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Single-component organic molecular ferroelectrics based on disk- or wheel-like rotation

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Electronic Supplementary Information

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1. Crystallography

Crystallographic data collection and structural refinement information for MSMA at room temperature.

Crystal data

$C_4H_8N_2O_4S$; M_r = 424.34

Orthorhombic, $Pna2_1$ (No. 33)

a = 9.2973(4) Å

b = 6.9862(3) Å

c = 11.4143(4) Å

V = 741.39(5) Å^3

Z = 4 (Z' = 1)

Mo$K\alpha$ radiation (λ = 0.71073 Å)

T = 296 K

0.40 × 0.16 × 0.14 mm^3

Calculated crystal density, 1.614 g/cm^3

Data collection and refinement

Four-circle diffractometer (Rigaku AFC10) equipped with a hybrid pixel detector (PILATUS200K).

R_{int} = 0.0059

$2\theta_{max}$ = 55°

$R[F^2 > 2\sigma(F^2)]$ = 0.024

$wR(F^2)$ = 0.063

S =1.090

1266 reflections

118 parameters

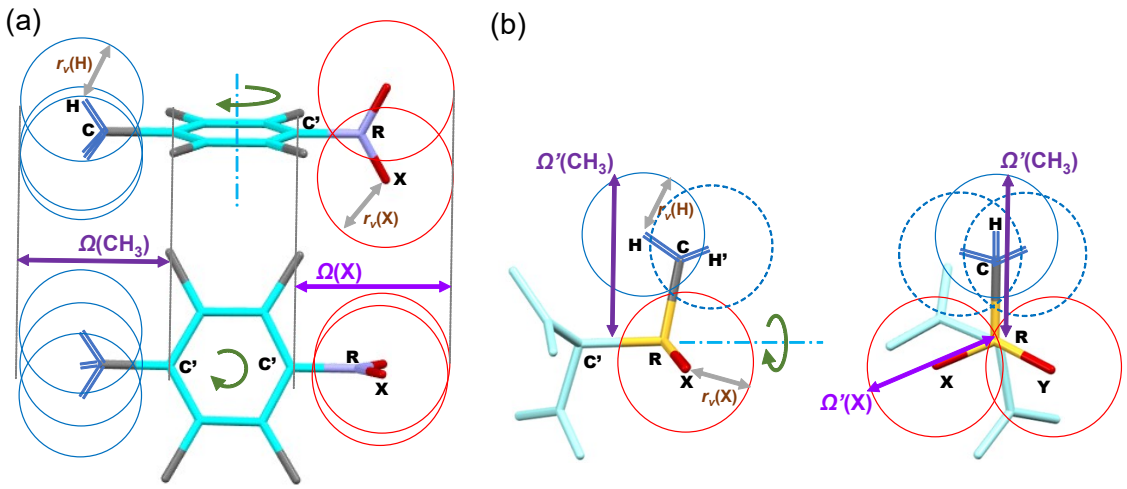

Figure S1. Schematic illustrations of substituent's structural parameters Ω and Ω' defined as the magnitude of projection (overhanging) along the radial direction of the rotator. (a) Distances Ω measured from the root carbon atom on the ring for a disk-like rotator. Example is PMNB (R = N and X = O). (b) Distances Ω' measured from the rotation axis for a wheel-like rotator. Example is MSMA (R = S, X = Y = O). The circles represent the van der Waals radii r_v(X) and r_v(H) of the terminal X and hydrogen atoms.

2. Thermal and Electric Properties

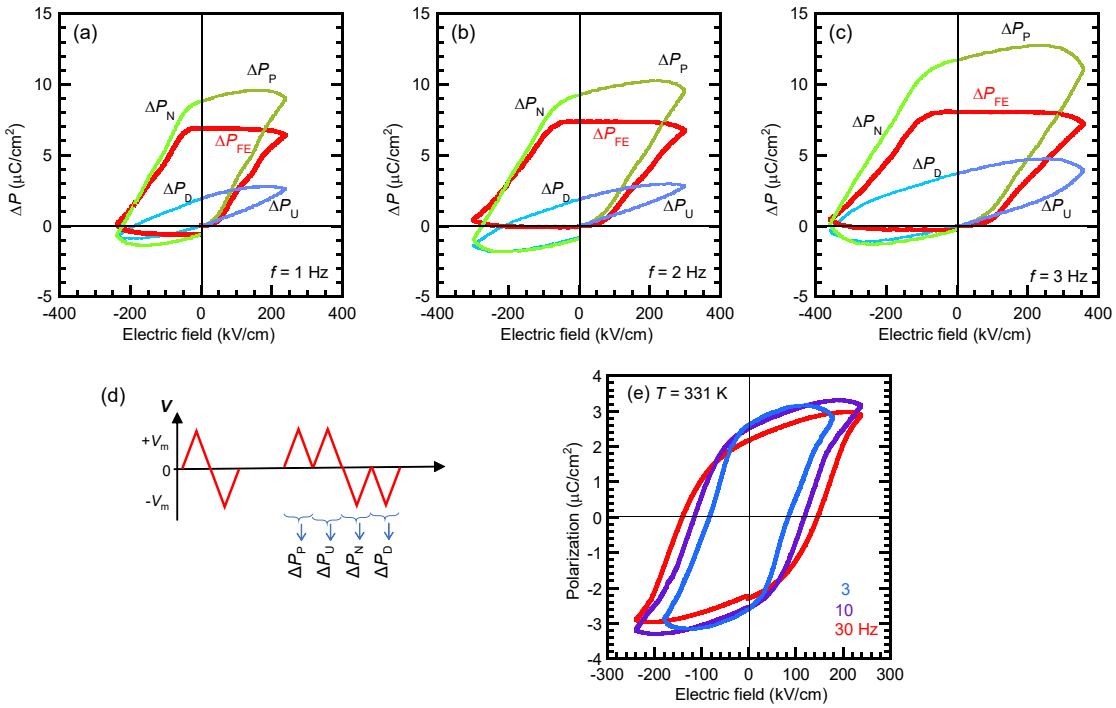

Figure S2. Indication of intrinsic ferroelectricity of a PMNB crystal. (a-c) Correction of polarization hysteresis loops (a) at frequency f = 1 Hz, (b) 2 Hz, and (c) 3 Hz using the positive-up-negative-down (PUND) procedure (also called "double-wave method": for details, see also M. Fukunaga and Y. Noda, *J. Phys. Soc. Jpn*. 2008, **77**, 064706). The panel (d) schematically illustrates the voltage waveform with ac electric field of triangular waveform. In the double wave, the first and second positive voltage waves are called "positive (P)" and "up (U)", respectively, and the first and second negative ones are "negative (N)" and "down (D)", respectively. The polarization reversal occurs during the processes P and N, which measure the total polarization changes ΔP_P and ΔP_N, respectively. The processes U and D retain the polarity and then can extract the non-hysteresis contributions ΔP_U and ΔP_D, respectively. The intrinsic ferroelectric hysteresis contribution ΔP_{FE} was obtained as ΔP_P - ΔP_U and ΔP_N - ΔP_D. (e) The *P*-*E* hysteresis curves at various frequencies at T = 331 K.

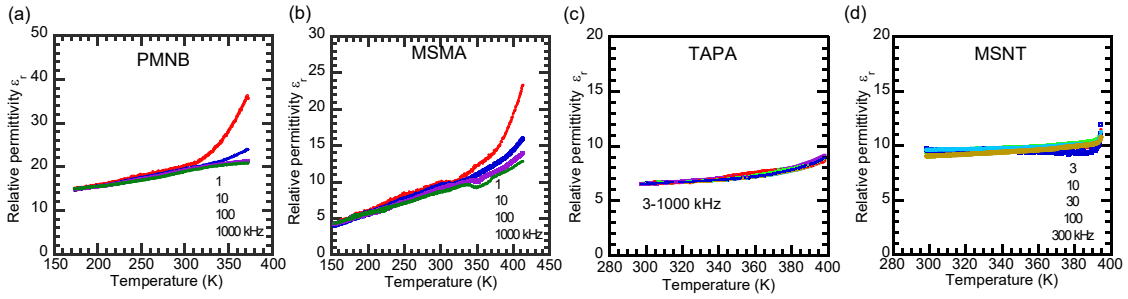

Figure S3. Temperature-dependent relative permittivity ε_r measured with an ac field of various frequencies: (a) PMNB with an $E\|c^*$ configuration, (b) MSMA with an $E\perp(011)$ configuration, (c) TAPA with an $E\perp(011)$ configuration, and (d) MSNT with an $E\|c$ configuration.

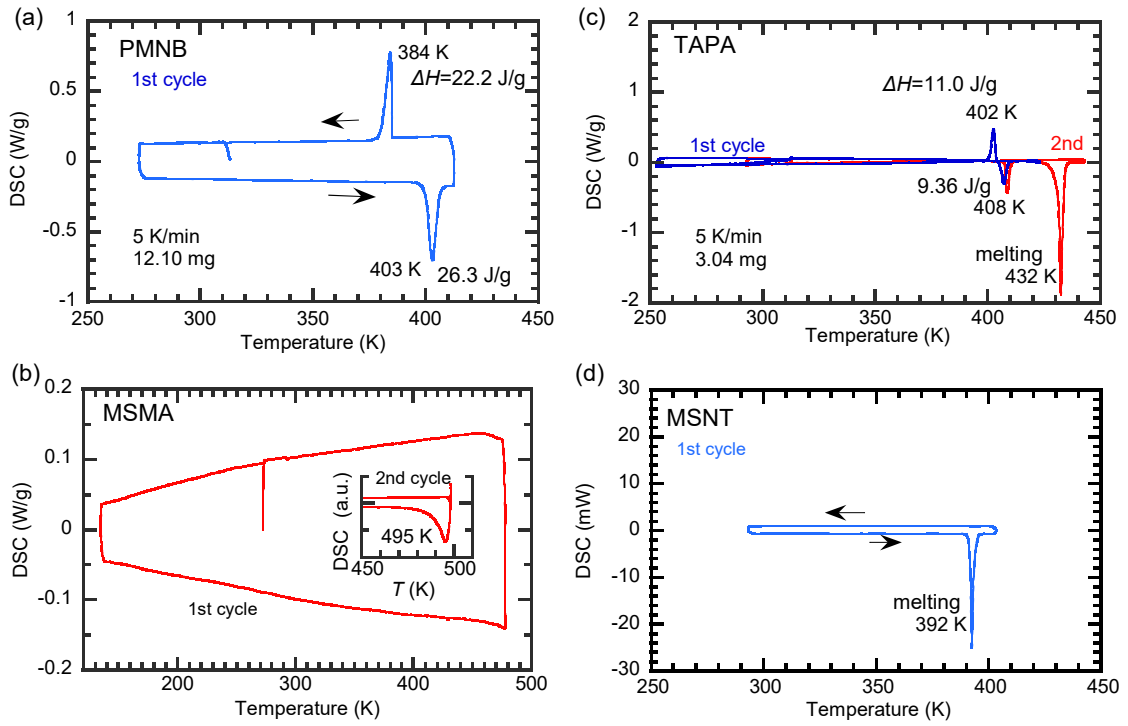

Figure S4. Differential scanning calorimetry (DSC) thermograms of (a) PMNB, (b) MSMA, (c) TAPA, and (d) MSNT crystals measured at a heating and cooling rate of 5 K/min. ΔH represents the transition enthalpy of the orientational order-disorder phase transitions.