

## Poster Presentation

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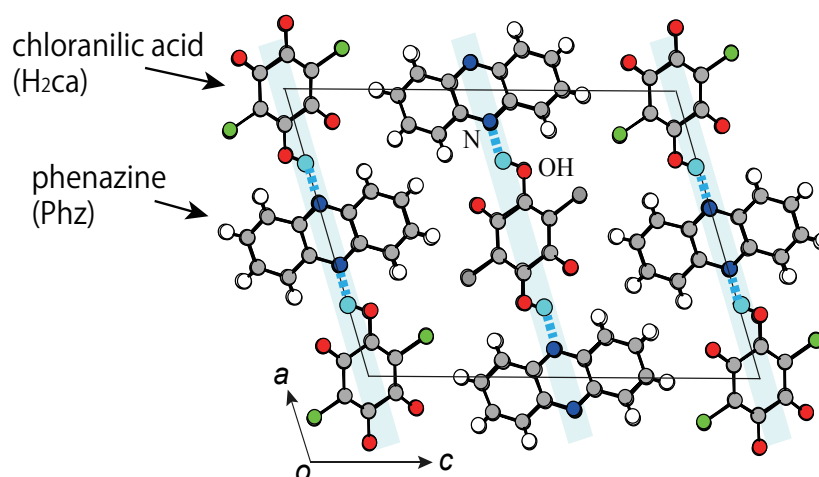
### Structural Study of Ferroelectric Phase in Acid-Base Supramolecule

A. Nakao<sup>1</sup>, R. Kumai<sup>2</sup>, S. Horiuchi<sup>3</sup>, Y. Tokura<sup>4,5</sup>, T. Ohhara<sup>6</sup>, T. Hanashima<sup>1</sup>, K. Munakata<sup>1</sup>, R. Kiyonagi<sup>6</sup>, T. Kawasaki<sup>6</sup>, K. Oikawa<sup>6</sup>, K. Kaneko<sup>6</sup>, I. Mamura<sup>6</sup>

<sup>1</sup>Research Center for Neutron Science and Technology, Comprehensive Research Organization for Science and Society, Ibaraki, Japan., <sup>2</sup>High Energy Accelerator Research Organization, Ibaraki, Japan, <sup>3</sup>National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan, <sup>4</sup>RIEN, Saitama, 351-0198, Japan., <sup>5</sup>Department of Applied Physics, University of Tokyo, Tokyo, Japan, <sup>6</sup>Japan Atomic Energy Agency, Ibaraki, Japan.

Supramolecular ferroelectric cocrystal of phenazine (Phz) with chloranilic acid (H<sub>2</sub>ca), which exhibits three successive phase transitions, have been characterized by the interplay between their structural transformations and solid-state acid-base (proton transfer) reactions (Figure) [1]. This material undergoes a ferroelectric phase (FE-I phase) transition of displacive-type at 253 K followed by successive phase transitions to the lattice modulated phases with incommensurate periodicities and with commensurate 2-fold periodicity (FE-II phase) at lower temperature [2]. To elucidate the origin of the ferroelectricity in the FE-I phase, it is crucial to study the crystal structure using single crystals. The synchrotron x-ray diffraction experiment was carried out on the imaging-plate diffractometer at BL-8A of Photon Factory in KEK. Superstructure reflections with the modulation wave vector  $q=(1/2\ 1/2\ 1/2)$  were clearly observed below 103 K. Considering the preserved 2/m Laue symmetry, the lattice can be transformed to a C-centered monoclinic lattice, which is related by  $(-2a, -2b, a + c)$  or  $(2a, -2b, -a - c)$  with the FE-I structure. Although the lattice distortion and the intensities of the superlattice reflections are consistent with the 2/m Laue symmetry, the space group C1 is deduced from the polar nature and a subgroup symmetry of the FE-I structure. Moreover, we performed single-crystal neutron diffraction experiments at SENJU of MLF/J-PARC in order to determine the displacement of the hydrogen atom. The crystal structure analysis at 10 K was carried out using the reflections measured in a half-sphere of reciprocal space at  $d > 0.4$ . The structure analysis was performed on the basis of the space group C1, where four Phz and four H<sub>2</sub>ca become crystallographically inequivalent. Finally, all the structural parameters including all hydrogen atoms were successfully refined. In the FE-II phase, the neutral and ionic molecules alternately align along the  $\pi$ -molecular stack.

[1] S. Horiuchi et al., *J. Mater. Chem.*, 19, 4421, 2009., [2] R. Kumai et al., *J. Am. Chem. Soc.*, 129, 43, 12921, 2007.



The molecular packing with hydrogen bond in the paraelectric phase.

**Keywords:** ferroelectric phase transition