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Ferroelectric Transition in an Organic Superconductor: Nonlinear Optical property and its Ultrafast Photocontrol

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1. Introduction

Conductive organic charge-transfer (CT) complexes have drawn much interest for a wide range of unusual physical properties. Of particular importance is two-dimensional (2D) systems based on 2:1 donor-acceptor ratio, which have produced almost all organic superconductors except fullerene and its derivatives.

Although a number of such complexes have metallic band structure, some compounds transform to be insulator due to strong influence of electron correlations. Recently, we discovered that one of such a complex generates permanent electrical polarization by unconventional ferroelectric transition associated with an electron localization.¹

Spontaneous polarization in crystal is a unique property of ferroelectrics—one of the most important dielectric materials for industrial applications. In this presentation, we report evidence for the generation of spontaneous polarization in the complex obtained by second-harmonic generation (SHG) measurements, and propose potential applications of such polar matters for fast driving optoelectronic devices.

2. Results and Discussion

Wigner-crystallization of electrons

In the 2:1 CT complexes, donors receive fractional charge ($+0.5e$) from counter anions. The charges transferred from anions are delocalized in donor layer; thereby, the valence level of donors is averaged between neutral and monocationic states ($D^+ + D^0 \rightarrow D^{+0.5}$).

The charges transferred from anions are delocalized in donor layer. In some complexes, however, the charges cannot delocalize for several reasons. During the past decade, it is increasingly recognized that charge localizations in large number of the 2D complexes are attributable to Wigner-crystal-like charge ordering (CO),² in which charges are localized on molecules in an alternating order to avoid repulsive Coulomb interaction between charges.

In this study, we focus upon such a CO in a CT complex α -(ET)₂I₃ [ET: bis(ethylenedithio)tetrathiafulvalene].

Charge ordering in α -(ET)₂I₃

Figure 1 shows the structure of donor (ET) of the complex and the molecular arrangement in the crystal. The triclinic unit cell contains four ETs; two of them denoted by A and A' are crystallographically equivalent each other by

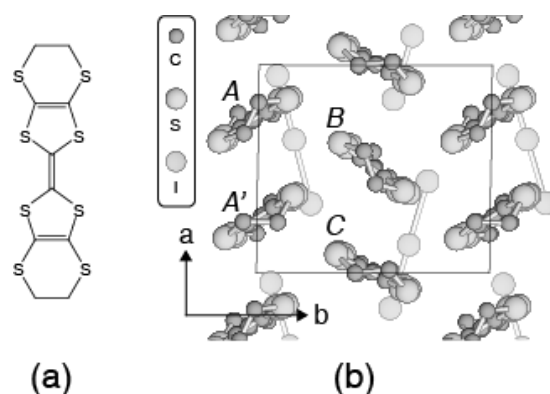


Fig. 1. (a) Molecular structure of ET. (b) Molecular arrangement in the crystal unit cell of α -(ET)₂I₃ viewed along the long axis of ETs. The unit cell contains four ETs (A, A', B and C).

the inversion symmetry.

This complex undergoes a metal-to-insulator transition. From the detection of the break of the mixed valency of donor molecules,^{3,4} the transition is identified to be CO. X-ray diffraction studies had argued that the crystal remains to be centrosymmetric below the phase transition temperature.⁵ However, according to theoretical calculations,^{6,7} there is a strong tendency that the charges are arranged in alternating manner in the molecular columns.

Such a CO pattern is incompatible with the arrangement of crystallographically equivalent molecules A and A', thus inconsistent with the argument of the x-ray studies. However, our spectroscopic data suggested that the crystal symmetry changed at the transition.⁴ Note that if the CO pattern breaks the inversion symmetry, it is expected that the crystal will induce ferroelectric polarization. To examine the possibility of the ferroelectric polarization, we have performed optical SHG measurements.

Dispersion of SHG coherence length

Harmonic generations, including SHG, are an interference phenomenon between propagating and newly induced harmonic waves in nonlinear optical medium. Therefore, the conversion efficiency from fundamental wave to harmonic one largely depends on the phase matching condition, which is conventionally measured by coherence length

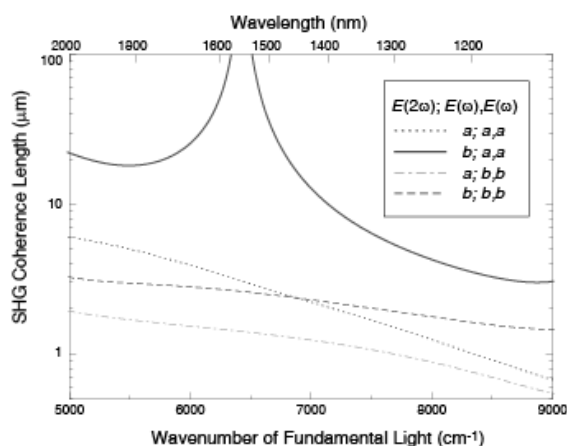


Fig. 2. Dispersion of SHG coherence length under type-I phase match condition.

$$[l_c = |2\pi / (k_{\omega}' - k_{2\omega}')|].$$

We estimated the coherence length of SHG l_c for the type-I phase-matching condition from the Kramers-Kronig analysis of reflection spectra of a single crystal. Figure 2 shows the obtained dispersion of l_c for near-IR region [$\lambda(\omega)$ =5000–9000 cm⁻¹]. The four curves represent l_c corresponding to the light polarizations described in the legend.

As shown by the solid curve, l_c for $E_{\omega} // a$ and $E_{2\omega} // b$ is increased in near IR region. It is noteworthy that l_c diverges at $\lambda(\omega)$ =1.55 nm, that is an important wavelength for optoelectronics. Taking this feature into account, we measured the SHG signal using a near IR pulse laser (λ =1400 nm, pulse width: 4 ps).

Temperature dependence of SHG

The SHG measurement was performed for a filmy single crystal under transmission geometry. Figure 3 shows the recorded SHG intensity as a function of temperature. The plot demonstrates that there is no SHG signal above the phase transition (T_{CO} =135 K). This is consistent with the centrosymmetric structure determined by the x-ray diffraction. With decreasing temperature, however, SHG signal critically emerges at T_{CO} , and develops to a saturated value. The emergence of SHG is a strong evidence that the centric symmetry is broken and finite spontaneous polarization is induced by the CO.

3. Conclusions

In this report, we discussed the optical SHG properties of α -(ET)₂I₃, and manifested that (1) ferroelectric polarization is generated by the Wigner-crystal-like CO and (2) non-critical phase matching for SHG is established at $\lambda(\omega)$ =1.55 nm. The finding of ferroelectric transition in a CT complex expands the range of the study on the organic materials toward functional dielectrics. One should note that α -(ET)₂I₃ shows superconductivity under application of proper pressure.¹⁰ The fact that the ferroelectric polarization, which is a contradictory physi-

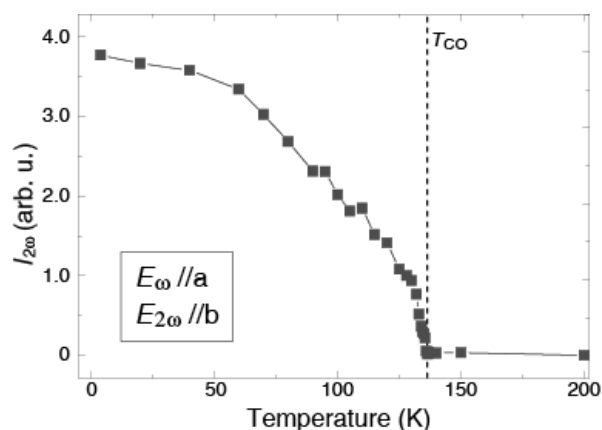


Fig. 3. Temperature dependence of SHG intensity measured from a filmy single crystal.

cal property to superconductivity, is obtained from the same compound is important for developing the study of electron correlation phenomena.

In addition to the importance for fundamental physics, we wish to stress the significance of the potential application of the ferroelectric phenomenon. As is widely known, controllability of permanent polarization is essential feature of ferroelectrics. However, because of slow response of the polarization against external perturbations, the feature has not been fully exploited. In addition to the above results, we will report very fast photoresponses of the electronically induced ferroelectric polarization;^{1,8} the polarization is quenched by the application of a femtosecond laser pulse, then shows picosecond-scale recovering.

Acknowledgements

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