Supporting Information: Weaving a two-dimensional Net of Hydrogen and Halogen Bonds: Cocrystal of a Pyrazolium Bromide with Tetrafluorodiiodobenzene

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Additional figures

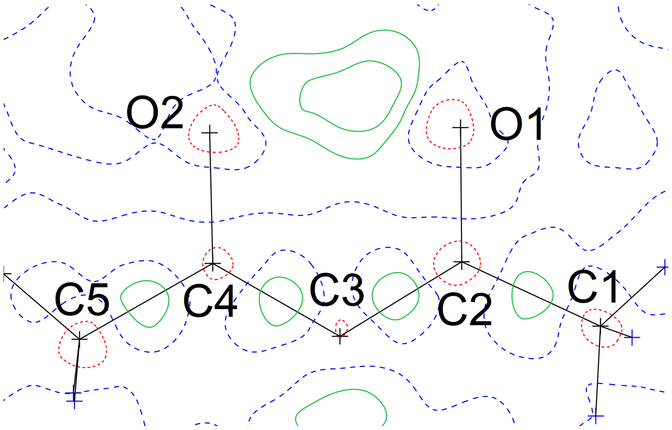

Figure S1: Difference Fourier synthesis map[S1] of **1** before including the enol hydrogen; contour lines drawn at 0.2 e Å^{-3}.

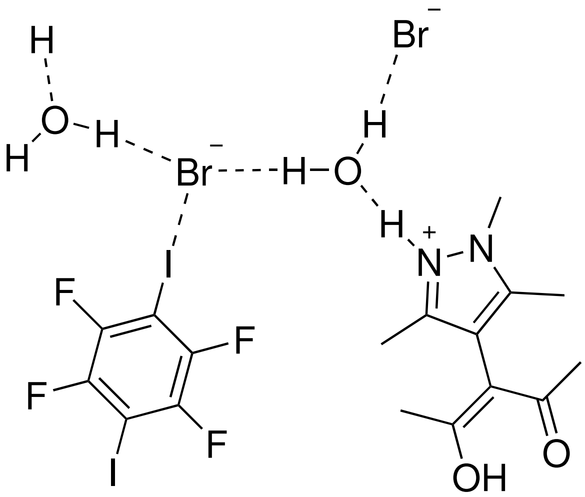

Figure S2: Fragment used for the single point calculation.

Database searches

Database searches in the CCDC[S2] were conducted with ConQuest 2021.2.0, build 327809. The exact structures and constraints are compiled in Figure S3. Van der Waals radii (r_{vdW}) were used as defined in ConQuest.

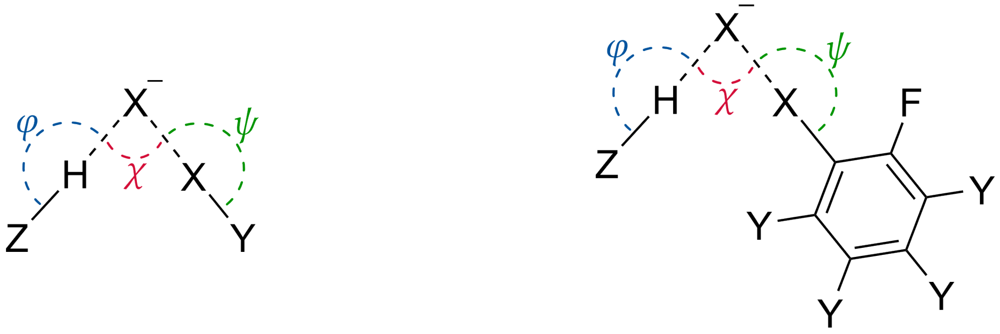

Figure S3: Left: More general query used to classify **3** in the range of related compounds. Right: Query limited to fluorinated halobenzenes as halogen bond donors with only twelve hits. Constraints: $d_{\max}(\mathrm{H}\cdots\mathrm{X}^-) = \sum(r_{\mathrm{vdW}})$; $d_{\max}(\mathrm{X}^-\cdots\mathrm{X}) = \sum(r_{\mathrm{vdW}}) - 0.2$ Å; $\varphi = 150°$ to $180°$; $\chi = 60°$ to $120°$; $\psi = 150°$ to $180°$; X = F, Cl, Br, I; Y = any atom; Z = O, N.

Powder X-ray diffractograms

Experimental X-ray powder patterns depicted below were collected at room temperature while simulated patterns correspond to the single crystal data obtained at 100 K. This leads to a shift of the lines in the experimental pattern to lower 2θ values due to the lattice expansion at higher temperature. Reflection intensities of **1** only fit the simulated data if the microcrystalline powder is ground; otherwise the intensities suffer from preferred orientation.

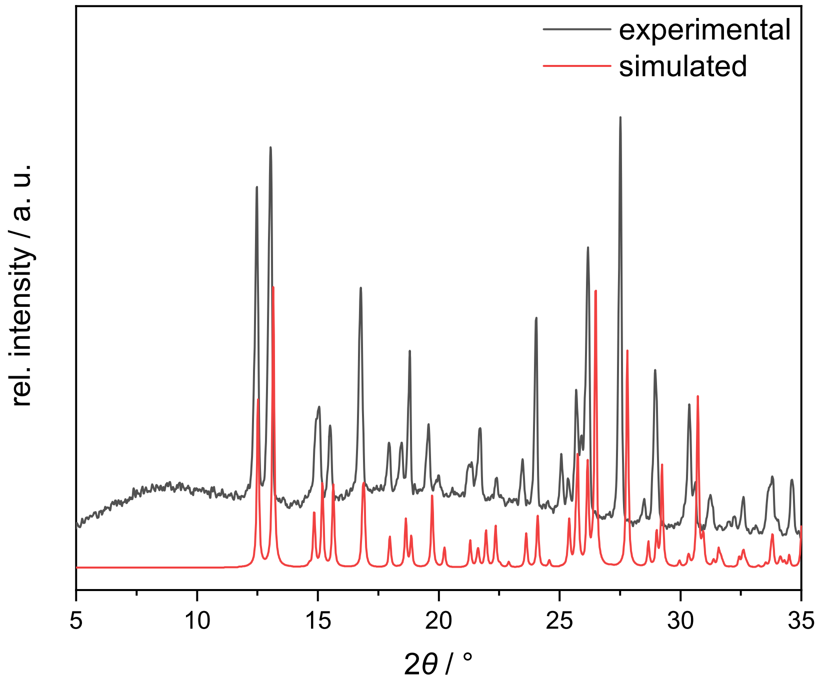

Figure S4: Experimental and simulated powder X-ray diffractogram of **1**.

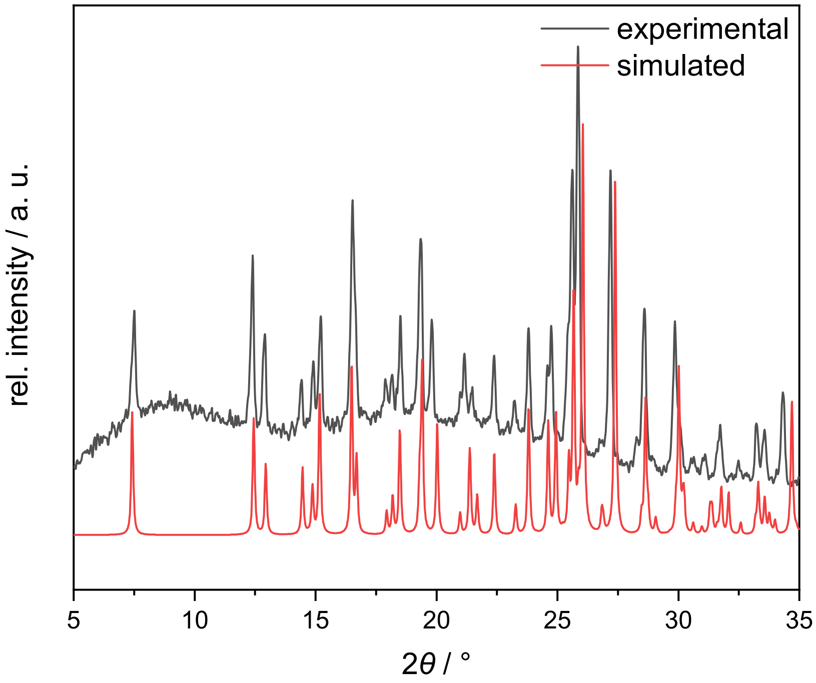

Figure S5: Experimental and simulated powder X-ray diffractogram of **2**.

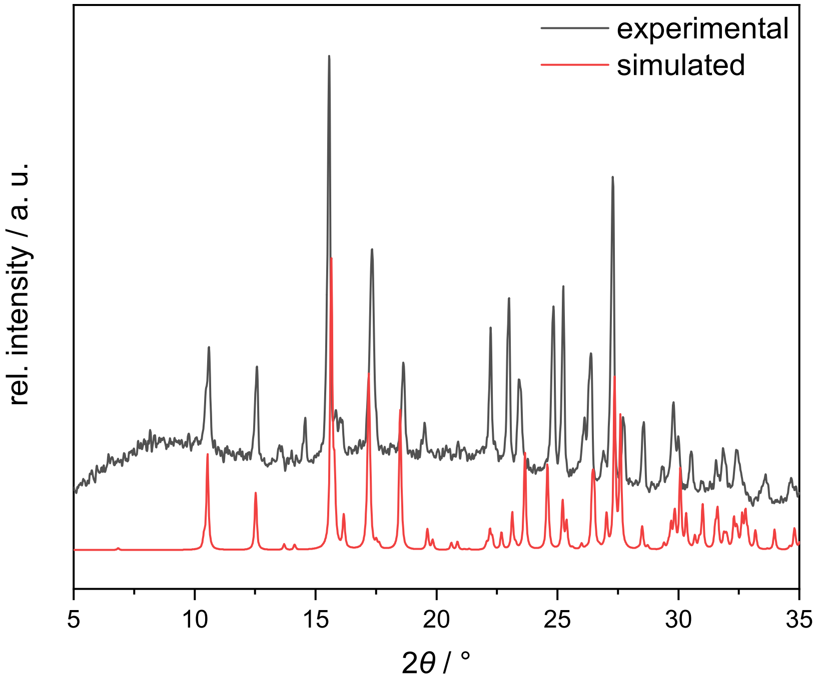

Figure S6: Experimental and simulated powder X-ray diffractogram of **3**.

References

(S1) Spek, A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* **2009**, *D65*, 148–155.

(S2) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr.* **2016**, *B72*, 171–179.