

## Successive phase transitions in organic ferroelectrics, phenazine-anilic acids

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### Introduction

Ferroelectrics have a spontaneous polarization that is switchable by an applied electric field, and have long constituted numerous technological applications such as capacitors, sensors, and information storages. Linear chain cocrystals of phenazine (Phz) with chloranilic acid (H<sub>2</sub>ca) and bromanilic acid (H<sub>2</sub>ba) have exhibited large polarization under small electric field in spite of the use of originally neutral and nonpolar constituents. Here we report the synchrotron x-ray diffractions studies on their successive phase transitions, indicating novel interplay between ferroelectricity and proton dynamics on hydrogen bonds.

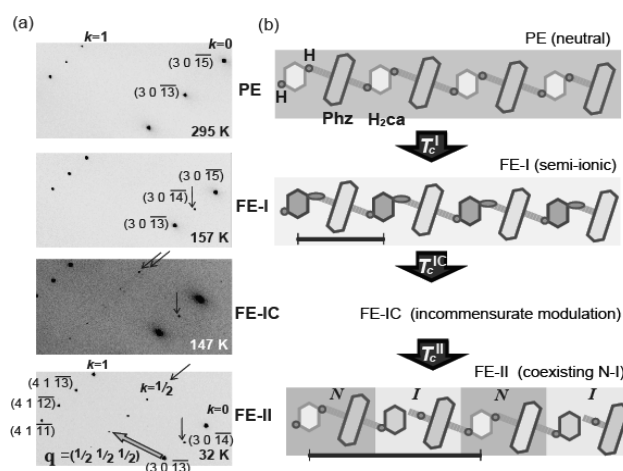
### Experiments

Synchrotron x-ray diffractions were collected on a Rigaku DSC imaging plate system by using Si-double-crystal monochromatized radiation ( $\lambda=0.9979$  Å for Phz-H<sub>2</sub>ba and 0.6873 Å for Phz-H<sub>2</sub>ca) at the beam line BL-1A. Monochromatized beam was focused using a bent cylindrical mirror made of Si crystal coated with Rh, with a focused beam size of 0.3 (vertical) × 0.7 (horizontal) mm. Temperature of the crystal attached on a glass fiber was controlled under flow of helium gas.

### Results and Discussion

According to the dielectric and pyroelectric properties, the Phz-H<sub>2</sub>ca (Phz-H<sub>2</sub>ba) undergo a transition from the paraelectric (PE) to ferroelectric (FE-I) phase at  $T_c^I = 253$  (138) K and also additional transitions at  $T_c^{IC} = 147$  (101) K and  $T_c^{II} = 137$  (98) K. These phase transitions are characterized by the change of x-ray diffraction as shown in Fig. 1a. The sudden appearance of  $(h0l)$  ( $h+l$ =odd) reflections at  $T_c^I$  (Fig.1a) indicates the symmetry-breaking from the space group  $P2_1/n$  to  $P2_1$ , posing the uniaxial polarity along the  $b$ -directions. The lowest-temperature ferroelectric (FE-II) phase ( $T < T_c^{II}$ ) exhibits a doubled cell volume for Phz-H<sub>2</sub>ca as proved by the additional spots at reciprocal wave vector  $\mathbf{Q} = \mathbf{G} \pm \mathbf{q}$  with modulation wave vector  $\mathbf{q} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$  for each  $\mathbf{G}$ , a reciprocal-lattice wave vector of original cell. On the other hand, the distinct modulation wave vector  $\mathbf{q}'$  of either  $(\frac{1}{3} \frac{1}{3} 0)$  or  $(\frac{1}{3} -\frac{1}{3} 0)$  (not shown) indicates a formation of threefold periodicity along the  $[110]$  or  $[\bar{1}\bar{1}0]$  direction for the Phz-H<sub>2</sub>ba. In quite a narrow temperature interval,  $T_c^{IC} > T > T_c^{II}$ , there exists an incommensurately modulated (FE-IC) phase for both Phz-H<sub>2</sub>ca and Phz-H<sub>2</sub>ba crystals as seen in Fig. 1a.

As a clue for understanding the successive phase transitions, we recall that one of the two acidic protons is displacing toward a nearly centered position over O··H··N bond with disordered nature in the FE-I phase [2] (see Fig. 1b). Then, it is natural to expect that the unusually elongated thermal ellipsoids reflect the time- and/or space-averaged distribution between different equilibrium positions that would be occupied as a periodic order in the FE-II phase. For the case of Phz-H<sub>2</sub>ca, half of displacing protons would be back to more neutral O–H··N form ( $N$ ) and the rest forward to more ionic O<sup>-</sup>··H–N<sup>+</sup> form ( $I$ ). Then, their alternation as .. $N$ - $I$ - $N$ - $I$ .. can constitute a doubled lattice periodicity of the FE-II structure. Similarly for the Phz-H<sub>2</sub>ba crystal with the weaker ionicity, the observed threefold periodicity would reflect, for instance, a .. $N$ - $N$ - $I$ - $N$ - $I$ .. sequence. As the intrinsic origin, we consider that the  $pK$  matching between the acid and base molecules should be crucial for such the fractional transformations from neutral to ionic form. For detail, see also ref. [3].



**Fig. 1** (a) Synchrotron x-ray diffraction photographs representing the PE, FE-I, FE-IC, and FE-II phases and (b) schematic drawings of proton locations on acid-base supramolecular chain for Phz-H<sub>2</sub>ca.

### References

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