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Structural, spectroscopic, nonlinear optical and electronic properties of calcium N-phthaloylglycinate: A combined experimental and theoretical study

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ABSTRACT

A calcium complex of N-phthaloylglycine (CaNPG) has been synthesized, and its crystal structure has been characterized by X-ray diffraction method. The FT-IR and fluorescence spectra for CaNPG have been recorded. N-phthaloylglycine ligand coordinates to Ca ion through the carboxylate O atoms as a bidentate ligand, and Ca ion does not play an important role in florescence spectrum. In order to support experimental findings and also investigate molecular surfaces, natural bond orbital (NBO) and nonlinear optical (NLO) optical properties of CaNPG complex, density functional theory calculations have been performed by hybrid B3LYP level. The very small energy gap between α-spin frontier molecular orbitals (FMOs) is demonstrated that CaNPG is a very reactive, chemically soft and optically active complex. The high stabilization energies of hyperconjugative interactions are also demonstrate that the charge mobility in CaNPG is very high. As consistent with above findings, first static hyperpolarizability of CaNPG has been found to be 10 times higher than pNA which is a NLO material.

1. Introduction

Phthalimides and its derivatives are one of the important class of organic molecules that possess diverse structural and biological applications [1,2]. Among phthalimides derivatives, N-Phthaloylamino acids are used for the synthesis of peptide bonds in solid phase synthesis [3]. Such phthalimide derivatives undergo photochemical reactions such as photochemical decomposition and decarboxylation [4]. Among the N-phthaloylamino acids, N-phthaloylglycine has been most widely studied with reference to cleavage with various amines, metal complexes with interesting supramolecular structures and adducts formations with various aromatics amines and hydroxyl aromatic compounds [5–7]. The heterocyclic derivatives of N-Phthaloylglycine are also reported in literature such as oxadiazole [8] and benzoxazinone [9]. Previously, we have reported the synthesis, characterization and crystal structure of 12,4-triazole of N-phthaloylglycine and its Schiff and Mannich bases [10,11]. In addition, we have also reported the synthesis and DNA binding studies of Ni(II), Cu(II) and Zn(II) complexes of N-Phthaloylglycine [12].

Metal organic frameworks (MOFs) offer an opportunity for combining the characteristics of both organic and inorganic ligands in order to obtain better nonlinear optical materials for the possible applications in telecommunication, high optical disk data storage, optical information processing and optical computing. Combining the high optical nonlinearity and chemical flexibility properties of organic ligands with thermal stability and perfect transmittance of inorganic materials have been attracted a great deal of attention in the field of nonlinear optics [13–15]. Additionally, the syntheses and characterizations of new materials with higher nonlinearities have gathered great interest in these days in order to satisfy the increasing technological requirements. One of the ways in which an organic molecule shows a large optical nonlinearity is that the extension of aromatic rings increasing the number of π electrons as well as their delocalization length [16,17]. Additionally, the

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substitution of aromatic rings with electron donor and acceptor atom and/or atom groups has let to remarkable increase in the first order hyperpolarizability (β).

It is well known that phthalimide is an aromatic cyclic compound and has strong π-bond delocalization. Additionally, two carbonyl (C═O) which is known as a powerful electron withdrawing group have been located on opposite sides of the molecule. Therefore, phthalimide derivates seems to be appropriate for nonlinear optical applications. It is also known that the coordination to metal atom enhances the nonlinear optical properties of organic molecules [18–20]. Considering that above mentioned conditions, the nonlinear optical properties of CaNPG complex have been investigated by density functional theory (DFT) calculations.

2. Experimental procedures

2.1. Synthesis of CaNPG complex

N-phthaloylglycine was prepared by the reported method [21]. The title compound was prepared by treating the N-phthaloylglycine (7.5 mmol, 1.54 g) with calcium oxide (3.75 mmol, 0.21 g). The reactants were placed in a beaker with 100 ml of distilled water and stirred for about 2 h. The reaction was carried out with the ratio of 2:1 of N-phthaloylglycine and calcium oxide, respectively (Fig. 1). The resulting solution was filtered and cooled at room temperature. After a few days colorless crystals were formed (Yield: 73%), which were washed with distilled water and characterized further.

2.2. Materials and instrumentation

All chemicals used in this work were analytical grade and purchased from Aldrich or Merck. Melting points were determined on Gallen Kamp, an electro thermal apparatus, Cat No.MPD350, sanyo, UK and is uncorrected. Infrared spectra were recorded on Nicolet iS 10 FTIR Spectrophotometer (4000–400 cm^{-1}) in KBr discs. Thermal gravimetry (TG) was measured DTG-60H Simultaneous DTA-TG Analyzer utilizing a heating rate of 10 °C/min. Fluorescent Emission spectra (DMSO) were recorded on F-7000 FL Spectrophotometer.

2.3. Crystal data

The crystals of title compound were grown by slow evaporation of water at room temperature. The colorless plate crystals were mounted on a sealed tube and all X-ray crystallographic data were collected on a Bruker AXS Smart Apex diffractometer. Correction for semi-empirical from equivalents was applied, and the structure was solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 Program System [22–25]. All data were collected with graphite-monochromated M_oK_α radiation (λ = 0.71073 Å) at 100 K.

3. Computational procedure

All of the calculations carried out in this study have been performed by using Gaussian 09 Revisions D.01 program [26] and the obtained theoretical data visualized by means of GaussView 5 [27]. First of all, $[Ca(Gly)_2(H_2O)_2]$ complex has been optimized in ground state energy level by using B3LYP level [28,29] of density functional theory (DFT) and 6-311++G(d,p) basis set [30]. Based on the obtained geometry, the vibrational frequencies for CaNPG complex have been computed by using the same method and basis set. It is well known that DFT levels predict vibration frequencies larger than experimental corresponding, so the obtained vibration frequencies were scaled down with the scaling factor of 0.9614 [31]. The electronic absorption spectrum for CaNPG in gas phase and ethanol solvent were simulated by using time dependent DFT (TD-DFT) level [32]. Solvent models allow simulations and calculations of reactions and processes which take place in solvated phases. For this purpose, conductor-like polarizable continuum model (CPCM) [33] has been used to calculate solvent (ethanol) effect. NBO analysis [34] has been performed to investigate the intermolecular charge transfer, rehybridization and delocalization of electron density. The nonlinear optical properties of CaNPG has been also investigated by the determining of dipole moment (μ), polarizability (α), anisotropy of polarizability (Δα) and first hyperpolarizability (β). Finally, Molecular Electrostatic Potential surface (MEP) [35] has been simulated to demonstrate polarizability, intramolecular charge transfers and reactive sides of CaNPG.

4. Result and discussion

4.1. Structural analysis

A calcium complex of N-phthaloylglycine was prepared and its crystal structure which reported by Bhatti et al. [36]. In CaNPG complex, the calcium atom was located to the center of distorted octahedron. In this study, CaNPG complex has been optimized in ground state energy, and the obtained geometric data have been compared with experimental ones. The XRD and optimized

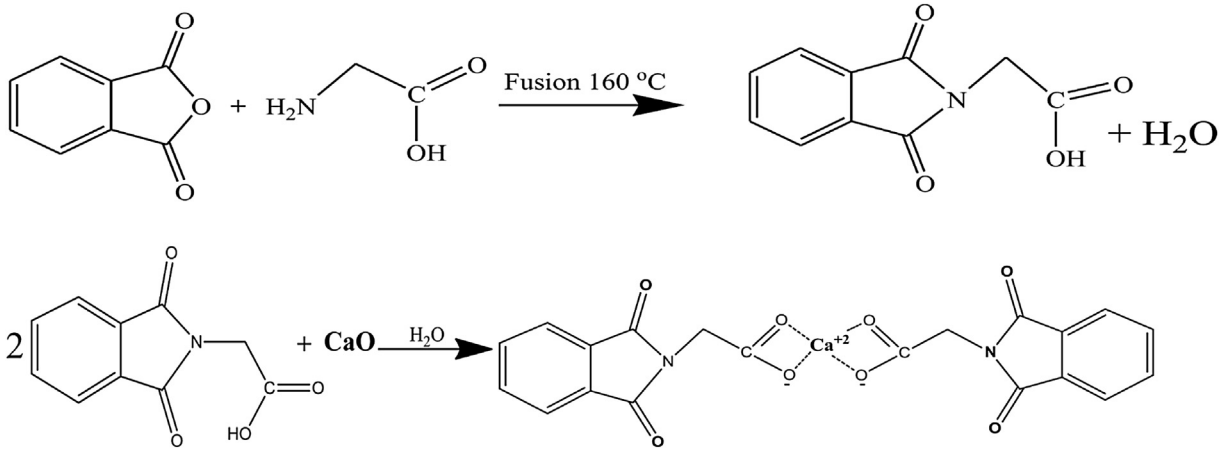

Fig. 1. Synthesis and characterization of NPG and CaNPG complex.