Communication

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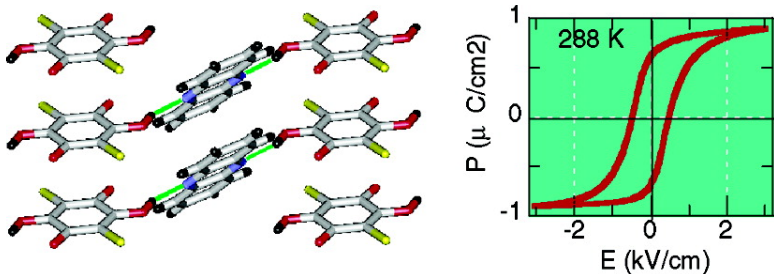

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Room-Temperature Ferroelectricity and Gigantic Dielectric Susceptibility on a Supramolecular Architecture of Phenazine and Deuterated Chloranilic Acid

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Ferroelectrics are versatile materials for applications to electronics and optics.[1] Especially, the reversible electric polarization in response to an external electric field is the essential property for application to the nonvolatile memory elements.[2,3] Therefore, the high Curie temperature (T_c) exceeding room temperature in ferroelectric organic materials is quite an important characteristic for ongoing design of all-organic electronics.

Recently, we have developed new ferroelectrics of low molecular-weight organic solids, the adducts of phenazine (Phz) with chloranilic acid (H_2ca) or bromanilic acid (H_2ba), in which intermolecular O−H⋯N hydrogen bonds form supramolecular structure.[4] Among these, the Phz−H_2ca crystal having the higher Curie temperature ($T_c = 253$ K) shows significant spontaneous polarization at low temperature as well as the dielectric constant exceeding 100 near room temperature. Furthermore, its much lower coercive field compared with that of the ferroelectric polymers[5] is advantageous for low-voltage operation. In this communication, we report the room-temperature ferroelectricity with huge dielectric response as the purely organic crystal by exchanging hydrogen with deuterium on the hydrogen bonds. The observed effect of deuteration between T_c and crystal structure was found to address distinguished features from the conventional models on the hydrogen-bonded ferroelectrics.

The cocrystals of Phz and deuterated chloranilic acid (D_2ca) or bromanilic acid (D_2ba) were prepared from the deuterated methanol. Figure 1 shows the temperature-dependent dielectric constant (ϵ) measured using an LCR meter along the crystallographic *b*- and *c*-axes of the cocrystals. The ϵ at the high-temperature paraelectric phase obeys Curie−Weiss law, where the Weiss temperature (θ) almost coincides with the Curie point as a pretransitional phenomenon of ferroelectricity. The T_c is elevated by as much as 51 and 66 K for Phz−D_2ca ($T_c = 304$ K) and Phz−D_2ba (204 K) with an increment of degree of deuteration (x) up to $x = 0.89$ and 0.80, respectively. The sizable isotope effect, as shown by the inset, indicates the importance of hydrogen bonds on the phase transition. Importantly, for the Phz−D_2ca crystals with x larger than 0.7, the T_c exceeds room temperature [shown by the shaded (yellow) area in Figure 1]. The room-temperature ϵ becomes extremely large, exceeding 2000 due to the vicinity of the peak at the ferroelectric phase transition. As far as we know, this is the highest room-temperature value among the purely organic ferroelectric solids.

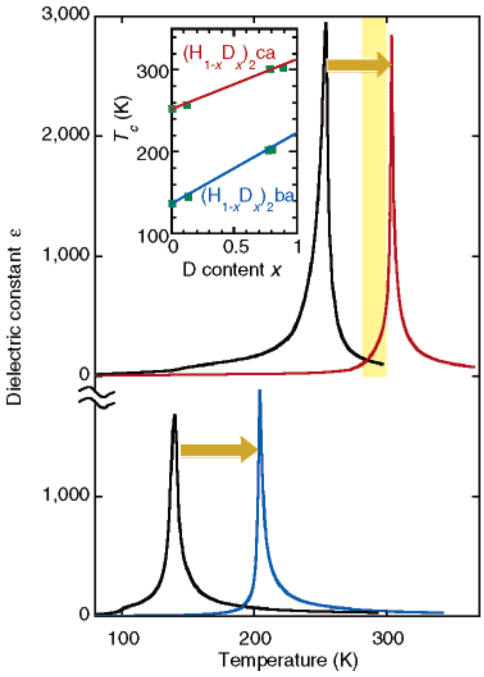

Figure 1. The dielectric constant (ϵ) of Phz−H_2ca and Phz−D_2ca ($x = 0.89$) (upper) and Phz−H_2ba and Phz−D_2ba ($x = 0.80$) (lower) at 1 MHz as a function of temperature. Arrows show the effect of deuterium substitution. The inset plots the Curie temperatures of the ferroelectric cocrystals as a function of degree of deuteration x.

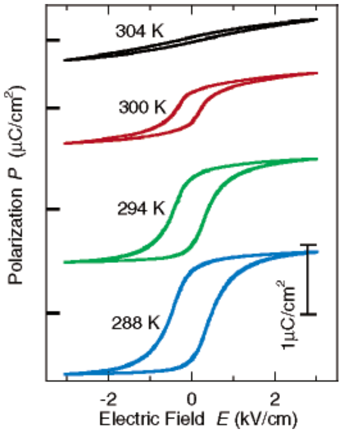

Figure 2. Thermal variation of the hysteresis loops of electric polarization on the Phz−D_2ca ($x = 0.89$) crystal near room temperature.

To verify the ferroelectricity near room temperature, the hysteresis of electric polarization was measured using a current/charge-to-voltage converter, while the triangle waveform voltage was applied along the polar (b) axis of the crystal in helium gas atmosphere. We show in Figure 2 the thermal variation of the polarization (P)−electric field (E) hysteresis curves of the Phz−D_2ca ($x = 0.89$). Upon cooling below $T_c = 304$ K, the hysteresis loop rapidly develops, and the spontaneous polarization reaches a large value, 0.64 μC/cm^2 at 288 K. The coercive field is very low;

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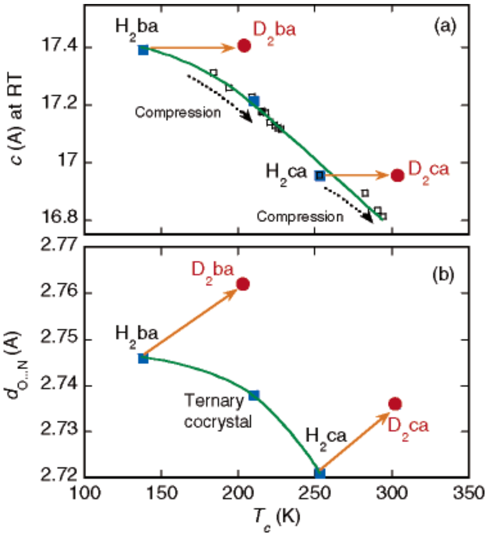

Figure 3. Relation between the ferroelectric phase transition temperature T_c and structural changes under hydrostatic pressure or upon deuteration; (a) the hydrogen-bonded O···N atomic distance, $d_{O\cdots N}$, and (b) the unit cell parameter, c, at room temperature. Filled squares denote Phz−H_2ca, Phz−H_2ba, and ternary Phz−$(H_2ba)_{1-y}(H_2ca)_y$ ($y = 0.55$) cocrystals, and orange arrows indicate their deuteration effect. Open squares plot the relation between T_c and the lattice constant c under hydrostatic pressures calculated with the experimentally determined c-axis compressibility for the Phz−H_2ca and Phz−H_2ba cocrystals.

even the values at 288 K (0.48 kV/cm) remain lower by 2−3 orders of magnitude than those for the typical ferroelectric polymers.[5] The hysteresis can be easily observed at room temperature also in air without electric discharge.

Such a huge deuteration effect has been observed for the conventional ferroelectrics having proton-transferable hydrogen bonds,[1] although its origin has long been the subject of controversy. In the typical material KDP (KH_2PO_4), for example, a different $H^+(D^+)$-tunneling frequency due to the mass change,[6] a geometric change of the hydrogen bond,[7] and recently, their combined roles[8] have been proposed as the possible mechanism for the significant increment of T_c upon deuteration. From these viewpoints, we examine the possible structural effects on T_c in the present series of ferroelectric cocrystals.

Figure 3 displays the relation between T_c and the unit cell parameter c and the hydrogen-bonded O···N atomic distance, $d_{O\cdots N}$.[9] The green lines indicate the structural changes in going from Phz−H_2ca to Phz−H_2ba crystal via their ternary crystal Phz−$(H_2ba)_{1-y}(H_2ca)_y$ ($y = 0.55$). The parameter c under hydrostatic pressure, which was found to show nonlinear pressure-dependence in a manner similar to T_c, appears to change with T_c along the same green line, as shown by the open squares in Figure 3a. Here, the T_c and compressibility of the single crystals were independently obtained from the $\epsilon - T$ measurements and the synchrotron X-ray diffraction, respectively, in the clamp-type high-pressure cell. On the other hand, deuterium substitution obeys distinct T_c versus crystal structure relationship from the cases of Cl/Br substitution and hydrostatic-pressure application, as shown by the orange arrows in the figure. Furthermore, for the geometry of the hydrogen bond, the increase of T_c accompanies the elongation of the O···N distance upon deuteration but shrinkage upon halogen substitution (Figure 3b). Whereas the KDP-type ferroelectrics involve the proton-transfer between the double potential minima, the hydrogen bond in Phz cocrystals is associated with no proton transfer from OH···N to $O^-\cdots NH^+$ form, as noted previously.[4] This may partly explain why the conventional pictures for the hydrogen-bonded ferroelectrics cannot be applied to the present system.

In summary, ferroelectricity and large dielectric susceptibility at room temperature are realized in hydrogen-bonded adducts of phenazine and deuterated chloranilic acids. The effective improvement of T_c by deuteration, in analogy with the conventional hydrogen-bonded ferroelectrics, such as KDP, manifests the importance of hydrogen bonds for the ferroelectricity. The observed relationship between T_c and crystal structure, however, precludes the conventional description in terms of the geometric effect, including the change of hydrogen bond length. The presently observed large deuteration effect thus provides a new challenge to the elucidation of the novel mechanism of ferroelectricity in the hydrogen-bonded π-molecular cocrystals.

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Supporting Information Available: Experimental procedures (PDF) and X-ray crystallography files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The lattice constant, c, and the distance, $d_{O\cdots N}$, were obtained at room temperature ($T = 298$ K), except for the Phz−D_2ca, which was measured at slightly higher $T = 305$ K (just above T_c) in order to compare the structures consistently within the same symmetry (space group $P2_1/n$). For the structural analysis, X-ray intensity data were collected on a Rigaku DSC imaging plate system by using Si-monochromated synchrotron radiation ($\lambda = 0.6868$ Å) at beam line BL-1A of Photon Factory (PF), High-Energy Accelerator Research Organization (KEK).

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