

# Engineering Ternary Cocrystals by Orthogonal Hydrogen and Halogen Bonds

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In the still maturing field of halogen bonding, we have been especially interested in discovering new halogen bonding motifs<sup>1,2</sup> and applying them in crystal engineering.<sup>3</sup>

The particular robustness of C–I⋯S halogen bond with thioureas has recently been highlighted, persisting even in solution.<sup>4</sup> In addition to that, the orthogonality of such interaction to hydrogen bonds has also been demonstrated,<sup>5</sup> offering the possibility of constructing complex systems where the two can operate independently.

Also knowing that the crown ethers reliably cocrystallize with thioureas,<sup>6,7</sup> this prompted us to combine thioureas with crown ethers and various (aromatic and non-aromatic) perfluorinated halogen bond donors, resulting in a large number of ternary cocrystals with high supramolecular yield. Besides the success of the strategy and the aesthetically appealing structures, these systems present other intriguing aspects, such as differing behavior of bromine- and iodine-based donors, tunable metrics and, finally, the possibility of constructing porous materials.

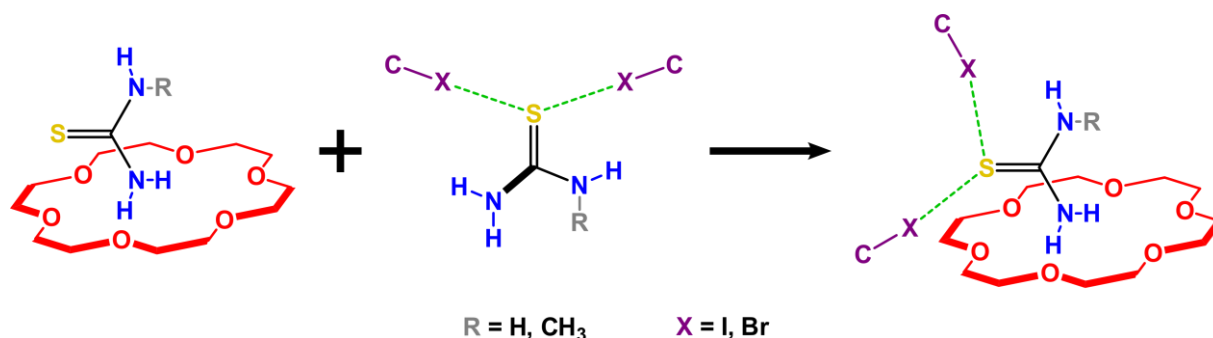


Figure 1. Hydrogen and halogen bonded motifs are combined in the studied ternary cocrystals.

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