Ultrafast modulation of polarization amplitude by terahertz fields in electronic-type organic ferroelectrics

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Abstract: Using strong terahertz fields, we succeeded in rapidly modulating ferroelectric polarizations in electronic-type ferroelectrics of molecular crystals, TTF-CA and croconic acid. Polarization modulations are attributable to collective inter- or intra-molecular charge-transfers induced by terahertz field.

1. Introduction

An important property of ferroelectrics is second-order optical nonlinearity, which is used for the controls of lights such as polarization rotations and frequency conversions. If polarization amplitude or a ferroelectric domain itself is rapidly controlled by photoirradiation, advanced controls of lights would be achieved. Recently, a new type of ferroelectrics in which ferroelectric polarizations are produced by intra- or inter-molecular charge transfers (CTs) is attracting much attention and called "electronic-type ferroelectrics". An organic molecular compound, tetrathiafulvalene-*p*-chloranil (TTF-CA), and a hydrogen-bonded organic crystal, croconic acid ($H_2C_5O_5$), are its typical examples. In TTF-CA, collective inter-molecular CT processes and resultant changes of the ferroelectricity can be induced by a femtosecond laser pulse, which is known as a photoinduced neutral to ionic transition [1–3]. In this paper, we report a new approach for the rapid control of ferroelectricity using a THz electric field in TTF-CA [4] and croconic acid. By the THz-pump optical-probe [5] and second-harmonic-generation(SHG)-probe spectroscopy, we show that the ferroelectric polarizations can be rapidly modulated via THz-field-induced collective CT processes.

2. Ultrafast modulation of ferroelectric-polarization amplitude in an organic CT compound, TTF-CA

In TTF-CA, donor (*D*) molecules of TTF and acceptor (*A*) molecules of CA arrange altanately, forming one-dimensional stacks (Fig. 1(a)). By lowering temperature, it shows a neutral to ionic phase transition at 81 K and the degree of CT ρ is changed from 0.3 to 0.6. In the ionic phase, *DA* molecules are dimerized due to the spin-Peierls mechanism. In addition, the dimeric molecular displacements are three-dimensionally orderd showing a ferroelectric nature. Ferroelectric polarization is dominated by intermolecular CT($\delta\rho$) within each dimer as shown in Fig. 1(a) [6].

Fig. 1(b) (the black line) shows the time evolution of the reflectivity change ($\Delta R/R$) induced by a THz electric field E_{THz} (the red line) at 2.2 eV (the intramolecular transition band). The reflectivity at this energy is known to depend sensitively on ρ. The initial reflectivity change up to 0.5 ps is in good agreement with the THz waveform (E_{THz}), indicating that ρ is directly modulated by E_{THz}. Subsequently, $\Delta R/R$ shows an oscillation with 54 cm^{-1} (Fig. 1(c)), which was obtained by subtracting the normalized E_{THz} from $\Delta R/R$. This mode can be assigned to the dimeric molecular oscillations, that is, the spin-Peierls mode, which is driven by the initial changes of ρ. THz-pump SHG-probe measurements revealed that the polarization amplitude was modulated by THz field through the changes of ρ.

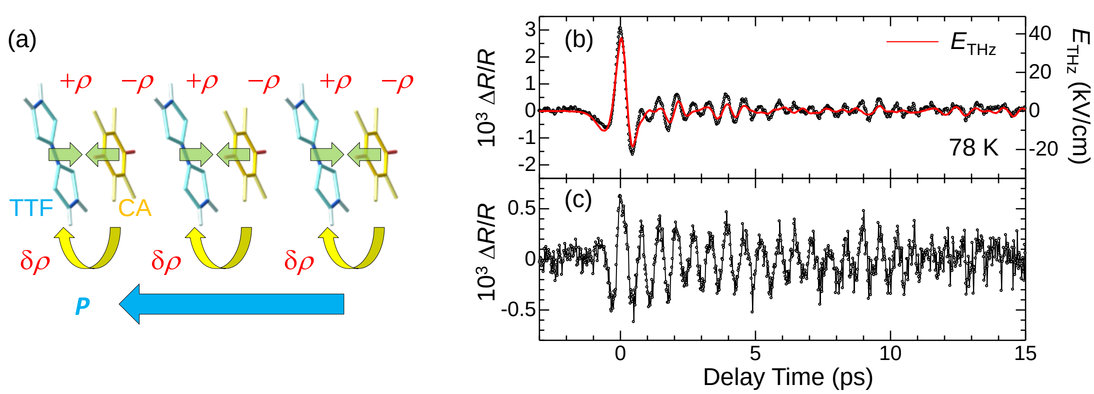

Fig. 1. (a) Schematic of ferroelectric polarization in TTF-CA. (b) THz electric field (red line) and reflectivity change (black line). (c) Oscillatory component of reflectivity change.

3. Ultrafast modulation of ferroelectric polarization in a hydrogen-bonded molecular crystal, croconic acid

Croconic acid is an above-room-temperature ferroelectric, which is composed of zigzag molecular sheets with hydrogen bonds [7] [Fig. 2(a)-(c)]. Application of quasi-static electric field along **c** axis (the polarization direction) causes collective proton transfers with the switching of π-electron bonds to reverse ferroelectric polarization. The theoretical study revealed that intra-molecular CT is an important factor for the ferroelectric polarization as well as the proton transfers. Moreover, in the previous study, we showed that croconic acid has large second-order optical nonlinearity originating from the lowest π-π* transition [8]. These results make us expect that croconic acid shows large responses to THz fields.

First, we measured the domain image using a THz radiation by an irradiation of femtosecond laser pulse with 1.55 eV. A domain image is shown in Fig. 2(e) together with a visible image in Fig. 2(d). A typical size of ferroelectric domains in as-grown samples is larger than the square of 200 μm. By selecting a homogeneous area in a crystal, we performed THz-pump SHG-probe measurement. The THz-field-induced change of SHG, $\Delta I_{SHG}/I_{SHG}$, is shown in Fig. 2(f). Its time profile is almost in agreement with the THz waveform (E_{THz}) shown by the red line, indicating the rapid modulation of the ferroelectric polarization. The maximum of the change of SHG, $\Delta I_{SHG}/I_{SHG}$, reaches 27 % at E_{THz}~120 kV/cm, which corresponds to the polarization change of ~14 %. Such large changes of SHG and polarization is attributable to the large responses of the π electron part.

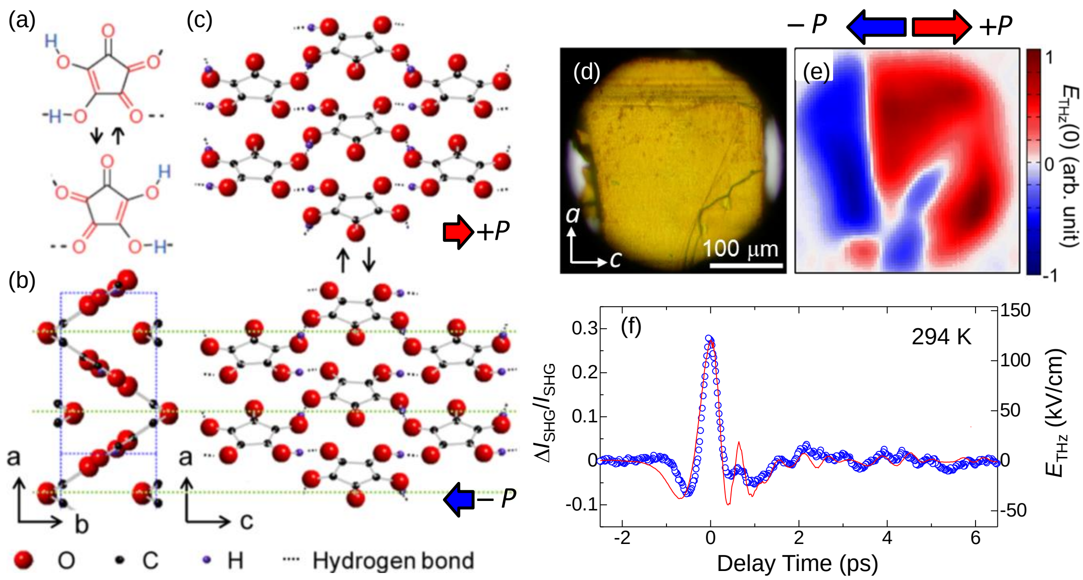

Fig. 2. (a) Molecular structure of $H_2C_5O_5$. (b) and (c) show crystal structure of $H_2C_5O_5$.(d) Visible image of a $H_2C_5O_5$ sample. (e) Polarization image of (d) obtained by THz radiation.(f) THz electric field (red line) and SHG intensity change (blue circles).

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