

Co-crystals prepared from a pyridine/azine spacer with a series of halogen-bond and hydrogen-bond donors

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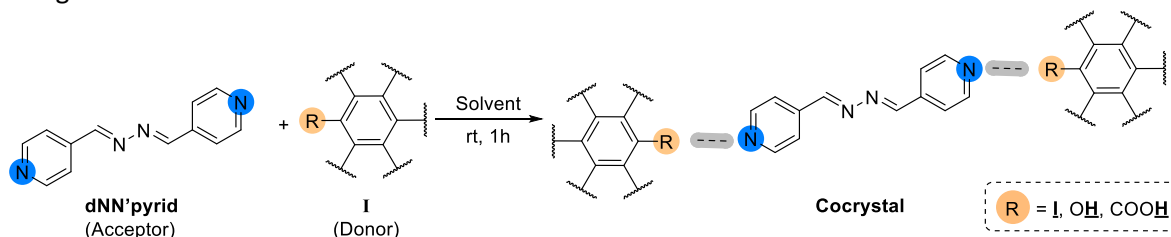
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Halogen bonding has proven to be a tool of great significance in supramolecular chemistry for designing organic, ionic and metal-organic materials. Halogen bonds (XBs) are attractive interactions involving the partially positively charged σ -hole of a halogen moiety with a partially negatively charged region. These anisotropic intermolecular interactions are highly significant and comparable to hydrogen bonds. Nitrogen and oxygen atoms have been reported as viable halogen-bond acceptors. The most used acceptors to date are those containing nitrogen atoms, particularly as part of an aromatic system, such as pyridine derivatives.^{1,2} Another noteworthy class is supramolecular synthons, particularly within the heterosynthetic category, where it encompasses different acceptor-donor molecules forming hydrogen-bonded entities. The predominant structural motif comprises supramolecular heterosynthons involving systems of the carboxylic acid-pyridine or phenol-pyridine types. In this work we prepare halogen- and hydrogen-bonding cocrystals using (1*E*,2*E*)-1,2-bis(pyridin-4-ylmethylene)hydrazine (dNN'pyrid) as a spacer in order to obtain different supramolecular arrangements. The XB donors used were 1,3,5-triiodo-2,4,6-trifluorobenzene, 1,4-diiodotetrafluorobenzene, and 1,2-diiodotetrafluorobenzene, while 4,4'-biphenol and tricarboxylic acid were used as H-bond donor. The proposed co-crystals were obtained by dissolving dNN'pyrid in methanol and mixing it with the appropriate donor, dissolved in methanol or CH₃OH:CHCl₃ solvent mixture. The resulting mixture was stirred at room temperature for one hour, Scheme 1. After a day of slow evaporation at room temperature, single crystals were obtained and their structures were determined by single-crystal X-ray diffraction. Five new co-crystal structures were obtained and the supramolecular arrangement for halogen-bonding co-crystals shows I...N interactions, C-H...F, and π - π interactions of the aromatic units. In the H-bonding systems OH...N and COOH...N interactions were observed, as expected, while π - π interactions between the aromatic units in supramolecular arrangement, were also observed. The obtained systems will have their Hirshfeld surfaces area analyzed and will be further evaluated according to their optical properties, thermal stability, and porosity. Additionally, other azine/pyridine-type spacers will be assessed in the future with the same co-ligands.



Scheme 1. Synthetic route to obtain of the cocrystals.

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