

Proton Ordering in Ferroelectric Anilate Salts with a Proton Sponge

Reiji KUMAI*¹, Sachio HORIUCHI¹, Yoshinori TOKURA^{1,2}

¹Correlated Electron Research Center (CERC), AIST, Tsukuba, Ibaraki 305-8562, Japan

²The Univ. of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Introduction

Renewed interest on anilic acids (or 2,5-dihydroxy-*p*-benzoquinones, H₂xa) stems from recent discoveries of ferroelectricity by hydrogen-bonding with organic dibasic bases such as phenazine and 5,5'-dimethyl-2,2'-bipyridine [1]. Polarization reversal has been achieved by the cooperative transfer or displacement of protons on the hydrogen-bonded chains of alternating acid and base molecules [2,3].

Recently, we have developed new ferroelectrics with distinct H-bonding modules using the 2,3,5,6-tetra(2'-pyridyl)pyrazine (TPPZ) molecule [4]. In the salt with anilic acids, the H₂-TPPZ²⁺ dication acts as a proton sponge. Dielectric measurements revealed phase transitions at $T_c = 334$ K and 172 K for bromanilate (Hba⁻) and chloranilate (Hca⁻) salts, respectively. The room-temperature ferroelectricity of the (H₂-TPPZ)(Hba)₂ crystal is evidenced by the slow polarization reversal with modest pyroelectricity (0.06-0.11 μCcm⁻²). Here we report on the synchrotron x-ray diffraction studies that disclosed proton dynamics in both intramolecular N•••H•••N bond of the dication and in an O-H•••O bonded dimer.

Experimental

All the x-ray diffraction data at various temperatures were collected with a Rigaku DSC imaging plate system by using Si-double-crystal monochromatized and focused synchrotron radiation ($\lambda = 0.9979$ or 0.6877 Å) at the beam line BL-1A of PF, KEK. In order to probe a delicate change of the H-bonding, we calculated the electron distribution by the maximum entropy method (MEM) analysis as well as the differential MEM analysis.

Results and Discussion

General structural features

The two TPPZ salts show the isomorphous unit cell of monoclinic crystal system accommodating as many as four H₂-TPPZ²⁺ dications and eight Hxa⁻ monoanions ($Z = 4$). While the mono-deprotonated anilic acids (Hxa⁻, Fig.1a) of the ortho-quinoid form a cyclic dimer, the H₂-TPPZ²⁺ has two intramolecular N•••H•••N hydrogen bridges between the pyridyl units with a very short N•••N distance (Fig. 2a). There are no inter-unit H-bonding between the acid and base. The paraelectric phase (PE) and ferroelectric phase (FE) structures belong to the centric type (space group $C2/c$) and its acentric subgroup (Cc), respectively. In the PE structure, a 2-fold rotation axis emerges between two Hxa⁻ molecules and the H₂-TPPZ²⁺ molecule is located on an inversion.

Molecular Structural Changes

The C_2 symmetry of the (Hxa⁻)₂ dimer demands each proton evenly disordered on both oxygen atoms (Fig. 1b) and manifests its double-proton transfer process above T_c . In contrast, these protons are ordered in the FE structure.

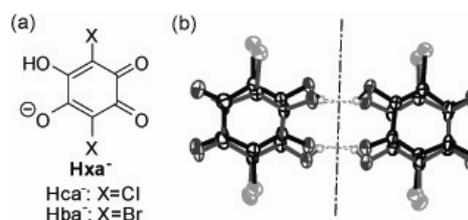


Fig. 1 (a) Hxa⁻ anions and (b) their disordered dimer in the PE structure.

The dication in the PE structure adopts a nonpolar geometry. Below T_c , only one of the two protons gets localized (b-site in Fig.2). For the disordered a-site, differential MEM analysis exhibited a broad electron distribution around the middle of H-bond and a slight splitting into double maxima indicates the positional disorder of the hydrogen. The resultant acentric H₂-TPPZ²⁺ ion generates the dipole moment responsible for the ferroelectricity.

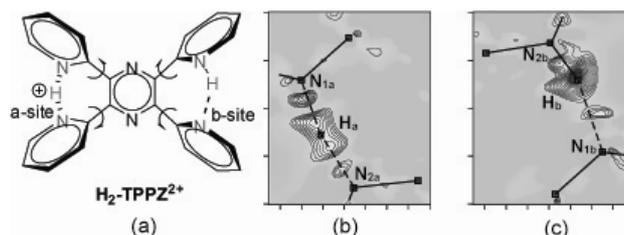


Fig. 2 (a) H₂-TPPZ²⁺ ion and (b) its a-site and (c) b-site electron density distributions deduced by the differential MEM analysis for the FE structure in [H₂-TPPZ][Hca]₂.

References

- [1] S. Horiuchi & Y. Tokura, Nat. Mater. 7, 357 (2008).
- [2] S. Horiuchi et al., Angew. Chem. Int. Ed. 46, 3497 (2007).
- [3] R. Kumai et al., J. Am. Chem. Soc., 129, 12920 (2007).
- [4] S. Horiuchi et al., to be published.

* r-kumai@aist.go.jp