Oral presentation

Unravelling Proton Dynamics: Discovering Organic Ferroelectricity and the Fascinating World of Incommensurate Phase Transitions

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We will present recent advancements in the field of modulated molecular ferroelectric crystals, focusing on the intricate connections between incommensurability, intermolecular interactions, and the ferroelectric properties of these materials. Highlighting the significance of understanding the modulated structure for comprehending crystal chemistry and functional properties.

Supramolecular compounds hold promise as ferroelectric materials due to their low density and potential cost-effectiveness, offering versatility in design based on the acidity and base strength of their constituent building blocks. Among these, co-crystals formed by 5,5′-dimethyl-2,2′-bipyridine (55DMBP: base) or Phenazine (base) with haloanilic acids (H_2xa, x= Cl, Br, I) represent a significant discovery in the realm of hydrogen-bonded organic ferroelectrics, wherein the acid and base blocks are interconnected through O—H…N bonds [1-2]. These co-crystals exhibit paraelectric-ferroelectric transitions upon cooling and heating. We have investigated the temperature-dependent structural phase transitions of the co-crystal comprising 5,5′-dimethyl-2,2′-bipyridine (55DMBP) and bromanilic acid (H_2ba, H_2ia) using synchrotron X-ray diffraction at the P24 beamline, DESY. Below T = 250 K, the crystal displays ferroelectric behavior (FE), transitioning to a paraelectric phase (PE) at higher temperatures up to 360 K, while passing through two PE-PE phase transitions [3].

Analysis of X-ray diffraction data at 120 K reveals a ferroelectric phase (FE-I), characterized by a commensurately modulated structure with a superspace group $P\bar{1}(\sigma1\ \sigma2\ \sigma3)0$ and a modulation wave vector (q =1/2 1/2 1/2). At 250 K, the crystal transforms into the paraelectric phase PE-II, retaining the same modulation wave vector. Above 320 K, the modulation wave vector becomes incommensurate (q =1/2±σ, 1/2±σ, 1/2±σ). Above 338 K the satellite Bragg reflections disappear. The crystal structure at 346 K of this PE-III phase is periodic with space group $P\bar{1}$ and a unit cell that acts as basic structure for the modulated phases. While the centrosymmetric superspace group remains consistent across FE-I, PE-II, and PE-IC phases, there are variations in the value for the phase of modulation. This variation enables the presence of an acentric space group in the FE phases [3].

Crystal-chemistry analysis reveals that the phase transitions originate from proton dynamics in intermolecular O—H…N or intramolecular 3-centered hydrogen bonds (bifurcated) in C=O... H(O)…N configurations. Our study, employing superspace formalism, not only allows comparison of phase transition mechanisms across all phases but also facilitates refinement of parameters for the twofold superstructures of the PE-II and FE-I phases, enhancing the accuracy of the structure model and, notably, the positioning of hydrogen atoms within hydrogen bonds [3].

[1] Horiuchi, S., Ishibashi, S., Kobayasshi, K. & Kumai, R. (2019) RSC. Adv. **9**, 39662.

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[3] Noohinejad, L., van Smaalen, S., Paulmann, C., & Tolkiehn, M. (2023) CrystEngComm, **25**, 4539.