Poster

Ternary halogen-bonded cocrystal design using Ni(II) complex containing isothiocyanate ligands as halogen bond acceptor species

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In recent years, the design strategy of binary cocrystals has been established by utilizing specific intermolecular interactions and using the knowledge of supramolecular synthons. However, the synthesis of higher-order cocrystals remains a challenging task, since balancing more components and controlling specific interactions in a crystal is difficult [1,2]. For the design of hydrogen-bonded ternary cocrystals, four synthetic strategies are known: 1) synthon hierarchy, where the best donor is connected to the best acceptor and the next best donor to the next best acceptor, 2) shape-size mimicry, where the third molecule (a mimic) enters a site occupied by one of two molecules already in a binary cocrystal, 3) structural inequivalence implies substitution of molecules situated in two distinct crystallographic environments in the same crystal structure, 4) combinatorial crystal synthesis, where the system itself selects the fittest interactions or sets of interactions out of multiple competing interactions [3]. On the other hand, obtaining higher-order halogen bonded cocrystals presents a significant challenge in crystal engineering. Only 10 ternary halogen-bonded cocrystals have been reported in the literature so far [4]. Out of those cocrystals, only 4 ternary cocrystals contain two different donor molecules. The mentioned cocrystals are based on small organic molecules or π-systems which served as a halogen bond acceptor and two perhalogenated molecules as donor moieties. To the best of our knowledge, there are no ternary metal-organic cocrystals known in the literature that contain two different donor molecules.

Our approach to this topic was focused on using metal coordination compound as the main building block for obtaining ternary cocrystals. We synthesized the Werner coordination compound with two trans-isothiocyanate groups, which are flexible and sterically unhindered, $Ni(CH_3C_5H_5N)_4(NCS)_2$ - **1**. This way we designed a ditopic metal-organic acceptor, which can interact with perfluorinated benzenes to form halogen bonds. To build ternary cocrystals, we used a combination of the following halogen bond donors: 1,3-diiodotetrafluorobenzene (**13tfib**), 1,4-diiodotetrafluorobenzene (**14tfib**) and 1,3,5-trifluoro-2,4,6-triiodobenzene (**135tfib**). Cocrystallization experiments were performed both mechanochemically and from the solution. Four different ternary cocrystals were synthesized and compared to previously synthesized binary cocrystals containing the same donor molecules. For both binary and ternary cocrystals, dispersion-corrected periodic density-functional theory (DFT) calculations were performed in plane-wave DFT code CASTEP [5,6]. These calculations were used to compute cocrystal formation energies, as well as intermolecular interaction energies. Isothiocyanate sulfur in **1** proved to be a very good and dependable halogen bond acceptor capable of forming multiple halogen bonds, which enabled the formation of ternary cocrystals. This work shows the progression from binary to ternary cocrystals using strategies of structural inequivalence and combinatorial crystal synthesis. The crystal structure of ternary cocrystal (**1**)(**135tfib**)(**13tfib**) is a result of a substitution of one symmetrically inequivalent **135tfib** molecule present in the crystal structure of binary with a **13tfib** molecule. As for the progression of the binary cocrystals containing **14tfib**, the formation of ternary cocrystals is based on interaction hierarchies of donor molecules, which are validated by calculations (Fig.1).

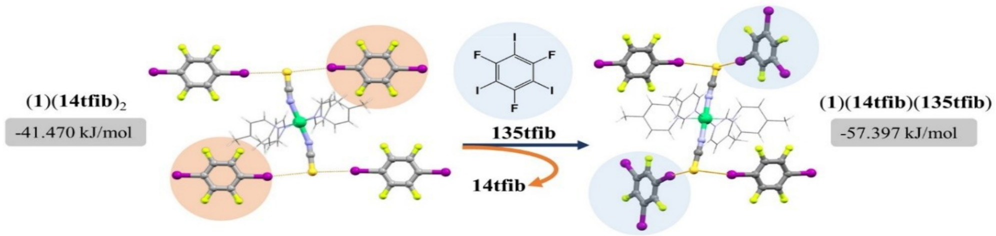

Figure 1. Cocrystal formation energies for (**1**)(**14tfib**)$_2$ (binary) and (**1**)(**14tfib**)(**135tfib**) (ternary cocrystal).

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