Crystal engineering based on short hydrogen bonds; cocrystallization of a highly nonlinear optical merocyanine dye with nitrophenol derivatives

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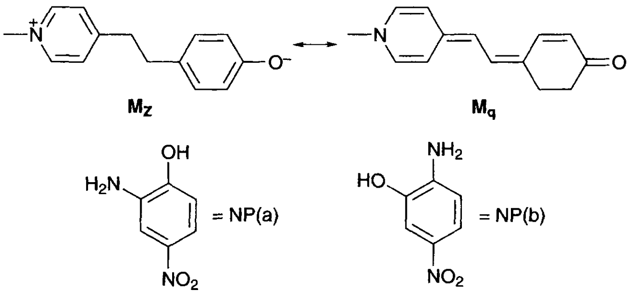
Short hydrogen bonds [$R_{\mathrm{O-H-O}}$ *ca.* 2.46(1) Å, $R_{\mathrm{H-O}}$ *ca.* 1.2(1) Å] in cocrystals of merocyanine dyes and nitrophenol derivatives are an interesting design element for crystal engineering in both framework and application-oriented considerations due to their high bonding strength and high degree of flexibility.

The rational design and synthesis of specific structural aggregates in the solid state, crystal engineering,[1] have been recently motivated by framework (symmetry, topology, and network properties)[2] or application-oriented [nonlinear optics (NLO), ferromagnetics, electronics][3] considerations. For NLO applications, crystal engineering has been successful for nitroaniline derivatives in the last decade.[4] Meanwhile, the interest for further development has been concentrated on crystals (*i*) containing more active NLO chromophores with highly extended π-electron conjugated systems, (*ii*) with certain chromophoric arrangements for favourable physical properties, and (*iii*) with good crystallinity.[5]

The use of hydrogen bonds as a steering force is now beginning to emerge as one of the most important strategies in crystal engineering.[6] A single hydrogen bond is not always perceived to be strong enough to dominate intermolecular aggregates.[6–8] Instead, cooperative hydrogen bonds or hydrogen bond networks are widely used in assemblies of supramolecular aggregates.[6,8] In contrast, there is another class of hydrogen bonds, so-called 'very short',[9a] 'very strong'[9b] or 'symmetric'[9c] hydrogen bonds, in which the bonding energy could be unusually strong, even comparable to the lower limit of covalent bonds. Most of these kinds of hydrogen bonds have been found in the aggregates of small molecules or ions in crystals.[9a,b] In this work, we show that with a short hydrogen bond, highly NLO active chromophores, merocyanine dyes and nitrophenol derivatives are assembled as salt or semi-salt crystals, leading to improvement of crystallinity and interesting physical properties.

Our interest in the merocyanine dye, **M**, was motivated by the fact that **M** is one of the best NLO chromophores with a very large molecular first-order hyperopolarizability and very good photo and thermal stabilities.[10] The merocyanine dye electronic structure depends on the relative contribution of its two resonance structures, a quinonoid form, $\mathbf{M_q}$, and a zwitterionic form, $\mathbf{M_z}$, the relative amounts of which are very sensitive to modification of its dielectric environment.[11] It was found that the crystallinities of compound **M** and its derivatives were too poor to grow single crystals with good optical quality. One of the strategies in crystal engineering is to dissect and insulate different types of intermolecular interactions from one another[1] which motivated us to introduce a guest molecule to cocrystallize with **M** to improve its crystallinity and to induce a certain packing motif. For this purpose, nitroaniline and nitrophenol derivatives, which may interact with each other or/and with **M** by means of hydrogen bonds, were chosen as guest molecules. They are also traditional NLO chromophores, which may even increase the density of useful NLO elements.[4]

Cocrystallization of equimolar amounts of nitroaniline (or nitrophenol) derivatives and **M** was carried out by cooling of methanol or ethanol solutions or slowly evaporating the solvents. Nitroaniline derivatives seem not to interact with **M** but crystallize independently. In contrast, cocrystallization of nitrophenol derivatives, such as 2-amino-4-nitrophenol [NP(*a*)] and 2-amino-5-nitrophenol [NP(*b*)], with **M** yielded red or black crystals in the form of needles, plates or bulk structures. These crystals can be grown large enough (3 × 3 × 3 mm) for optical devices. Furthermore, we found that **M** could cocrystallize with most phenol derivatives with good crystallinity. Insight into the cocrystallization can be obtained from the single-crystal X-ray structures of the cocrystals **1** [NP(*a*)M] and **2** [NP(*b*)M].†



1 = NP(a)•**M**; **2** = NP(a)•**M**

There are two dimeric aggregate structures in cocrystals **1** and **2** (Figs. 1 and 2). First, we have the hydrogen-bonded dimeric cation [*MHM*]$^+$ and anion [*XHX*]$^-$ (Fig. 1) in cocrystal **1**. Second, there is the hydrogen-bonded neutral dimeric aggregate, *MHX*, formed between **M** and NP(*b*) in cocrystal **2** (Fig. 2). Note that the three types of aggregates, [*MHM*]$^+$, [*XHX*]$^-$ and *MHX*, show an attractive common feature, namely

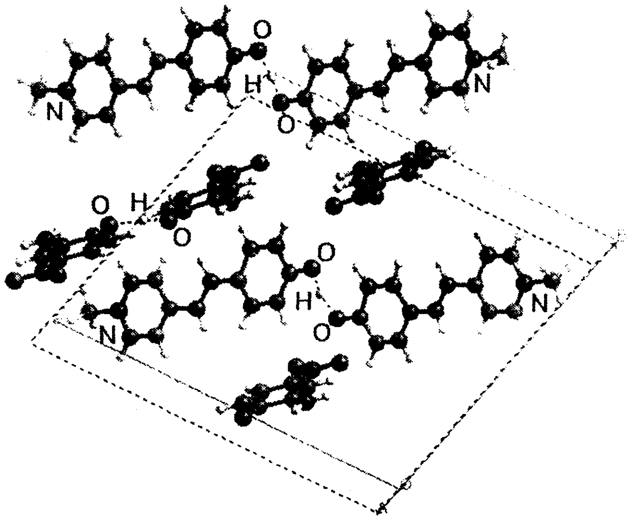


Fig. 1 Dimeric cations [*MHM*]$^+$ and anions [*XHX*]$^-$ bound by short hydrogen bonds in alternating layers in the lattice of crystal **1**

that the hydrogen bonds between the two phenolic oxygen atoms, $R_{O–H–O}$, are very short, 2.46(1) Å, and that the protons are nearly equidistant to the two phenolic oxygen atoms [$R_{H–O}$ *ca.* 1.2(1) Å]. According to an empirical evaluation,[12] the bonding energy of this kind of short hydrogen bond could be unusually strong [20 kcal mol^{-1} (cal = 4.184 J)], comparable to the lower limit for covalent bonds. These aggregates play important roles in construction of the three-dimensional structures of the cocrystals (see below), leading to their high melting (decomposition) points: 222(2) °C (**1**), 205(2) °C (**2**).

In cocrystal **1**, the dimeric cation $[MHM]^+$ and the anion $[XHX]^-$ are both almost coplanar, with an angle between the two **M** (or **X**) planes of only 7°. The three-dimensional structure of cocrystal **1** consists of alternating layers of cations and anions (Fig. 1). The dimeric cation $[MHM]^+$ lies in a plane with an angle of about 65° to the plane of the dimeric anions $[XHX]^-$. The charge-transfer axes ($O \rightarrow N$) of the highly hyperpolarizable chromophores **M** are almost antiparallel to one another with an angle of 178.8° between them, which is an ideal packing for third-order NLO applications. Hence crystal **1** is a special organic salt consisting of alternating layers of the dimeric cation $[MHM]^+$ and the dimeric anions, $[XHX]^-$, respectively, with strong Coulombic interactions that help in building up stable structures.

In the neutral dimeric aggregate, *MHX*, of cocrystal **2**, the chromophores *M* and *X* share one proton. Therefore *M* and *X* each possess half a negative charge, $M^{-0.5\,\delta}$ and $X^{-0.5\,\delta}$. Hence crystal **2** is only a semi-salt with the 'symmetric' hydrogen-bonded aggregate, $M^{-0.5\,\delta}H^{+1}X^{-0.5\,\delta}$. In this dimeric aggregate, the *M* plane is nearly perpendicular (86°) to the *X* plane. The *M* and *X* planes build alternating layers in the three dimensional structure of the cocrystal **2**.

In point of view of supramolecular synthons in crystal engineering,[13] cocrystallization of nitrophenol derivatives and **M** through the interaction with the phenolic group is a synthon between a hard acid and a hard base to yield a salt or a semi-salt. In contrast, the hardness of the amino group of nitroaniline derivatives is much weaker than that of the phenolic group of nitrophenol derivatives, leading to less successful cocrystallization properties of nitroaniline derivatives with **M**.

Note that the angle between the two charge-transfer axes ($O \rightarrow N$ of **M** and $NO_2 \rightarrow NH_2$ of *X*) is 36.8°, and the electron-donor groups (phenolic oxygen atoms) of the chromophores **M** and *X* are very close to each other in $M^{-0.5\,\delta}H^{+1}X^{-0.5\,\delta}$. It is believed that the electron conjugation between **M** and *X* is enhanced in $M^{-0.5\,\delta}H^{+1}X^{-0.5\,\delta}$, which can enhance the molecular first-order (β) and second-order (γ) hyperpolarizabilities. Additionally, by examination of the molecular structures of **M** in crystals with the long and short hydrogen bonding to the phenolic oxygen atom, we found that the bond lengths, C–O, of **M** are significantly different.[‡] This means that the balance of the resonance structures of **M**, $\mathbf{M_q}$ and $\mathbf{M_z}$ will be shifted when the proton is driven close to the phenolic oxygen atom.

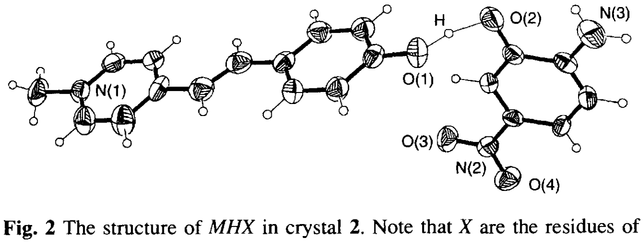


Fig. 2 The structure of *MHX* in crystal **2**. Note that *X* are the residues of NP(*a*) or NP(*b*) where protons are removed from the phenolic groups.

In summary, compared with a covalent bond for a molecule, the short (O···H···O) hydrogen bond for supermolecules shows not only the high bonding strength but also a higher degree of flexibility, which can adapt its bonding directions to fit the three dimensional packing for stabilization of the crystals. For example, it can drive chromophore aggregates into a co-plane such as in cocrystal **1**, or into planes perpendicular to each other such as in crystal **2**. Hence, with the advantages of the high bonding strength and high degree of flexibility, the short hydrogen bond is an interesting design element for crystal engineering in both framework and application-oriented considerations.

Footnotes

[†] *Crystal data*: for **1**, $C_{20}H_{19}N_3O_4$, $M = 365.4$, triclinic, space group $P1$; $a = 8.714(14)$, $b = 13.67(2)$, $c = 16.18(2)$ Å, $\alpha = 103.75(11)$, $\beta = 97.71(11)$, $\gamma = 101.92(13)°$, $U = 1798(5)$ Å^3, $Z = 4$, $D_c = 1.350$ g cm^{-3}, $R = 0.0478$, $wR = 0.0523$. For **2**, $C_{20}H_{19}N_3O_4$, $M = 365.4$, monoclinic, space group $P2_1/c$; $a = 9.087(8)$, $b = 10.208(9)$, $c = 19.14(3)$ Å, $\beta = 103.23(8)°$, $U = 1728(3)$ Å^3, $Z = 4$, $D_c = 1.404$ g cm^{-3}, $R = 0.0355$, $wR = 0.0438$, $w^{-1} = \sigma^2(F) + 0.0010\,F^2$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/104.

[‡] There is a structure of crystal $\mathbf{M}\cdot H_2O$,[14] in which a hydrogen bond occurs between H_2O and the phenolic oxygen of **M** with a hydrogen bonding length of $R_{O–H–O} = 2.78$ Å, and the C–O bond length of **M** is $R_{C–O} = 1.304(5)$ Å. In contrast, in cocrystals **1** and **2**,[†] the strong hydrogen bonds between the phenolic oxygen, $R_{O–H–O} = 2.46(1)$ Å, lead to longer C–O bonds of **M**, such as $R_{C–O} = 1.34(1)$ Å. In this case, the contribution of the resonance structure, $\mathbf{M_z}$ of **M**, should increase.

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Received, 5th March 1996; Com. 6/01585I