[MS24-P13] Molecular Disorder as a Tool in the Crystal Engineering Toolkit.

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Defects in inorganic systems are routinely exploited as a route to enhancing or introducing physical properties such as conductivity, ferroelectricity and optical properties in solid materials. Similar effects in organic systems are yet to be properly exploited, in spite of the fact that disorder is frequently present in such materials. Multi-component complexes have found widespread applications in areas such as pharmaceuticals, agrichemicals and optical materials, but to date these have focused on the precise control of the supramolecular assembly by carefully matching the functional groups of the active molecule with its partner molecule. By seeking to combine disorder with the synthesis of multi-component molecular complexes where intermolecular interactions are engineered into the solid form, this work targets enhancement of material properties. Controlling the nature of defects in molecular systems is difficult due to the complex balance of kinetics and thermodynamics but crystal disorder can be engineered into multicomponent molecular complexes through molecular level control of the intermolecular interactions by introducing many competing, similar energy interactions or by utilising symmetric molecules. This provides an alternative route to modifying the physical properties of the composite material in addition to the benefits obtainable by moving into a multi-component solid form. As a recent example of this, the intergrowth of the two polymorphs of aspirin – effectively a designed disorder – can lead to increased solubility of the resultant materials compared to either of the pure polymorphs. [1] It is possible to crystallographically model multiple orientations for such disordered components, and most commonly, the disorder is not random and local, short-range order can be rationalised by consideration of the intermolecular interactions between molecules. Structured diffuse scattering is also often observable in the diffraction patterns and incorporation of this additional information can lead to a more complete description of the crystal packing. We will present examples of the controlled introduction of molecular defects into multicomponent molecular materials applied to active pharmaceutical ingredients and optically active materials. This includes examples of slip-layer defect materials with enhanced compaction and solubility and a single-crystal to single-crystal thermochromic phase transition in the molecular complex of 2- iodoaniline with 3,4-dinitrobenzoic acid which exhibits an exceptional molecular rearrangement made possible by disordered 2-iodoaniline molecules acting as a lubricant. In these cases, the disorder is a crucial aspect in lending these materials their physical properties.

[1] A.D. Bond, CrystEngComm (2012), 14, 2363.

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