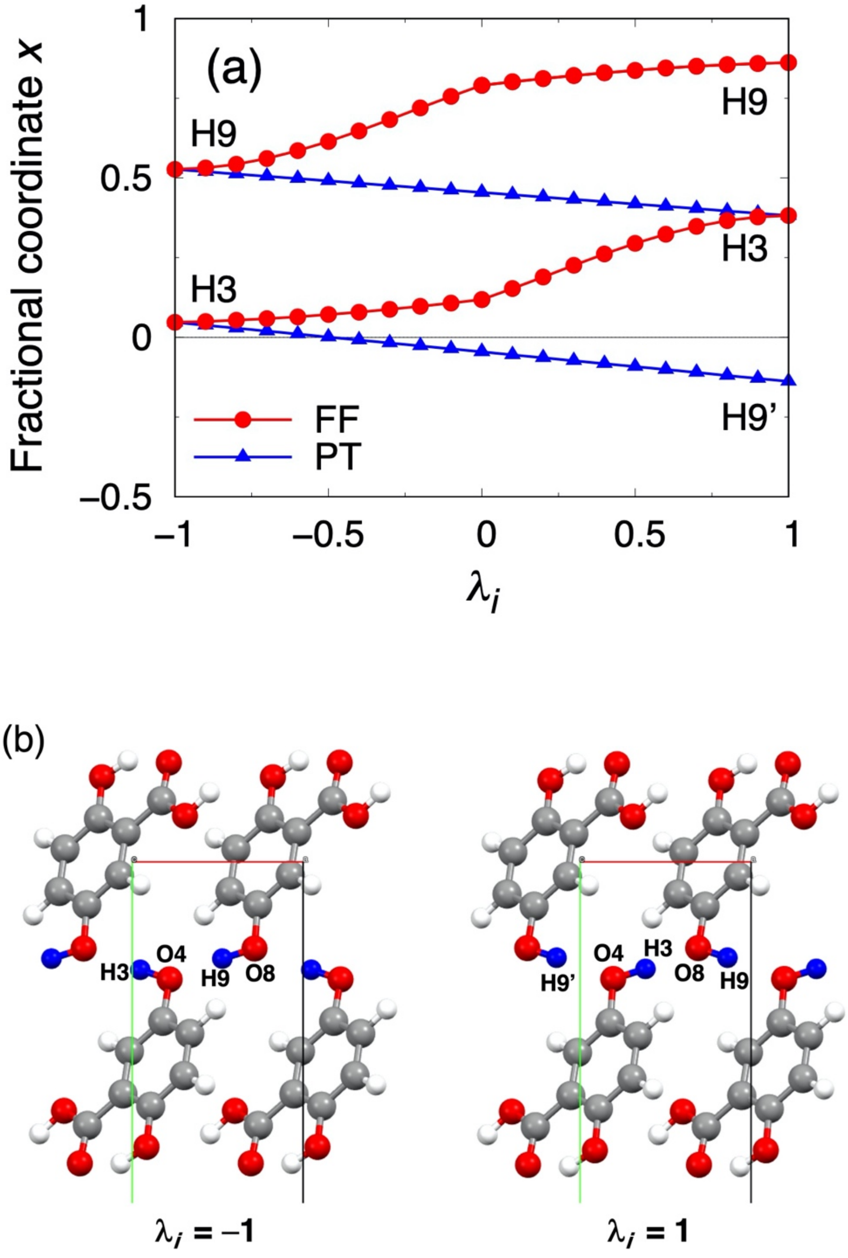


Figure S7. (a) Fractional coordinates x of the protons in the hydrogen-bonding chain as a function of polar distortion λ_i (FF: i = f, PT: i = p) in DHBA. For the labels of the protons, see (b). The coordinates of H3 and H9 at $\lambda_i = 1$coincide with those in the CIF data presented in this work. The coordinate of H9', x(H9') = x(H9) – 1 at $\lambda_i = 1$. Note that H3 and H9 are converted between $\lambda_p = -1$ and 1 in the PT process, because H3 (H9) are defined the protons bonded to O4 (O8).

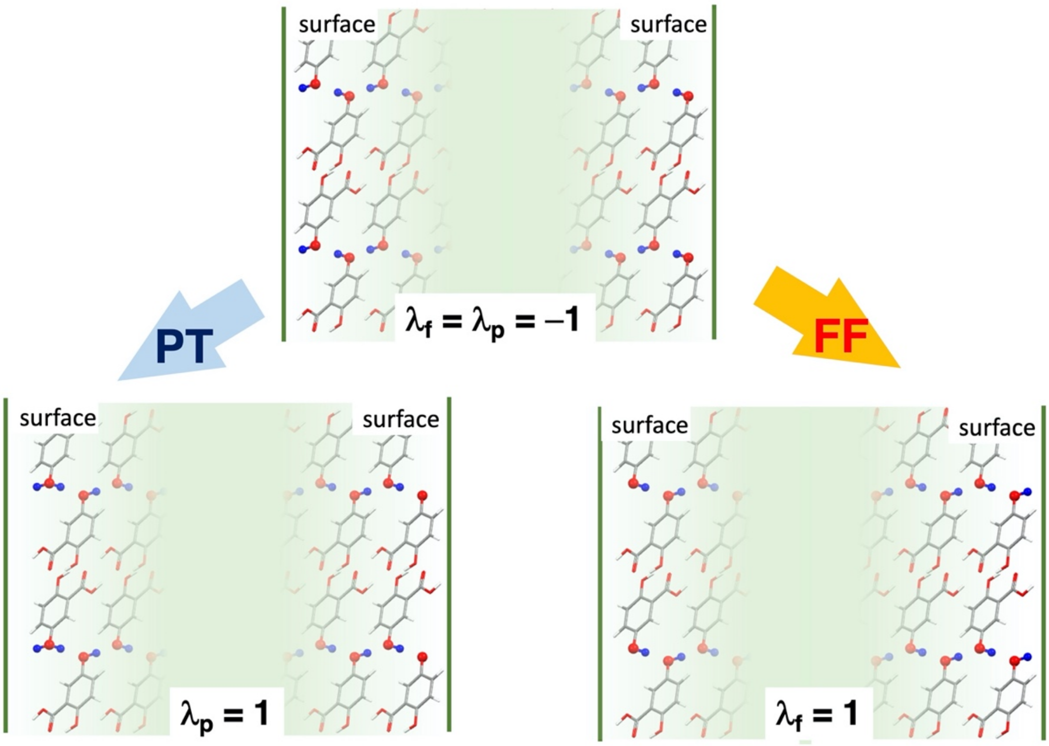


Figure S8. Schematic illustrations of surface states at $\lambda_i = \pm 1$ (FF: i = f, PT: i = p). The protons in the hydrogen-bonding chains are exposed on the right hand surface at $\lambda_f = 1$. Meanwhile, they appear on the left hand surface as the protonated form of DHBA molecule at $\lambda_p = 1$.

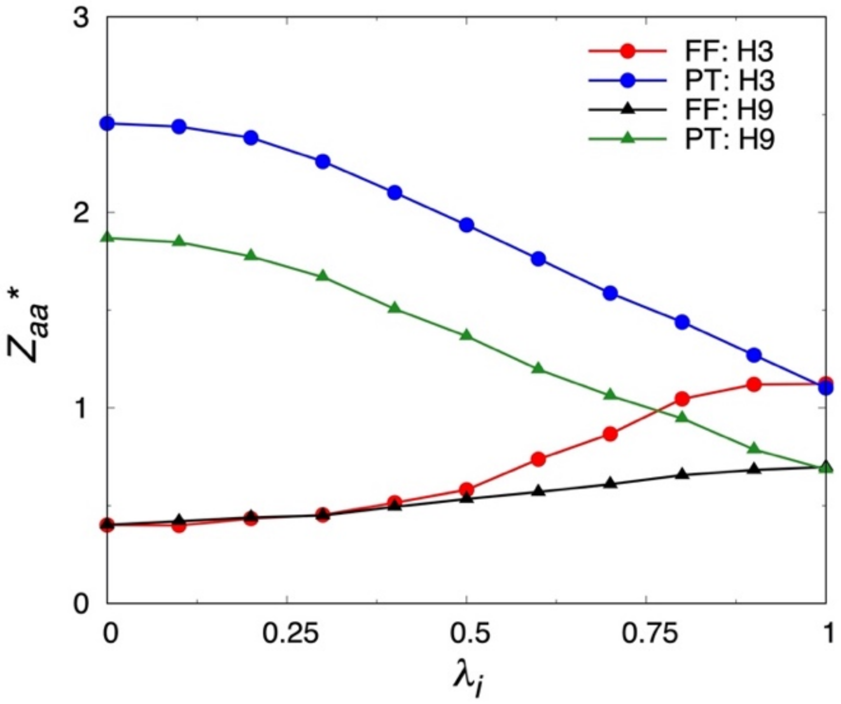


Figure S9. Born effective charge Z_{aa}* as a function of polar distortion λ_i (FF: i = f, PT: i = p) in DHBA. Here, Z_{jk}* means the charge for polarization direction j and deformation directions k. Z_{aa}* is plotted for the two symmetrically inequivalent protons in the hydrogen-bonding chains (atoms H3 and H9 are defined in the CIF file presented in this work). The effective charge of each proton averaged over λ_i is estimated as 0.42 (H3) and 0.37 (H9) for FF and 2.00 (H3) and 1.50 (H9) for PT, respectively, by taking account of Z_{ab}* and Z_{ac*}* as well as the deformation direction. (The a component of the deformation is chosen to be positive). The mean value is 1.06 over the two kinds of protons and the two mechanisms.

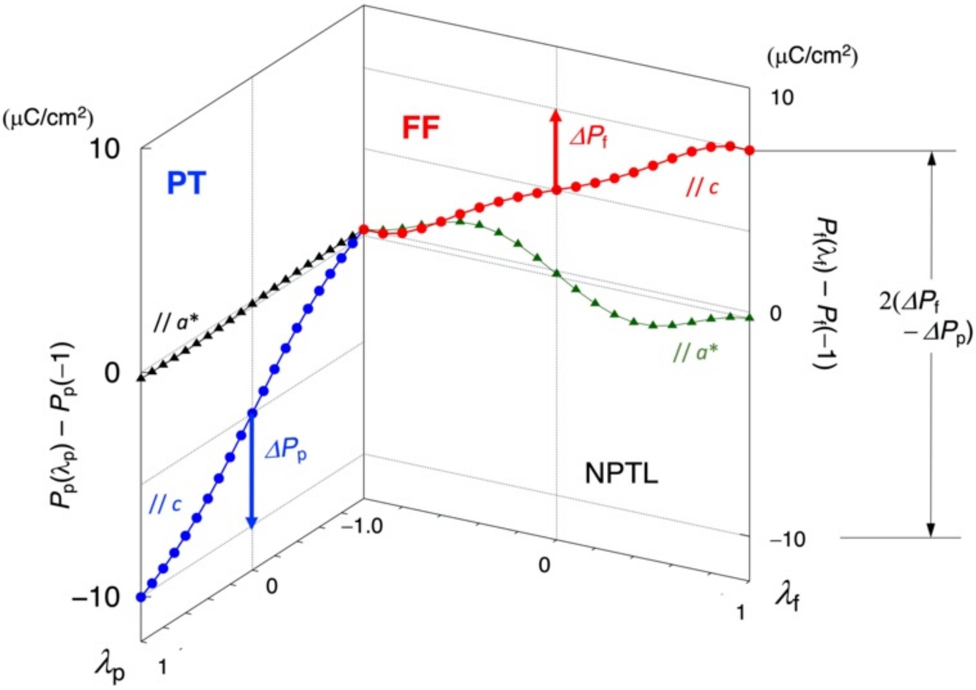


Figure S10. The evolution of theoretical spontaneous polarization along the crystal *a** and *c* axes in NPTL is plotted for the FF and PT mechanisms against the degree of polar distortion λ_i (FF: i = f, PT: i =p). $\lambda_i = \pm 1$ correspond to fully ferroelectric states with opposite directions in polarizations and $\lambda_i = 0$ is a centrosymmetric reference (hypothetical paraelectric state).

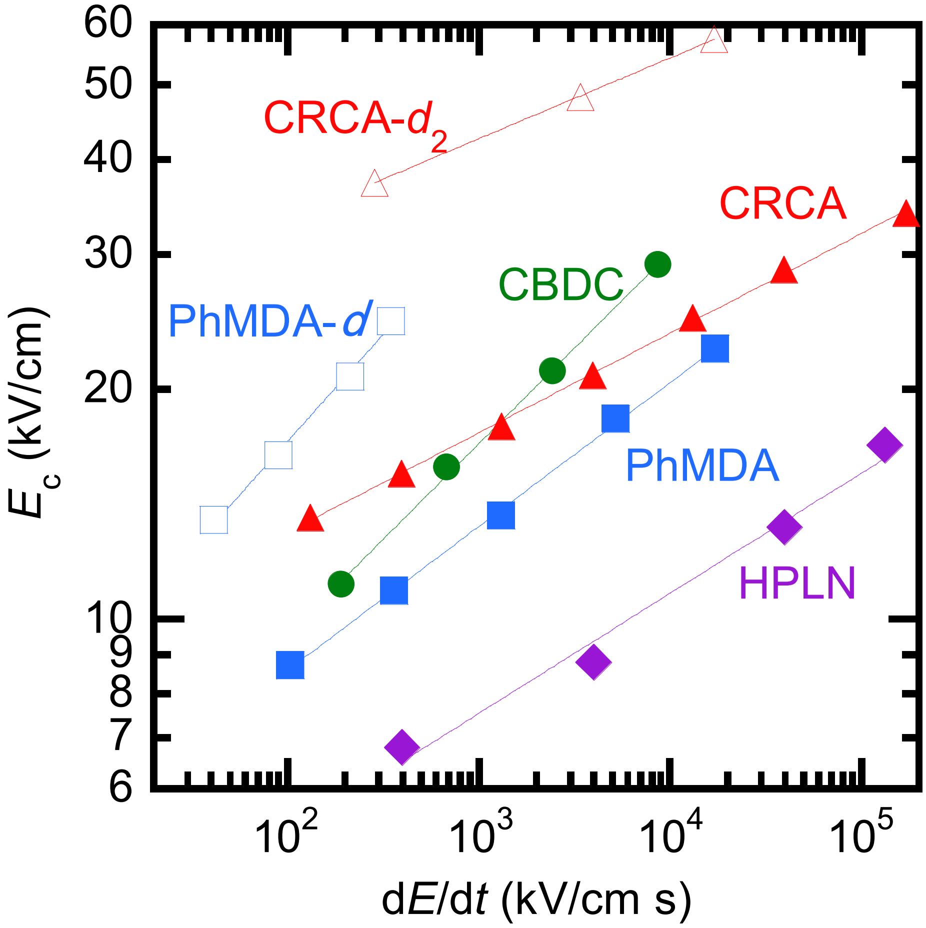


Figure S11. Comparison of switching fields of OH···O bonded prototropic ferroelectrics at various sweep rates.