

Real-Space Observation of Ferroelectric Domains in Organic Charge-Transfer Complexes by Electromodulation Method

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One-dimensional organic charge-transfer (CT) complex, tetrathiafulvalene-*p*-chloranil (TTF-CA), shows neutral-to-ionic phase transition at $T_c = 81\text{K}$. In TTF-CA, TTF (donor) and CA (acceptor) molecules are stacked alternately to form one-dimensional columns. In the ionic phase below T_c , the ionized donor and acceptor molecules are displaced and dimerized. The in-phase dimerization makes the crystal polarized and ferroelectric. In order to clarify the ferroelectric nature in TTF-CA, which is characterized by the CT, dimerization, and domain structures, we have measured the electric-field induced reflectivity change by electromodulation method. The applied electric field enhances the degree of CT (ρ) in the domains polarized parallel to the external field, while it suppresses ρ in antiparallel domains. The change of ρ can be probed by the shift of the peak positions of the intramolecular transition bands in the visible region. By mapping the electric-field induced change of reflectivity, we obtained the real-space patterns of ferroelectric domains in TTF-CA.

Key words: TTF-CA, electromodulation, ferroelectric domain,

1. INTRODUCTION

Organic charge-transfer (CT) complexes composed of donor (D) and acceptor (A) molecules have been widely studied since they show various intriguing physical properties such as superconductivity and metal-insulator transition. In the CT complexes consisting of donors with large ionization energy and acceptors with large electron affinity, the ionic ground state is realized where the electron is transferred from donors to acceptors.

The target CT complex in this study is tetrathiafulvalene-*p*-chloranil (TTF-CA), in which donor molecules, TTF, and acceptor, CA, [Fig. 1(a)] are alternately stacked to form one-dimensional chains [Fig. 1(b) and (c)]. At room temperature, the degree of CT from donors to acceptors, ρ , is low (around 0.3) and the ground state is essentially neutral (N), while below the critical temperature $T_c=81\text{K}$, the ground state is changed to be ionic ($\rho=0.7$). Such N-I transitions can be triggered

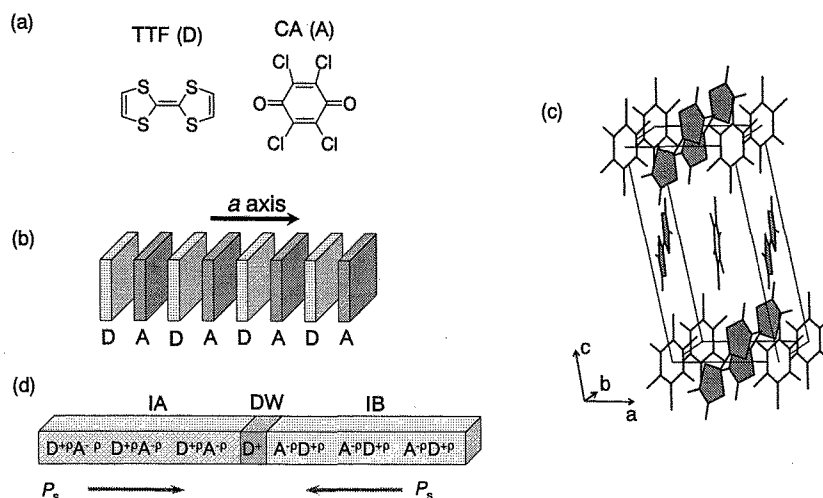
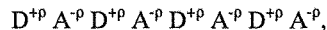
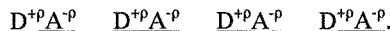


Fig. 1 (a) Chemical structures of tetrathiafulvalene (TTF) and chloranil (CA). (b) Schematic of the alternate stack of donor (D) and acceptor (A) molecules. (c) Crystal structures of TTF-CA. (d) Two ionic phases, IA and IB, with the opposite polarizations. Between IA and IB, domain walls (DW) exist.

by various perturbations such as the application of pressure and the light irradiation [7-9]. Particularly, the photoinduced I-to-N transitions are intensively studied [9-16]. In the ionic phase of TTF-CA, the isolated spins on the TTF and CA molecules are paired by the spin-Peierls mechanism. The pairing of the spins is accompanied with the dimerization of the DA lattice. In the N-phase, the D and A molecules are equally spaced as



while the D and A molecules forming a singlet pair approach each other in the I phase. The spacing in the DA chain is modulated as



The D and A molecules move to the opposite sides and produce the microscopic dipole moment. Neutron diffraction experiments clarified that the phase of dimerization is three-dimensionally in-phase and that the inversion symmetry is broken, which indicate that the crystal can be ferroelectric [4]. Actually, the second harmonic generation in the visible region is observed, which can be only seen in the case that the inversion symmetry is macroscopically broken [13]. However, the real macroscopic image of the ferroelectric domains has not been obtained yet. Here, we performed the electromodulation experiments on TTF-CA in order to observe the real-space ferroelectric domain structures.

2. EXPERIMENTAL

TTF-CA crystals are obtained by co-sublimation of TTF and CA molecules. On the surface of the crystal, the two symmetric electrodes are made of carbon paste. In this study, we have two types of ER experiments. The first configuration is the macroscopic ER measurement. In this experiment, the light from a tungsten lamp is monochromated and then shaped with an aperture to a 500- μm spot. The light is irradiated between the electrodes whose gap is larger than 500 μm . The amplitude of the applied alternating electric field is 0.25-10 kV/cm, and the frequency is 1 kHz. The second configuration is the microscopic ER measurements for mapping measurements, in which the ER signals are obtained by the microscope-equipped spectrometers. In the above two experiments, the electric-field-induced change of the reflectivity is observed using the lock-in detection method. The electric-field-induced change, ΔR , induced by the alternating field, $F_0 \cos(\omega t)$, is written as follows:

$$\Delta R(F) = R'(0)F_0 \cos \omega t + 1/2R''(0)(F_0)^2(1 + \cos 2\omega t)/2 + \dots$$

The first term appears only in the case that the inversion symmetry is broken. The first and second terms can be separated by the observed frequencies used in lock-in detection and called 1f and 2f signal, respectively. All the ER experiments are performed at 77K. The samples are mounted in cryostats. Simultaneously with the ER measurements, the dielectric constants are measured.

3. RESULTS AND DISCUSSIONS

Reflectivity spectra perpendicular to the one-dimensional axis at 77K and 4K are shown in Fig. 2(a). Three peaks are observed at 2.25, 3.0, and 4.0 eV. These peaks are all assigned to be intramolecular

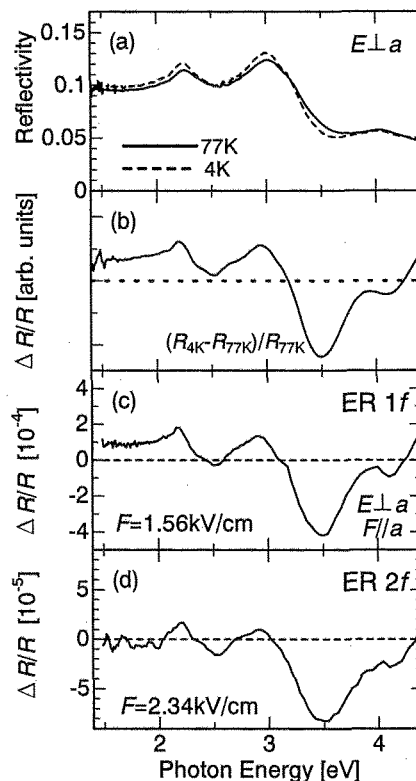


Fig. 2(a) Reflectivity spectra of TTF-CA perpendicular to the one-dimensional chain measured at 77K (solid line) and 4K (broken line). (b) Difference spectrum of reflectivity between 77K and 4K, $(R_{4K}-R_{77K})/R_{77K}$. (c) 1f component of ER spectrum. (d) 2f component of ER spectrum.

transitions in TTF [3]. The 2.25-eV peak is assigned to the transition from the second-highest doubly occupied b_{2g} molecular orbital to the topmost half occupied b_{1u} molecular orbital in TTF^{+p} molecules. The transition from the topmost half occupied b_{1u} molecular orbital to the lowest unoccupied molecular orbital in TTF is split into 3.0-eV and 4.0-eV peaks by the CT interaction along the chain. With a decrease of the temperature, these peaks are shifted to the lower energy side, which is due to the increase of the degree of CT. In order to make clear the change of the reflectivity, we show the difference spectra $(R_{4K}-R_{77K})/R_{77K}$ in Fig. 2(b). The increase of the reflectivity around 2.25 and 3 eV and the decrease around 3.5 eV are clearly seen. The 1f and 2f components of macroscopic ER spectra are shown in Fig. 2(c) and (d), respectively. In both spectra, there are positive signals around 2.25 and 3.0 eV, and a negative signal at 3.5 eV. These spectral features are very similar to the difference spectrum shown in Fig. 2(b). This strongly indicates that the direct origin of the ER signals is the electromodulation effect on ρ . The fact that the 1f signal appears indicates that the inversion symmetry is broken in the scale of the spot size of the light.

The electric-field dependence of the ER signals is shown in Fig. 3(b). The 1f signal appears from the lower electric field, while the 2f signal rises at approximately 0.9 kV/cm. This difference suggests that the different

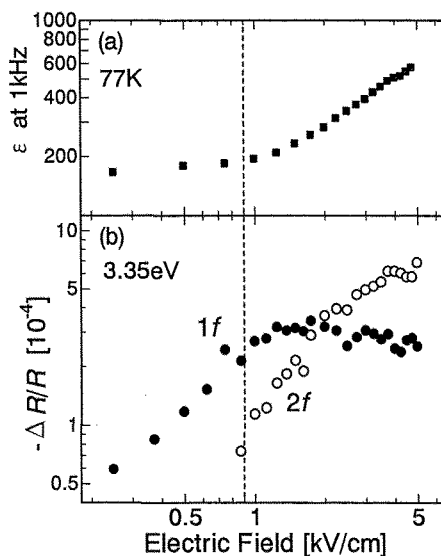


Fig. 3 (a) Electric-field dependence of dielectric constant, ϵ , measured at 1 kHz. (b) Electric-field dependence of ER $1f$ (filled circles) and $2f$ (open circles) signals measured at 3.35eV.

mechanisms work between $1f$ and $2f$ response.

First, we will discuss the origin of the $1f$ signal. The $1f$ signal directly indicates the breaking of the inversion symmetry. As shown in Fig. 1(d), there are two types of ionic phases, IA and IB, depending on the direction of the pairing of DA. In the IA chain, the positive charge shifts to the right and the negative to the left. Accordingly, the dipole moment P_s is right-pointing. On the other hand, in the IB chain, the molecules move to the opposite directions compared with IA chains and P_s is left-pointing. Considering that the IA and IB chains coexist, the $1f$ signal appears so that the sizes of IA and IB domains are not balanced. In the IA domains, the rightward electric field increases the polarization, which corresponds to the increase of the degree of CT, while the same electric field decreases the degree of CT in the IB domains. The increase and decrease of the degree of CT should lead to the opposite shifts of the reflectivity spectra. These two effects should be cancelled. However, considering the fact that the $1f$ signal is observed, the sizes of IA and IB are not balanced and the cancellation is not completed. The ER signal from the larger domain is predominantly observed. The dominant domains are dependent on the samples. Actually, the sign and intensity of the $1f$ signals is sample-dependent.

Next, let us discuss the origin of the $2f$ signals. The $2f$ signal is observed only in the stronger electric field regions. Generally, the $2f$ response is observed when the positive and negative electric fields have the same effect. The sign of the $2f$ signal in the experimental results indicates that the degree of CT always increases under both the rightward and leftward electric fields. This suggests that the dominant domains switch between IA and IB synchronizing with the reverse of electric field. In this case, the domain walls between IA and IB should be movable. Actually, it was reported that there exist the spin-solitons, which is the domain boundary between IA and IB in the ionic phase [16], and that they have

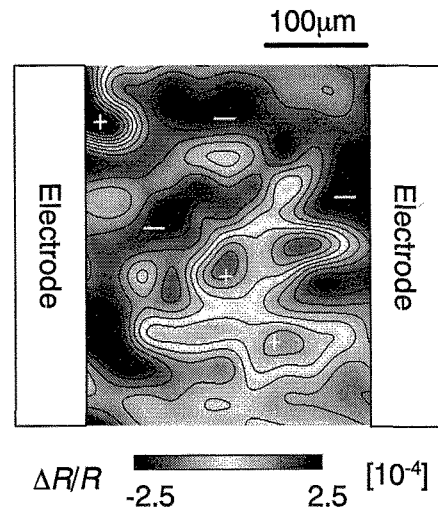


Fig. 4 Map of the ER $1f$ signal of TTF-CA measured at 77K. The symbol, + and -, indicates the sign of the signals and the gray scale the intensity of the signal. The + (-) sign indicates IB (IA) domains.

fractional charges. The movement of a domain wall reverses the polarization of the domain from IA to IB or from IB to IA. In the traveling area of the domain wall, the polarization is always parallel to the electric field. Accordingly, the electric field always increases the degree of CT and produces the $2f$ signals. The movement of domain walls and the reverse of the polarization should be reflected in the dielectric constant, ϵ . In Fig. 3(a), we show the electric-field dependence of the dielectric constant measured at 1 kHz. In the region of the lower electric field, ϵ is around 170, which is consistent with the reported value [8]. The value of ϵ increases above 0.9 kV/cm where the $2f$ signal appears. This behavior of the dielectric constants supports the electric-field induced motion of the domain walls accompanied with the reverse of the polarization. This threshold behavior is probably due to some pinning effects of the domain walls.

The sign of the $1f$ signal reflects the direction of the polarization of the domain. In order to observe the ferroelectric domain structure, we have performed the mapping measurements of the ER signals using an optical microscope. We observe the $1f$ signal at 3.35eV for the 143 sampling points. Each sampling area is $25 \times 25 \mu\text{m}$. The experimental results are shown in Fig. 4. In this figure, the data are spatially smoothed by the spline procedure. As clearly seen in Fig. 4, the large IA domains are formed, the size of which is over $100 \mu\text{m}$. In the figure, the ER signal is weak at the white area, in which the domain walls between IA and IB are expected to exist. Considering that the size of the domain is comparable to the spot size of macroscopic ER measurements, we can understand that the averaged polarization and the $1f$ signal remains in the macroscopic ER measurements. It is clear from Fig. 4 that the domain structure is not one-dimensional, but two- or

three-dimensional. This means that the domain walls on the adjacent chains are correlated and pinned with each other. Such a pinning effect will be a main origin for the threshold behavior of the $2f$ signals observed in Fig. 3(b).

4. CONCLUSIONS

We have performed the ER measurement on TTF-CA crystals. The macroscopic measurements reveal that the ER signals appear due to the modulation effects on the degree of CT. The ER measurements using the optical microscope clarifies that the domains in TTF-CA crystal are not one-dimensional but two- or three- dimensional and that the size is larger than $100\mu\text{m}$. The electric field dependence of the ER signals shows that the domain walls between the IA and IB phases are pinned by the interchain interaction and that the application of the higher electric field than 0.9 kV/cm makes the domain walls movable.

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