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Nanosecond optical limiting response of sandwich-type neodymium dyphthalocyanine in a co-polymer host

B. Aneeshkumar [a,*], Pramod Gopinath [a], Jayan Thomas [b],
C.P.G. Vallabhan [a], V.P.N. Nampoori [a], P. Radhakrishnan [a]

[a] *International School of Photonics, Cochin University of Science and Technology, Cochin 682 022, India*
[b] *Optical Science Center, The University of Arizona, Tucson, AZ 85721, USA*

Abstract

The nanosecond optical limiting characteristics of sandwich-type neodymium diphthalocyanine in a co-polymer matrix of polymethyl methacrylate (PMMA) and methyl-2-cyanoacrylate have been studied for the first time. The measurements were performed using 9 ns laser pulses generated from a frequency-doubled Nd:YAG laser at 532 nm wavelength. The optical limiting performance of neodymium diphthalocyanine in co-polymer host was studied at different linear transmission. Laser damage threshold was also measured for the doped and undoped co-polymer samples. The optical limiting response is attributed to reverse saturable absorption which is due to excited-state absorption.
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1. Introduction

Over the last decade, many research groups have been involved in the research for effective optical limiting materials in the visible wavelength region [1–4]. These optical limiting materials have potential applications in strong laser modulation and the protection of optical sensors and human eyes from intense laser light. A good optical limiting material should possess high linear transmission at very low incident light energy and low transmission under intense light radiation. Materials with weak ground-state absorption and strong excited-state absorption are ideal material for a good optical limiter. Here the optical limiting response is caused by a mechanism known as reverse saturable absorption (RSA) [5]. It results from population of the excited states with a large absorption cross-section in comparison with that of the ground state, which generally has an extremely fast response for involving electronic transitions. Singlet and triplet excited states can cause reverse saturable absorption. At short laser pulses, on the picosecond timescale, singlet-state absorption provides nonlinear attenuation. If the laser pulses are in the nanosecond timescale (~10 ns),

the molecules should posses high triplet yields and long triplet lifetimes to attenuate the laser pulses [6].

Recently, RSA has been found in many organic and organometallic compounds like organometallic cluster compounds, porphyrins, metallo-phthalocyanines and fullerenes [7–9]. Among these materials, metallo-phthalocyanines exhibit very good RSA and they are considered to be one of the benchmark materials for optical limiting [9–14]. Metallo-phthalocyanines are characterized by an extremely delocalyzed π-conjugated electron system. It is a two-dimensional large molecule with D_{4h} symmetry. The physical and chemical properties of these materials can be easily tailored by substituting various functional groups at peripheral sites and by incorporating different metal atoms into the ring. All metallo-phthalocyanines do have two similar ground-state absorption bands: the Q-band in the visible region in the 600–800 nm range and a B-band (Soret-band) in the 300–400 nm range [6]. In the spectral window between these two bands, all metallo-phthalocyanines have large excited-state absorption. Therefore, the RSA in metallo-phthalocyanines can be observed in this spectral window.

The excited-state absorption of metallo-phthalocyanines can be greatly enhanced by substituting the central metal atom with a heavy metal atom. Perry et al. [3] have shown that phthalocyanine complexes with paramagnetic coordinating groups or with heavy metal atoms covalently attached

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* Corresponding author. Tel.: +91-484-2575848;
fax: +91-484-2576714.
E-mail address: b.aneeshkumar@tuc.nl (B. Aneeshkumar).

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to the conjugated ring exhibit enhanced triplet–triplet absorption and optical limiting response for nanosecond laser pulses because of the increased intersystem crossing rates and quantum yields of excited triplet states. In this article, we report what are to our knowledge the first experimental observation of optical limiting response of neodymium diphthalocyanine (Nd(Pc)$_2$) in a co-polymer matrix of methyl-2-cyanoacrylate and methyl methacrylate.

2. Molecular structure and sample preparation

The optical limiting response of many chromophores have been studied in different solid matrices [15–19]. A solid-state optical limiter is simpler to implement for applications in imaging systems, night vision goggles, and coated or bulk windows. It also helps to make concentration gradient materials. The co-polymer solid host used in this work has excellent optical quality, high mechanical strength and reasonably high laser damage threshold. Moreover, all the lanthanide phthalocyanines show very good solubility in the monomer mixture. So, this matrix can be also used to host other rare earth phthalocyanines. A further advantage of this co-polymer host is the absence of elevated temperature during the co-polymerization process. This reduces the risk of temperature induced degradation of the dopant materials.

As a rare earth phthalocyanine, neodymium phthalocyanine has a diphthalocyanine structure [20]. Diphthalocyanine is a sandwich compound with two phthalocyanine (Pc) rings coordinated to a central metal atom. The two Pc ligands, which are rotated 45° with respect to each other. Furthermore, one of the Pc rings is virtually planar while the other is significantly distorted [21]. Sandwich-type metal diphthalocyanines have found many applications in material science, especially in molecular conductivity, gas sensing property, electrochromism and optical limiting property. The UV-Vis spectra of metallo-phthalocyanines showed complex spectra

compared to that of planar Pc monomers [22]. The complex nature of the spectra is due to the fact that π–π interaction between the two Pc ligands might lead to a splitting of the degenerate molecular orbitals of each monomer. The molecular structure of Nd(Pc)$_2$ is shown in Fig. 1.

Nd(Pc)$_2$ was prepared by a modification of a known method [23]. A mixture of 3 g of 2,3-dicyanobenzene and 1 g of neodymium acetate was heated to 280 °C in a nitrogen flushed evacuated glass ampoule. The dark shinning product was isolated from the mixture by Soxhlet extraction with chloroform. The sample so obtained in powder form was carefully washed with acetic anhydride and acetone to remove traces of persistent impurities. Final chemical purification was done by dissolving the sample in dimethyl formaldehyde and passing it through a column of aluminum oxide. It was then eluted using methanol. The solution was evaporated to dryness and the residue was vacuum dried at 100 °C for 1 h. The purified sample was identified by elemental analysis, UV-Vis and IR spectroscopic techniques.

The solid transparent matrix chosen for doping the Nd(Pc)$_2$ was a co-polymer of methyl-2-cyanoacrylate and methyl methacrylate. The undoped co-polymer host was transparent in the entire visible and near IR range. In order to fabricate the co-polymer host impregnated with the Nd(Pc)$_2$, a casting solution was prepared by dissolving the Nd(Pc)$_2$ in a homogeneous mixture of methyl-2-cyanoacrylate and methyl methacrylate monomer. This diphthalocyanine showed very good solubility in this monomer mixture. This uniform mixture was filled in a clean glass mold made out of optically flat glass plates. Large samples, completely free of air bubbles were obtained after a co-polymerization reaction. Since the mould was fabricated from optically flat glass plates the samples have extremely high surface quality, so that no polishing was required and hence, there was minimum scattering of the laser beam at large angles from the sample. Thus, in the absence of scattering at large angles, the system measured change in transmission due to change
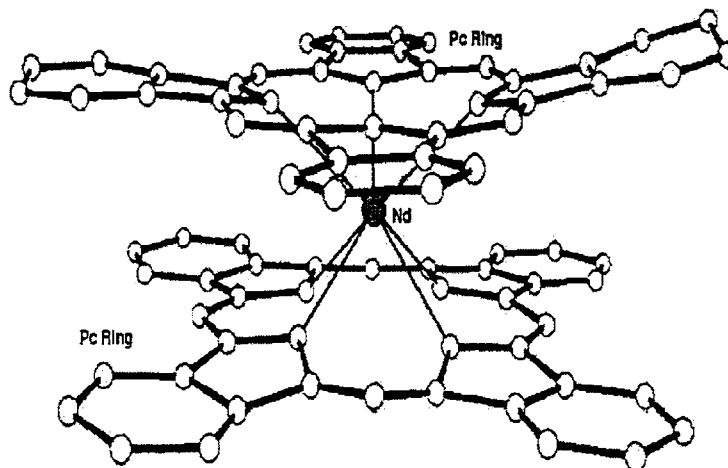

Fig. 1. Perspective view of the molecular structure of the sandwich-type neodymium diphthalocyanine.
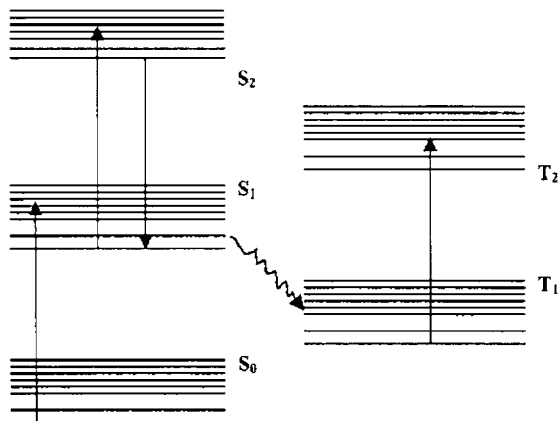
Fig. 2. Five level energy level model for the reverse saturable absorption in metallo-phthalocyanines.

in absorption only. The main advantages are the ease of high quality sample preparation and the rapid co-polymerization process in the absence of elevated temperature.

The $Nd(Pc)_2$ doped matrix has a dark green color. The ground-state absorption spectrum at room temperature of the doped polymer host is shown in Fig. 2. The Q-band at the 590–780 nm in the visible region is due to the electronic transitions to the π–π^* states. The Soret-band in the near UV region shows strong features and is very intense. The absorption valley is around 532 nm, so at this wavelength for nanosecond laser pulses, $Nd(Pc)_2$ will show reverse saturable absorption.

3. Experimental set-up

The optical limiting response of the doped co-polymer samples were performed using a standard experimental configuration. Laser wavelength at 532 nm from a frequency doubled Nd:YAG laser (Quanta Ray DCR-11) with a pulse width of 9 ns and repetition rate of 10 Hz was used to excite the sample. All the samples have a thickness of 2.2 mm, which is comparable to the sample thickness used by different groups [15,18,24]. The laser pulses were focused using a 15 cm focal length convex lens and the sample was placed in such a way that it was slightly away from the focal plane of the convex lens. This was to prevent the rapid optical breakdown of the co-polymer sample at the focal plane. The incident and transmitted energy was measured using energy detectors after averaging over 10 pulses. Compared with the light spot dimension, the much larger acceptance area of the energy probes ensured that a collection of all the energy of the pulse and thus the factor of nonlinear refraction was excluded. The optical limiting response was studied by varying the input energy with a laser beam attenuator arrangement and by monitoring the incident and transmitted energy. The maximum input energy was limited by the damage threshold of the $Nd(Pc)_2$ doped co-polymer host.

4. Results and discussions

The reverse saturable absorption of many chromophores can be described by a three-level model for the situation where the sample medium is excited by picosecond laser pulses. However, in this work, we used nanosecond laser pulses and therefore the intersystem crossing can be used to extend the optical limiting for longer laser pulses because of the added contribution to the absorption by the triplet states. Many authors [6,12,25,26] proposed a five-level model to describe the interaction of metallo-phthalocyanines with nanosecond laser pulses, which is depicted in Fig. 3. S_n and T_n are the singlet and triplet state, respectively, where $n = 0$, 1 or 2 and every electronic energy levels involve many vibronic sublevels. When interacting with a laser pulse at 532 nm, atoms from the $S_0(\nu = 0)$ level get excited to the upper vibrational level of S_1. Through a nonradiative decay within picoseconds, they can relax to the lowest vibrational level of $S_1(\nu = 0)$. Since Pc's have very low fluorescence [6] the transition from $S_1(\nu = 0)$ to S_0 can be neglected. There for the main decay mechanism is the intersystem crossing from $S_1(\nu = 0)$ to $T_1(\nu = 0)$. Here we assume that the intersystem crossing is fast compared to the laser pulse width (9 ns) and virtually all the atoms excited from S_0 reach first excited triplet state, T_1. In fact, the intersystem crossing is higher for heavy atom substituted Pc's due to large spin-orbit coupling of the metal orbital and their mixing with the orbitals of the conjugated ring [3]. There for under nanosecond pulse excitation, the main contribution to RSA comes from triplet states.

The experimental result of the output–input characteristics are shown in Fig. 4 for linear transmittances of 52 and 35% at 532 nm, respectively. At very low input fluence, the transmission obeys Ber-Lambert law. As the input fluence increases, the output fluence decreases and decreases with increase in input fluence. We observed an optical limiting response with saturated or clamped output fluency. The
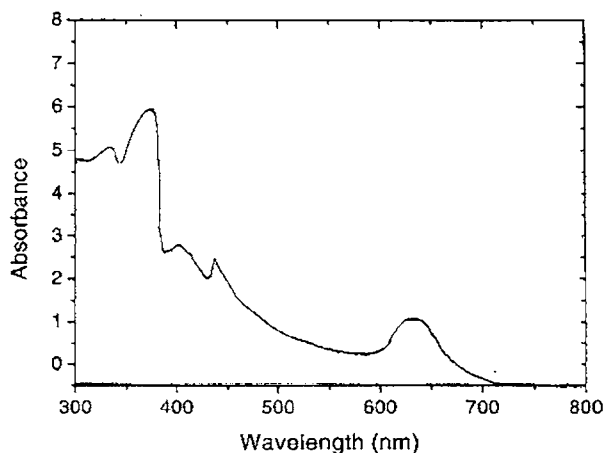

Fig. 3. Ground-state absorption spectrum of neodymium diphthalocyanine doped co-polymer host.
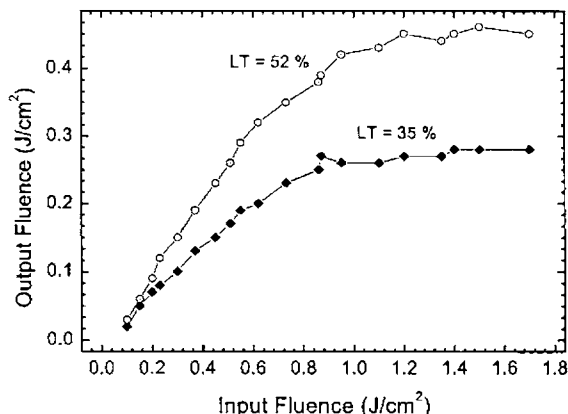
Fig. 4. Optical limiting response of neodymium diphthalocyanine doped co-polymer samples for 9 ns laser pulse at 532 nm. The linear transmittance was 35 and 52%, respectively.

Fig. 5. Plot of $\ln(I_0/I)$ vs. $(I_0 - I)$ for $Nd(Pc)_2$ doped co-polymer sample for two different linear transmittance. The straight line is the best linear fit to the experimental data points.

transmittance of both samples decreases remarkably with increased laser intensity, but the optical limiting response of the sample with 35% linear transmittance is better compared to the sample with 52% linear transmittance. The data shows that as the concentration increases, a reduction in linear transmittance as well as the clamping level is observed.

Reverse saturable absorption is due to excited-state absorption is the main mechanism for metallo-phthalocyanine molecules to produce an optical limiting effect. The ratio of effective excited- to ground-state absorption cross-section σ_{eff}/σ_0 can be used as a figure of merit for optical limiting based on reverse saturable absorption [27]. This can be defined as

$$\frac{\sigma_{eff}}{\sigma_0} = \ln\frac{T_{sat}}{\ln T_{lin}} \tag{1}$$

with

$$T_{sat} = \exp(-\sigma_{eff}N_0 l) \tag{2}$$

where T_{lin} is the linear transmittance at very low excitation power, T_{sat} is the saturated transmittance for high degree of excitation, N_0 is the total molecular population and l is the length of the laser pass through the doped co-polymer sample. As shown in Fig. 4, for a linear transmittance of 0.35, the saturated transmittance is 0.16. The estimated figure of merit is 1.7 from Eq. (1). Compared to the reported value of ~3 for C_{60} and >10 for phthalocyanine complexes [3,27] the figure of merit for the neodymium diphthalocyanine doped co-polymer sample is not large enough. However, a wide range of structural modifications at the molecular level is possible in metallo-phthalocyanines by substituting various functional groups at peripheral sites, which can dramatically improve the optical limiting performance [28–31]. Further studies of this influence on the optical limiting properties are deserved.
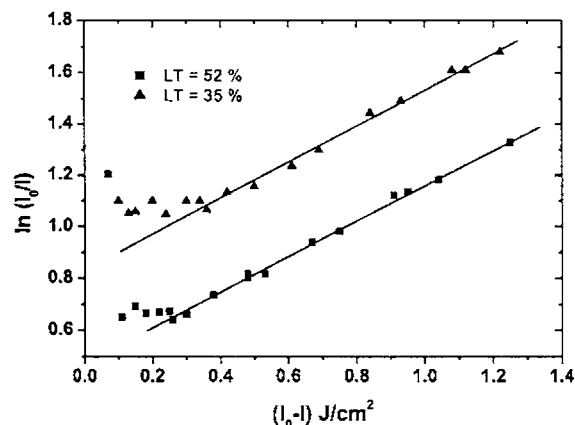
In the case of reverse saturable absorption, the incident laser intensity I_0 and the transmitted laser intensity I obeys the relation

$$\ln\left(\frac{I_0}{I}\right) = k(I_0 - I) + Ag \tag{3}$$

where k is a constant, which depends on the absorption cross-section and lifetimes of the ground, excited singlet and excited triplet states and Ag is the ground-state absorbance [32]. Eq. (3) says that the plot of $\ln(I_0/I)$ versus $(I_0 - I)$ should be a straight line with slope k and intercept Ag. Fig. 5 shows the plot of $\ln(I_0/I)$ versus $(I_0 - I)$ for the $Nd(Pc)_2$ doped co-polymer samples. The straight line nature of the graph is a clear indication that reverse saturable absorption is the main mechanism causing optical limiting in these samples.

Unnikrishnan et al. [33] already done the wavelength dependent nonlinear absorption studies in $Nd(Pc)_2$ using open aperture z-scan technique. Their measurements were done in a solution of $Nd(Pc)_2$ for wavelengths of 632, 624, 618, 612, 604 and 532 nm. The open aperture z-scan data show an increase in transmittance at the focal point for wavelength up to 612 nm. As the wavelength is decreased to 532 nm the transmittance at the focal point exhibit a decreasing behavior, which is typical of reverse saturable absorption. Phthalocyanines have large excited-state absorption cross-section around 532 nm [6]. So, the RSA observed in their measurements is attributed to excited-state absorption. In our optical limiting studies, the $Nd(Pc)_2$ is doped in a co-polymer host, which will not change the molecular structure of this compound. So, in our case also it is reasonable to believe that RSA due to excited-state absorption is the main mechanism responsible for the optical limiting response.

Laser damage thresholds for the $Nd(Pc)_2$ doped co-polymer samples; defined here to be the fluency required to cause a permanent measurable change in the sample transmission measurements. The damage threshold of the

mple is larger if the samples are translated laterally after
ery few shots during testing. The damage threshold of
samples ranged between 1.8 and 2 J/cm^2. The damage
eshold for the undoped co-polymer host was 2 J/cm^2. It
found that the presence of Nd(Pc)$_2$ in the co-polymer ma-
x reduces its damage threshold. For the Nd(Pc)$_2$-doped
polymer samples, the measured laser damage threshold
s 1.8 J/cm^2.

Conclusions

In summary, the optical limiting response of a sandwich-
pe neodymium diphthalocyanine in a co-polymer matrix of
ethyl methacrylate and methyl-2-cyanoacrylate has been
easured by using 9 ns laser pulses at 532 nm for differ-
nt linear transmittance. The laser damage threshold of the
ped co-polymer matrix was also reported. It was found
hat the damage threshold for the doped sample is reduced
y 10 % compared to the undoped sample.

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