

Degenerate four wave mixing in some metal phthalocyanines and naphthalocyanines

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Abstract

Here we report measurements of third-order susceptibility $\chi^{(3)}$, figure of merit F defined as $\chi^{(3)}/\alpha$ (where α is the absorption coefficient) and second hyperpolarizability $\langle\gamma\rangle$ of some metal substituted phthalocyanines and a naphthalocyanine in solutions of dimethyl formamide using degenerate four wave mixing at 532 nm under nanosecond excitation. It was found that among samples investigated, bis-naphthalocyanine possessed the highest value of $\langle\gamma\rangle$ followed by the bis-phthalocyanine. This observation is explained on the basis that bis-naphthalocyanine followed by bis-phthalocyanine has higher degree of π electron conjugation. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Experimental investigation of nonlinear optical (NLO) properties is of paramount importance considering the fact that NLO effects are being increasingly exploited in a number of technological applications such as optical computing, passive optical power limiting and design of logic gates [1,2]. In fact innovations in technological applications of NLO effects have a symbiotic relationship with synthesis of suitable NLO materials and their proper characterization. For technological applications large and fast acting

nonresonant optical nonlinearity is usually preferred. Besides, there are a number of other desired properties for NLO materials like thermal and chemical stability and ease of molecular structural engineering. Organic macromolecules with extensive π electron conjugation like porphyrins, phthalocyanines (Pcs), naphthalocyanines (Ncs) and their different types of derivatives form a class of compounds which satisfy many of these requirements [3]. Therefore investigation of NLO properties of this class of compounds is very relevant and highly desirable. Here we report the measurements of third-order susceptibility $\chi^{(3)}$, figure of merit F [$F = \chi^{(3)}/\alpha$, where α is the absorption coefficient] and second hyperpolarizability $\langle\gamma\rangle$ of some metal Pcs (MPcs) and a metal Nc (MNc) using nanosecond degenerate four wave mixing in optical phase conjugation geometry. The samples selected include mono Pc [FePc, LaPc and MoOPc], a bis-Pc [Sm(Pc)₂] and

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a bis-Nc [Eu(Nc)₂]. It is worth noticing that samples selected have different levels of π electron conjugation due to their structural differences. The central metal ion of each sample also varies. Both the extent of π electron conjugation and nature of central metal ion are known to influence the NLO properties of this class of compounds significantly [4–6]. Therefore measurements reported here can give some insight in to the contribution of these two factors to third-order NLO parameters.

2. Experimental

DFWM experiment was carried out at 532 nm using the second harmonic of a Nd:YAG laser (GCR 170 Quanta Ray) in standard optical phase conjugation geometry (back scattering geometry). Here we are interested in the nonlinearity, which arises mainly out of the electronic response. Therefore in the present experimental set up the polarizations of the interacting beams were appropriately chosen so as to avoid the formation of a thermal grating. The two pump beams were s polarized and probe beam was π polarized. The two pump beams were of nearly equal intensity and pump–probe intensity ratio was adjusted to be about five. The angle between the pump and probe beam was about 8°. Samples were taken in cuvette of path length 1 mm. Pump beam intensity and probe beam intensity were measured in arbitrary units using photodiodes (Newport UV 818 and Melles Griot 13DAS 007) and were averaged over hundred shots using a digital storage oscilloscope (Tektronix TDS 220). The experimental setup was calibrated using CS₂ by measuring the ratio of χ_{yyxx} to χ_{xxxx} . The measured value was 0.695, which is very close to the value reported in the literature 0.706 [7]. The interacting beams had a diameter of about 8 mm and these were used in the experiment without further focusing.

Structures of the samples investigated here are given in Fig. 1. MPcs are planar molecules with D_{4h} symmetry containing 18 π electrons per ring [8]. Both bis-Pcs and bis-Ncs have identical structures where metal ion is sandwiched between two Pc or Nc planes. It is to be noted that Ncs contain

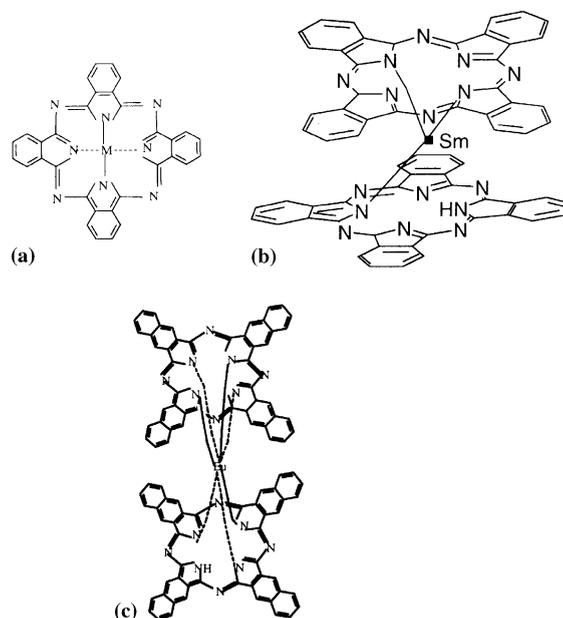


Fig. 1. (a) Structure of MPc ($M \equiv Mo = O, La$ and Fe); (b) structure of $Sm(Pc)_2$; (c) structure of $Eu(Nc)_2$.

four additional benzene rings and hence they possess higher degree of π electron conjugation in comparison with Pcs. The samples were dissolved in dimethyl formamide (DMF). Concentration of the samples varied from 0.1 to 0.3 mM. Absorption spectrum of each sample was recorded (Jasco V 570) and these are given in Fig. 2. Pump beam energy was varied from 2 mJ to a maximum of 7 mJ depending on the sample.

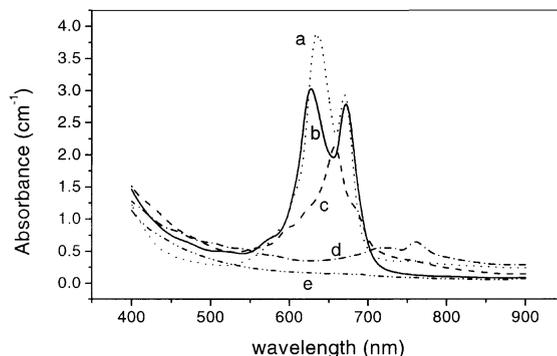


Fig. 2. Absorption spectra of the samples in solutions of DMF: (a) LaPc, (b) $Sm(Pc)_2$, (c) MoOPc, (d) $Eu(Nc)_2$, (e) FePc.

3. Results and discussion

Phase conjugate signal intensity $I(\omega)$ depends on the pump beam intensity $I_0(\omega)$ as given by the relation

$$I(\omega) \propto \left(\frac{\omega}{2\varepsilon_0 cn^2} \right)^2 |\chi^{(3)}|^2 I_0^3(\omega). \quad (1)$$

This relation shows that there is a cubic dependence for signal intensity on pump beam intensity. Fig. 3 shows the log–log plot of phase conjugate signal intensity measured against pump beam intensity for MoOPc. Similar plots were obtained for all other samples also. All the plots had a slope nearly equal to 3 (within the limit 3 ± 0.3), which is characteristic of third-order process involved. This also suggests that there is no saturation of nonlinearity in the measurements. The phase conjugate signal intensity from the solvent was also

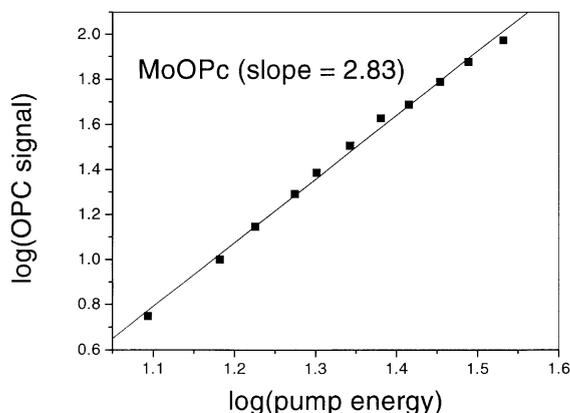


Fig. 3. Log–log plot of phase conjugate intensity against pump beam intensity for MoOPc in arbitrary units.

measured under identical condition. This is essential to understand contribution of the solvent to observed phase conjugate signal from the sample. $\chi^{(3)}$ of the sample was calculated with respect to a reference sample CS_2 using the equation [9]

$$\chi^{(3)} = \chi_{\text{ref}}^{(3)} \left[\frac{(I/I_0^3)}{(I/I_0^3)_{\text{ref}}} \right]^{1/2} \left[\frac{n}{n_{\text{ref}}} \right]^2 \frac{l_{\text{ref}}}{l} \times \frac{\alpha l}{(1 - e^{-\alpha l})e^{-\alpha l/2}}. \quad (2)$$

Here n is the refractive index, α is the linear absorption coefficient and l is the sample length. $\chi_{\text{ref}}^{(3)}$ was taken to be 2.73×10^{-13} esu [7]. In absorbing samples we can define the figure of merit (F) of third-order nonlinearity as $\chi^{(3)}/\alpha$. F is a measure of the maximum nonlinearity that can be achieved in the sample for a given absorption loss. F is very often used for comparing the third-order nonlinearity of different absorbing samples.

Second hyperpolarizability $\langle \gamma \rangle$ is a measure of microscopic third-order nonlinearity. Second hyperpolarizability of the solute can be calculated from the measured values of $\chi^{(3)}$ of the sample and that of the solvent using the equation [10]

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

Here N_{solute} is the number density of the solute per cm^3 , and $L = (n^2 + 2)/3$ is the local field correction factor. Measured values of $\chi^{(3)}$, F and $\langle \gamma \rangle$ are given in Table 1. From Table 1 it is clear that the $\chi^{(3)}$ of all the samples are at least three times higher than that of the solvent. Among the samples investigated, LaPc possessed the highest F value and $\text{Eu}(\text{Nc})_2$ had the lowest F value. $\text{Eu}(\text{Nc})_2$ have highest $\langle \gamma \rangle$ value followed by $\text{Sm}(\text{Pc})_2$. Measured

Table 1

Measured values of third-order susceptibility $\chi^{(3)}$, figure of merit F and second hyperpolarizability $\langle \gamma \rangle$ of the samples investigated

Sample	α (cm^{-1})	$\chi^{(3)}$ ($\times 10^{-13}$ esu)	F ($\times 10^{-13}$ esu-cm)	$\langle \gamma \rangle$ ($\times 10^{-32}$ esu)
$\text{Eu}(\text{Nc})_2$	0.55	1.6	2.9	55
$\text{Sm}(\text{Pc})_2$	0.48	1.8	3.75	43.6
MoOPc	0.5	1.86	3.72	31
LaPc	0.3	1.39	4.6	24
FePc	0.3	1.14	3.8	13
DMF (solvent)		0.35		

$\chi^{(3)}$ value of the solvent is also given.

$\langle\gamma\rangle$ values of mono Pcs are smaller than those of $\text{Sm}(\text{Pc})_2$ and $\text{Eu}(\text{Nc})_2$.

$\langle\gamma\rangle$ values depend on a number of factors. In the context of the samples investigated here, important parameters that can influence $\langle\gamma\rangle$ values are: (1) the level of π electron conjugation, and (2) extent of distortion of the same by metal ion. Possibility of one-photon or multiphoton absorption also needs to be considered at the excitation wavelength. In the case of Pcs and Ncs, linear absorption is very weak around 532 nm but many of these compounds exhibit fairly strong reverse saturable absorption (RSA) [also known as excited state absorption (ESA)] in this wavelength region [11]. ESA can contribute to imaginary part $\chi^{(3)}$, which in turn influences measured $\langle\gamma\rangle$ values.

The highest values of $\langle\gamma\rangle$ obtained for $\text{Eu}(\text{Nc})_2$ followed by $\text{Sm}(\text{Pc})_2$ can be most probably due to the fact that these two compounds have the highest degree of π electron conjugation in that order with respect to all the other samples mentioned here. This obviously implies that lower $\langle\gamma\rangle$ values of MoOPc, LaPc, FePc with respect to $\text{Eu}(\text{Pc})_2$ and $\text{Sm}(\text{Pc})_2$ are mainly due to reduced level of π electron conjugation of these compounds. Among mono Pcs studied here MoOPc and FePc were observed to have highest and the lowest $\langle\gamma\rangle$ values, respectively. LaPc has a $\langle\gamma\rangle$ value in between MoOPc and FePc. These three samples differ by the nature of central metal atom and therefore we can attribute observed differences in $\langle\gamma\rangle$ values mainly to the varying influence of the metal ions in respective samples.

Mo and Fe are transition metals. Transition metal substitution can result in several charge-transfer (CT) mechanisms. They include metal–ligand charge transfer (MLCT), ligand–metal charge transfer (LMCT) and metal–metal charge transfer. These mechanisms can result in the formation of some new energy states in the HOMO–LUMO gap, which eventually modifies the NLO properties of the compound significantly [12,13]. Large $\langle\gamma\rangle$ value of MoOPc in comparison with FePc can be due to the possible presence of such CT process occurring in it. However CT processes are not reported in nontransition metal substituted compounds and therefore higher $\langle\gamma\rangle$ of LaPc with

respect to FePc can be due to different mechanisms. A probable reason is the enhanced contribution from ESA because in compounds with identical structures, ESA is usually higher in the case of heavy metal substituted compounds [14].

Reji et al. [9] have reported the F and $\langle\gamma\rangle$ values of FePc dissolved in dichloromethane at 532 nm itself as 6.9×10^{-13} esu-cm and 27×10^{-32} esu, respectively. They have not subtracted the $\chi^{(3)}$ value of the solvent as in Eq. (3). If $\chi^{(3)}$ value of the solvent is not subtracted, $\langle\gamma\rangle$ values for FePc in the present case is obtained from Eq. (3) as 19×10^{-32} esu. This value is less than 27×10^{-32} . Difference in measured values can be partly due to differences in experimental conditions. Reji et al. measured $\langle\gamma\rangle$ value at 35 ps. In Pcs nonlinear and other photo-physical properties strongly depend on excited states. When pulse width changes from picoseconds to nanoseconds the behaviour of excited states will vary. Besides the polarizations of the interacting beams are also different from those in the present case. Therefore direct comparisons of these two results may not be entirely appropriate.

4. Conclusion

Third order nonlinear susceptibility, figure of merit and second hyperpolarizability were measured for a number of Pcs and Ncs dissolved in DMF with DFWM technique at 532 nm. It was observed that among the samples investigated, bis-Nc [$\text{Eu}(\text{Nc})_2$] followed by bis-Pc [$\text{Sm}(\text{Pc})_2$] possessed higher $\langle\gamma\rangle$ values. This is attributed to the presence of higher π electron conjugation in these molecules. Among mono Pcs, MoOPc was found to have higher $\langle\gamma\rangle$ value, which is attributed to the presence of CT processes occurring in it.

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