MS32. Halogen bonding in the solid state

Chairs: Christer Aakeröy, Lee Brammer

MS32-O1 Perfluorinated azobenzenes for the design of new halogen-bonding molecules and photomechanical materials

Tomislav Friščić[1], Oleksandr S. Bushuyev[1], Christopher J. Barrett[1]

1. McGill University

email: tomislav.friscic@mcgill.ca

Over the past decade, halogen bonding has developed from a laboratory curiosity to a powerful tool of crystal engineering, allowing the deliberate and controlled assembly of cocrystals, 1-, 2- or 3-dimensional supramolecular architectures and design of systems for molecular recognition and separation.[1] This presentation will focus on our recent exploration of solvent-free methodologies for the synthesis of multi-component materials based on halogen bonds, as well as the use of perfluorinated azobenzenes as building blocks for the synthesis of halogen-bonded cocrystals. In particular, we will describe how the extensive fluorination of the azobenzene moiety leads to new and attractive opportunities both in the design of photo-mechanical materials capable of mechanical response to visible light stimuli,[2] as well as in the synthesis of new molecular building blocks pre-designed for halogen-bonded self-assembly.[3] The photo-mechanical properties of the herein described halogen-bonded materials are based on the previously never reported irreversible crystal-to-crystal cis-to-trans isomerization in the solid state. Whereas we find that this photo-mechanical effect is readily exhibited by several crystalline perfluorinated cis-azobenzenes, the use of halogen bond-driven cocrystallization allows, for the first time, the modulation and fine-tuning of their photo-mechanical behavior. The variation of different halogen bond acceptors in combination with a limited set of perfluorinated cis-azobenzene halogen bond donors as photo-mechanically active building blocks enabled the synthesis of a library of cocrystals with a range of photo- and thermo-chemical properties: from those that exhibit cis-trans isomerization without any change in crystal shape to those that undergo crystal-to-crystal isomerization accompanied by large scale bending. As an example of such tuning of photo-mechanical behavior of crystalline solids, the presentation will highlight a photo-mechanical halogen-bonded cocrystal that allows the *in situ* study of solid-state azobenzene isomerization by single crystal X-ray diffraction.[4]

1) Priimagi et al. Acc. Chem. Res. 2013, 46, 2686; 2) Bushuyev et al. J. Am. Chem. Soc. 2013, 135, 12556; 3) Bushuyev et al. CrystEngComm 2015, 17. 73; 4) Bushuyev et al. Chem. Sci. 2014, 5, 3158.

Keywords: halogen bonding, photo-mechanical effect, cocrystals, supramolecular, self-assembly, crystal-to-crystal