Electronic Ferroelectricity with Large Polarization Directed Antiparallel to Molecular Displacement in an Organic Crystal

Macroscopic electric polarization in displacive-type ferroelectrics is often considered within the traditional simplest framework described by an atomic displacement and static point charge. Here we show that intermolecular charge-transfer instead governs the ferroelectricity of a molecular crystal, in which electron donor and acceptor nonpolar molecules having incompletely ionic charges ($\pm0.60e$) dimerize along the molecular stacking chain. The observed large polarization was consistent with recent first-principles calculations and the poling effect on the absolute structural configuration can be interpreted in terms of electronic ferroelectricity, which not only exhibits polarity antiparallel to the ionic displacement but also enhances the polarization significantly more than that given by the point-charge model. Such a strongly interacting molecular system will lead to the future design of ferroelectrics for high-performance and high-frequency operations through the fast electronic processes.

The organic charge-transfer complex TTF-CA which comprises an electron donor, tetrathiafulvalene (TTF) and an acceptor, *p*-chloranil (CA) has been attracting much attention because of a novel neutral-to-ionic phase transition (NIT) [1]. The TTF-CA can be regarded as a displacive-type ferroelectrics because the crystal structure is symmetry-broken to the polar space group of *Pn* upon NIT. The donor and acceptor molecules displace pairwise in the alternately stacking chain along the crystallographic *a*-axis. Recently, in contrast to a conventional point-charge model (0.27 μCcm^{-2} along the *a*-axis), first-principles calculations suggested a much larger spontaneous polarization (3-10 μCcm^{-2} along the *a*-axis) with two contrasting candidates of electronic states in TTF-CA [2, 3]. The total polarization was predicted to be directed either parallel or antiparallel to the ionic polarization, depending on the antiferromagnetic or nonmagnetic state, respectively. Here we report the experimental determination of both the magnitude and the direction of the spontaneous polarization in TTF-CA [4].

The ferroelectric nature of TTF-CA was evident from a sharp peak anomaly on the temperature-dependent permittivity and large value of dielectric constant (ε_r) and Curie constant (*C*) are suggestive of a large spontaneous polarization as a proper ferroelectric. However, experimental evaluation of the spontaneous polarization (P_s) value has long been hindered by its narrow charge gap of ~0.7 eV and electric leakage caused by current-induced resistance switching under electric field higher than 10 kVcm^{-1}. We found that satisfactory observations of hysteresis were limited in a narrow range of both frequency and temperature. The coercive field (E_c) increases with increasing frequency or lowering temperature. The observed values from a well-defined parallelogram-like hysteresis were P_s of 6.3 μCcm^{-2} and E_c of 5.4 kVcm^{-1} at 59 K.
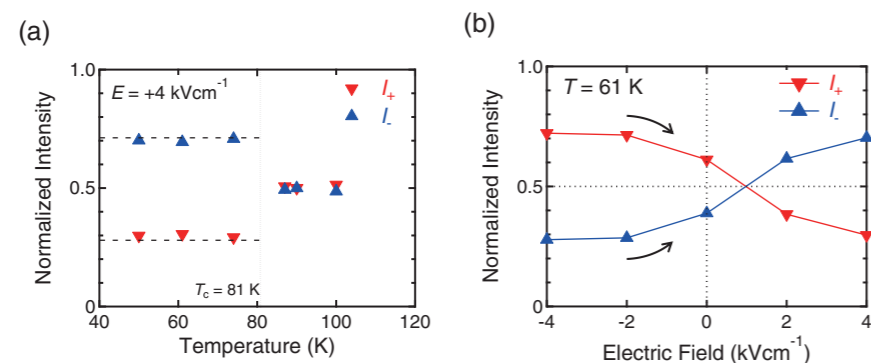
To investigate the direction of spontaneous polarization, the degrees of symmetry-breaking in bulk and absolute configurations of the polar TTF-CA crystal structure under an electric field were examined by probing the difference in intensity between Bijvoet pair reflections. The synchrotron radiated X-ray of relatively long wavelength (λ = 1.55 Å) was used to exploit large anomalous scattering factors of the sulfur and chlorine atoms. The Bijvoet pair reflections 101 and $\overline{1}0\overline{1}$ exhibited the largest intensity difference according to a simulation based on the atomic coordinates obtained at *T* = 15 K [5] and 40 K [6]. Figure 1(a) depicts the temperature dependence of their normalized integrated intensity $I_+ \equiv I(101)/\{I(101) + I(\overline{1}0\overline{1})\}$ and $I_- \equiv I(\overline{1}0\overline{1})/\{I(101) + I(\overline{1}0\overline{1})\}$. Just below T_c, the observed I_+ and I_- readily approach 0.705 or 0.295 [horizontal broken lines in Fig. 1(a)], which correspond to the full polarization into either polarity according to the simulation. Therefore, the poling field of +4 kVcm^{-1} is regarded as sufficient for developing a single-domain state. The intensities of Bijvoet pair (I_+ and I_-) were interchanged by inverting the applied electric field direction due to polarization switching as shown in Fig. 1(b). By comparing the observed intensity of the Bijvoet pair with that obtained by the simulation, we found that the positively charged TTF molecules shift toward the positive electrode and the negatively charged CA toward the negative electrode as shown in Fig. 2(a).

These experimental observations confirm the recent first-principles calculations predicting an extreme contribution of the electronic polarization, which is directed antiparallel to the ionic displacement and governs the magnitude of polarization. The electronic ferroelectricity itself is currently one of the key issues for multiferroelectrics. The electronic response with lower energetic cost of lattice deformations promises both high-performance and high-frequency operations as well as new functionalities.

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BL-8A

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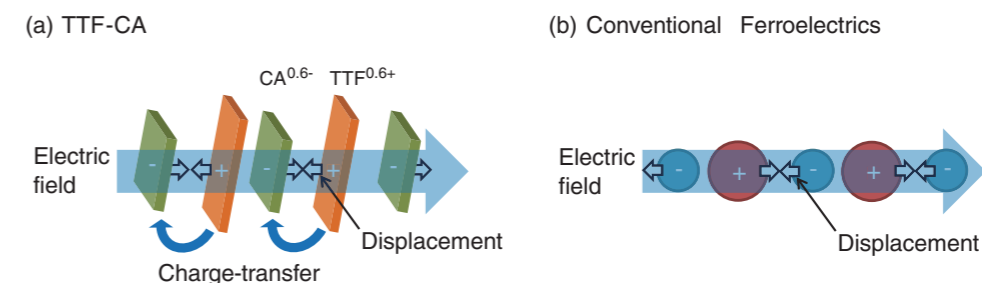
(a) TTF-CA (b) Conventional Ferroelectrics

Figure 2: Schematic drawing of the ionic displacement under an electric field. (a) TTF-CA. Deep blue and open arrows indicate charge-transfer from TTF to CA and molecular displacement under the electric field, respectively. (b) Conventional displacive-type ferroelectrics.

Figure 1: Normalized integrated intensity of Bijvoet pair reflection 101 and $\overline{1}0\overline{1}$. (a) Temperature dependence under constant electric field E = +4 kVcm^{-1} parallel to the *a*-axis. Horizontal broken lines correspond to the single domain values. (b) Electric field dependence increasing from E = −4 kVcm^{-1} to +4 kVcm^{-1} at 61 K.