Nonlinear optical co-crystal of analogous polyene chromophores with tailored physical properties†

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A new organic nonlinear optical co-crystal based on analogous configurationally locked polyene chromophores with noncentrosymmetric packing exhibits a large macroscopic second-order nonlinearity with tailored physical properties.

Crystallization of organic molecules with extended π-conjugation showing large nonlinearity is still a challenging topic. In particular, for second-order nonlinear optical applications a noncentrosymmetric arrangement of long π-conjugated chromophores in the crystals is required.[1] However, due to the tendency for antiparallel aggregation of highly nonlinear optical molecules with large dipole moment, crystal engineering strategies for acentric crystals are more complex than in general for small molecules. In order to overcome this limitation many different approaches have been investigated such as use of molecular asymmetry, chirality, hydrogen bonds, strong Coulomb interactions, non-rod-shaped π-conjugated cores, octupolar compounds and photochromism.[2,3]
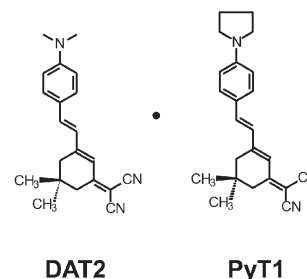
Another interesting approach for achieving acentric crystals is supramolecular synthetic co-crystallization. It offers more design feasibility as one or both constituent molecules can be modified to fit one another and to acquire the desirable macroscopic properties in the solid state. Furthermore, the physical properties such as the melting temperature and solubility, as well as the nonlinear optical and electro-optical properties can be improved or changed compared to those of single-component crystals.[2] Most studies have introduced a non-analogous guest molecule, which was usually a unit that is not nonlinear optically active, to co-crystallize with nonlinear optical host chromophore by ionic bonds and/or strong hydrogen bonds.[4–7] Except the merocyanine-based co-crystals,[4] most acentric co-crystals have shown relatively small macroscopic nonlinearities of less than two orders of magnitude second harmonic generation (SHG) efficiency of the urea standard. Furthermore, application of melt-based growth techniques for acentric co-crystals is often limited due to an insufficient thermal stability of the ionic forms, similar to that of the highly nonlinear optical ionic crystal DAST (4′-dimethylamino-N-methyl-4-stilbazolium tosylate) and its derivatives.[8] Acentric co-crystallization of analogous chromophores (*i.e.* the guest and the host molecule are both nonlinear optical chromophores with similar chemical structures) has not yet been reported. Recently a series of configurationally locked polyene (CLP) chromophores has been developed. They have large macroscopic second-order nonlinear susceptibilities, good thermal stability and the growth of single crystalline thin films by melt-based techniques has been demonstrated.[9] In this work, we report for the first time to our knowledge on an acentric co-crystal of analogous polyene chromophores with tailored physical properties.

The chemical structures of the constituent chromophores are shown in Fig. 1. They consist of the configurationally locked phenylhexatriene bridge with different electron donor groups, dimethylamino group for DAT2 and pyrrolidino group for PyT1. The ring in the π-conjugated polyene was introduced to improve the thermal stability of the chromophores.[9,10] The wavelength of maximum absorption is λ_{max} = 502 nm for DAT2 and λ_{max} = 521 nm for PyT1 in chloroform solutions. According to the so-called nonlinearity–transparency trade-off,[2] both chromophores show similar and large molecular nonlinearity of about $\beta_z = 1075 \times 10^{-40}$ m⁴ V⁻¹ at wavelength 1907 nm and a large dipole moment of about 3.3×10^{-29} C m.[9] In thermal gravimetric analysis (TGA) under nitrogen atmosphere at a scan rate of 10 °C min⁻¹, both the constituent chromophores exhibit high thermal stability with a decomposition temperature T_d of 290 °C.

Co-crystallization of equimolar amounts of the analogous DAT2 and PyT1 chromophores was carried out by the slow evaporation method. Due to a poor solubility of DAT2 molecule in methanol both chromophores were first dissolved completely in methylene chloride and then mixed with methanol (methylene chloride : methanol ∼ 1 : 1). The solution was kept at a constant temperature (30 °C) for the nucleation and growth. Using this method, red plate-like crystals were obtained.

Mixing several analogous chromophores with large dipole moments, the constituent molecules usually did not co-crystallize due to the tendency of dipole–dipole aggregation and the complicated intermolecular interactions, (*i.e.*, they formed an amorphous solid or different chromophores crystallized independently).

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Fig. 1 Chemical structures of the constituent analogous polyene chromophores.

In some cases co-crystals were formed, but with a centrosymmetric packing.‡ In order to check whether the crystals grown from DAT2 and PyT1 mixtures are co-crystals or pieces combining two single-component crystalline domains, we investigated them by thin layer chromatography, powder X-ray diffractometry and differential scanning calorimetry (DSC). Using thin layer chromatography, one piece of the grown crystal was shown to contain two components corresponding to each of the constituent molecules DAT2 and PyT1, implying that the grown crystals consist of both chromophores. Fig. 2 shows DSC thermodiagrams of the crystals grown. If the grown crystals were mechanical mixtures of two single-component crystals, the thermodiagram would show two independent sharp melting transitions at the temperatures of 178 °C and 235 °C, corresponding to the single-component DAT2 and PyT1 crystals, respectively. However, the grown crystals exhibit a melting transition that is between the transitions of two single-component crystals. Furthermore, the powder X-ray diffraction pattern of the grown crystals does not show a mixed pattern of two single-component crystals. Therefore, the grown DAT2–PyT1 crystals are evidently co-crystals of two analogous polyene chromophores.

The crystalline structure of the single-component DAT2 and PyT1 crystals and the DAT2–PyT1 co-crystal were determined by X-ray diffraction analysis. The single-component crystals with different donor groups, dimethylamino group for DAT2 and the pyrrolidino group for PyT1, have similar monoclinic $P2_1$ crystal structure (i.e., same space group and symmetry, similar cell parameters and crystallographic angles)§ and similar orientation of molecules based on weak hydrogen-bonds in the crystals (Fig. 3). The DAT2–PyT1 co-crystal has a triclinic noncentrosymmetric structure with space group symmetry $P1$. The constituent DAT2 and PyT1 chromophores form a noncentrosymmetric molecular pair aligned along the crystallographic polar b-axis as shown in Fig 4a. Compared to the monoclinic single-component crystals, the triclinic co-crystal has similar cell parameters and crystallographic angles, which are close to the monoclinic system ($\alpha = 89.87(3)°$, $\gamma = 90.02(3)°$). Moreover, the orientation of the constituent molecules is also similar, in the co-crystal only the two-fold rotational symmetry around the b-axis is not present since the molecular pairs consist of two different chromophores. The crystal structure of the co-crystal is therefore pronouncedly
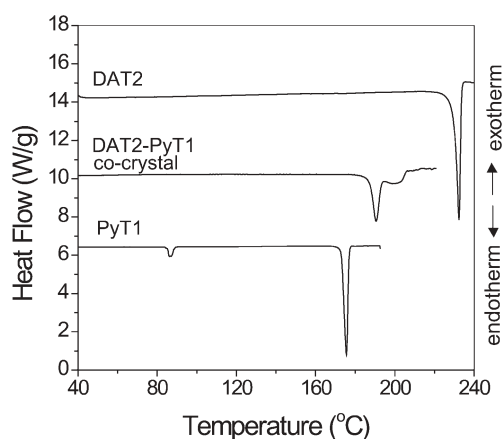
Fig. 2 DSC thermodiagrams of single-component PyT1 and DAT2 crystals and DAT2–PyT1 co-crystal.
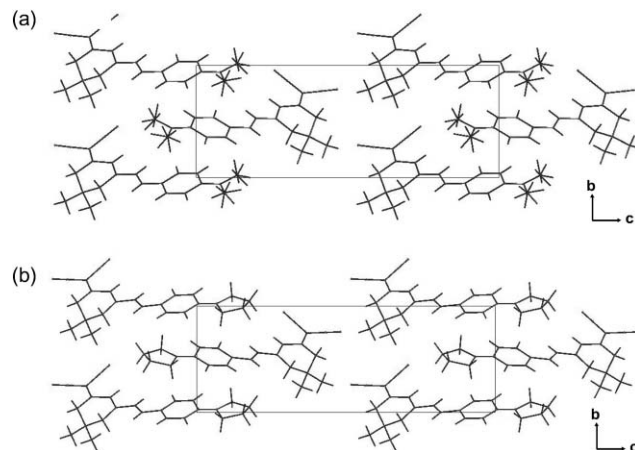
Fig. 3 Crystal packing diagram projected along the a-axis for monoclinic $P2_1$ phase of single-component DAT2 (a) and PyT1 (b) crystals. The occupancy of hydrogen of the dimethylamino $(CH_3)_2N-$ donor groups in DAT2 is 0.5, which is due to rotational CH_3 disorder modeled by the two most probable situations.
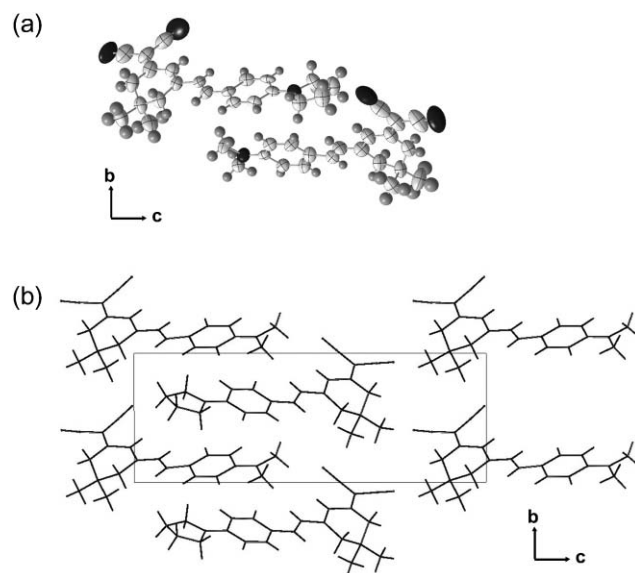
Fig. 4 (a) Noncentrosymmetric molecular pair of the DAT2 and PyT1 chromophores aligned along the crystallographic polar b-axis in crystalline state. (b) Crystal packing diagram projected along the a-axis for triclinic $P1$ phase of DAT2–PyT1 co-crystals.

pseudosymmetric $P2_1$. The disordered monoclinic option was considered in the X-ray analysis as well, but was ruled out because unsatisfactory results were obtained. Finally the triclinic ordered structure is confirmed by $Z = 1$ and by the fact that no trace of disorder could be detected in the refined triclinic structure.

To investigate the macroscopic nonlinearity of the grown co-crystal the Kurtz and Perry powder test[11] has been performed at a fundamental wavelength of 1.9 μm. The grown co-crystals exhibit very strong SHG signals of 130 times respective to that of urea, larger than the single-component PyT1 crystal (80 times) and similar as the single-component DAT2 crystal (140 times). To our knowledge this is the first observation of an acentric co-crystal of analogous chromophores with large macroscopic nonlinearity.
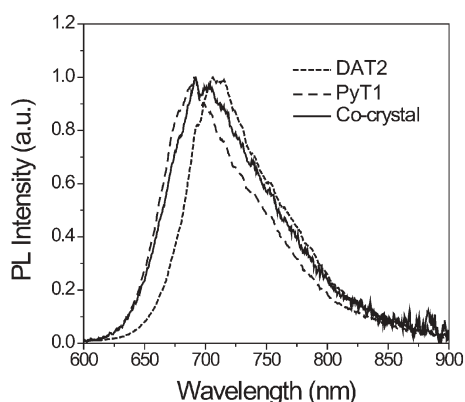
Fig. 5 Photoluminescence (PL) spectra (normalized scale) of single-component DAT2 (dotted line) and PyT1 (dashed line) crystals and DAT2–PyT1 co-crystal (solid line).

The physical properties as well as the macroscopic nonlinearity of the co-crystals of DAT2 and PyT1 are improved and changed compared to those of single-component crystals. The co-crystal still retains the advantage of a large SHG efficiency of the DAT2 crystal and a good thermal stability of both constituent molecules. By introducing the PyT1 chromophore with a lower melting temperature T_{m} and higher solubility in methanol as compared to DAT2, the melting temperature T_{m} of the co-crystal decreases (see Fig. 2) and the solubility in methanol increases with respect to the single-component DAT2 crystal. The lower melting temperature T_{m} is therefore beneficial for melt crystal growth and is high enough for environmental stability without sublimation at room temperature. The increased solubility is advantageous for solution crystal growth because DAT2 with a poor solubility in methanol suffers from a poor material transport and thus slow crystal growth.

Like the noncentrosymmetric DAT2–PyT1 co-crystal, the co-crystal of hydroxypiperidino-based polyene analogues, with centrosymmetric crystal structure,‡ also shows changes in its physical properties compared to those of single-component crystals. The melting temperature T_{m} of 193 °C for the co-crystal is between the values of 155 °C and 203 °C for the single-componenet crystals. The solubility is also changed. Due to a very high solubility the 4-hydroxypiperidine-based chromophore does not nucleate in methanol, but with the 3-hydroxypiperidine-based analogous chromophore having a lower solubility nucleation into a co-crystalline form is relatively easy.

Co-crystallization of analogues will also result in a modification of other physical properties beside the macroscopic optical nonlinearity, melting temperature and solubility. One example is the photoluminescence efficiency and wavelength. The long π-conjugated polyene molecules like our constituent chromophores of the co-crystal are well-known as red photoluminescence materials.[12] As shown in Fig. 5 the emission maximum wavelength λ_{em} of the co-crystal is between the 710 nm value for the DAT2 crystal and 692 nm for the PyT1 crystal, using an excitation wavelength of 550 nm.

In summary, we report for the first time to our knowledge on an acentric co-crystal of analogous polyene chromophores with a large macroscopic optical nonlinearity of about two orders of magnitude greater SHG signal than that of urea. Co-crystallization of analogous molecules is a very efficient crystal engineering approach for growing high quality acentric crystals with improved and tailored nonlinear optical and other physical properties.

Notes and references

‡ Example of a centrosymmetric co-crystal of two polyene analogues (isomers) 2-{3-[2-(4-(4-hydroxypiperidino)phenyl]vinyl]-5,5-dimethylcyclohex-2-enylidene}malononitrile (PiT2) and 2-{3-[2-(4-(3-hydroxypiperidino)-phenyl]vinyl]-5,5-dimethylcyclohex-2-enylidene}malononitrile (PiT3). **PiT2–PiT3 co-crystal (2 : 1)**: needles, $C_{24}H_{27}N_3O$ (one component), M_{r} = 372.48 (one component), monoclinic, space group $P2_1/c$, a = 5.8580(12) Å, b = 12.230(2) Å, c = 29.332(6) Å, α = 90°, β = 93.98(3)°, γ = 90°, V = 2096.4(7) Å^3, Z = 4, T = 295 K, CCDC 295447†.

§ Single crystal structures: **DAT2–PyT1 co-crystal**: plate, $C_{44}H_{48}N_6$, M_{r} = 660.88, triclinic, space group $P1$, a = 6.0670(12) Å, b = 7.5330(15) Å, c = 20.663(4) Å, α = 89.87(3)°, β = 96.60(3)°, γ = 90.02(3)°, V = 938.1(3) Å^3, Z = 1, T = 295 K, CCDC 297362. **DAT2**: plate, $C_{21}H_{23}N_3$, M_{r} = 317.42, monoclinic, space group $P2_1$, a = 6.1303(7) Å, b = 7.4239(9) Å, c = 20.258(4) Å, α = 90°, β = 96.750(8)°, γ = 90°, V = 915.6(2) Å^3, Z = 2, T = 295 K, CCDC 278087.† **PyT1**: plate, $C_{23}H_{25}N_3$, M_{r} = 343.46, monoclinic, space group $P2_1$, a = 5.9510(12) Å, b = 7.5960(15) Å, c = 21.590(4) Å, α = 90°, β = 96.82(3)°, γ = 90°, V = 969.0(3) Å^3, Z = 2, T = 295 K, CCDC 293252†.

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