1.4 Crystal Engineering Based on Short Hydrogen Bonds: Co-Crystallization of a Highly Nonlinear Optical Merocyanine Dye with Nitrophenol Derivatives

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The use of hydrogen bonds as a steering force is now beginning to emerge as one of the most important strategies in crystal engineering. Compared with the strong interaction of covalent bonds with a stabilization around 20~100 kcal/mol, a single hydrogen bond with a bonding enthalpy of less than 5 kcal/mol is not always perceived to be strong enough to dominate intermolecular aggregates. In one class of hydrogen bonds, however, so-called "very short", "very strong" or "symmetric" hydrogen bonds, the bonding energy could be unusually strong, even comparable to that of covalent bonds. Most of these kinds of hydrogen bonds have been found in the aggregates of small molecules or ions in crystals.

We found that the short hydrogen bond has the advantages of high bonding strength and high degree of flexibility, which is an interesting design element for crystal engineering using optimised nonlinear optical chromophores. Our newly developed co-crystals based on this approach show improved physical properties as compared to the crystals of its components. As an example, we first grew nice optical quality crystals of the merocyanine dye, which is one of the chromophores with the largest potential for second-order NLO, by co-crystallization with nitrophenol derivatives. These co-crystals show good crystallinity, easy crystal growth, and high melting points.