

**MS29-2-2 A temperature-dependent flexible proton-transfer system**

#MS29-2-2

L. Saunders<sup>1</sup>, P. Edwards<sup>2</sup>, J. Taylor<sup>3</sup>, D. Nye<sup>3</sup>, D. Grinter<sup>4</sup>, D. Allan<sup>4</sup>, S. Thompson<sup>4</sup>

<sup>1</sup>Diamond Light Source - Didcot (United Kingdom), <sup>2</sup>University of Leeds - Leeds (United Kingdom), <sup>3</sup>STFC - Didcot (United Kingdom), <sup>4</sup>Diamond - Didcot (United Kingdom)

**Abstract**

Molecular crystals are formed from the association of discrete organic molecules via intermolecular interactions and may be single or multi-component. Crystal engineering is used in their design to target specific structural features resulting from molecular association, including voids, stacking or charged species, with related material properties such as guest uptake, colour and switchable forms.

Hydrogen bonding interactions play an important role in the molecular assembly of organic components in the solid state. Proton transfer events may occur within molecular crystals when formed of organic acids and bases and is favoured across the shorter of the hydrogen bonding interactions, often those that are charge assisted and where a significant covalent component is found.<sup>1</sup> The proton transfer may be static, occurring on crystal formation and resulting in oppositely charged species connected by charge assisted hydrogen bonds, or be variable, such that multiple positions across the hydrogen bond are energetically favourable and/or are susceptible to external crystal environment.<sup>2</sup> Determining proton transfer state in the salt-cocrystal continuum has impact in pharmaceutical regulation whilst a shifting proton position as a function of an external variable can result in sensor (where a colour change is induced) or switchable (polarisation change) technology. Its study and where this type of behaviour is found is therefore of interest, to aid in incorporation into or its control within functional materials.

In this work, we present a study of the temperature dependent behaviour of multi-component molecular salt (1) 4,4'-bipyridinium 2,4-dinitrobenzoate (1:3), probed using a range of characterisation techniques. System (1) has resulted from a co-crystallisation study based on introducing a third-component to alter the proton transfer states and colour properties of the 4,4'-bipyridinium hydrogen squarate.<sup>3, 4</sup> We use differential scanning calorimetry alongside synchrotron single crystal and powder X-ray diffraction methods to characterise the thermal behaviour of (1). In the crystal structure of (1), molecular association of components occurs via charge assisted  $N^+—H\cdots O^-$  hydrogen bonds across which proton disorder is evident. Due to the weak scattering signal of the H-atoms from the X-rays, it is not possible to accurately resolve the nature of the disorder or how, if at all, it evolves as a function of temperature. In light of this, we implement a number of spectroscopic techniques including Near Edge X-ray Absorption Fine Structure and X-ray Photoelectron spectroscopy to explore the proton disorder of this system to determine what role, if any, it has in the thermally induced crystallographic phase transition.

**References**

1. L. K. Saunders, A. R. Pallipurath, M. J. Gutmann, H. Nowell, N. Zhang and D. R. Allan, CrystEngComm, 2021, 23, 6180-6190.
2. L. K. Saunders, H. Nowell, L. E. Hatcher, H. J. Shepherd, S. J. Teat, D. R. Allan, P. R. Raithby and C. C. Wilson, CrystEngComm, 2019, 21, 5249-5260.
3. D. M. S. Martins et al., J. Am. Chem. Soc., 2009, 131, 3884-3893.
4. J. S. Stevens, Cryst. Growth Des., 2022, 22, 779-787.