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Growth and characterization of an efficient nonlinear optical D–π–A–π–D type chalcone single crystal

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ABSTRACT

A chalcone molecule, p-methoxy dibenzylideneacetone (PDBA), with molecular formula $C_{19}H_{18}O_3$ having D–π–A–π–D type, lambda (Λ)-shape structure has been synthesized by Claisen–Schmidt condensation reaction. High-quality single crystals of PDBA were grown by slow evaporation solution growth technique using acetone, methanol and dimethyl formamide (DMF) as solvents. PDBA easily crystallizes in orthorhombic system with noncentrosymmetric space group, Aba2, and the cell parameters are $a = 7.2756(9)$ Å, $b = 33.583(6)$ Å, $c = 6.132(5)$ Å and $v = 1498.3$ Å^3. The powder second harmonic generation (SHG) efficiency of PDBA was determined to be 15.5 times that of urea. This large SHG efficiency of PDBA is due to (i) the Λ-shape of the molecule resulting in a head-to-tail molecular columns along the crystallographic *c*-direction where dipole moment of the individual molecule add up to establish a net macroscopic polarization and (ii) the C–H…π hydrogen bond interactions in PDBA crystal structure (which can extend molecular charge transfer into supramolecular realm in the exited state) which may partly contribute to the observed SHG. PDBA crystal is highly transparent in the visible to near infrared region and has lower optical cutoff of 440 nm. The thermal stability of PDBA is comparable with that of urea. High optical transparency down to blue region, better Vickers hardness value, higher powder SHG efficiency and laser damage resistance than that of urea, and the existence of phase-matching property in this chalcone make it a potential candidate for SHG applications.

1. Introduction

Organic nonlinear optical (NLO) materials with high NLO coefficients and ultra-fast response time are required for applications such as frequency conversion, frequency mixing, optical data storage, electro-optic modulation, optical parametric oscillations and photonic integrated circuitry [1,2]. In addition to their large NLO response, the advantage of organic materials is that they offer high degree of synthetic flexibility to tailor their optical properties through structural modification and exhibit very high laser damage threshold, and good chemical and thermal stability [3]. In order to achieve good macroscopic nonlinear response in organic crystals, one requires high molecular hyperpolarizability and also proper orientation of the molecule in the solid-state structure to facilitate high-frequency conversion efficiency. Most of the organic materials (e.g. derivatives of p-nitro aniline) reported so far possess D–π–A type structure. Though a modification of structure of p-nitro aniline (e.g., m-NA and 3-methyl-4-nitroaniline) and the derivatives (e.g., *N*-(4-nitrophenyl)-(L)-prolinol (NPP)) brought significant improvement in their second harmonic generation (SHG) efficiency, their longer cutoff wavelength precludes them for efficient blue light generation from current diode lasers [4]. Therefore materials transparent in the blue region with significantly high SHG efficiency compared to urea are of our current research interest.

Chalcones are a promising class of organic materials known for their excellent blue light transmittance and high SHG efficiency [5]. From the past investigations on these molecular systems, it is found that these molecules show high SHG efficiency when π-electron acceptor group is substituted on the benzoyl (Ph–CO-) group rather than on the phenyl group at the other end [6]. On the other hand, by placing an electron donor group on each phenyl ring one can substantially enhance the frequency conversion efficiency of these chalcones [7]. It is also realized in these molecules that the substitution of weak electron donors such as Cl, Br, CH_3 and methoxy (OCH_3) groups on phenyl group results in

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noncentrosymmetric structures and have been suggested as the best electron donor groups for designing NLO chromophores, considering the transparency and SHG efficiency [8]. A large number of donor/accepter-substituted chalcone derivatives have been reported for their high SHG efficiency [9,10]. Therefore, chalcones have been attractive due to their high nonlinearity as well as for their transparency, and the cross-conjugated path in these molecular system appears as a powerful electronic system for the molecular engineering of efficient SHG materials.

In the past few decades, large varieties of chalcone molecules have been synthesized and their single-crystal structures have been reported (see online journal Act. Crystallogr. Section E), but very few reports are available on their high-quality single-crystal growth for photonic applications. The powder SHG efficiency of 15.5 times that of urea motivated us to grow bulk single crystals of PDBA. In this article, we report the crystal growth and characterization of this D–π–A–π–D type chalcone, p-methoxy dibenzylideneacetone (PDBA) and its SHG efficiency.

2. Experimental procedure

2.1. Synthesis

PDBA was prepared by Claisen–Schmidt condensation reaction [11]. A solution of ethanol and 10% sodium hydroxide was taken in a conical flask. A previously prepared solution of p-methoxy benzaldehyde (0.002 mol) and acetone dissolved in ethanol (0.001 mol) was added to the conical flask with stirring while maintaining the temperature of solution between 20 and 25 °C. After completely adding the aldehyde–ketone mixture, the solution was stirred for another 60 min. The separated product was then filtered and washed with excess of water and finally dried. The synthesized crude sample was purified by successive recrystallization from acetone.

2.2. Solubility and crystal growth

The size of a crystal grown by solution growth technique depends on the amount of growth substance available in that solution, which in turn depends on the solubility of material in the solvent used for crystal growth. Inclusion of solvent molecules in the crystal lattice will often result in a decreased quality of crystal as time elapses. Hence, the choice of solvent plays a major role in the solution growth technique. In order to identify a suitable solvent and the growth method, the solubility of PDBA in methanol, acetone and dimethyl formamide (DMF) was determined at and above room temperature. The solubility of PDBA was found to be more in DMF when compared to that in other two solvents. As shown in Fig. 1, the solubility of PDBA in acetone and DMF varies almost linearly with increase in temperature. However, in order to grow high-quality single crystals of PDBA, either slow cooling or slow evaporation at constant temperature was realized to be the suitable method.

To grow single crystals of PDBA, solvent evaporation at constant temperature solution growth technique was employed. The purified compound was used to prepare saturated solutions of PDBA in acetone, methanol and DMF in separate beakers. The temperature of solutions was increased by 5 °C in order to obtain a homogeneous mixture. The solutions were then filtered to remove any suspended particles and were kept undisturbed in a dust-free environment. Macroscopic defect-free seed crystals, previously grown by fast evaporation of solvents, were used as seeds for growing large-size single crystals from the respective solutions. As the evaporation rates of acetone and methanol solvents were high,

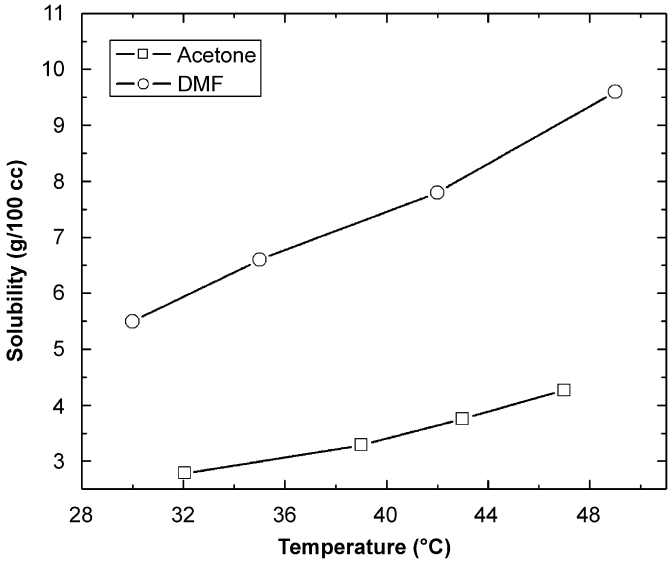

Fig. 1. Solubility of PDBA in acetone and DMF.

the beakers containing these two solvent–compound solutions were tightly covered with a polythene sheets using rubber tags and the growth was performed at ambient temperature. In the case of DMF, the growth solution temperature was maintained at 30 °C using a temperature-controlled water bath. The crystals grown from all three solvents were found to be elongated along crystallographic *c*-direction and had no remarkable difference in their morphology. We used DMF as the solvent for the subsequent single-crystal growth of PDBA for the following reasons: (i) the evaporation rate of DMF is very low and yields high-quality single crystals and (ii) the solubility of PDBA in DMF is better than that in other two solvents. The photographs of PDBA single crystals grown from methanol, acetone and DMF are shown in Fig. 2(a)–(c), respectively. The cleaved (0 1 0) crystal plates of PDBA grown from DMF are shown in Fig. 2(d). Single crystals of PDBA having a maximum size of $34 \times 9 \times 1.5\,mm^3$ (methanol), $30 \times 8 \times 1.3\,mm^3$ (acetone) and $16 \times 6 \times 1.7\,mm^3$ (DMF) were obtained in a period of 30 days. The crystals grown from acetone and methanol were found to be slightly opaque and the surface quality was not as good as that of the PDBA crystal grown from DMF.

3. Characterization

The single crystals of PDBA were characterized using elemental analysis, Fourier transform infrared (FTIR) spectroscopy and powder X-ray diffraction (XRD) techniques.

3.1. CHN analysis

The elemental analysis of PDBA powder sample was carried out using a Vario EL III carbon hydrogen nitrogen sulfur (CHNS) analyzer to determine the percentage composition of elements present in it. As listed in Table 1, both experimentally determined percentage compositions of elements in the PDBA molecule and the calculated ones from the PDBA molecular formula are in good agreement.

3.2. FTIR spectral analysis

In order to confirm the functional groups present in the PDBA molecule, FTIR spectrum was collected using a Shimadzu-8700