Third order nonlinear optical studies in europium naphthalocyanine using degenerate four wave mixing and Z-scan

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Abstract

Third order nonlinear susceptibility $\chi^{(3)}$ and second hyperpolarizability $\langle\gamma\rangle$ of a bis–naphthalocyanine viz. europium naphthalocyanines, $Eu(Nc)_2$, were measured in dimethyl formamide solution using degenerate four wave mixing at 532 nm under nanosecond pulse excitation. Effective nonlinear absorption coefficient, β_{eff} and imaginary part of nonlinear susceptibility, $Im(\chi^{(3)})$ were obtained using open aperture Z-scan technique at the same wavelength. Optical limiting property of the sample was also investigated. The role of excited state absorption in deciding the nonlinear properties of this material is discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Organic compounds like porphyrins and phthalocyanines (Pc's) have several advantages over inorganic materials as far as their third order nonlinear optical (NLO) properties are concerned. Some of the important features of this class of compounds are their large optical nonlinearity, ultrafast response time, chemical and thermal stability and structural flexibility. Metal Pc's are planar centrosymmetrical macromolecules with

D_{4h} symmetry containing 18π electrons per each Pc ring. Large nonlinearity is usually attributed to the presence of easily polarizable π electrons and owing to their flexibility, the structure of these systems can easily be modified [1–3]. Structural modifications that are very relevant in the context of the nonlinear and spectroscopic properties of these materials are (1) the presence of metal ions in the center, (2) nature of peripheral substituents and (3) presence of additional conjugation. Introduction of peripheral substituents as well as central metal ions alters the electronic structure of the molecules and results in effective intramolecular charge transfer processes and thus provides parameters to tailor suitably the nonlinear response [4,5]. Measurement of NLO parameters of different structural variants helps us to study the origin and extent of the nonlinearity as well as to exploit

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NLO effects in appropriate areas of optical technology like optical limiting, optical computing, and optical communication. For example, efforts are in progress in many laboratories for the realization of all optical devices [6]. Such devices can do away with electrical/optical/electrical conversion existing in the present communication system, which really limits the optimum use of available speed.

In the light of wide applications of NLO effects, a large number of materials have been synthesized and their NLO properties have been explored using different techniques like degenerate four wave mixing (DFWM), Z-scan and third harmonic generation (THG) [7–11]. Here we are interested in the third order NLO properties of electronic origin of a bis-naphthalocyanine viz. europium naphthalocyanine, $Eu(Nc)_2$ dissolved in dimethyl formamide (DMF). Naphthalocyanines (Nc's) are compounds with additional conjugation with respect to corresponding Pc's. In the present work second hyperpolarizability $\langle \gamma \rangle$ and figure of merit F which is defined as $\chi^{(3)}/\alpha$, (α is the linear absorption coefficient) have been measured for $Eu(Nc)_2$ using DFWM at 532 nm with a nanosecond laser. Nonlinear absorption was also studied using open aperture Z-scan technique. Nonlinear absorption coefficient β and imaginary part of nonlinear susceptibility, $Im(\chi^{(3)})$ have been calculated. Effect of nonlinear absorption on optical limiting was demonstrated in a separate and independent experiment.

2. Experimental

DFWM experiment was carried out at 532 nm using the second harmonic of a Nd:YAG laser (GCR 170, Quanta Ray, 7 ns pulse width). Standard back scattering configuration of DFWM was used for the experiment. In nanosecond regime usually thermal effect dominates. Here we are interested mainly in the nonlinearity, which arises from the electronic response. Therefore polarizations of the beams were so chosen so as to avoid thermal effects. The two pump beams were s polarized and probe beam was π polarized. In the present phase conjugation set up the pump-probe

angle was adjusted to be nearly 8°. The two pump beams were of nearly equal intensity. Pump-probe intensity ratio was about 5. The phase conjugate beam, which retraces the path of probe beam, was separated using a beam splitter. The experimental set up for DFWM was calibrated by measuring the ratio of $\chi^{(3)}_{yxyx}$ to $\chi^{(3)}_{xxxx}$ for CS_2. This ratio was found to be 0.695, which is very close to the literature value 0.706 [12]. The interacting beams had a diameter of nearly 8 mm and these were used in the experiment without focussing.

In the open aperture Z-scan experiment transmittance of the sample is measured as the sample is moved along the propagation direction (z) of a focused gaussian laser beam. In the present experiment the laser beam was focused with a lens of focal length of 20 cm producing a beam waist ω_0 of 13 μm and Rayleigh range z_0 of 1.5 mm at the sample. The sample was taken in a cuvette of path length 1 mm, which is less than the Rayleigh range in the sample. Therefore thin sample approximation is reasonably valid.

In both Z-scan and DFWM experiments input and output energy were measured using photodiodes (Newport 818 UV and Melles Griot 13DA 007) and were averaged over hundred shots using digital storage oscilloscope (Tektronix TDS 220)

3. Results and discussion

Fig. 1 shows the structure of $Eu(Nc)_2$. In this case metal ion is sandwiched between two Nc planes. Absorption spectrum of the sample is given in Fig. 2. It is to be noted that compared to the corresponding Pc's, $Eu(Nc)_2$ has higher degree of conjugation.

0.1 mM solution of $Eu(Nc)_2$ was used in the experiment. Pump beam energy was varied from 1 to 5 mJ. Fig. 3 shows the log–log plot of the phase conjugate intensity against pump beam intensity. The plot is a straight line with slope equal to 3. This value may be considered as close to three and hence it is indicative of the third order process involved in the phenomenon. It also suggests that there is no saturation of the nonlinearity. The $\chi^{(3)}$ was calculated with respect to a reference sample CS_2 using the equation [13]
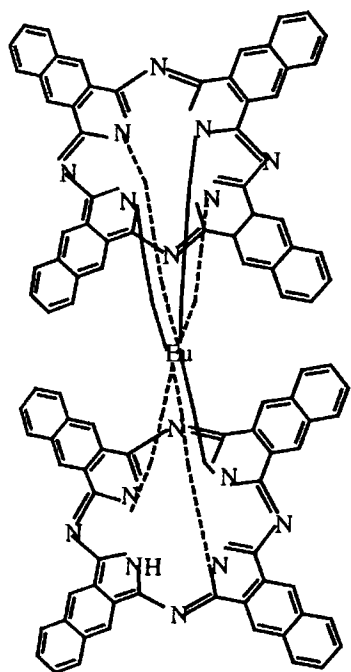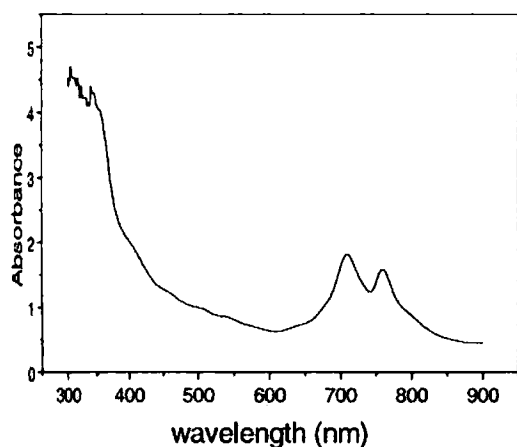
Fig. 1. Structure of europium naphthalocyanine.

Fig 2. Absorption spectrum of europium naphthalocyanine in solution of DMF.

$$I^{\prime} = \chi_{\text{ref}}^{(3)} \left[\frac{(I/I_0^3)}{(I/I_0^3)_{\text{ref}}} \right]^{1/2} \left[\frac{n}{n_{\text{ref}}} \right]^2 \frac{I_{\text{ref}}}{I}$$

$$\times \frac{\alpha l}{(1 - e^{-\alpha l})e^{-\alpha l/2}} . \qquad (1)$$

Here n is the refractive index, I is the sample length, I_0 and I are pump intensity and phase
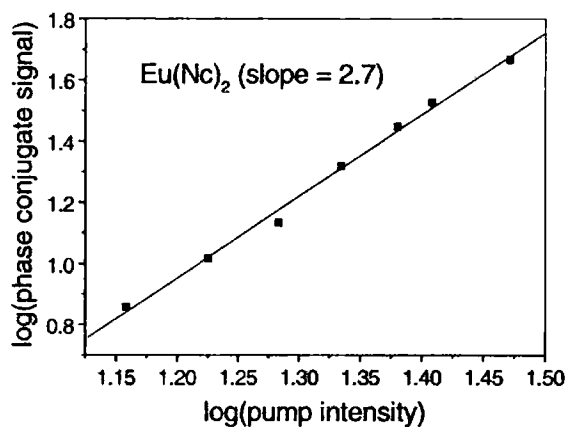

Fig. 3. Log–log plot of phase conjugate signal intensity against pump beam intensity (in arbitrary units).

conjugate signal intensity, respectively. $\chi_{\text{ref}}^{(3)}$ was taken to be 2.73×10^{-13} esu [12]. The $\chi^{(3)}$ of the solvent was also measured in the same experimental condition. In the case of absorbing sample we can define figure of merit F for third order nonlinearity which characterizes the nonlinear response that can be achieved for a given absorption loss. F values are very often used for comparing different types of absorbing samples.

Microscopic third order nonlinear response is characterized by second hyperpolarizability $\langle\gamma\rangle$. The second hyperpolarizability of solute can be calculated using pairwise additive model using the following equation [4]:

$$\langle\gamma\rangle = \frac{\chi_{\text{solution}}^{(3)} - \chi_{\text{solvent}}^{(3)}}{L^4 N_{\text{solute}}} . \qquad (2)$$

Here N_{solute} is the number density of the solute per cm^3 and $L = (n^2 + 2)/3$ is the local filed correction factor. The measured values of the nonlinear susceptibility, figure of merit and hyperpolarizability of the sample and solvent are given in Table 1.

In the case of metal substituted macromolecules second hyperpolarizability is dependant on the π electron conjugation as well as the extent of distortion of the same by central metal ion. It also depends on how closer the wavelength of excitation is with respect to absorption maximum of the sample. Around 532 nm, though linear absorption of this class of macromolecules is weak, they generally exhibit fairly good excited state absorption

Table 1
Measured values of third order susceptibility, figure of merit and second hyperpolarizability of the of europium naphthalocyanix DMF solution

Sample	α (cm^{-1})	$\chi^{(3)}$ ($\times 10^{-13}$) esu	$\chi^{(3)}/\alpha$ ($\times 10^{-13}$) esu cm	$\langle \gamma \rangle$ ($\times 10^{-32}$) esu
Solvent(DMF)		0.37		
Eu(Nc)$_2$ in DMF	0.55	1.6	2.9	55

Third order susceptibility of the DMF is also given.

(ESA) in this wavelength region [14], which can contribute to the imaginary part of $\chi^{(3)}$. Contribution of ESA to Im($\chi^{(3)}$) was measured using open aperture Z-scan technique and this is discussed in the following paragraph. Apart from that, measurement of DFWM gives combined contribution of central metal ion and π electron conjugation to nonlinearity. It is possible to separate the effect of π electron conjugation from that of central metal ion by studying the NLO properties of corresponding metal free naphthalocyanine and comparing the results with that of Eu(Nc)$_2$. Metal may introduce additional energy levels in HOMO–LOMO gap. This can result in some new weak absorption lines and/or small shift in absorption maxima with respect to corresponding metal free compound. Evidently these types of spectral changes effected by central metal ion can influence the NLO properties considerably. Here these contributions are not separated and therefore we wish to attribute observed nonlinearity to combined effect of conjugation, central metal ion and ESA.

Pc's and Nc's have an excited state absorption cross section that is higher than that of the ground state. Consequently these molecules exhibit ESA which can be used for passive optical power limiting. Nonlinear absorption present in the sample can be accounted for by defining the nonlinear absorption coefficient as β_{eff}. It is a measure of the over all nonlinear absorption, which may include ESA as well as instantaneous two-photon absorption (ITPA). Correspondingly Im($\chi^{(3)}$) is designated as Im($\chi^{(3)}_{eff}$) [15]. This is essential to take into account all the possible nonlinear absorption processes in the sample.

Effective nonlinear absorption coefficient was calculated from open aperture Z-scan experiment by fitting the experimental data to the normalized

transmittance (normalized to large values of given by the equation [16]

$$T(z) = \frac{C}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2})\, dt,$$

C is the normalizing constant, $q_0 = (\beta_0 I_0 d)$ $(1 + x^2)$, where I_0 is the irradiance at focus, z/z_0 and $I_{eff} = (1 - e^{-\alpha l})/\alpha$ is the effective length. Here α is the linear absorption coefficient and l the sample length.

Fig. 4 shows the open aperture Z-scan curve the sample of concentration 0.2 mM for an irradiance of 152 mW/cm^2 at focal region after corrected for front surface fresnel reflection. Decrease of transmission around the focal point is indicate of the presence of nonlinear absorption. From the fit to the experimental data, β_{eff} was calculated to be 39 cm GW^{-1} which gives Im($\chi^{(3)}_{eff}$) 0.25 × 10^{-13} esu. From Table 1, we get the difference between the $\chi^{(3)}$ values of the sample solvent as 1.23 × 10^{-13} esu. The Im($\chi^{(3)}_{eff}$) obtain
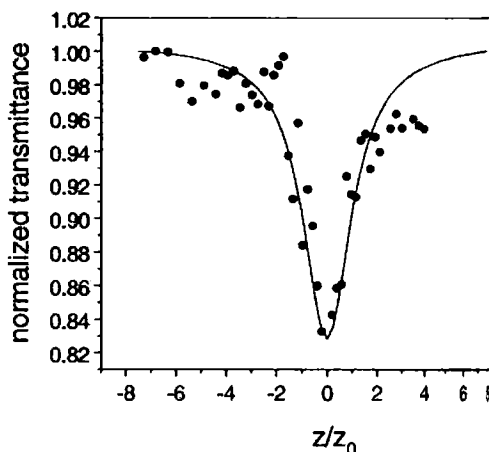

Fig. 4. Open aperture Z-scan curve: (•) experimental theoretical fit.

from Z-scan experiment is less than 1.23×10^{-13} esu, in spite of the fact that concentration of the sample used in Z-scan experiment is higher than that of the sample used in DFWM. This seems to indicate that though NL absorption do contribute to $\chi^{(3)}$, observed value of $\chi^{(3)}$ in DFWM experiment may not be due to nonlinear absorption alone. This conjecture can be verified by performing a closed aperture Z-scan measurements, as it gives only real part of $\chi^{(3)}$ [Re($\chi^{(3)}$)]. But under nanosecond excitation, closed aperture Z-scan measurements is dominated by thermal effects and hence picosecond measurements may be required for this purpose.

Presence of nonlinear absorption can result in passive optical power limiting. Fig. 5 shows throughput measured against input laser energy for 0.2 mM solution taken in a cuvette of path length 1.4 mm. Laser beam was focussed by a lens of focal length 20 cm. The sample was kept sufficiently away from the focal point to avoid surface damage. Corresponding nonlinear transmission (shown in inset) clearly shows that transmission decreases to 70% of the linear transmission as a result of nonlinear absorption.

Nonlinear absorption under nanosecond excitation can be easily explained using a five-level model involving S_0, S_1, S_2, T_1 and T_2 as shown in Fig. 6 [17]. Here S's and T's correspond to singlet and triplet manifold, each containing a number of vibrational levels. Molecules are initially excited
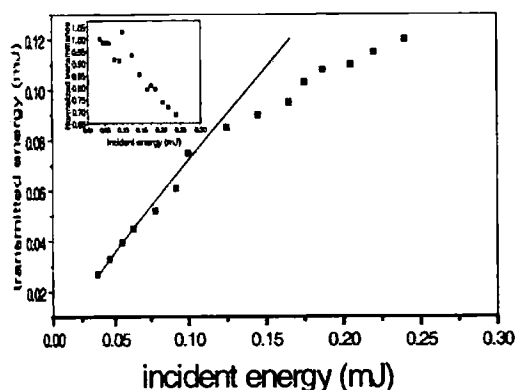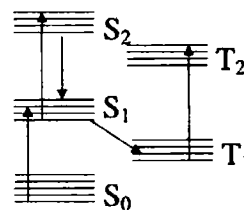

Fig. 6. Energy level diagram (five-level model) $T_1 \leftarrow S_1$ transition is nonradiative.

electronically from lowest vibrational level of S_0 to upper vibrational levels of $S_1 [S_1 \leftarrow S_0(v = 0)]$. Here v corresponds to vibrational quantum number. From there molecules will arrive at lowest vibrational level of $S_1(v = 0)$ in picoseconds by nonradiative decay. In nanosecond time scale $(S_2 \leftarrow S_1)$ singlet transition does not deplete population in S_1 appreciably as atoms excited to S_2 decay to S_1 itself within picoseconds. From S_1 molecules finally go to T_1 via intersystem crossing wherefrom they are excited to T_2. Nonlinear absorption observed here is a consequence of $T_2 \leftarrow T_1$ absorption $[T_2 \leftarrow T_0(v = 0)]$.

Bis-Pc's have a structure similar to that of $Eu(Nc)_2$. F and $\langle\gamma\rangle$ values for some bis-Pc's obtained are reproduced in Table 2 from [18]. F values are often used to compare the over all third order nonlinearity of a variety of samples. It can be seen that the sample in the present experiment exhibits fairly high F values compared to bis-Pc's given in Table 2. $\langle\gamma\rangle$ value is also higher in the present case. Mono Pc's, porphyrins, etc. generally have a structure considerably different from that of our sample. However FePc and some of its

Fig. 5. Throughput measured against input energy. Inset figure shows corresponding nonlinear transmission; (—) linear transmission.

Table 2
Values of figure of merit and second hyperpolarizability of some bis-Pc's at 1.06 μm

Sample	α (cm^{-1})	$\chi^{(3)}/\alpha$ ($\times 10^{-13}$) esu cm	$\langle\gamma\rangle$ ($\times 10^{-32}$) esu
Sc(Pc)$_2$	3.5	0.6	48
Lu(Pc)$_2$	1.3	1	34
Yb(Pc)$_2$	1.5	1	41
Y(Pc)$_2$	.62	2	26
Gd(Pc)$_2$	.58	2	22
Eu(Pc)$_2$	0.51	2	22
Nd(Pc)$_2$	0.53	1	15

Reproduced from [18].

derivatives reported in [13] show higher F values than that of our sample. Basket handled porphyrins have been studied by Kumar et al. [10] but F values have not been mentioned in their work. Within the scope of this paper, we have not evaluated the excited state absorption cross section σ_{ex} of $Eu(Nc)_2$. In order to compare the optical limiting property of different samples exhibiting excited state absorption, figure of merit of nonlinear absorption, which is the ratio of σ_{ex} to σ_g (σ_g is the ground state absorption cross section) is more appropriate parameter than β_{eff}. These aspects are under investigation.

4. Conclusions

Moderately strong phase conjugate reflections were observed from the solutions of $Eu(Nc)_2$ under DFWM configuration. Third order susceptibility, second hyperpolarizability and figure of merit were calculated for the sample at 532 nm. Imaginary part of $\chi^{(3)}$ was also obtained from open aperture Z-scan experiment. These measurements show that observed value of $\chi^{(3)}$ seen in DFWM may not be due to ESA alone. The sample exhibits optical limiting phenomenon.

Acknowledgements

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