

Halogen Bonded Co-crystals of a Pyridyl *Bis*-urea Macrocycle and Diiodotetrafluorobenzenes

*Som, B.¹, Salpage, S. R.¹, Son, J.¹, Gu, B.¹, Smith, M. D.¹, and Shimizu, L. S.¹

¹Graduate students, Undergraduate student, Crystallographer and Professor, Department of Chemistry and Biochemistry, University of South Carolina

bsom@email.sc.edu

Keywords: Supramolecular chemistry, Solid-state, Crystalline materials

Abstract: Halogen bonding has become a very important tool in the control and organization of small molecules into supramolecular assemblies, producing superior properties for materials that have various applications. The Shimizu group have previously demonstrated that a pyridyl bis-urea macrocycle (**1**) self-assembles into columnar 1D structures through two different hydrogen bonds (N-H \cdots N and N-H \cdots O) where the urea NHs interacts with the urea carbonyl oxygen and the pyridine nitrogen. This affords pillars with basic lone pairs from the carbonyl oxygen that can be used to absorb guest molecules in the solid-state through non-covalent interactions such as hydrogen bonding and halogen bonding. Here, we investigated these strong pillars as a co-crystal former for ditopic halogen bond donors [1,2-diiiodotetrafluorobenzene (*o*-DITFB), 1,3-diiiodotetrafluorobenzene (*m*-DITFB), and 1,4-diiiodotetrafluorobenzene (*p*-DITFB)] to test the robustness of this synthon and probe its ability to organize activated halides. These co-crystals were grown by the vapor diffusion technique, in which water was vapor diffused into a DMSO solution of the macrocycle and halogen bond donor (1:1 or 1:2 stoichiometric ratio). The formation of halogen bonding in the co-crystals was established using several techniques, including FT-IR, XPS and single crystal X-ray diffraction (SCXRD) and the strength of the halogen bonds (I \cdots O=C) were evaluated by DFT calculations. Single crystal XRD analysis of the co-crystals showed alternating segregated stacks of the halogen bond donors and the strong cylindrical pillars of **1** (halogen bond acceptor), which is a very important motif used in the development of molecular electronics. Our main goal is to use this halogen bond synthon to organize molecules and control their properties.