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An experimental and computational approach to electronic and optical properties of Diglycine barium chloride monohydrate crystal: Applications to NLO and OLED

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ABSTRACT

Diglycine Barium Chloride Monohydrate have been synthesized and characterized by the ^{13}C and ^{1}H NMR spectroscopy and single crystal X-ray structural studies with a detailed analysis of Hirshfeld surface and fingerprint plots facilitating the interactions within the crystal structure. The Protonated N—H···O and intermolecular interaction responsible for the NLO activity are studied using DFT studies as well as experimental spectroscopic techniques. The molecular geometry, first & second hyperpolarizability studies and harmonic vibrational wavenumbers were calculated using density functional theory with B3LYP/SDD methods. The detailed interpretation of the vibrational spectra (FTIR and Raman) was carried out with the Normal Coordinate Analysis (NCA) following the scaled quantum mechanical force field methodology. The inter and intra molecular interactions responsible for the stabilization of the molecule were revealed by the NBO and AIM analyses. Photoluminescence spectrum shows that the luminescence is at the blue region. The observed saturable absorption and self-defocusing effect lead to optical limiting action at 532 nm for a CW diode-pumped Nd: YAG laser (50 mW) beam. Optical nonlinearity studies (z-scan) give the nonlinear refractive index, nonlinear absorption coefficient, third order nonlinear susceptibility, second order hyperpolarizability and optical limiting. The obtained results indicate that the synthesised compound is a good candidate for optical limiting and OLED applications.

1. Introduction

Semi-organic NLO crystals have inherent high nonlinearity and synthetic flexibility to alter their properties making them highly attractive in the technological point of view [1,2]. Metal coordinated organic centrosymmetric structures have been studied as third-order NLO materials [3]. Third-order optical nonlinearities play essential role in high frequency ultra-fast optical systems [4]. A semi organic non-linear optical crystal possesses both the high optical non-linearity of a purely organic compound and the thermal and mechanical properties of an inorganic compound [5]. It is reported that the organic compounds containing proton donating carboxylic group and proton accepting amino group when hydrogen bonded to a metal complex led to the enhancement of NLO activity [6–8]. In optical fibre communication, transmission techniques with nonlinear response are preferred [9]. Likewise, most recently researchers have developed advanced techniques to improve fiber networking through multi-dimensional resources integration (MDRI) architecture [10].

The present study describes characterization of DGBCM crystal using single crystal X-ray and FT-NMR analyses along with their electronic structure evaluation by DFT studies. The DFT study describe the vibrational spectroscopic investigations aided by density functional computations followed by force field calculations, the correlation between the molecular structure and NLO property investigating the ICT interaction, hydrogen bonds, and static first & second hyperpolarizability of the DGBCM molecule. The third-order NLO susceptibilities for organometallic compounds principal role begins to play the charge transfer between the ligands and the metals [12,13]. The crystal structures and their bulk crystal growth are already reported [11,14,15]. This paper brings out luminescence behaviour investigated by photoluminescence and Life time analysis, TG-DTA, UV absorption study and the third order optical nonlinearity using Z-scan studies reveal nonlinear optical properties of title crystal.

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2. Methods

2.1. Experimental methods

2.1.1. Crystal growth for DGBCM

Diglycine barium chloride monohydrate (DGBCM) crystal was synthesized by the slow evaporation technique, with glycine and barium chloride dihydrate in the molar ratio 2:1 in double distilled water. The solution was filtered using Whatman filter paper. The filtrate was covered with perforated foil and allowed to evaporate slowly. Crystals are grown after three weeks. Optically transparent single crystals of DGBCM are obtained after three recrystallizations in water.

2.1.2. X-ray data collection & structure refinement

The measurement were done with Bruker AXS Kappa Apex II CMOS detector diffractometer using graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K, the dimension of the DGBCM crystal used for data collection was 0.492 × 0.382 × 0.292 mm^3. The data was reduced using the program SAINT [16] and empirical absorption corrections are done using SADABS [17]. The structure is solved by the direct method using SHELXS-2013 [15]. The structure was refined using the full-matrix least-squares method based on F^2 using SHELXL-2013 [18]. Materials for publications are prepared using PLATON [19] program.

2.1.3. Spectroscopic measurements

The ^1H and ^{13}C FT-NMR spectra of the samples in distilled water solutions were recorded on a Bruker AVANCE III 500 MHz (AV 500) multi nuclei solution NMR Spectrometer at 298.7 K. The spectrometer frequencies used for the ^1H and ^{13}C NMR measurements were at 500.23 MHz and 125.79 MHz respectively. The UV–Vis–NIR absorption spectral data of the samples in water solutions were measured using a JASCO V-760 Spectrophotometer in the region 187–800 nm. Fluromax-4 spectrofluorometer was used to obtain the fluorescence spectrum with fixed slit width using a xenon lamp for UV light generation. The solid state Fourier transform infrared (FT-IR) spectra of the sample were recorded using the Perkin Elmer Spectrum Two: FT-IR spectrometer in the scan range 4000–450 cm^{-1} with a resolution of 1 cm^{-1} by the KBr pellet method. The confocal Raman spectrometer system used for recording Raman spectra has a WITec Alpha 300 RA (Germany) confocal Raman microscope with a resolution of 4 cm^{-1} and the microscopic objective lens with a magnification of 10×. The laser source of wavelength 532 nm was used to record the spectra of the solid samples in the spectral range 4000–10 cm^{-1}.

2.1.4. Z-scan measurement

In our experiment, well-polished crystal of DGBCM about 1 mm thickness was irradiated by 50 mW continuous wave laser beam at 532 nm diode pumped Nd: YAG laser which was focused by a lens with 3.5 cm focal length. The crystal is translated in an axial direction to vary the incident intensity falling on the crystal surface. The third-order nonlinear refractive index (n_2) nonlinear absorption coefficient (β) and second order hyperpolarizability (γ) of the DGBCM crystal were evaluated by the Z-scan technique. In Z-scan measurements open aperture (OA) Z-scan gives the information of totality of the transmitted light collected by the detector and the closed aperture (CA) Z-scan measures only a small part of the transmitted light collected by passing through a small aperture [20,21].

2.2. Computational details

Quantum chemical computations for DGBCM molecule are performed by Gaussian 09 [22] program package. The geometric parameters IR, Raman, (^1H and ^{13}C) NMR, UV-vis spectra, first & second hyperpolarizability calculated with DFT/B3LYP level of theory with SDD basis set. The Gaussian input in the form of an isolated molecule were taken from crystal information file (CIF) obtained by single crystal XRD experiment. The positive theoretical frequencies confirm the optimized geometry to be at minima in the potential energy surface. Normal Coordinate Analysis (NCA) is used to transform the harmonic force field in the Gaussian output into a set of symmetry coordinates by using MOLVIB program version 7.0 [23,24]. To obtain better agreement between the theoretical and experimental IR and Raman frequencies by using scaled quantum mechanical procedure (SQM) performed according to selective scaling in the natural internal coordinates [25,26]. The Natural Bond Orbital (NBO) analysis gives inter and intra molecular bonding and interaction carried out on the optimized structure using the NBO 3.1 program [27]. The electron density at the bond critical points (BCP) was analyzed using the atoms in molecules (AIM) approach at B3LYP/SDD level by using the AIMALL package [28]. Time-dependent density function theory (TD-DFT) was used to calculate the excitation energies with basis set B3LYP/SDD. In addition to B3LYP, a highly correlated method M06 and CAM-B3LYP used to simulate electronic absorption phenomena. The electrophilic and nucleophilic attacks of DGBCM has been presented on molecular electrostatic potential (MEP) and electronic properties have been deduced from HOMO–LUMO analysis. The ^1H and ^{13}C NMR isotropic shielding are calculated with the help of GIAO method [29,30]. The DFT method also calculates dipole moment, mean polarizability and dynamic first and second hyperpolarizabilities are calculated at 532 nm ħω = 0.0857 a.u laser wavelength. The mathematical details used for the calculation of dipole moment, polarizability, hyperpolrizability, second harmonic generation, β(−2ω;ω,ω), the electro-optical Pockels effect, β(−ω,ω,0), second hyperpolarizability for quadratic electro- optic Kerr effect, γ(−ω;ω,0,0) and the DC electric field induced second harmonic generation, γ(−2ω;ω,ω,0) were reported in literature [31,32].

Table 1
Crystal data and structure refinement for DGBCM.

Identification code	DGBCM
Empirical formula	$C_4H_{12}BaCl_2N_2O_5$
Formula weight	376.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c n
Unit cell dimensions	a = 8.2415(6) Å (8.31 Å)* α = 90° b = 14.7056(13) Å (14.84 Å)* β = 90° c = 9.2229(8) Å (9.32 Å)* γ = 90°
Volume	1117.78(16) $Å^3$
Z	4
Density (calculated)	2.237 Mg/m^3
Absorption coefficient	4.030 mm^{-1}
F(000)	720
Crystal size	0.492 × 0.382 × 0.292 mm^3
Theta range for data collection	3.544–24.997°
Index ranges	$-9 \le h \le 9$, $-17 \le k \le 17$, $-10 \le l \le 10$
Reflections collected	7607
Independent reflections	981 [R(int) = 0.0698]
Completeness to theta = 24.997°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.34 and 0.21
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	981/0/71
Goodness-of-fit on F^2	1.119
Final R indices [I > 2sigma(I)]	R1 = 0.0196, wR2 = 0.0471
R indices (all data)	R1 = 0.0219, wR2 = 0.0485
Extinction coefficient	0.0292(10)
Largest diff. peak and hole	0.527 and −0.638 e·$Å^{-3}$

* Ref. [11].