Strong Polarization Switching with Low-Energy Loss in Hydrogen-Bonded Organic Antiferroelectrics

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Electronic Supplementary Information

Experimental details

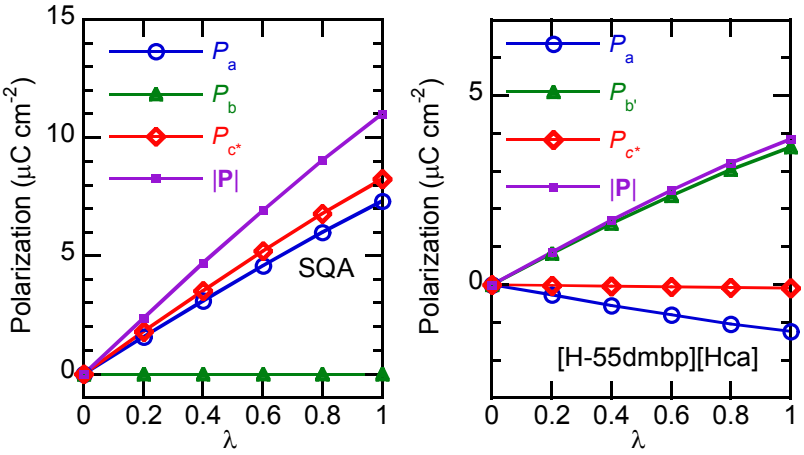

Figure S1. Evolution of the sublattice polarization as a function of the degree of polar distortion λ changing from the centrosymmetric reference (hypothetical paraelectric, λ = 0) to the fully polarized (ferroelectric, λ = 1) configuration. (a) Sheet polarization of the squaric acid (SQA) crystal and (b) ribbon polarization of the [H-55dmbp][Hca] crystal. In the λ = 1 structures of both crystals, the hydrogen positions were computationally relaxed. The polarization components were calculated using the Cartesian coordinate system; the *b*′-direction is taken as being perpendicular to the crystallographic *a* and *c** axes for the triclinic crystal of [H55dmbp][Hca].

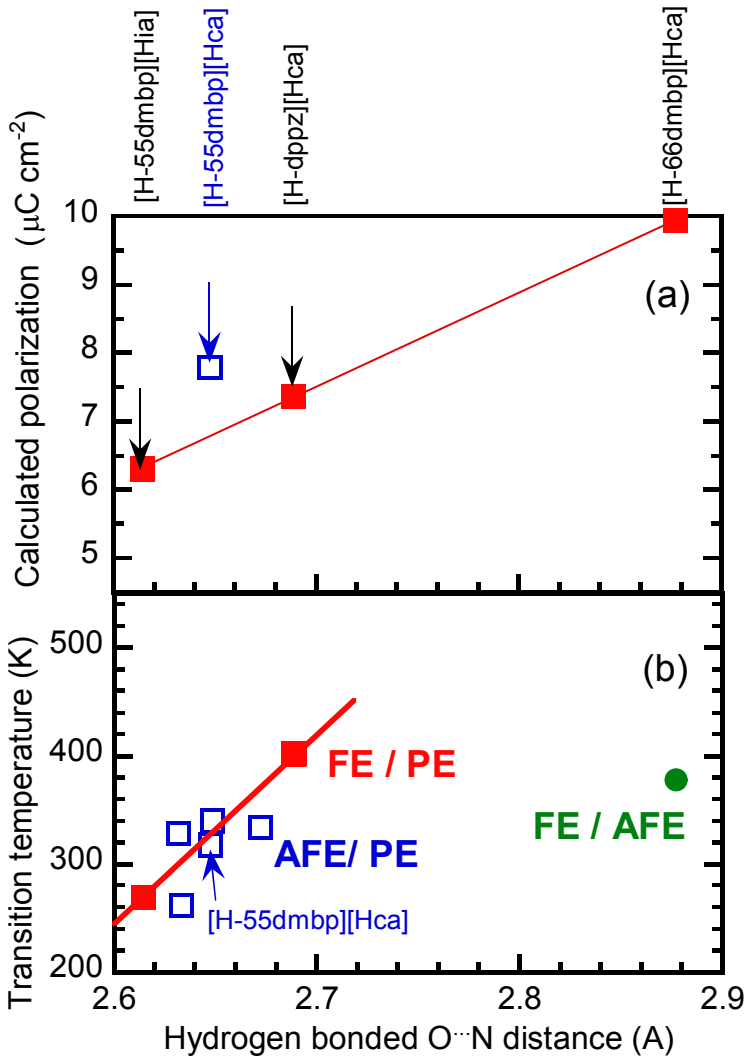

Figure S2. Comparison of the properties between the antiferroelectric [H-55dmbp][Hca] and ferroelectric acid/base supramolecular crystals of anilic acids as a function of the hydrogen-bonded O···N distance. (a) Induced polarization $2|\mathbf{P}_1|$ in the sublattice model (blue open squares) in comparison with the theoretical spontaneous polarization of the ferroelectric compounds (red filled squares). (b) Phase-transition temperature. Orange filled and open diamonds represent the ferroelectric and antiferroelectric transition (Curie) temperature T_c, respectively. The green circle indicates the ferroelectric-to-antiferroelectric phase-transition point of α-[H-66dmbp][Hca]. H_2ia = iodanilic acid, dppz = 2,3-di(2-pyridinyl)pyrazine, 66dmbp = 6,6'-dimethyl-2,2'-bipyridine. For a systematic comparison, the plot includes our previous data reported in ref. 1.

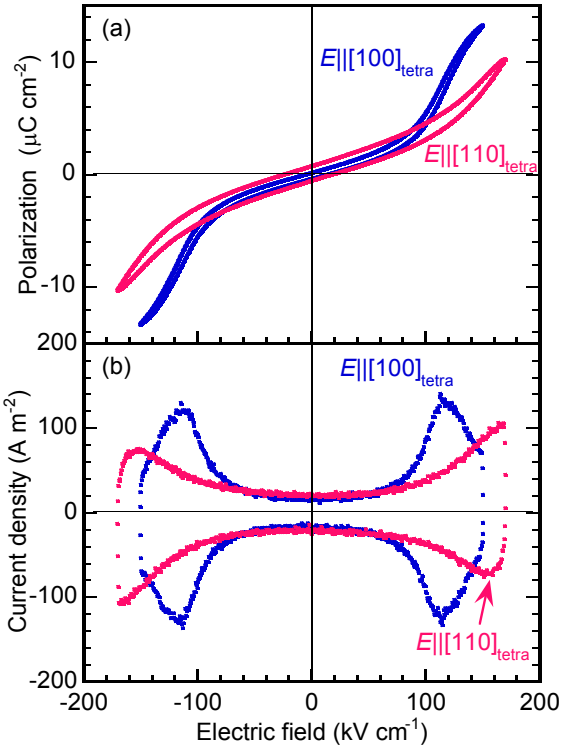

Figure S3. Antiferroelectric switching with **E**||[100]$_{tetra}$ and **E**||[110]$_{tetra}$ configurations in SQA crystal at T = 324 K and f = 100 Hz. (a) P–E hysteresis loops. (b) Corresponding J–E curves.

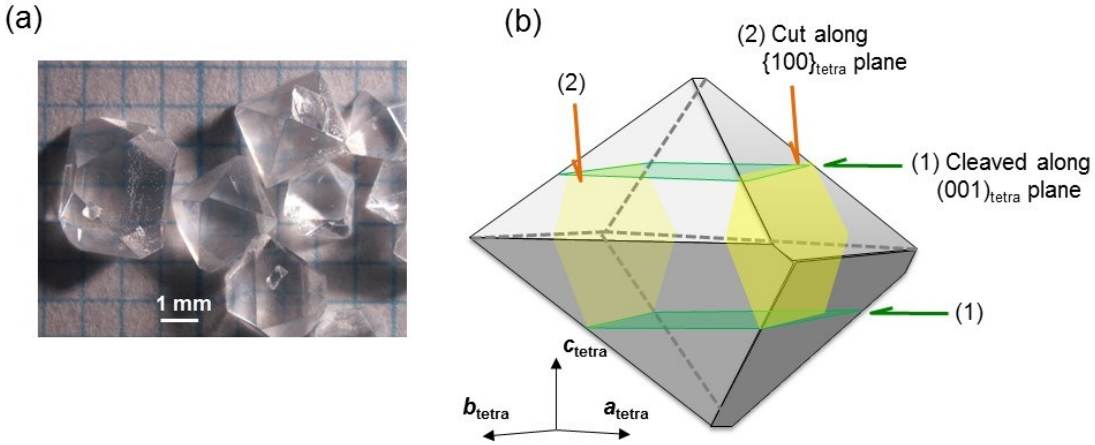

Figure S4. Squaric acid. (a) Photograph of crystals. (b) Schematic of the crystal cutting for the electric measurements.

1 K. Kobayashi, S. Horiuchi, S. Ishibashi, F. Kagawa, Y. Murakami and R. Kumai, *Chem. –Eur. J.*, 2014, **20**, 17515.