2 Phase Control of Molecular System Project

Controlling of physical properties in molecular systems –

In this project, electronic correlation in molecular crystal systems is investigated to elucidate novel phenomena such as superconductivity, ferroelectricity, and charge ordering. One of our goals is elucidating the origins of physical properties from crystal structural information. With this aim, we performed crystal structure analysis of various molecular systems, including organic thin films, under different external conditions.

Recently, we succeeded in producing highquality thin films made of organic materials and evaluated these by using synchrotron radiation diffraction and reflectivity. [1]

With regard to bulk materials, we have performed numerous structural studies using organic single crystals. Ferroelectric material has been one of our research targets in particular. In addition to the ferroelectrics, we have paid close attention to antiferroelectrics from the standpoint of application. For example, we have suggested that organic antiferroelectrics consisting of hydrogenbonded supramolecular assemblies, such as squaric acid, are promising for application in energy storage devices. [2] In this report, we introduce another possibility for application by achieving large electrostriction in organic antiferroelectrics. [3]

3-1 Field-induced antipolar-polar structural transformation and giant electrostriction in organic crystal

Over the past decades, electromechanical materials, which are capable of interconversion of mechanical and electrical energies, have been of significant interest owing to their potential for application in transducers, sensors, micro-actuators,

Project Leader: Reiji Kumai

energy storage, and mechanical energy harvesting. Strong electromechanical response often emerges owing to the coupling between electric polarization P and mechanical strain in ferroelectrics (FEs) and antiferroelectrics (AFEs), both of which are promising dielectric materials. Large strain can be induced in the FEs (or AFEs) during the stepwise flipping of P under an oppositely oriented electric field E, where the P-E curve exhibits a single (or double) hysteresis loop. To date, lead-based piezoelectric ceramics, in particular lead zirconate titanate (PZT) and its modified forms, have been widely used FEs for the abovementioned applications owing to their excellent electromechanical properties. However, because of environmental issues, it is of key importance to turn to nonhazardous substances for device fabrication. Therefore, lead-free electromechanical materials, alternatives to materials of the leadcontaining piezoelectric ceramics, should be proposed. Potential candidates for FE and AFE materials have been investigated among various molecular structures, in particular those appearing near morphotropic phase boundaries. Organic FE materials are suitable as environmentally benign alternatives that attract significant interest owing to their characteristics; they are lightweight, flexible, fusible, and low-cost materials. In electrostriction, a phenomenon observed in all dielectrics, strain emerges in the material proportional to the square of the polarization, and independent of the polarity of the externally applied electric field. In contrast, the piezoelectric effect is a linear effect and occurs only in specific dielectrics such as the polar and/or chiral crystals including FEs. Even though various organic polymer FEs, such as the poly(vinylidene fluoride) (PVDF), have been developed for piezoelectric applications, their piezoelectric coefficients are still smaller than 1/10 of those of piezoelectric ceramics. Moreover, the antiferroelectricity of organic materials has not attracted significant attention, and no extensive knowledge of electrostriction in these materials exists to date.

In this study, we report a field-induced antipolar-polar structural transition accompanied by a giant electrostriction in an organic AFE. Over the past several years, various organic AFE crystals and an increasing number of organic FEs have been developed from imidazole derivatives. The microscopic origin of their ferroelectric switching is the polarity reversal of hydrogen-bonded chains, driven by cooperative prototropy, which involves intermolecular proton transfer and simultaneous switching of double bonds in the π -conjugated system. Experimental determination of the field-induced polar structure in the organic AFEs has not been reported to date. Among AFE imidazoles, 2-trifluoromethylbenzimidazole (TFMBI) exhibits the lowest switching field, which is sufficiently low to avoid atmospheric discharge in diffraction experiments (~30 kV/cm). Unfortunately, crystal twinning has prevented complete determination of its field-induced crystal structure. We developed an alternative of the low-field AFE, based on its naphthimidazole analogue. 2-trifluoromethylnaphthimidazole (TFMNI) forms an antipolar crystal with alternating polarities of the hydrogen-bonded chains, which can be forced to align with a relatively low electric field. We investigated the field-induced structural changes using in-situ single-crystal X-ray diffraction in the presence of an electric field. The theoretically calculated polarization of this polar crystal structure is in a good agreement with the observed field-induced polarization in the P-E hysteresis measurements. The corresponding electrostriction strain is one order of magnitude larger than the piezoelectric strain of croconic acid (CRCA), which shows the largest spontaneous polarization among organic materials. Therefore, organic AFEs are promising electrostrictive materials with potential for electromechanical applications.

At ambient conditions, the crystal structure of TFMNI belongs to the monoclinic centric space group $P2_1/n$. Its molecules are NH···N hydrogenbonded, constructing linear chains along the [101] direction of the crystal (Figure 1a). Each chain



Fig. 1: (a) Chemical structure of the hydrogenbonded chain of TFMNI. (b) Crystal structure of the antiferroelectric TFMNI single crystal, viewed along the [101] crystallographic direction. All hydrogen atoms, except for those in NH, are omitted for clarity. The arrows indicate the direction of the polarization.

is dipolar, and its polarity is antiparallel to that of a neighboring chain along the *b*-direction as a result of the inversion symmetry (Figure 1b). The trifluoromethyl group, which has a large thermal factor, is disordered over two orientations with occupancy factors of 0.80 and 0.20. For simplicity, only its major orientation is illustrated in the figure.

In order to investigate the antiferroelectric phase transition, the dielectric constant was measured at various temperatures and frequencies (Figure 2a). The applied electric field was parallel to the dipolar hydrogen-bonded chains in all of the experiments discussed below. Although the dielectric constant becomes larger with temperature increase, the sharp peak anomaly characteristic of the phase transition (if present) was beyond the highest temperature considered in the measurements. The frequency dispersion emerged due to dielectric relaxation processes, such as local dipolar fluctuations in the chain. The P-E hysteresis measurements revealed double loops, as expected for AFEs (Figure 2b) at room temperature. The field-induced polarization rapidly increased

around 30-40 kV/cm and saturated at ~ 50 kV/ cm.

In order to determine the field-induced structure, we performed synchrotron X-ray single-crystal analysis in the presence of an electric field. As indicated by the red arrow in Figure 2b, the applied field was set to 40 kV/cm, which is almost equal to the maximum allowed value to avoid electric discharge in air, but close enough to the field amplitude required to achieve a fully polarized state. Figure 3a shows the crystal structure in the presence of the electric field. With application of the electric field, the Bravais lattice transforms from a primitive monoclinic into to an Acentered orthorhombic crystal form, the transition described by: $(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{b}, \mathbf{c} - \mathbf{a}, \mathbf{a} + \mathbf{c})$ (Figure 3b). For the crystal structure in the electric field, the space group of Aea2 was consistent with the extinction rules of reflections and also gave the best reliability factor. The experimentally determined locations of NH hydrogen atoms were consistent with the bond alternation C-N(H)-C=N-C



Fig. 2: (a) Temperature dependences of the relative permittivity ε of TFMNI. The inset shows temperature dependence obtained by differential scanning calorimetry (DSC) data. (b) Hysteresis loops of the electric polarization (*P*) as a function of the electric field (*E*) for TFMNI measured at various frequencies at room temperature. The polar structure was determined in the presence of an electric field of 40 kV/cm (denoted with the red arrow).

geometry of the imidazole ring as revealed by the corresponding bond lengths (1.34-5 Å for N(H)-C and 1.30 Å for C=N) for both crystal forms. The length of the hydrogen-bonded NH···N and size of the dihedral angle between the molecules were almost unchanged after the structural transition. It is worth noting that the trifluoromethyl group remains disordered without changes in the occupancy even in the presence of the electric field. This indicates that the disorder of the trifluoromethyl group is not related to the antipolar-polar transition.

As illustrated by the thick arrows in Figure 3b, antiparallel dipoles of the hydrogen-bonded chains are flipped; all the dipoles are forced to be parallel with each other and constitute the field-induced polar structure. Using our computational code QMAS, based on the Berry phase formalism, we calculated the fully polarized value of *P* to be 7.5 μ C/cm². This value was obtained by computational relaxation of hydrogen atom positions using the experimentally determined structure, under the assumption of minimum total energy. This theoretical prediction for the polarization is in good agreement with the experimentally measured maximum value of *P* ~ 6 μ C/cm², which



Fig. 3: (a) Polar crystal structure of TFMNI in the presence of an electric field. All hydrogen atoms, except those in NH, are omitted for clarity. (b) Arrangement of the polarized hydrogen-bonded chains in TFMNI in the polar (left) and antipolar (right) structure. Red and blue arrows represent the polarities of the chains.

demonstrates validity of the structural analysis.

Least square refinement of lattice parameters using approximately 80 Bragg reflections revealed a lattice expansion along the a-axis and shrinkage along the *c*-axis (Figure 4a) with increasing field amplitude. The b-axis, along which the molecules are arranged side-by-side, was almost unchanged. On the other hand, both longitudinal strain along the hydrogen-bonded a + c direction (c' direction in the FE form) and transverse strain along the molecular stacking c - a direction (b' direction) are very small owing to the cancellation of the a- and c-direction components with each other (Figure 4c). The lattice strain of the TFMNI crystal has the largest value along the a-direction of 0.07% at 25 kV/cm, which corresponds to a piezoelectric coefficient of 280 pm/V, assuming linearly induced strain. As a reference, we also measured the piezoelectric strain along the polar *c*-axis of the fully poled CRCA crystal (Figure 4b). The obtained strain of 0.008% induced at 25 kV/ cm in CRCA was one order of magnitude smaller than that of TFMNI. In TFMNI, the value of the lat-



Fig. 4: (a) Dependence of the lattice strain in a TFMNI as a function of the electric field. Error bars are smaller than the symbol size for data points. (b) Dependence of the lattice strain along the c-axis in the electrically poled CRCA crystal as a function of the electric field. The inset shows the hysteresis curve of the polarization of the same crystal specimen. (c) Shear strain dependence in TFMNI as a function of the electric field.

tice strain along the *a*-direction at the maximum field of 40 kV/cm reaches 0.15%, which corresponds to a piezoelectric coefficient of 376 pm/V. This value is one order of magnitude larger than the longitudinal piezoelectric coefficient d_{33} of PVDF (-31 pm/V) and comparable to the d_{33} coefficient of commonly used piezoelectric ceramics (~ 370 pm/V).

Taking into account the structural change in the Bravais lattice, as discussed above, one of the most representative parameters describing the observed transformation should be the degree of deviation from the orthorhombic cell, defined as $\Delta \alpha' = 90^{\circ} - \alpha'$, where α' is the angle between the **a** + *c* and *a* – *c* directions. Thus, $\Delta \alpha^{\prime}$ corresponds to the shear strain. As shown in Figure 4c, with the increase in field magnitude, $\Delta \alpha'$ decreased toward zero, whereas the variation of the unit cell volume $\Delta V/V$ remained negligibly small. Figure 5 shows a schematic drawing of the field-induced transformation from antipolar to polar structures. The red lines outline the antipolar crystal structure, while the blue lines outline the polar structure. Comparison between the two structures shows that the giant electrostriction in TFMNI originates from the shear strain generated by relative molecular displacements along the hydrogen-bonded chain direction.

In summary, TFMNI is the first reported organic AFE crystal that exhibits a field-induced structure, demonstrated by in-situ X-ray diffraction studies, which demonstrated substantial evidence of the antipolar-polar structural transition. This



Fig. 5: Molecular displacements during the structural transformation from antipolar to polar phase, viewed along the *b*-axis (*a*'-axis). Red and blue molecules belong to the antipolar and polar structures, respectively.

electrical phase-change phenomenon was accompanied by a giant electrostriction, which was approximately one order of magnitude larger than the reported piezoelectric strains of organic ferroelectrics CRCA and PVDF, but comparable to those of piezoelectric ceramics. As phase switching occurs at a relatively low electric field, organic AFEs are promising materials for electrostrictive applications.

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