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Investigating the nonlinear behavior of cobalt (II) phthalocyanine using visible CW laser beam

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ABSTRACT

Experimental and theoretical results of the diffraction ring patterns in cobalt (II) phthalocyanine (PcCo(II)) in dimethyl formamide solution using visible low power continuous wave CW laser beam are reported. The wave-front curvature of the used laser beam seem to modify the spatial phase modulation of the beam. The upward convection modify each pattern by reducing the vertical diameter of each ring in comparison with horizontal one. At low input power the effect of convection is minimized. Simulation results given are based on the Fresnel-Kirchhoff diffraction integral. The nonlinear refractive index of the solution of PcCo(II) was measured using Z-scan technique, by exciting with CW laser at 473 nm wavelength. The effect of concentration of the sample on nonlinear refractive index has been investigated.

1. Introduction

Organic molecules with nonlinear optical process continue to attract attention because of their potential applications in a wide variety of optoelectronic and photonic devices [1–3].The nonlinear response of these organic molecules at low intensity lasers results in a large third order nonlinear optical (NLO) susceptibilities. Extensive work has been carried out and the reports have been published for the organic molecules in liquid solutions [4,5].

When a laser beam propagates in an absorbing medium a spatial distribution of temperature is generated according to the light beam irradiance spatial profile. Since the local refraction index values of the absorbing medium depend on the temperature, a spatial distribution of the refraction index or thermal lens (TL) [6] is induced. As a direct consequence of (TL) effect and the change of phase of the propagating laser beam diffracting ring patterns (DRPs) [7] resulted. Based on the (DRP) the nonlinear refractive index, n_2, of the nonlinear medium can be evaluated. The Z-scan technique, developed by Sheik Bahae et al. [8] is another simple and effective tool that can be used to measure the nonlinear refractive index, n_2.

During the last fifteen years, extensive works have been directed towards the study of nonlinear properties of phthalocyanine, viz., bis- phthalocyanine [9], alkyl phthalocyanine [10], Lu(111) phthalocyanine [11], alkoxy phthalocyanine [12], 4-tetra and oct-substituted lead phthalocyanine [13], copper phthalocyanine [14], zinc phthalocyanine [15–17], Lanthanide

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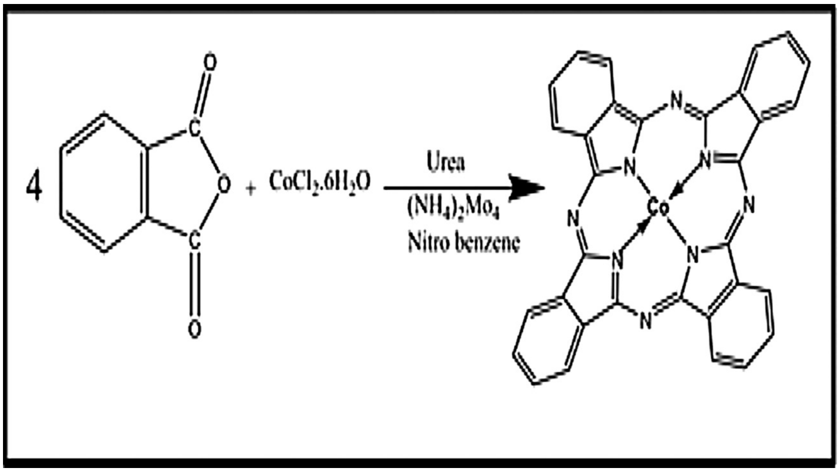

Fig. 1. Synthesis of PcCo(II).

bis- phthalocyanine [18], In(111) and Ga (111) [19,20] chlorinated tetrasubstituted phthalocyanine [21], prophyrin-appended europium (111) bis phthalocyanine [22], thiophene phthalocyanine [23], etc. The Z-scan was the main tool used to investigate the nonlinear response in these materials. The nonlinear absorption coefficient, the third order susceptibility, the second hyper polarizability, nonlinear refractive index and optical limiting were among the nonlinear parameters measured.

There are many kinds of phthalocyanine molecles(Pc), depending on the linkage of the phthalocyanine molecules. Phthalocyanine molecules could be unimolecular, bimolecular with metal atom sandwiched between two phthalocyanine molecules, multimolecular as side linked phthalocyanine molecules to form planer structure(eka-linked) and face to face stacked phthalocyanines (μ-bridged).

Metal phthalocyanine complexes (PcM) are macro cyclic ring contains four iso indole units and central metal atom. They are nearly planar molecules with D_{4h} symmetry. Phthalocyanines with different central metal atoms have been intensively investigated since their discovery in the beginning of the twentieth century [24]. Phthalocyanines have industrial applications as pigments and dyeing agents due to their intense colours. They are chemically inert and thermal stability tall 300 °C under normal pressure and more that 500 °C under vacuum [25]. They can be prepared by number of methods because of their electronic and optical properties and proccessability. They have been established in many applied fields, as sensitizers for photodynamic therapy (PDT) and electronics [26].

In the present work the study of nonlinear optical properties of PcCo(II) using continuous wave (CW) visible low power laser beam having fundamental transverse (TEM_{00}) mode are presented. The Z-scan is used in the measurement of the nonlinear refractive index of the sample. The effect of concentration on nonlinear refractive index have also been investigated.

2. Experimental

2.1. Preparation of cobalt (II) phthalocyanine, PcCo(II)

A mixture of 2.795 g(0.02 mol) of phthalic unhydride, 1.19 g(0.005 mol) of hydrated cobaltous chloride($CoCl_2{\cdot}6H_2O$), 5 g of urea and 0.01 g of ammonium molybdate [$(NH_4)_2MoO_4$] were dissolved in 25 ml of redistilled quinoline. The mixture was refluxed with mechanical stirring for 2 h. The reaction mixture then cooled and filtered. The solid product could not be dissolved in many solvents, so, it was refluxed with distilled water for 10 min, cooled and filtered. Same procedure was repeated with hexane, chloroform and carbon tetrachloride respectively. The blue final product then dried at 100 °C. The yield is 74.2% and its decomposition temperature is 227 °C. Molecular formula, $C_{32}H_{16}N_8$, CHN analysis; Calculated: C(67.25%), H(2.8%), N(19.6%). Found:C(67.1%), H(2.68%), N(19.12%). The reaction is shown in Fig. 1. The yield is dissolved in dimethyl formamide (DMF) to obtain 5 mM, 7 mM and 10 mM concentrations of solutions of PcCo(II). Fig. 2 is a photograph of the solution of PcCo(II) with 10 mM concentration.

2.2. Spectroscopic study

The UV–vis spectroscopy was carried-out using a 6800 UV–vis spectrophotometer (Jenway-England). These measurements were all performed at room temperature. Fig. 3 shows the spectral distributions of absorbance (A) for 5, 7, and 10 mM concentrations of the solution of PcCo(II) in the spectral range (300–800) nm. Inset in Fig. 3 shows the variation of absorption coefficient, α, against sample concentration.

Electronic spectroscopy shows the two main characteristic bands, the Q band,(600–700) nm and Soret band (300–400 nm) [25–27]. Both bands are related to π-π^* transition, due to the π electrons on the rings and n-π^* transition, due to the n