Supporting Information

Dipole Fluctuation and Structural Phase Transition in Hydrogen-Bonding Molecular Assemblies of Mononuclear Cu^{II} Complexes with Polar Fluorobenzoate Ligands

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Experimental Section

DFT calculations. Potential energy curves for the molecular rotations of 4-FBA, 3-FBA, and 3,4-F_2BA ligands were obtained by a theoretical DFT calculation based on a B3LYP/3-21G(*d*) basis set. Atomic coordinates for the calculations were obtained from each crystal structures **1** at 300 K, **2** at 250 K, and **3** at 300 K. One fluorobenzoate (F_xBA) molecule surrounding by neighboring four F_xBA ligands was rotated every 30 ° along the C–COO^- axis, and a single point energy for every rotation was obtained. The potential energy at a rotation angle $\phi = 0°$ was defined as $\Delta E = 0$ kJ mol^{-1}, and the ϕ - ΔE plots were determined for crystals **1**, **2**, and **3**.

Differential Scanning Calorimetry

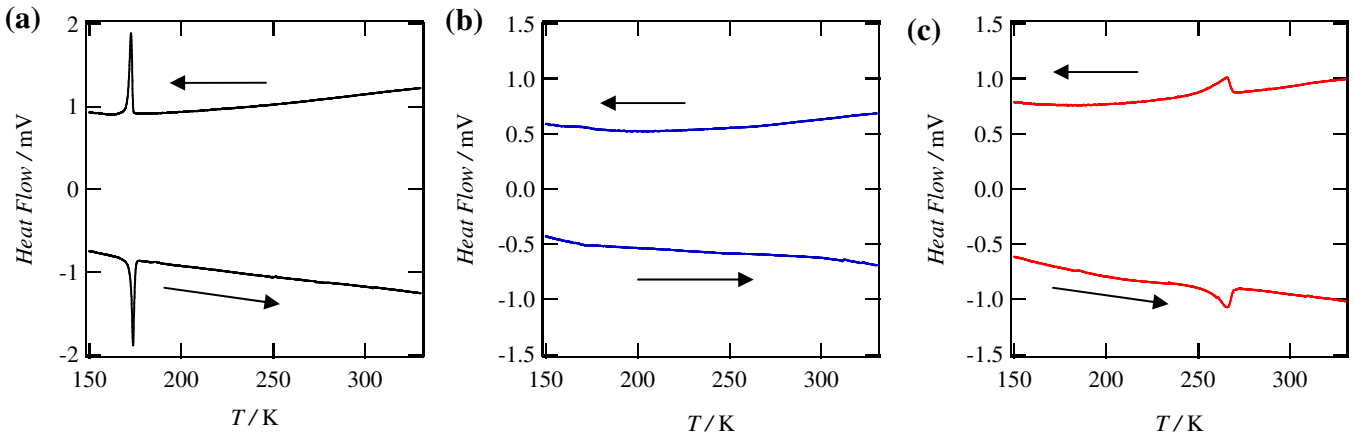

Figure S1. DSC charts of crystals of (a) **1**, (b) **2**, and (c) **3** at the temperature range from 150 to 320 K.

X-ray Oscillation Photograph

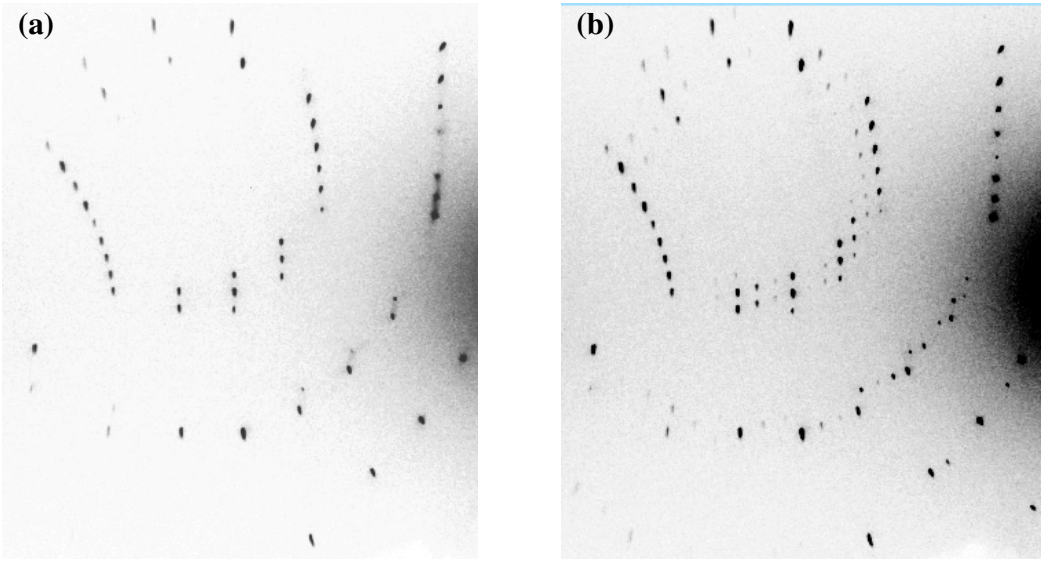

Figure S2. Changes in diffraction spots for crystal **2** with temperature changes. X-ray oscillation photograph of the same sample measured under the same conditions except for the temperature at (a) 180 and (b) 170 K.

Crystallographically Independent Molecules in the Crystals.

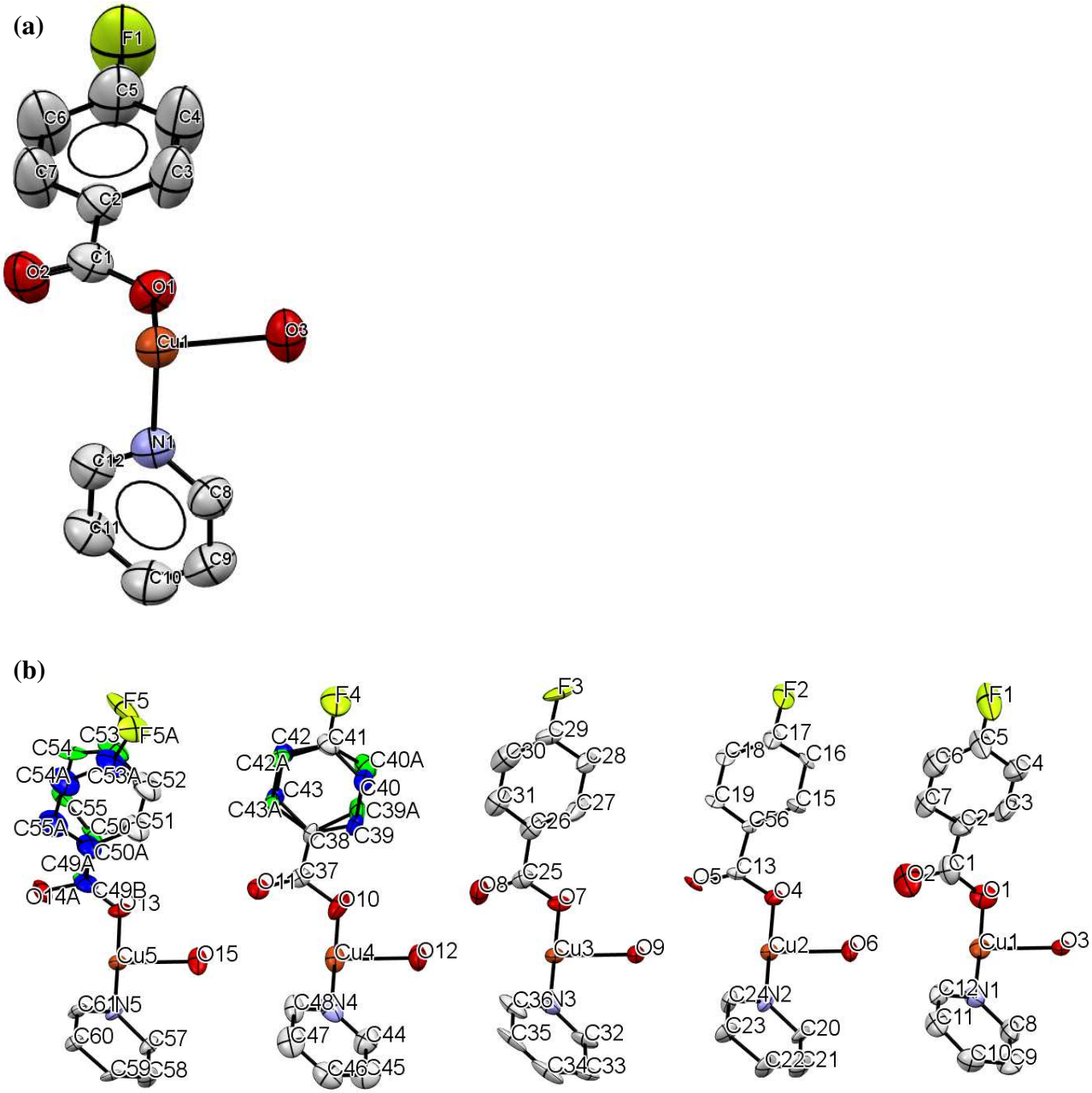

Figure S3. Crystallographically independent molecular structures and atomic numbers of the crystal **1** for (a) the high and (b) low temperature phases, respectively. Gray, red, purple, blown, and yellow atoms correspond to carbon, oxygen, copper, fluorine, respectively. Hydrogen atoms are omitted for the clarity.

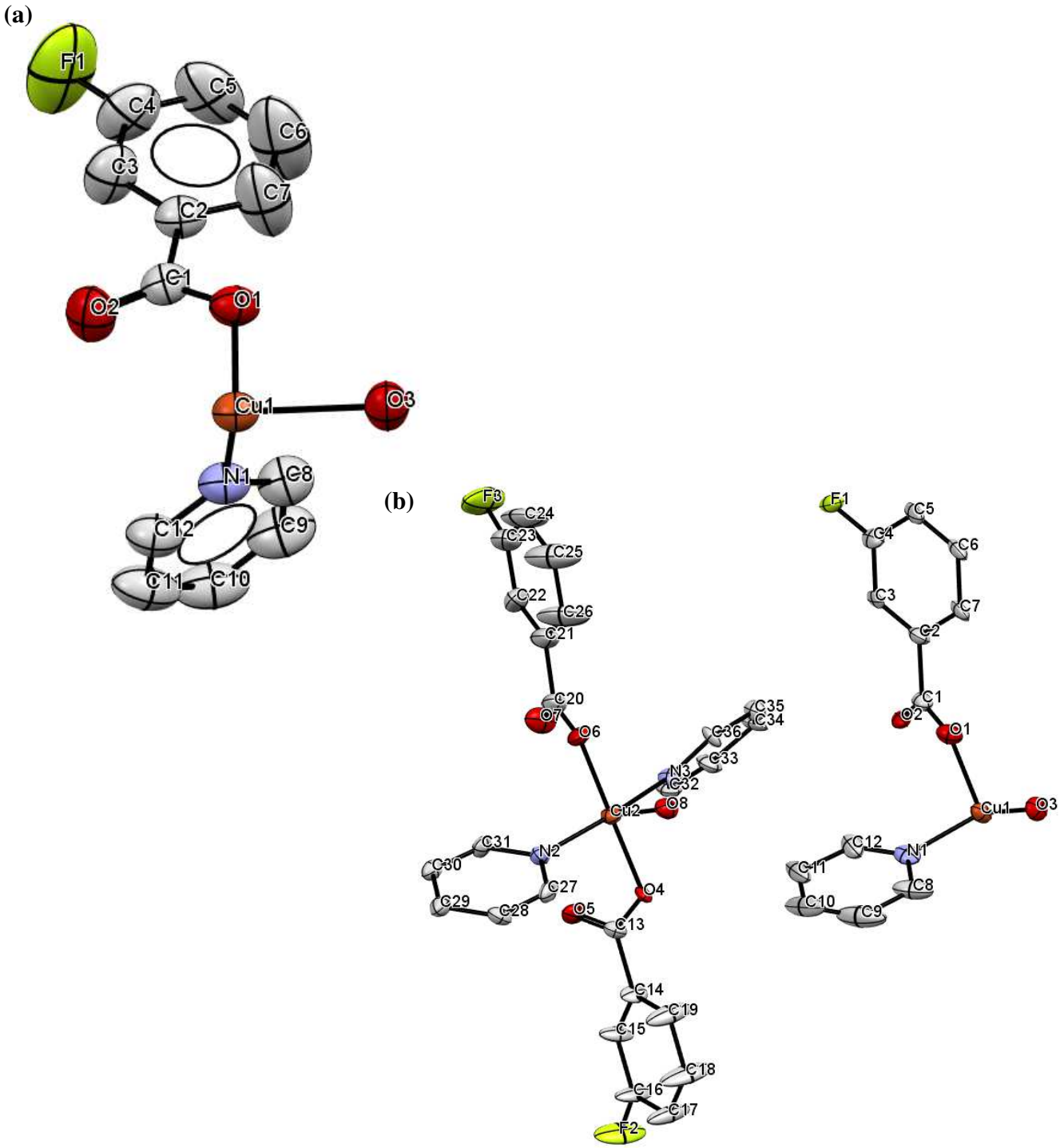

Figure S4. Crystallographically independent molecular structures and atomic numbers of the crystal **2** for (a) the high and (b) low temperature phases, respectively. Gray, red, purple, blown, and yellow atoms correspond to carbon, oxygen, copper, fluorine, respectively. Hydrogen atoms are omitted for the clarity.

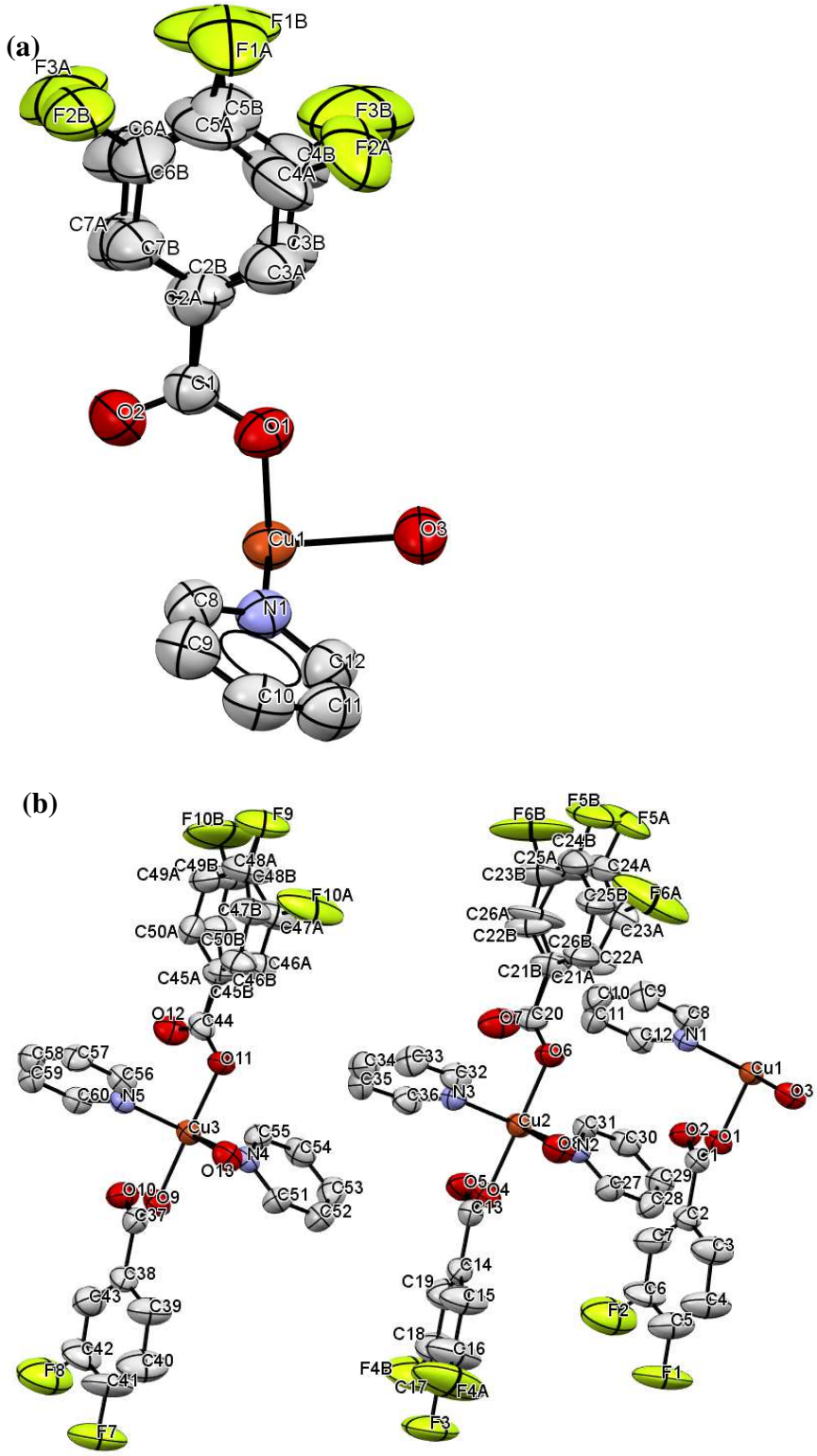

Figure S5. Crystallographically independent molecular structures and atomic numbers of the crystal **3** for (a) the high and (b) low temperature phases, respectively. Gray, red, purple, blown, and yellow atoms correspond to carbon, oxygen, copper, fluorine, respectively. Hydrogen atoms are omitted for the clarity.

Table S1 Hydrogen bonding distance between oxygen atom in H_2O ligand and free oxygen in F_xBA.

Crystal	Oxygen in H_2O	Free oxygen in F_xBA	$d_{O\text{-}O}$ / Å	Percentage difference (%)
1 in HTP (300 K)	O3	O2	2.772	0
1 in LTP (170 K)	O2	O6	2.707	-2.34
	O5	O9	2.83	2.09
	O8	O12	2.751	-0.76
	O11	O15	2.761	-0.40
	O14A	O3	2.779	0.25
2 in HTP (300 K)	O3	O2	2.808	0
2 in LTP (100 K)	O5	O2	2.746	-2.21
	O5	O4	2.875	2.39
	O10	O7	2.88	2.56
	O10	O9	2.743	-2.31
	O15	O12	2.724	-2.99
	O15	O14	2.736	-2.56
3 in HTP (300 K)	O3	O2	2.76	0
3 in LTP (240 K)	O3	O2	2.796	1.30
	O8	O5	2.733	-0.978
	O8	O7	2.712	-1.74
	O13	O10	2.815	1.99
	O13	O12	2.761	0.03

Temperature- and Frequency-Dependent Dielectric Constant for crystals 1 and 2

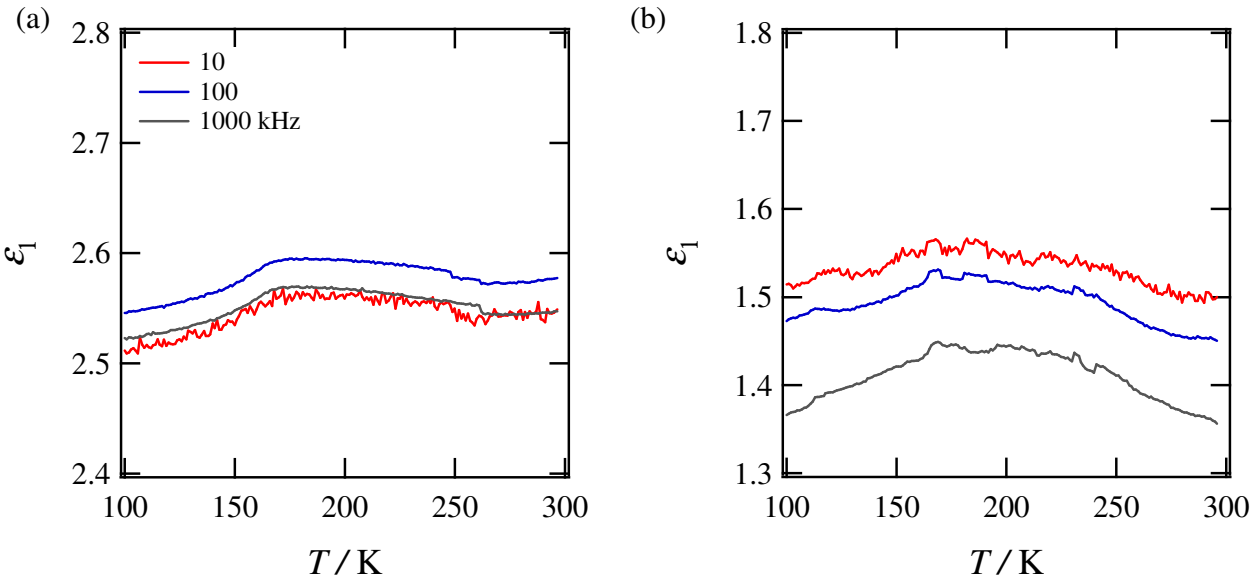

Figure S6. Temperature- and frequency dependent real part of dielectric constant for crystals of (a) **1** and (b) **2**, respectively. Red, blue and grey lines correspond to the plot for the frequencies of 10, 100 and 1000 kHz, respectively.

Potential Energy Curves for F_xBA Ligand Rotation.

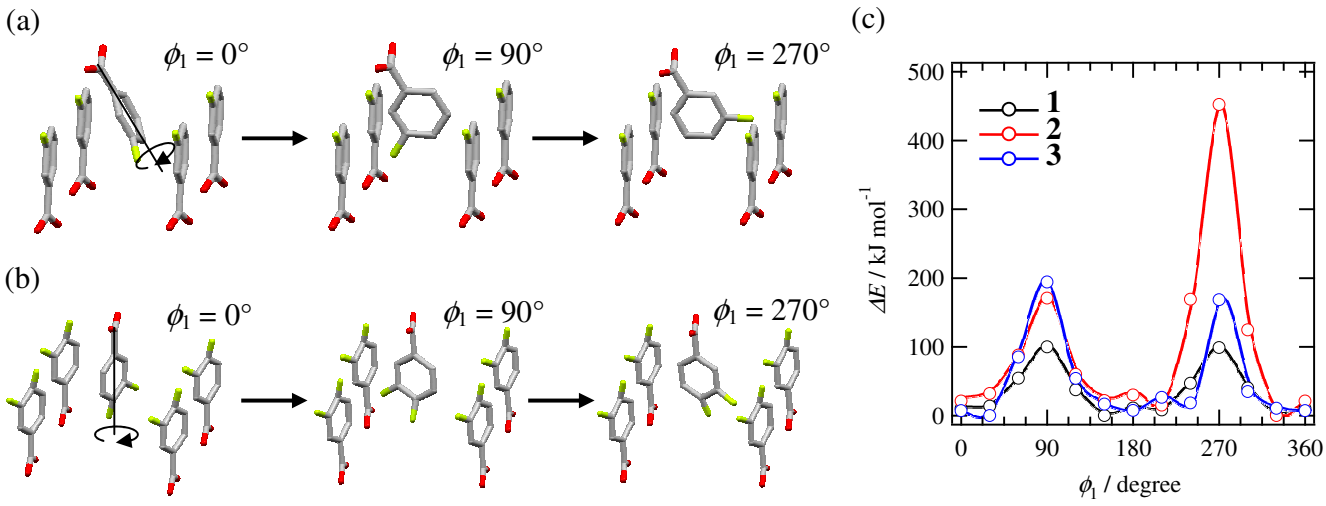

Figure S7. Potential energy curves for the molecular rotations of polar F_xBA ligands in crystals **1**, **2**, and **3**. Model structures of (a) $(3\text{-FBA})_5$ and (b) $(2,3\text{-F}_2\text{BA})_5$ assemblies in crystals **2** and **3**, where the rotation of central 3-FBA and 2,3-F_2BA ligands were calculated in the fixed arrangement of the neighboring four ligands. (c) Relative energy ΔE vs rotation angle ϕ_1 plots for the molecular rotations of three polar F_xBA ligands in crystals **1**, **2** and **3** using a B3LYP/3-21G(d) basis set. Each line was a guide for eye.

To evaluate the possible molecular motions in each crystal, the DFT calculation was carried out based on a B3LYP/3-21G(*d*) basis set. One F_xBA ligand was rotated every 30° with a rotation angle ϕ_1 along the C–COO^- bond, which was surrounded by four neighboring independent F_xBA ligands (Figures S7a and S7b). Although the cooperative molecular motions should be assumed in the crystalline state, the potential energy in the present theoretical calculations overestimated the magnitude of potential energy barrier. Figure S7 summarizes the potential energy curves for ligand rotation of 4-FBA, 3-FBA, and 3,4-F_2BA. The double minimum type potential energy curve with two energy minima at $\phi = 0$ and 180° were obtained in all crystals, where the potential energy barriers (ΔE) were appeared at $\phi = 90$ and 270°. Although the arrangement of F_xBA ligands in crystals **1** and **3** was parallel due to the dipole-dipole

interaction induced by fluorine atom at the *para*-position in benzoate, the ΔE ~100 kJmol^{-1} at $\phi = 90°$ in crystal **1** was almost the half of that of ΔE ~ 200 kJ mol^{-1} in crystal **2** due to less steric repulsive effect for the rotations of *p*-FBA. On the contrary, asymmetrical potential energy curve at different ΔE-maxima at ϕ = 90 and 270° was observed in the molecular rotation of crystal **2**, which completely suppressed the fully 360°-rotation from $\phi = 0$ to 360°. The asymmetry was arose from the asymmetrical repulsion between the 3-FBA ligands (Figure S7a). The two-fold flip-flop rotation above 350 K has been reported in the ΔE ~ 270 kJmol^{-1} of the ferroelectric supramolecular rotator in (*m*-FAni^{+})(DB[18]crown-6)[Ni(dmit)$_2$]$^{-}$ crystal. From the magnitude of ΔE, the two-fold flip-flop motion of polar 4-FBA ligands can be assumed in crystal **1**, whereas relatively large ΔE > 200 kJ mol^{-1} for crystal **3** should be difficult to rotate fully in the molecular assemblies. Therefore, the thermally activated dipole fluctuations of polar 3,4-F$_2$BA ligands occurred around the structural phase transition temperatures of crystals **3**.