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A dual approach to study the electro-optical properties of a noncentrosymmetric L-asparagine monohydrate

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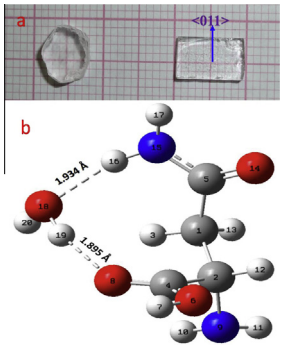
HIGHLIGHTS

- A new design has been made for growth of LAM single crystals.
- Experimental and theoretical spectroscopy has been studied.
- The grown crystals are highly transparent i.e. ~80%.
- Theoretically obtained results are found in semi-quantitative agreement with experimental.
- First hyperpolarizability has been found to be 0.883×10^{-30} esu which is twice than urea.

GRAPHICAL ABSTRACT

Cut and polished specimens of LAM crystal and its molecular geometry.



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ABSTRACT

In this work we reports the experimental and theoretical investigation on an organic noncentrosymmetric monohydrated L-asparagine (LAM) molecule. LAM single crystals were grown in specially designed beaker for the first time. Structural confirmation was done by identifying the vibrational modes using IR and FT-Raman spectroscopic studies. The ultra violet–visible–near infrared absorbance, diffuse reflectance spectra were recorded in the spectral range 190–2500 nm. The optical transparency was calculated and found to be ~80%. Its optical band gap was calculated found to be ~5.100 eV. Density functional theory (DFT) was employed to optimize the molecular geometry of LAM using B3LYP/6-31G* basis set of theory. The HOMO–LUMO energy gap of 6.047 eV and transition energy of 176 nm ($f_0 = 0.024$) have been found in semi-quantitative agreement with our experimental results. The dipole moment, polarizability and first hyperpolarizability were calculated at the same level of theory. The obtained results reveals that the titled compound can be a decent contender for nonlinear applications.

Introduction

Amino acid family crystals are of great interest due to their attractive nonlinear optical properties. L-asparagine monohydrate (LAM) is an organic nonlinear optical (ONLO) compound from amino acid family and also named as monohydrated L-asparagine. It is also known by other names such as monohydrated (S)-2-Aminosuccinic

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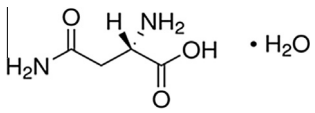
acid 4-amide, (S)-(+)-2-Amino succinamic acid, L-Aspartic acid 4-amide and its structure is shown below:



It is a very important material among other biological substances because it plays a vital role in the metabolic control of some cell functions in nerve and brain tissues, and is also used by many plants as a nitrogen reserve source [1] among other biological materials. In last few years the titled material has been of great interest of study in pure as well as with dopants [2–7]. The titled material is also having very good tendancy to form the new stable compounds/crystals and are well studied [8–14].

In recent past decade the optoelectronic industries, researchers and scientists are exceedingly fascinated toward the ONLO materials because of their wide applications such as high speed electro-optic modulators, optical data processing devices, second harmonic generation (SHG) elements, color display, electro-optic switches, and high-energy lasers for inertial confinement fusion research. Such NLO crystals with proficient optical frequency conversion are the fundamental components for the development of laser systems, which are of enormous importance as wide spread assortment tunable sources of articulate illumination all the wavelength spectral regions. ONLO materials display gigantic optical nonlinearity in single crystal form, which is of prodigious interest for above mentioned applications as well as in information technology, telecommunication, optical information processing and high optical data storage, etc. Because of large nonlinear response over a wide frequency range, inherent synthetic flexibility and large optical damage threshold for laser power and low frequency dispersion the organic materials show prominent properties. The key advantage of these materials is that they can be tailored to get the desired NLO properties [15,16] and also we can say that they have large structural diversity. Due to the presence of active π bonds the organic compounds shows excellent NLO properties, which help in the molecular engineering of tailor-made applications specially the family of organic amino acids shows interesting NLO properties [17,18]. Amino acids pageant a zwitterionic nature, hold a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH_3^+) in solid state form. Due to this dipolar nature, amino acids lead to some interesting physical and chemical properties making them suitable applicant for NLO applications. Therefore, there is an inordinate requirement to grow their good quality defect free single crystals for such applications. The available literature on the titled materials shows that much effort has been focused on the experimental studies such as infrared (IR), vibrational (Raman), crystal structure by single crystal X-ray diffraction, and second harmonic generation. For example, Yogam et al., [19] have performed experimental study on the growth, thermal, and optical properties of L-asparagine monohydrate NLO single crystal and found the SHG efficiency seven times higher than KDP. Similarly, we have previously reported the unidirectional growth of L-asparagine monohydrate along with first experimental observation of its SHG nature.[13] Recently, Sylvestre et al. [20] have performed a theoretical study of vibrational and NBO analysis of L-asparagine monohydrate (with H_2O close to COOH). They found that the stability of L-asparagine monohydrate molecule arised from hyperconjugation.

However, in present investigation, the authors aim to spotlight a molecular level structure–property relationship of LAM using a dual approach comprising of experimental and theoretical methodologies. In the experimental part, we have indigenously designed an assembly for the first time (see Fig. 1) for crystal growth by solution method (temperature lowering) to grow good quality crystal of LAM based on previous studies [11,21–24]. In computational part, we have also used DFT method combined with finite field approach to calculate the molecular level polarizability (α), anisotropy of polarizability ($\Delta\alpha$), static first hyperpolarizability (β) of L-asparagine monohydrate. Additionally, a structure–property relationship has been further explained using frontier molecular orbitals and molecular electrostatic potential (MEP) maps of L-asparagine monohydrate molecule. In contemporary science, computational chemistry has been considered as an advance tool to calculate the molecular geometries, IR, and vibrational frequencies in a cost effective way [11,25]. Recently, we have used computational approaches to investigate structure–NLO property relationships in a variety of novel classes of organic, inorganic and organic–inorganic hybrid molecules [26–34].

Experimental and theoretical details

Crystal growth

L-asparagine monohydrate of ⩾99% purity was purchased from Sigma Aldrich (A8381 SIGMA). As the quality of single crystals is based on the purity of material therefore, before using the as purchased materials for crystal growth it was crystallized then recrystallized in double distilled water and filtered for more than three times to increase the purity of material. After that the purified material was used to prepare the saturated solution at 305 K for crystal growth by temperature lowering technique using continuous stirring (500 rpm) for more than 36 h. Then the prepared solution was equally filtered in four beakers with Whatman filter paper in a close environment to avoid any nucleation due to temperature variation and covered with a plastic sheet out of which three were specially designed for LAM crystal growth as shown in Fig. 1(b–d).

Fig. 1(a) is of normal beaker in which we have grown a seed crystal of LAM with concave bottom surface shows that the crystal is not able to grow at the bottom portion as it is unable to get the solution while in the designed beakers we have made an arrangement to put the seed crystal in the middle of the solution inside the beaker. The crosses of different angles (i.e. 60, 30, 15 °C) with a small pin hole at the center were made of Teflon material and fixed inside the beakers. The bottom surface of the crystal was also found to grow and becomes flat and also by changing the angle we can have good possibility to grow the crystal all around with natural facets too. To grow the good quality crystals of the titled materials, few micron size holes were made in the aluminum foil for slow evaporation of solvent. Finally the prepared solution was kept inside the constant temperature bath of accuracy (±0.001 °C) at the same solution prepared temperature. After more than 12 h we have started to reduce the temperature of the bath at the rate of 0.03 °C/h and kept under the microscope (by which we can see the nucleation at micro meter level) to know the start of nucleation. The very first nucleation was observed after two days the temperature reduction was keep continue for further growth. The good quality single crystals of LAM were harvested from the mother solution after 12 days and the cut and polished specimens

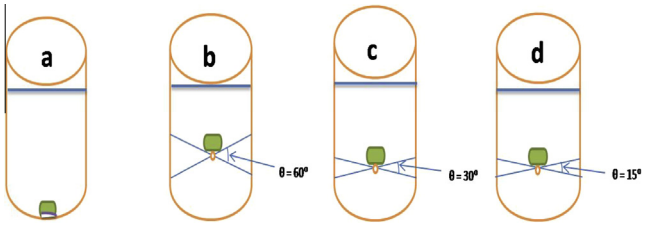


Fig. 1. Designs for good quality crystal growth of LAM.