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Synthesis, Hirshfeld surface analysis, laser damage threshold, third-order nonlinear optical property and DFT computation studies ofDichlorobis(DL-valine)zinc(II): A spectroscopic approach

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Abstract

The organometallic crystal of Dichlorobis(DL-valine)zinc(II) was grown by solution growth method. The computed structural geometry, vibrational wavenumbers and UV–visible spectra were compared with experimental results. Hirshfeld surface map was used to locate electron density and the fingerprint plots percentages are responsible for the stabilization of intermolecular interactions in molecular crystal. The second-order hyperpolarizability value of the molecule was also calculated at density functional theory method. The surface resistance and third-order nonlinear optical property of the crystal were studied by laser induced surface damage threshold and Z-scan techniques, respectively using Nd:YAG laser with wavelength 532 nm. The open aperture result exhibits the reverse saturation absorption, which indicate that this material has potential candidate for optical limiting and optoelectronic applications.

Introduction

Nonlinear optical (NLO) properties of organometallic compounds are considerable interest because of their applications in telecommunication, image processing, data storage, optical modulation, optical switching and optical limiting [1], [2]. A large number of organometallic complexes with efficient NLO properties have been synthesized and studied over the past thirty years [2], [3], [4], [5], [6]. The metal-ligand binding interactions plays an important role in increasing their NLO efficiency of the organometallic compounds. The nonlinear response in transition metal-organic compound may be due to the combinations of central metal and ligand as well as the charge transfer nature of the metal to ligand coordination bonds [7]. Therefore, transition metal-ligand coordination has been expected to be one of the new candidates for

nonlinear optical materials, and it has been found that metal-ligand coordination exhibits good third-order NLO effects. Several papers have reported the NLO responses in the transition metal cluster family including optical absorption coefficient (β), refractive index (n_2), susceptibility ($\chi^{(3)}$), second-order hyperpolarizability (γ) and optical limiting effects [8], [9], [10], [11], [12]. Recently, crystal growth combination of amino acid with a transition metal compound has been proposed as a new candidate for NLO applications [13], [14], [15], [16]. The crystal structure of Dichlorobis(DL-valine)zinc(II) (DLVZC) was reported by Natarajan etal. [17]. Density functional theory (DFT) is very widely used to predict the structure of systems containing transition metals, vibrational wavenumbers and molecular hyperpolarizabilities [18], [19], [20], [21], [22], [23], [24].

In the present work, the structural geometry, vibrational spectra of synthesized DLVZC compound using both theoretical and experimental technique have been analyzed and reported. The natural bond orbital (NBO) analysis has been performed to explore interaction between (metal-ligands) inter- and intramolecular charge transfer and hydrogen bonding is explained. The global electrophilicity, chemical potential, hardness and softness have been calculated by Frontier molecular orbitals (FMOs) analysis. Hirshfeld surface maps and fingerprint plots to understand the various types of intermolecular interactions in a molecular crystal package are plotted. UV–Visible (UV–vis) spectral analysis has been carried out to identify the various electronic transitions. The second-order hyperpolarizability of the synthesized DLVZC solution have been measured by open aperture (OA) and closed aperture (CA) methods using Z-scan technique.

Section snippets

Synthesis

The saturated aqueous solution of a mixture of DL-Valine and Zinc chloride in the stoichiometric ratio 1:1 was prepared with double distilled water. This prepared solution was stirred continuously for about 4hours using a magnetic stirrer. Then the solution was filtered and kept at room temperature. After 45 days crystals were grown, which were purified by further recrystallization process and finally good quality crystals were obtained.…

Characterization details

The powder X-ray diffraction (XRD) pattern of the…

Computational details

Quantum chemical computations were performed using the Gaussian 09 [25] program and visualize the results using GaussView 3.0 program [26]. The DLVZC molecular geometry and vibrational wavenumbers were computed by the DFT/Becke-3-Lee-Yang-Parr (B3LYP) [27] with 6–311++G(d,p) and LANL2DZ (Los Alamos National Laboratory 2 double ζ) level of basis sets. Furthermore, the vibrational modes were identified by potential energy distribution (PED) by VEDA4 program [28]. The calculated harmonic…

Structural geometry

The X-ray data were collected using the X'Pert-Pro diffractometer. The powder X-ray diffraction data indicates that the DLVZC single crystal crystallizes in monoclinic system and space group $C2/c$. The lattice parameters are a=20.5104Å, b=6.2143Å, c=13.4125Å, cell angles $\alpha=\gamma=90°$, β=102.3465° and Volume (V)=1669.99Å^3. The powder XRD pattern of DLVZC is shown in Fig.1. When they are compared, the powder XRD data is in well matched with the reported value [17]. The observed…

Conclusion

The computed molecular structural geometry, vibrational and electronic absorption spectra are in good agreement with the experimental data results. Hirshfeld surface analysis of DLVZC reveals that the strong close and weak longer intermolecular interactions in the crystalline state. Further, the fingerprint 2D plots confirm the percentage of interaction present in the DLVZC molecule. Third-order NLO parameters of absorption coefficient, refraction index, nonlinear susceptibility and…

Acknowledgements

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> …The chemical potential value is negative which indicates that the compound is stable [47]. The decreased value of chemical hardness (reciprocal gives softness) measures the charge transfer, which indicates a high polarizability in the molecule [41,48]. This study describes that the grown crystals is the potential candidate for NLO applications.…

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> …Curvedness estimates “how much shape”, areas of sharp curvature retains high curvedness while low values of curvedness corresponds to flat areas and tends to divide the surface into patches associated with contacts between near by molecules.Shape index is a measure of “ which shape” and is most sensitive to the delicate changes in surface shape. The 2D fingerprint plots(combination of de and di) provide a summary of intermolecular transitions in the solid [54]. Hirshfeld surface and the 2D fingerprint plots were generated using Crystal Explorer 17.5 and is illustrated in Fig. S2 and Fig. S3(supporting information),respectively.…

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