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Theoretical and Experimental Evaluation of Structural and Optical Properties of Novel Zinc-Benzimidazole Metal Complex Doped in Polystyrene Matrices

P. A. Praveen and R. Ramesh Babu*

Crystal Growth and Thin Film Laboratory, Department of Physics, Bharathidasan University, Tiruchirappalli – 620 024, Tamilnadu, India.

**Email: rampap2k@yahoo.co.in*

Abstract. A novel zinc incorporated benzimidazole metal complex (diacetobis (1H-benzimidazole) Zn(II)) is synthesized by a simple chemical route. The structure of the obtained complex is predicted using FTIR and EPR spectroscopy and further confirmed using semiempirical simulation of vibrational frequencies. Theoretical energy gap of the complex is about 3.2 eV and the hyperpolarizability calculations show that the third harmonic generation dominates over other mechanisms in the complex. Recorded absorption spectrum of the complex shows a broad absorption band between 200 and 300 nm corresponding to π - π transitions. To evaluate the third order nonlinear optical properties experimentally, the complex is doped into a polystyrene matrix with different weight percentages and fabricated as freestanding films. The films are subjected to Z-scan analysis and from the open and closed aperture scans the samples are found to have a reverse saturable absorption and self focusing effect. The calculated third order susceptibilities are of the order of 10^{-4} esu, which is one of the largest values reported in literature.

Keywords: Thin films, Nonlinear Optical Materials, Chemical Synthesis, Organometallic materials.

PACS: 81.15.-z, 68.60.Dv, 78.68.+m, 42.70.Mp, 42.70.Nq, 81.20.Ka, 81.05.Lg

INTRODUCTION

In the recent past, metal organic materials are extensively investigated for their combined advantages of both organic and inorganic material properties [1]. For nonlinear optical considerations, the conjugated π -electron system of organic moieties could rapidly response to the applied field resulting large and extremely fast nonlinearities. On the other hand, metal ions in the organic medium often enhances the physical properties of the complex such as thermal stability, mechanical durability and laser damage threshold etc., Metal ions will induce additional electronic transitions in the complex which is advantageous for third order nonlinear optical applications. Benzimidazole (BMZ), a heterocyclic aromatic compound, is well known for its anti-bacterial and anti-fungal activity. Recently, it has been identified as a potential second harmonic generation (SHG) material with a SHG efficiency of 4.5 times better than that of KDP crystal. There is a growing interest of study the coordination behavior of Benzimidazole towards transition metal ions, especially to tune its optical properties. In this paper,

we report on the theoretical and experimental studies of structural and optical properties of diacetobis (1H-Benzimidazole) Zn (II) (Zn-BMZ) complex.

EXPERIMENT

Analytical grade zinc acetate tetrahydrate (0.1 M) and BMZ (0.2 M) were dissolved separately in ethanol. The prepared metal solution was slightly heated with stirring for 5 minutes and then the ligand solution was added drop wise into it. After few minutes, clear white precipitate was settled at the bottom of the beaker. The precipitate was filtered, washed with ethanol and dried in hot air oven for an hour. The synthesized material was subjected to FTIR and EPR analysis to predict the molecular structure. Semiempirical quantum chemistry package MOPAC2012 was used for computational analysis of the predicted structure. The intrinsic reaction coordinates of the molecule was adjusted to obtain a global minimum and the geometry of the complex was optimized at PM6 level. Optimized structure was used to generate the vibrational frequencies, energy gap and polarizability and hyperpolarizability values. Since the

obtained product was not soluble in any of the commercially available solvents it was doped into polystyrene (PS) matrices and fabricated as freestanding films to record the Z-Scan spectra. For the preparation of Zn-BMZ doped PS films, 0.5 M of PS was dissolved in toluene and stirred well till the PS completely dissolves in the solvent. 0.05, 0.1 and 0.15 weight percentage of Zn-BMZ was added to that solution and ultrasonically treated for 15 minutes. For higher wt% (more than 0.15) the Zn-BMZ powder was not homogeneously dispersed over PS solution and hence 0.15 was chosen as the maximum dopant percentage. The obtained clear whitish gel was then casted onto a petri dish and allowed to dry in open air atmosphere for 48 hrs. After that the free standing films were peeled off from the petri dish and used for Z-Scan analysis.

RESULTS AND DISCUSSION

Structural Identification

The EPR spectrum of Zn-BMZ complex is shown Figure 1. The position of the line and nature of the spectrum is a characteristic curve of low spin zinc complexes. The broad nature of the signal indicates that the Zn ion exhibits a tetragonal geometry with the ligand. 'g' values of the present study shows the exchange coupling effects are operative in the complex.

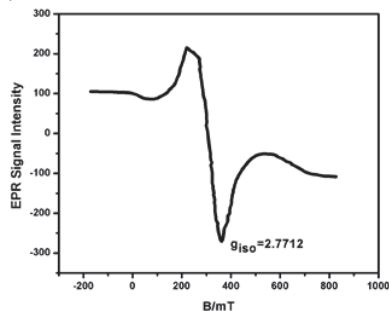


FIGURE 1. EPR spectrum of Zn-BMZ

The observed FTIR spectrum of the complex is shown in Figure 2. Presence of strong absorption in the region 300 cm^{-1} can be inferred to the tetragonal coordination of metal ion with the ligand. Due to the heavy mass of the metal atom, the absorption frequencies are shifted to the lower wavenumber region compared to the other metal complexes. Presence of $\nu(\text{N-H})$ vibrations in the region 3071 cm^{-1} and the shift in $\nu(\text{C=N})$ in the region 1381 cm^{-1} confirms the coordination of metal atom through nitrogen atom of the imidazole ring. The vibrational peak observed in the region 1472 cm^{-1} can be assigned to C=O stretching of acetate ion. Predicted structure

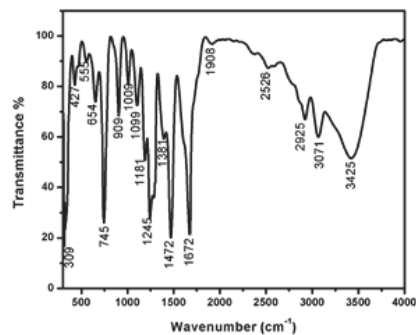


FIGURE 2. FTIR Spectrum of Zn-BMZ

of the complex is shown in Figure 3. This has been used to calculate the theoretical vibrational frequencies and they are in good agreement with the observed frequencies. The percentage of error calculated from fit (Figure 4) is approximated about less than 2%.

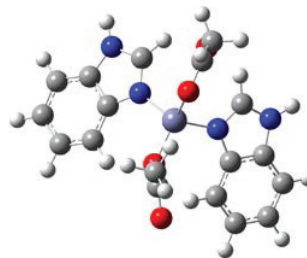


FIGURE 3. Predicted structure of Zn-BMZ complex

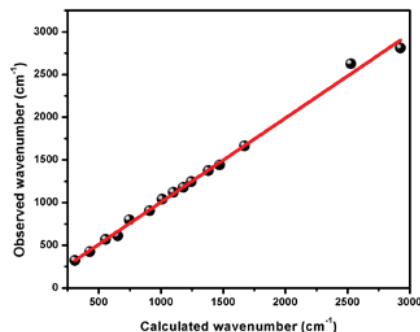


FIGURE 4. Fitted values of observed and calculated frequencies

Linear and Nonlinear Optical Properties

UV-Vis spectrum of the Zn-BMZ complex was recorded using diffused reflectance spectroscopy (DRS) in the range between 200 and 800 nm, and the spectral data is shown in Figure 5. A broad absorption peak observed in the range 200 to 300 nm corresponding to $\pi \rightarrow \pi^*$ interligand transitions. The theoretical HOMO (Higher Occupied Molecular Orbital)-LUMO (Lower Unoccupied Molecular Orbital) difference (3.2 eV) is simulated and shown in the Figure 6.

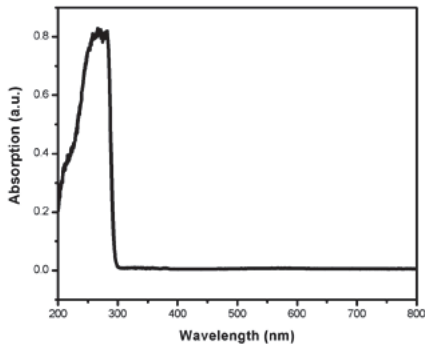


FIGURE 5. Absorption spectrum of Zn-BMZ sample



FIGURE 6. HOMO-LUMO orbitals of Zn-BMZ

The static values of polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) values of Zn-BMZ molecule are calculated about 263.15 A.U., 1.8748×10^{-30} esu and 1.9384×10^{-35} esu respectively. Contribution of different third order mechanisms such as third harmonic generation (THG), electric field induced second harmonic generation (DC-EFISH), intensity dependent refractive index (IDRI) and optical Kerr effect (OKE) to the overall third order susceptibility can be identified by calculating susceptibility values for each mechanism. The obtained values of Zn-BMZ are plotted in Figure 7 for different incident frequencies ($\omega=0.0, .025, 0.5, 0.75, 1.0$ eV) and THG dominates over other mechanisms. From the Z-scan analysis, all the films are found to exhibit a valley-peak configuration corresponding to positive nonlinearity (i.e., self-focusing) in closed aperture (CA) scans. Reverse saturable absorption (RSA) behavior of the films is observed from the open aperture (OA) scans. The RSA behavior of PS:Zn-BMZ thin films can be inferred with the help of five-level model. Based on which the RSA behavior of the samples is due to weak ground state absorption between $S_0 \rightarrow S_1$ followed by an intersystem crossing to T_1 energy level, followed by a $T_1 \rightarrow T_2$ excited state absorption (ESA). Observation of RSA can be interpreted that the excited state ($T_1 \rightarrow T_2$) absorption cross-section is larger than that of the ground state ($S_0 \rightarrow S_1$) absorption cross-section. The major contribution of third order nonlinearity in PS:Zn-BMZ films arises due to thermal effect i.e., the

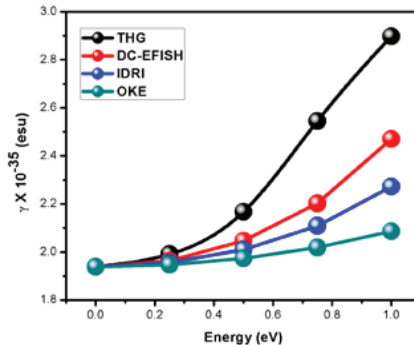


FIGURE 7. Third order susceptibility values of Zn-BMZ for different mechanisms

energy of the focused light beam on the sample induce a heating effect in the medium. Due to heating there appears a thermal gradient induced refractive index change in the sample which acts as a thermal lens and distorts the phase of propagating beam through it. This is one of the common phenomena observed in CW Z-scan operation.

TABLE 1. Third order nonlinear optical parameters of PS:Zn-BMZ films

Sample	β	$n_2 \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-3}$ esu
0.05	18.27	6.63	6.08
0.1	23.50	11.80	7.83
0.15	28.18	14.84	9.40

Conclusion Zinc complex of benzimidazole was synthesized chemically and the product was confirmed by means of FTIR, EPR and semiempirical computational studies. Theoretical hyperpolarizability values showed that the THG dominates over other mechanisms. From the Z-Scan analysis samples were found to exhibit reverse saturable absorption and positive nonlinear refractive index at all the dopant concentrations. The obtained susceptibility values are one of the largest values reported in literature.

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