A Novel and Perfectly Aligned Highly Electro−Optic Organic Cocrystal of a Merocyanine Dye and 2,4-Dihydroxybenzaldehyde

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Organic nonlinear optical (NLO) materials, both single crystals and polymers, based on extended π-electron systems have been proposed for electro−optical applications, especially for fast electro−optical modulation, due to the large electronic contribution to the electro−optic effects and the low dielectric constant of organic materials.[1] Two key parameters of optimal electro−optical organic materials are that they contain stable chromophoric molecules with large molecular hyperpolarizabilities and that these molecules are aligned with the vector part of the molecular hyperpolarizabilities parallel to each other in a non-centrosymmetric packing.[2] Compared with polymer materials,[3] organic crystals are of great interest since a reliable and a time independent orientation of NLO chromophores in the lattice can be imposed.

Difficulties of organic crystals for practical second-order NLO applications are due to the fact that most of these chromophores (90% of the achiral organic molecules) crystallize centrosymmetrically, leading to a cancellation of the second-order NLO effects. In addition, most optimized NLO chromophores normally show poor crystallinity, which limits the growth of good quality crystals. In this work we report on a novel organic electro−optic crystal in which the dipole moments of the NLO chromophores (merocyanine, **M2**, and protonated merocyanine, [H-**M2**]⁺) are in an antiparallel orientation similar to that in a pseudo-centrosymmetric structure. However, based on a proton asymmetry, the vector parts of the first hyperpolarizabilities of NLO chromophores (**M2** and [H-**M2**]⁺) are in a completely parallel orientation. This work also presents a successful example to improve the crystallinity of a highly hyperpolarizable chromophore.

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 hyperpolarizability, $\beta_{\text{vec}}^{\text{M}}$,[4] and with very good photo and thermal stabilities. The merocyanine dye's electronic structure depends on the relative contribution of its two resonance structures, a quinonoid form, $\mathbf{M_q}$, and a zwitterionic form, $\mathbf{M_z}$, which are very sensitive to a modification of its dielectric environment.[5] In a polar medium, the highly polar aromatic resonance structure $\mathbf{M_z}$ is stabilized relative to the quinonoid form $\mathbf{M_q}$. This leads to a dipole moment of the excited state ($\mu_{\text{e}}^{\text{M}} = +13.7$ D) that is smaller than that of the

Mq ↔ **Mz**

M1: R = CH₃
M2: R = CH₂CH₂OH

DB

1 = **M2**·**DB**·0.5H₂O = Mero-DBA
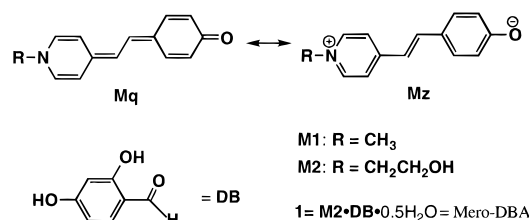
ground state ($\mu_{\text{g}}^{\text{M}} = +22.6$ D), giving rise to a negative $\Delta\mu^{\text{M}}$ (-8.9 D).[6a] This results in a negative solvatochromic behavior[7] and a negative first-order molecular hyperpolarizability, $-\beta_{\text{vec}}^{\text{M}}$.[6] This negative value implies that $\beta_{\text{vec}}^{\text{M}}$ is in an antiparallel orientation to the ground state dipole moment of **M**, $\mu_{\text{g}}^{\text{M}}$. These properties are different from most stilbenoid derivatives, such as the protonated form of **M**, 4-hydroxy-4′-*N*′-methylstilbazolium cation ([H-**M**]⁺), which shows a positive first-order hyperpolarizability value.[6a]

Hence it is of considerable interest to develop potentially useful nonlinear optical crystals based on merocyanine dyes. However, in addition to a centrosymmetric packing, it was found that the crystallinity of the compound **M** and its derivatives was 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[8] to induce a desired chromophoric alignment and to improve crystallinity, which motivated us to introduce a guest molecule to cocrystallize with **M**. We have found that by cocrystallization with nitrophenol derivatives based on the short hydrogen bond the cocrystal properties of the merocyanine dye, **M1**, are greatly improved.[9]

In this work, cocrystallization of equimolar of 2,4-dihydroxybenzaldehyde (**DB**) and **M2** was carried out by cooling of methanol solutions or slowly evaporating the solvent. Deep red cocrystals **1** in the form of needles were obtained. The good optical quality of these crystals was checked with polarized light microscopy to show homogeneous extinction. The cocrystal **1** shows a strong second-harmonic generation (SHG) signal, comparable to that of 2-(*N*-prolinol)-5-nitropyridine (PNP)[1a] in the powder test at 1.3 μm, suggesting a highly non-centrosymmetric molecular arrangement of the chromophores in the cocrystal lattice.

Single-crystal X-ray structure analysis shows that the unit cell of cocrystal **1** contains two molecules of **M2** and **DB** together with one H₂O molecule, in a non-centrosymmetric packing with space group $P1$.[10] The frameworks, except for the hydrogen bonds of **M2** as well as **DB**, are oriented in an antiparallel fashion with respect to each other and appear as pseudo-"centrosymmetric" structures within a unit cell (see Figure 1a). Further crystal structure analysis reveals that in the three-dimensional structure of the cocrystal **1** there are two types of hydrogen-bonded aggregates formed by **DB** and **M2**, respectively. Importantly, the proton plays different roles in the two aggregates.

The dimeric **DB** aggregate (Figure 1a) is formed by two **DB** molecules which loose a proton to self-assemble as a hydrogen-

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(10) (a) Crystal data for **1**, $C_{44}H_{44}N_2O_{11}$: red prismatic crystal, triclinic, $P1$, $a = 8.262(3)$ Å, $b = 10.039(4)$ Å, $c = 13.491(4)$ Å, $\alpha = 69.73(2)°$, $\beta = 82.99(11)°$, $\gamma = 66.06(3)°$, $V = 959.1(6)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.345$ mg cm⁻³, $R = 0.0291$, w$R = 0.0397$, GOF = 1.19, residual electron density $0.12/-0.12$ eÅ⁻³. (b) H₂O in crystal **1** is lost at $T = 90(1)$ °C, measured by thermal gravitate (TG) analysis.
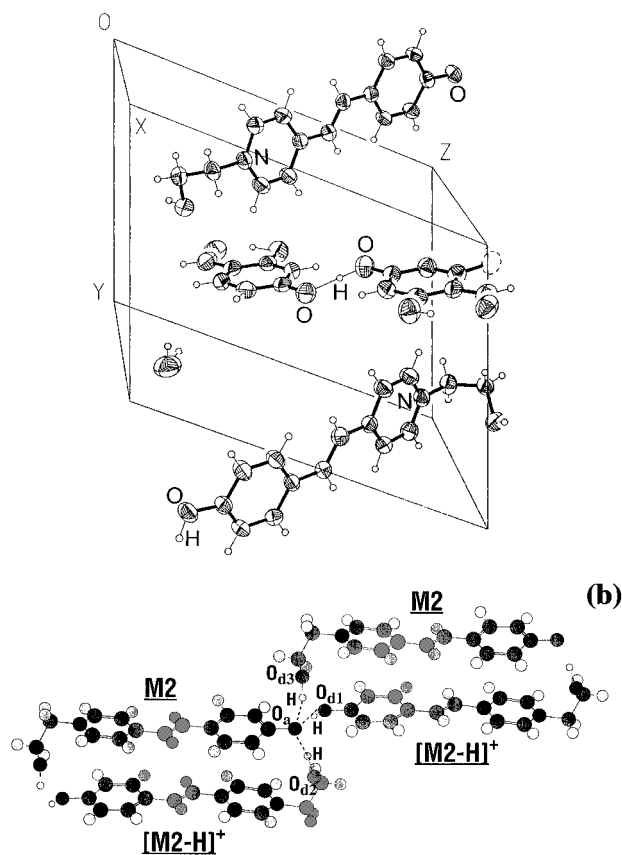
Figure 1. (a) Shows a unit cell of crystal **1**, where the non-hydrogen-bonded molecular frameworks of **M2**, as well as **DB** (assembled as a dimeric aggregate, [XHX]⁻), are oriented in an antiparallel fashion with respect to each other and appear as pseudo-"centrosymmetric" structures. Note that disorder of the oxygen atom of the **DB** molecule was found (shown as dotted circle). (b) Shows the **M2** aggregate with a four-center (oxygen atoms) three-hydrogen bond.

bonded dimeric anion [XHX]⁻ (X is an anion of **DB** which lost one proton), in which the distance between the two phenolic oxygen atoms, R_{O-H-O}, is very short, 2.46(1) Å, and the proton stays nearly equidistant to the two phenolic oxygen atoms (R_{H-O} ∼ 1.2(1) Å), as determined by Fourier synthesis . This short hydrogen bond is called a "very short",[11a] "very strong",[11b] or "symmetric"[11c] hydrogen bond, because the bonding energy is unusually strong (20 kcal/mol),[12] even comparable to the lower limit of that of covalent bonds.

On the contrary, the **M2** aggregate (see Figure 1b) is formed by four **M2** molecules which accept two protons to self-assemble as a multiple hydrogen bond network kept together by a four-center (oxygen atoms) three-hydrogen bond.[13] Compared with a short hydrogen bond in the dimeric anion [XHX]⁻ the interaction of these multiple hydrogen bonds leads to an increase in the length of the hydrogen bond between two phenolic oxygen atoms of the **M2**, R_{Oa-Od1}. It also causes the proton not to stay at the center but to localize at one of the phenolic oxygen atoms of **M2**.[14] Hence, both the neutral merocyanine, **M2**, and cationic protonated merocyanine, [H-**M2**]⁺, exist in this aggregate (see Figure 1). This can be further shown by comparing the bond

lengths of **M2** and [H-**M2**]⁺. For example, the C−O bond length in **M2** ($R_{C-O}^- = 1.329(5)$ Å) is obviously shorter than that of the related C−OH bond length of [H-**M2**]⁺ ($R_{C-OH} = 1.351(5)$ Å). These results are in agreement with the fact that the significant contribution of the resonance structure **M_q** of **M** should shorten the bond C−O⁻. In addition, the structural details of **M2** and [H-**M2**]⁺ in crystal **1** are in a good agreement with the structure found in the neutral merocyanine crystal ($R_{C-O} = 1.309(5)$ Å)[15] and the corresponding cation, the protonated merocyanine crystals ($R_{C-OH} = 1.352(4)$ Å),[16] respectively.

The highly active SHG efficiency of the cocrystal **1** in the Kurtz and Perry powder test further convinced us that the vector part of first-order molecular hyperpolarizabilities of the chromophores in the cocrystal add up to contribute to the macroscopic susceptibilities. Note that in the unit cell of crystal **1** the ground-state dipole moments of **M2** and [H-**M2**]⁺, μ_g^{M2} and $\mu_g^{[H-M2]+}$, are almost completely antiparallel to one another with a dihedral angle of 189.4(5)° between them.[17] In contrast, the vector parts of the first-order hyperpolarizabilities of **M2** and [H-**M2**]⁺, β_{vec}^{M2} and $\beta_g^{[H-M2]+}$, are almost completely parallel to one another with a dihedral angle of 0.6(5)° between them,[17] which is the ideal packing for an electro−optic crystal.
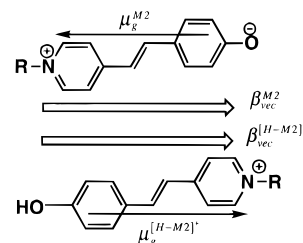
Two distinctive features are noted in the cocrystal structure. One is that the **M2** and the **DB** aggregates are self-assembled as stable elements by strong hydrogen bonds, such as a multiple hydrogen bonding network and the short hydrogen bonds, respectively. The second one is that the three-dimensional structure of cocrystal **1** consists of alternating layers of the **M2** and **DB** aggregates with a positive and negative charge, respectively, resulting in Coulombic interactions between the alternating layers. In addition water molecules also link the alternating layers with hydrogen bonds.

In summary, we have demonstrated for the first time to our knowledge that an electro−optic crystal with an ideal chromophoric alignment and constructively reinforced first-order hyperpolarizability, β, can be prepared by taking advantage of the antiparallel arrangement of two chrmophores bearing opposite sign of the hyperpolarizability. Moreover, the cocrystal **1** is a novel interesting electro−optic crystal due to completely parallel vector parts of the first-order molecular hyperpolarizabilities of the chromophores **M2** and [H-**M2**]⁺ in the cocrystal. The stable **M2** and **DB** aggregates self-assembled by strong hydrogen bonds and the alternating layers isolated from each other in the three-dimensional structure are the key parameters to improve the merocyanine dye's crystallinity in cocrystal **1**.

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(13) The phenolic oxygen (O$_a$) of **M2** plays the role of a hydrogen bond acceptor and bonds with three hydrogen-bond-donating groups (HO group) with three different bonding lengths, $R_{Oa-HOd1}$ = 2.56(1) Å (R_{H-Oa} ∼ 1.6(1) Å), $R_{Oa-HOd2}$ = 2.59(1) Å (R_{H-Oa} ∼ 1.5(1) Å), and $R_{Oa-HOd3}$ = 2.75(1) Å (R_{H-Oa} ∼ 1.6(1) Å).

(14) Here hydrogens at oxygen atoms were taken from a difference Fourier synthesis and refined isotropically. In addition, low-temperture neutron diffraction data confirmed that the proton will be asymmetric and fixed at the oxygen atom when $d_{O-H\cdots O}$ = 2.55 Å (see: Steiner, T.; Saenger, W. *Acta Crystallogr.* **1994**, *B50*, 348−357).

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