[MS24-P31] Towards Tunable Optical Properties: Thermochromism in Haloaniline Complexes.

Charlotte L. Jones, Lynne H. Thomas and Chick C. Wilson.

Department of Chemistry, University of Bath, Bath, BA2 7AY
E-mail: clj22@bath.ac.uk

Thermochromism is the temperature-dependent change in the colour of a material which can occur in both the solution and solid state in various types of materials, and offers potential for applications as sensors and indicators and in optical devices.[1] In the solid state a number of mechanisms are known for thermochromism, such as a molecular rearrangement or proton transfer;[2,3] the exact origin of the colour change depends on the type of material. A currently under-explored potential route towards solid-state thermochromism is through multi-component crystallisation. Multi-component complexes are a rich potential source of synthesising and understanding solid state materials with distinct or tunable physical properties, while also providing an ideal framework for their full characterisation and understanding. Combining molecules using crystal engineering principles not only allows the design of architectures that extract the best attributes for both components, if the arrangement of the molecules can be controlled, but also provides an environment that offers potential for evolution of properties by optimising the co-component. As part of an investigation into the tunability of colour using multi-component crystallisation routes, based on the known thermochromic material 2-iodoanilinium picrate,[3] the cocrystallisation of iodoanilines and bromoanilines with dinitrosubstituted benzoic acids has been studied extensively. A series of molecular complexes have been formed, whereby simple, colourless co-molecules have been cocrystallised to form strongly coloured crystalline multi-component materials. There is a particular focus on controlling the important hydrogen and halogen bonding and π-π stacking interactions. Disorder of one or more of the molecular components occurs in many of the coloured multi-component materials, and the disorder in these systems may be playing a significant role in inducing colour in the solid-state. To date, two thermochromic two-component materials have been developed. Both 2iodoaniline 3,4-dinitrobenzoic acid and 2bromoaniline 3,4-dinitrobenzoic acid undergo a temperature-induced colour change (at 85°C and 95°C, respectively). The crystal packing in the two multi-component materials is extremely similar, however the colour change is irreversible in the 2-iodoaniline complex but reversible in the 2-bromoaniline complex. Disorder of the haloaniline is present in the low temperature form of each of the systems; a massive structural rearrangement occurs on heating, resulting from a single crystal-single crystal phase transition, as characterised by single crystal X-ray diffraction. This rearrangement is likely to be driven by more efficient packing in the solid state, and is facilitated by the disordered haloaniline molecules present in the low temperature phase. This has therefore highlighted the importance of understanding, introducing and controlling defects as an alternative route to favourable properties in organic multi-component solid-state materials.

[1] White, M.A. & LeBlanc, M. (1999). *J. Chem. Educ.*, **76**, 1201-1205.
[2] Lee, S.C., Jeong, Y.G., Jo, W.H., K, H-J., Jang, J., Park, K-M. & Chung, I.H. (2006). *J. Mol. Struct.* **825**, 70-78.
[3] Tanaka, M., Matsui, H., Mizoguchi, J-I. & Kashino, S. (1994). *Bull. Chem. Soc. Jpn.* **67**, 1572-1579.

Keywords: thermochromism; crystal engineering; disorder