

Invited Paper

Nonlinear optical absorption of zinc-phthalocyanines in polymeric matrix

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Abstract

We realized and investigated films of zinc-phthalocyanines into poly(methylmethacrylate) (PMMA) for optical limiting applications. The ratio by weight of the compound to the host polymer was 0.083% and 0.15%. Linear optical characterization of films, performed by spectrophotometry, show a low degree of molecular aggregation of zinc-phthalocyanines in the polymeric matrix.

Two different type of nonlinear optical investigation were performed separately on the obtained films. Measurements of nonlinear transmission were carried out using a ns Nd:Yag laser followed by OPO (532 nm) and a nonlinear response was observed. From the experimental data, the nonlinear absorption coefficient β was retrieved and found to be 29 and 43 cm/GW, respectively. The measurements of β was also performed via the z-scan technique on the same films, using 100 fs pulses at 800 nm. At this wavelength, the nonlinear absorption coefficient was evaluated to be 0.40 and 0.23 cm/GW.

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1. Introduction

An optical limiter is an optical device pertaining high transmission up to a certain input intensity while switches to low transmission above this threshold. This behaviour offer sensor and eye protection from laser radiation over a wide range of wavelengths, provided the wide range of existing laser wavelengths. Materials with strong nonlinear optical properties are extensively investigated and generally well suited for the realization

of passive optical limiters, i.e. where the switching process between two different transmission regimes is determined only by the intensity of the incoming light. Nevertheless, the ideal material for an optical limiter must meet several specifications as a high optical nonlinearity, a broadband response, a high threshold for laser induced damage and a low intensity threshold to activate the nonlinear process. Finally, the linear absorption must meet a compromise between low value, to reduce losses, and high value to drive the nonlinear effect that provides the limiting action. As a consequence, the realization of an optical limiter with a single bulk material is still an open task.

In the last years, much interest has been devoted to some organic macromolecules, as phthalocyanines (Pc) and their metal complexes (M-Pc), showing nonlinear

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optical properties of both second [1] and third order [2]. Their strong nonlinear optical properties are related to the system of delocalized π -electrons typical of their macrocyclic core, which gives rise to excited state absorption. Specifically, this accumulative nonlinearity is produced through the polarization of the electronic ground state and the successive absorption, from this polarized state, as determined by the intensity of the applied electric field. The mechanism of nonlinear absorption in these molecules, known as a reverse saturable absorption, can be described by a system possessing four relevant electronic energy levels [3,4].

The Pcs present the further advantage of a great structural flexibility and versatility since they can host different elements in their central site, thus offering a wide range of linear optical properties, related to the central atom nature. Specifically the presence of a heavy central atom, as a metal, has the effect to increase the optical nonlinearities [5].

On the other hand, the main limit to the use of these molecules is their low solubility in common solvents, which give rise to molecular aggregation both in solution and in the solid state, thus causing a drastic decay of their optical properties. In order to overcome the aggregation problem many solutions have been already proposed by introducing appropriate substituents into the cavity of the macrocycle or in the periphery [6], varying axial [7] and peripheral ligands and substituents [8], changing the symmetry of the macrocycle [9].

We introduced zinc-phthalocyanine (Zn-Pc) into a polymeric matrix and characterized the nonlinear optical behaviour of the obtained films. The investigated Zn-Pc has a planar structure, since the central zinc atom does not distort the phthalocyanine ring. Since the planarity of this structure may increase the undesired aggregation effects, in a previous work we characterized the spectral properties of both solutions and films at increasing concentration by a spectroscopic analysis. This preliminary study was crucial for the realization of films with the maximum allowed concentration of Zn-Pc, being the efficiency of the nonlinear absorption process directly proportional to the concentration of the nonlinear molecules. Molecular aggregation, in fact, is evidenced in the linear absorption spectra by a blue-shift and broadening of the Q-Band with respect to that of the monomeric species. For film realization, we entrapped Zn-Pc molecules in a poly(methyl methacrylate) (PMMA) matrix after stirring and heating of many different solutions [13]. Finally, two different types of nonlinear optical measurements were carried out on the realized samples, i.e. nonlinear optical transmission and z -scan, in order to characterize the

nonlinear optical absorption coefficient of the films at the investigation wavelengths.

In what follows, we will firstly introduce the process of samples preparation and the corresponding linear optical characterization. Afterwards, we will describe the experimental setups employed for nonlinear optical measurements, together with the obtained results.

2. Sample preparation and linear characterization

The investigated Zn-Pc molecules (Sigma–Aldrich) have no peripheral substitutes and their molecular weight is 577.91 u. Toluene was used as a solvent, and homogeneous solutions of different Zn-Pc concentrations (in the range 1.73×10^{-5} to 2.60×10^{-4} M) were obtained, after stirring for several hours. In order to avoid molecular aggregation we analysed their linear optical properties by evaluating the solutions absorbance spectra in the visible range. Linear optical characterisation was carried out with a standard spectrophotometer, using a wide spectrum light source (QTH 250), and an optical spectral analyser. Transmittance spectra of different solutions in a 1 mm thick quartz cuvette, were carried out and the absorbance spectra were then retrieved, being the reflectance from the quartz cuvette neglectable.

The two absorption bands which are characteristics of these molecules, i.e. the B-band in the UV and the Q-band in the visible range, are evidenced in Fig. 1. In agreement with literature [14], the peak in the Q-band, corresponding to monomer species (680 nm), is slightly shifted to 671 nm. Two other peaks (641 and 606 nm)

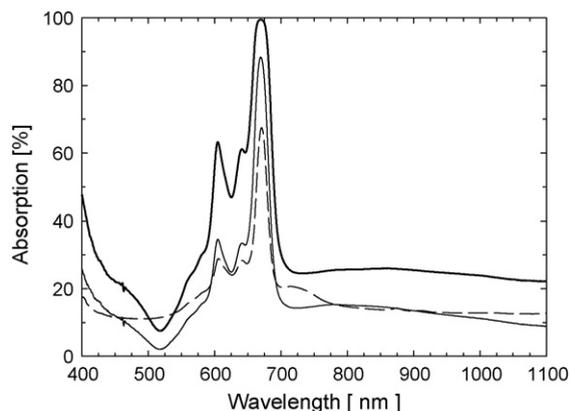


Fig. 1. Comparison between linear optical absorbance spectra of Zn-Pc/toluene solution 2.88×10^{-5} M in a 1 mm thick quartz cuvette (dashed line) and Zn-Pc polymeric films (continuous lines). The Zn-Pc to PMMA weight ratios in the films are 0.15% (thick solid line) and 0.083% (thin solid line).

corresponding to monomer overtones are also visible in the reported spectra. The reduced width of the main peak indicates the homogeneity and good solubility of the investigated solutions.

The solutions with PMMA, ZnPc and toluene were prepared and subsequently heated and stirred for some hours, in order to avoid molecular aggregation. The films were cast into Petri dishes and kept under thermal heating in order to evaporate the residual solvent.

The ratio by weight of the compound to the host polymer was chosen to be between 0.083% and 0.15%, in order to evaluate the relationship between Pc concentration and nonlinear absorption coefficient (β). Films thicknesses were measured with a profilometer and found to be 74 μm for sample A and 57 μm for sample B. The linear absorption spectra of different films are also reported in Fig. 1. The evident Q-band peak, at the same wavelength as for solutions, is an indication of a very low degree of aggregation, corresponding to a great majority of monomeric species entrapped in the polymeric matrix. The presence of the resonances, at the same wavelengths, in the Q-band, underlines the good maintenance of the linear properties of the solutions in the polymer matrix state.

3. Nonlinear optical transmission measurements

The transmission of a laser beam at different intensities through the obtained films, was measured, in order to evidence optical limiting effects in Zn-Pc entrapped into polymeric matrix related to molecule concentration. Linear optical absorption is given by the Beer–Lambert law:

$$\frac{I_{\text{out}}}{I_0} = \exp(-\alpha L) \quad (1)$$

where I_{out} and I_0 are the output and input laser intensities, respectively, α_0 the absorption coefficient (given in cm^{-1}), while L represents the sample thickness. When nonlinear absorption is taken into account, Eq. (1) is modified by including the light induced absorption changes, $\alpha = \alpha_0 + \beta I_0$, where α_0 is now the linear absorption coefficient and β is the nonlinear absorption coefficient (given in cm W^{-1}). For $\beta > 0$, the induced nonlinear absorption results in transmission decreasing with increasing input intensity.

Specifically, under excitation of a laser beam whose wavelength is lower than the Q-band peak, the nonlinear mechanism that takes place in this macromolecules is the so called reverse saturable absorption. This nonlinear absorption is consecutive to the excited triplet state absorption taking place when the laser pulse

duration, τ , is longer than the intersystem crossing rate τ_{ISC} [15–17].

In order to measure the optical-limiting responses and then to obtain a β value, we performed the measurements with the experimental setup described elsewhere [18]. The beam was provided by the output of an OPO after a Nd:YAG laser, with a pulse width of 5 ns ($\tau > \tau_{\text{ISC}}$) and a repetition rate of 10 Hz. The selected wavelength was 532 nm, corresponding to the minimum value of nonresonant response for all the samples. After the Variable Attenuator (V.A.), a first beam splitter (BS_1) divided the beam: a part of it (4%) was focused onto a photodiode (Thorlab DET 210) (PD_1) by a lens, and the residual part (96%) was focused onto the sample after passing through a pinhole. The latter beam was sent to a second beam splitter (BS_2): the main part was sent to a beam stopper (BS) while the other part was focused onto a second identical photodiode (PD_2). Both detectors were connected with a 300 MHz digital phosphor oscilloscope while their saturation was prevented using a set of linear neutral density filters, whose transmittance value was taken into account in the data fitting process. An accurate set up calibration was performed by using a power-meter with a Helio-Neon laser as reference.

Both investigated films show a nonlinear response under increasing input intensity and the experimental data are reported in Fig. 2. In particular, at very low input incident intensity the transmission obeys to linear Lambert–Beer law, as evidenced by the lines included in Fig. 2 as an indication of linear sample transmittances. When the input intensity increases, we observed a

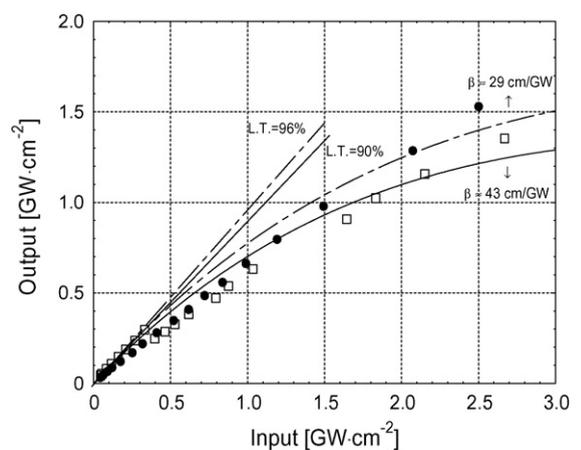


Fig. 2. Nonlinear transmission of film1 (0.15 wt%/□ mark) and film2 (0.083 wt%/● mark) measured for increasing incident intensity. The curve lines represent the best fit of experimental data. The straight lines represents the slopes of the fitting curves, corresponding to the linear transmission of both samples (respectively L.T. = 96%, L.T. = 90%).

Table 1

Films data together with measured linear and nonlinear optical properties, at 532 and 800 nm, respectively

Sample	Zn-Pc ratio in weight (%)	Thickness (μm)	$\lambda = 532 \text{ nm}$			$\lambda = 800 \text{ nm}$		
			Linear transmission (%)	$\alpha_0 \text{ (cm}^{-1}\text{)}$	$\beta \text{ (cm/GW)}$	Linear transmission (%)	$\alpha_0 \text{ (cm}^{-1}\text{)}$	$\beta \text{ (cm/GW)}$
A	0.15	74	90	19.46	43	76	54	0.40
B	0.083	57	96	5.28	29	87	19	0.23

deviation from the linear behaviour, more pronounced for the most concentrated sample. Since the film thickness was known and the linear absorption values could be retrieved from linear spectra, the experimental data were fitted assuming the only parameter to be the nonlinear absorption coefficient, β . From the experimental data, the nonlinear absorption coefficient β was retrieved and found to be 43 and 29 cm/GW for sample A and B, respectively. Sample data, together with the obtained results for β are summarized in Table 1.

4. z-Scan measurements

z-Scan [19,20] is a sensitive technique which is essentially a derivative of the input/output intensity measurements previously reported. It is based on the nonlinear transverse modification of the laser beam throughout its focal length, resulting in the intensity variation experienced by a sample which is translated around the focal point of the laser beam. Any optical nonlinearity in the sample would modify the beam profile and, as a consequence, in the far field the modified laser beam would present different spot size, curvature and intensity, determined by the nonlinear refractive and absorptive properties of the tested material. Specifically, when a small aperture is placed

in front of the detector, this technique provides a measurement of the refractive nonlinearity while open aperture z-scan experiments are sensitive to intensity-dependent absorption, i.e. β coefficient.

The z-scan experimental set-up here employed was already described previously [21,22]. The laser source was a Ti-sapphire, in CW regimes, therefore thermal contributions to the nonlinear optical signal could eventually arise. In order to avoid these undesired effects, the sample was scanned around the focal point of a laser beam at a frequency of about 5 Hz and the transmitted signal was directly monitored on a scope. Furthermore, the power beam for all measurements was never exceeding 1 mW in CW. Four diffraction-lengths after the focal point, the laser beam was focused with a long-focal lens on the detector, thus excluding any nonlinearity arising from beam profile variation on the detector. Detector saturation was prevented by an accurate calibration with neutral density filters. Eventual Fabry-Perot like resonances due to multiple interference from film surfaces were avoided by tilting the sample from the orthogonal direction of about 20° , until the low intensity regime gave a completely flat response over the complete sample translation.

The measured transmittance as a function of sample position along the z-axis is shown in Figs. 3 and 4 for the

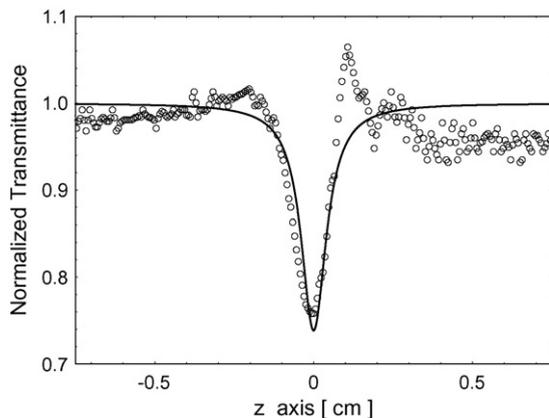


Fig. 3. Open aperture z-scan signal of sample A (0.15 wt%): measurements (\circ) and theoretical fit (solid line).

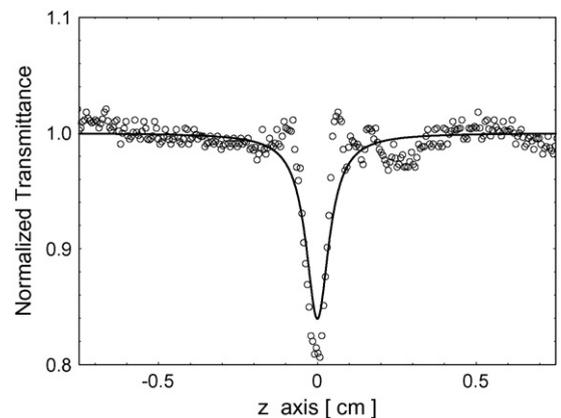


Fig. 4. Open aperture z-scan signal of sample B (0.083 wt%): measurements (\circ) and theoretical fit (solid line).

two samples, respectively. As expected, the effect of nonlinear absorption in the investigated samples is responsible for transmittance decreasing close to the beam focus. Transmittance reduction is more pronounced for sample A which is at the same time thicker and has a higher weight ratio of nonlinear molecules.

From theoretical point of view, the normalized transmittance as a function of the z -axis coordinate in the open aperture z -scan measurements, can be written as [23]:

$$T(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)} \quad (2)$$

being q_0 the adimensional parameter:

$$q_0(z) = \beta I_0 \frac{1 - e^{-\alpha_0 L}}{(1 + (z/z_0)^2)\alpha_0} \quad (3)$$

L is sample thickness, I_0 the peak beam intensity at the focus, w_0 the beam radius at focus, and z_0 is the Rayleigh length ($z_0 = \pi\omega_0^2/\lambda$). To interpolate the z -scan experimental curves according to Eqs. (2) and (3), the fundamental beam intensity term, I_0 , was determined from the measurements of the beam power, 1 mW, and beam spot-size, $\sim 50 \mu\text{m}$. The sample data which are necessary are the sample thickness ($L = 57$ and $74 \mu\text{m}$, respectively) and the linear absorption coefficients at 800 nm. With the given data, which for simplicity are also reported in Table 1, the only fitting parameter is then reduced to the nonlinear absorption coefficient, β . We have therefore fitted the experimental data and obtained the solid curves shown in Figs. 3 and 4. The nonlinear parameter were found to be 0.40 cm/GW for sample A and 0.23 cm/W for sample B.

It is worth to note that the nonlinear absorption coefficient values obtained at 800 nm are quite lower, if compared to those obtained at 532 nm. As a matter of fact, the wavelength of investigation, 800 nm, is well above the Q-band. As a consequence the Zn-Pc molecules are not behaving as reverse saturable absorbers, thus the observed nonlinear absorption at the investigated wavelength is determined by a type of two-photon absorption rather than excited triplet state absorption followed by intersystem crossing. Investigation in the range of wavelengths above the Q-band peak will be object of further study, in order to better explain the mechanism of nonlinear absorption here evidenced.

5. Conclusions

Polymeric films containing Zn-Pc were realized by entrapping the molecules in a PMMA matrix by stirring

and heating different starting solutions, obtained in toluene. The ratio by weight of the compound to the host polymer was 0.083% and 0.15% and the linear optical measurements of the samples underline the good optical quality of the films with a very low degree of aggregation.

Measurements of nonlinear optical transmittance were recorded at 532 nm in nanosecond regime, and optical limiting effects were observed for both samples. Theoretical fit of the experimental data, i.e. input versus output intensity, was obtained and the nonlinear optical coefficient, β , was calculated to be 29 and 43 cm/GW, respectively for film B and film A.

A second kind of nonlinear measurements via z -scan technique, were performed on same samples, using 100 fs pulses at 800 nm, thus showing transmittance decreasing around the focus, in the open aperture scheme. Following some theoretical considerations, the experimental data were fitted and the value of β at 800 nm was found to be reduced to 0.40 and 0.23 cm/GW, respectively for film A and film B.

In conclusion, the comparison between the nonlinear absorption coefficient of the films below, 532 nm, and above, 800 nm, the Q-band peak is evidence of the different nonlinear optical mechanisms which are activated depending on the spectral region which is investigated. Specifically, for wavelength < 670 nm the strong effect of reverse saturable absorption typical of these molecules is active, while the weaker optical nonlinearity in the near infrared is ascribed to two photon absorption mechanism.

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References

- [1] T. Yamada, T. Manaka, H. Hoshi, K. Ishikawa, H. Takezoe, J. Porphyrins Phtalocyanines 2 (1998) 133–137.
- [2] M. Hanack, D. Dini, M. Barthel, S. Vagin, Chem. Rec. 2 (2002) 129–148.
- [3] D. Dini, M. Barthel, M. Hanack, Eur. J. Org. Chem. 2001. 375923769.
- [4] M. Calvete, G.Y. Yang, M. Hanack, Synth. Met. 141 (2004) 231–243.
- [5] J.W. Perry, K. Mansour, S.R. Marder, K.J. Perry, D. Alvarez Jr., I. Choong, Opt. Lett. 19 (9) (1994) 625–627.

- [6] X. Àlvarez Micó, S.I. Vagin, L.R. Subramanian, T. Ziegler, M. Hanack, *Eur. J. Org. Chem.* (2005) 4328–4337.
- [7] H.-J. Kang, E.-H. Kang, S.-W. Park, J.-W. Lee, J.-K. Lee, *Macromol. Symp.* 235 (2006) 195–200.
- [8] G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* 104 (2004) 3723–3750.
- [9] D. Dini, G.Y. Yang, M. Hanack, *J. Chem. Phys.* 119 (9) (2003) 4857–4864.
- [13] A. Kost, L. Tutt, M.B. Klein, T.K. Dougherty, W.E. Elias, *Opt. Lett.* 18 (5) (1993) 334–336.
- [14] S. Subbiah, R. Mokaya, *J. Phys. Chem. B* 109 (2005) 5079–5084.
- [15] P. Zhu, P. Wang, W. Qiu, Y. Liu, C. Ye, G. Fang, Y. Song, *Appl. Phys. Lett.* 78 (10) (2001).
- [16] Q. Gan, S. Li, F. Morlet-Savary, S. Wang, S. Shen, H. Xu, G. Yang, *Opt. Express* 13 (14) (2005) 5424–5433.
- [17] D. Dini, *Int. J. Mol. Sci.* 4 (2003) 291–300.
- [18] R. Ostuni, M.C. Larciprete, G. Leahu, A. Belardini, C. Sibilìa, M. Bertolotti, Optical limiting behavior of zinc phthalocyanines in polymeric matrix, *J. Appl. Phys.* 101 (2007) 33116–33120.
- [19] M. Sheik-Bahae, A.A. Said, E.W. Van Stryland, *Opt. Lett.* 14 (1989) 955.
- [20] M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagan, E.W. Van Stryland, *IEEE J. Quantum Electron.* 26 (1990) 760.
- [21] E. Fazio, P. Bevilacqua, M. Bertolotti, *Proc. SPIE* 2775 (1996) 135–139.
- [22] E. Fazio, A. Passaseo, M. Alonzo, A. Belardini, C. Sibilìa, M.C. Larciprete, M. Bertolotti, Measurement of pure Kerr nonlinearity in GaN thin films at 800 nm by means of eclipsing z -scan experiments, *J. Opt. A: Pure Appl. Opt.* 9 (2007) L3–L4. , doi:10.1088/1464-4258/9/2/L01.
- [23] *Chem. Phys.* 324 (2006) 699–704.