

## Resonant Nonlinear Absorption in Zn-Phthalocyanines

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In this work, we investigate the nonlinear absorption dynamics of Zn phthalocyanine in dimethyl sulfoxide (DMSO). We used single pulse and pulse train Z-scan techniques to determine the dynamics and absorption cross-sections of singlet and triplet states at 532 nm. The excited singlet state absorption cross-section was determined to be 3.2 times higher than the ground state one, giving rise to reverse saturable absorption. We also observed that reverse saturable absorption occurs from the triplet state, after its population by intersystem crossing, whose characteristic time was determined to be 8.9 ns. The triplet state absorption cross-section determined is 2.6 times higher than the ground state one. In addition, we used the white light continuum Z-scan to evaluate the singlet excited state spectrum from 450 to 710 nm. The results show two well-defined regions, one above 600 nm, where reverse saturable absorption is predominant. Below 600 nm, we detected a strong saturable absorption. A three-energy-level diagram was used to explain the experimental results, leading to the excited state absorption cross-section determination from 450 nm up to 710 nm.

### Introduction

Phthalocyanines are organic macrocyclic compounds that present excellent stability, and whose optical and electrical properties can be tuned by varying the peripheral groups and the central metal ion. Such features make phthalocyanines promising candidates for a broad range of applications, from organic solar cells<sup>1–3</sup> to photodynamic therapy of cancer.<sup>4–7</sup> Macrocyclic compounds, such as phthalocyanines, exhibit large optical nonlinearities in general.<sup>8–11</sup> Thanks to the intense reverse saturable absorption (RSA) exhibited by these compounds,<sup>12</sup> they have been employed in a number of applications with emphasis on optical limiting.<sup>13,14</sup> For instance, lead<sup>12,14</sup> and indium<sup>15</sup> phthalocyanines are two of the most successful materials for optical limiting operating with the RSA process. As mentioned before, these materials can be synthesized in a wide variety, with the attachment of functional groups. In this way, fine-tuning of the physical and chemical properties can be achieved with the molecular control of the compound itself, or by the way the molecules are assembled.

The RSA process occurs when the absorption cross-section of the excited state exceeds that of the ground state. Usually, for macrocyclic compounds RSA follows from an intersystem crossing from a higher excited singlet state to an excited triplet state. The RSA efficiency depends upon the properties of excited states, such as excited states relaxation times, intersystem crossing time and cross-sections. Therefore, to select the most suitable candidates for a given application, the knowledge of the compound's excited state properties is of foremost importance.

In this work, we used single pulse<sup>16</sup> and pulse train Z-scan (PTZ-Scan)<sup>17</sup> techniques, both at 532 nm, to investigate the

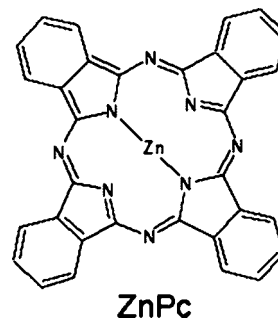


Figure 1. Molecular structure of ZnPc.

dynamics and excited state properties of phthalocyanines containing Zn, namely ZnPc, whose molecular structures is presented in Figure 1. To gain further insight into the character and processes of the excited states of ZnPc, we also carried out nonlinear absorption spectrum measurements from 450 to 710 nm using the WLC Z-scan technique.<sup>18</sup> The resonant nonlinear absorption spectrum of ZnPc presents saturable absorption (SA) and reverse saturable absorption (RSA), depending on the excitation wavelength. The understanding of the influence of chemical structure on the excited state spectroscopic parameters, may lead us to the development of compounds with better optical properties.

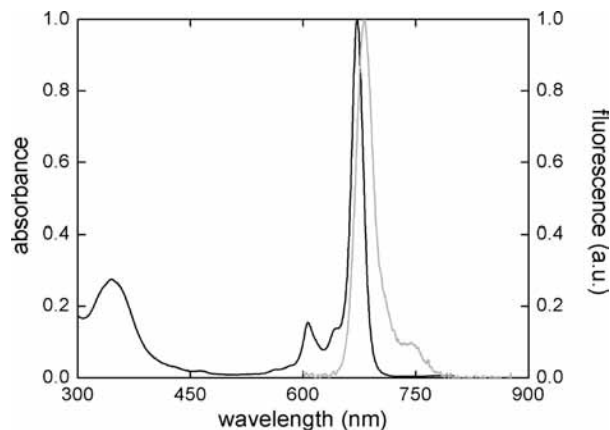
### Experiments

To measure the nonlinear optical process of ZnPc, we prepared DMSO solution in a concentration of  $1.2 \times 10^{17}$  molecules/cm<sup>3</sup> ( $\sim 2.0 \times 10^{-4}$  mol/L). The UV–vis absorption, at room temperature, was measured with a Cary-17A spectrometer, using a solution concentration 6 times smaller than that

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**Figure 2.** Absorption (black) and fluorescence (dark gray) spectrum of ZnPc in DMSO.

used in nonlinear optical experiments. The linear and nonlinear experiments were performed in a 2 mm quartz cuvette.

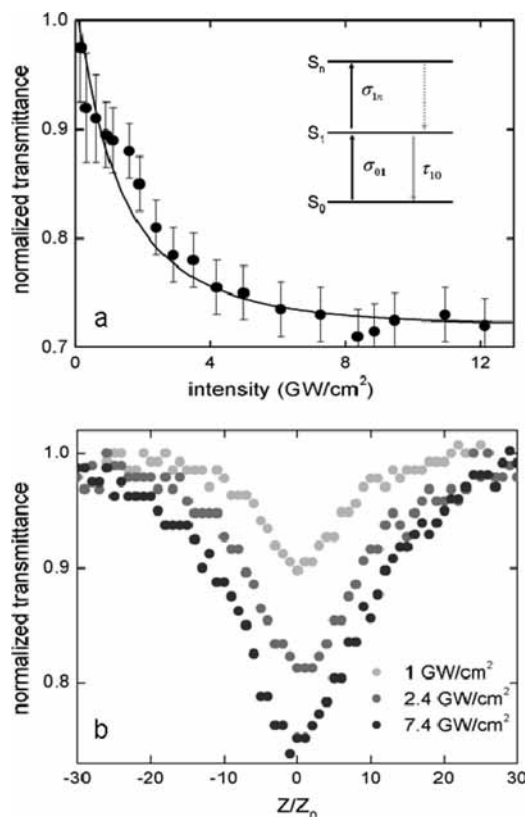
To measure the fluorescence lifetime  $\tau_f$ , the ZnPc solution was pumped at 532 nm with 70 ps Q-switched/mode-locked Nd:YAG laser. The fluorescence signal was collected with optical fiber that is attached a fast detector ( $\sim 500$  ps) connected a 1 GHz digital oscilloscope. The fluorescence spectrum was measured using an optical fiber spectrometer ( $\sim 2$  nm resolution).

The nonlinear absorption dynamics of Zn-phthalocyanine were measured using two configurations of the Z-scan technique at 532 nm. The first one was the conventional single pulse Z-scan technique,<sup>16</sup> which consists of monitoring changes in the normalized transmittance while translating the sample through the focus of the laser beam ( $z$ -axis). The normalized transmittance is obtained through the ratio of the transmittance at a given  $z$ -position by the transmittance far from the focal plane (linear transmittance). The second configuration employed was the PTZ-scan technique,<sup>19</sup> which is able to map the nonlinear dynamics in nanosecond time scale. In this last, while the sample is moved along the laser beam focal axis, the pulse train of a Q-switched/mode-locked laser is acquired. In the end of the measurement, a Z-scan signature is obtained for each individual pulse. The PTZ-scan technique has a pulse train with 20 pulses, each one with 70 ps and separated by 13 ns. For a single pulse Z-scan, a Pockels cell, between two crossed polarizers, is used to extract one pulse from the pulse train. To avoid the cumulative thermal effect, a repetition rate of 10 Hz was applied.

Also, the nonlinear absorption spectrum of phthalocyanines was carried out using the WLC Z-scan technique.<sup>18</sup> The white light continuum is generated by focusing 150 fs pulses at 775 nm in a 3 cm water cell. Typically, 8  $\mu$ J of WLC in the visible is generated by employing approximately 0.3 mJ at 775 nm. The WLC beam is recollimated using a 10 cm focal distance lens, and a low pass filter is used to remove the pump pulse and the infrared portion of the WLC spectrum. The WLC spectrum employed in our experiment presents a 300 nm band in the visible region (450–750 nm), with about 5 ps of positive chirp. The general procedure of the WLC Z-scan technique is same of the conventional Z-scan.<sup>16</sup> However, in the WLC Z-scan a spectrometer (resolution of  $\sim 2$  nm) must be used instead of the photodetector generally employed, yielding Z-scan curve for each wavelength.

## Results and Discussion

Figure 2 shows the linear absorption and fluorescence spectra of ZnPc in DMSO. From this figure, we observe a strong absorption



**Figure 3.** (a) Normalized transmittance as a function of the pulse intensity obtained from the single pulse Z-scan experiment at 532 nm. The inset in this figure shows the three-energy-level diagram used to model the single-pulse Z-scan result. (b) Open-aperture Z-scan signatures obtained with single 70 ps pulses for three distinct pulse intensities.

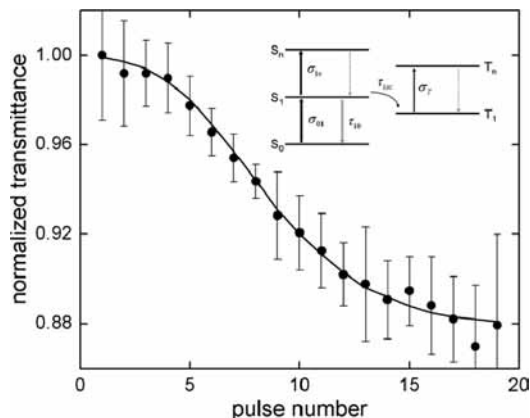
band around 670 nm, related to the  $\pi \rightarrow \pi^*$  transition of the Q-band. It is worth noting that at 532 nm, wavelength employed in nonlinear optical measurements with picosecond pulses, only a small absorption is observed. The fluorescence spectrum (gray line in Figure 2), obtained with excitation at 532 nm, presents a strong peak around 700 nm. The fluorescence lifetime  $\tau_f = (4.3 \pm 0.2)$  ns was determined by fitting the fluorescence decay with a fast detector, using a single exponential.

Figure 3a shows the decrease of the normalized transmittance as a function of the pulse intensity for the single pulse experiment, characterizing a RSA. In Figure 3a, each point corresponds to the minimum value of the normalized transmittance obtained from single pulse open-aperture Z-scan measurements, illustrated in the inset of Figure 3b for three distinct intensities. To fit this data, we employed the three-energy-level diagram showed in the inset of Figure 3a, representing only the singlet states ( $S$ ) of the molecule. The triplet states can be neglected because the pulse duration (70 ps) is much shorter than the intersystem crossing time. We also assumed that a small population is created in  $S_n$  for low irradiances. Besides, the  $S_n$  lifetime is in the femtosecond time scale. Accordingly, the rate equations that describe the fraction of molecules in the first two singlet states are given by

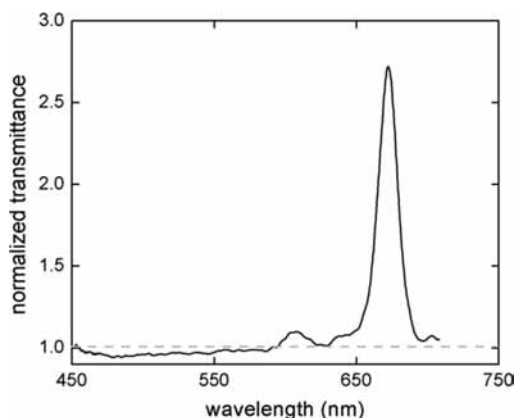
$$\frac{dn_{S_0}}{dt} = -W_{01}n_{S_0} + \frac{n_{S_1}}{\tau_{10}} \quad (1)$$

$$\frac{dn_{S_1}}{dt} = W_{01}n_{S_0} - \frac{n_{S_1}}{\tau_{10}} \quad (2)$$

where  $1/\tau_{10} = 1/\tau_r + 1/\tau_{ic}$  is the lifetime of the first excited state,  $\tau_r \approx 20$  ns and  $\tau_{ic} \approx 13$  ns are radiative and internal



**Figure 4.** Normalized transmittance along the pulse train for ZnPc at 532 nm for a pulse intensity of MW/cm<sup>2</sup>. The solid line represents the fitting obtained using the five-energy-level diagram (inset), with the parameters given in the text.



**Figure 5.** Normalized transmittance spectrum ZnPc in DMSO obtained using the WLC Z-scan.

conversion lifetimes respectively. These times are calculated according to ref 20  $n_{S_i}$  are the population fractions of the singlet states ( $S_i$ ), with  $n_{S_0} + n_1 = 1$ .  $W_{01} = \sigma_{01}I(t)/h\nu$  is the one-photon transition rate, where  $\sigma_{01}$  is the ground state cross-sections at 532 nm,  $h$  is the Planck constant, and  $\nu$  is the light frequency. The set of differential equations is numerically solved using a Gaussian temporal profile for the laser pulse. The time dependence of the absorption during the excitation is given by:

$$\alpha(t) = N[n_{S_0}(t)\sigma_{01} + n_{S_1}(t)\sigma_{1n}] \quad (3)$$

where  $N$  is the concentration and  $\sigma_{1n}$  is the excited state cross-section. The transmittance can be calculated by integrating the Beer's law,  $dI/dz = -\alpha(t)I(t)$ , over the sample thickness. Because the detection system in our experiment measures the pulse fluence, we also have to carry out integration over the full pulse width. Such result is then normalized to the linearly transmitted energy, and used to fit the data in Figure 3a (solid line). The absorption coefficient,  $\alpha_{01}$ , is obtained from the linear absorption spectrum and then used to calculate the ground state absorption cross-section through  $\sigma_{01} = \alpha_{01}/N$ . Therefore, the only adjustable parameter is  $\sigma_{1n}$ . The value determined from the fitting was  $\sigma_{1n} = (1.6 \pm 0.1) \times 10^{-17} \text{ cm}^2$ , which is 3.2 times higher than the ground state cross-section ( $\sigma_{01} = 0.5 \times 10^{-17} \text{ cm}^2$ ).

In Figure 4, we present the results obtained for ZnPc with the PTZ-scan technique. As seen, the sample presents a decrease of the normalized transmittance with the pulse number, indicating the accumulative nature of the nonlinear absorption (reverse

storable absorption). This data is modeled using the five-energy-level diagram presented in the inset of Figure 4. After being excited by a single pulse of the pulse train to  $S_1$ , the molecule can relax back to  $S_0$ , be promoted to  $S_n$  or undergo an intersystem crossing to the triplet state  $T_1$ . When the next pulse of the pulse train arrives in the sample, accumulative contributions due to the population buildup at the long-lived triplet state  $T_1$  start to occur. Molecules in this state can be promoted to another triplet state,  $T_n$ , resulting in a change in the molecule absorption. Because of the low intensity of each pulse of the pulse train, and the short lifetime of  $S_n$  and  $T_n$ , their population can be neglected. Considering this model, the fraction of molecules in each state are given by

$$\frac{dn_{S_0}}{dt} = -W_{01}n_{S_0} + \frac{n_{S_1}}{\tau_{10}} \quad (4)$$

$$\frac{dn_{S_1}}{dt} = W_{01}n_{S_0} - \frac{n_{S_1}}{\tau_f} \quad (5)$$

$$\frac{dn_{T_1}}{dt} = \frac{n_{S_1}}{\tau_{isc}} \quad (6)$$

where  $n_{T_1}$  is the population fraction of the first triplet state, with  $n_{S_0} + n_{S_1} + n_{T_1} = 1$  (normalization condition). The  $S_1 \rightarrow S_0$  transition lifetime,  $\tau_{10}$ , can be described by  $1/\tau_{10} = 1/\tau_f - 1/\tau_{isc}$ , in which  $\tau_f$  and  $\tau_{isc}$  are the fluorescence lifetime and the intersystem crossing time, respectively. These equations are numerically solved using the temporal and intensity profile of the pulse train, which allows determining the population of each state. The temporal evolution of the absorption can be then calculated using

$$\alpha(t) = N[n_{S_0}(t)\sigma_{01} + n_{S_1}(t)\sigma_{1n} + n_{T_1}\sigma_T] \quad (7)$$

where  $\sigma_T$  is the triplet state absorption cross-section. Using the same procedure described previously for the single-pulse experiment, we are able to obtain the transmittance evolution of the sample. In this case, however, the fitting parameters are  $\sigma_T$  and  $\tau_{isc}$ , because  $\sigma_{01}$  and  $\sigma_{1n}$  are already known from the linear absorption and single-pulse Z-scan analysis respectively. The solid line in Figure 4 represents the best fittings obtained with this procedure.

The intersystem crossing time obtained through the fitting is  $\tau_{isc} \approx (8.9 \pm 0.4) \text{ ns}$ . This value is in good agreement with the ones reported in the literature for similar phthalocyanines.<sup>21</sup> The quantum yield of triplet formation,  $\phi_T$ , was calculated using  $\phi_T = \tau_f/\tau_{isc}$ ,<sup>22</sup> giving  $\phi_T \approx 48\%$ . This result is close to the values obtained in the literature, and 2.4 times higher than the fluorescence quantum yield reported in the ref 21. The absorption cross-section of the triplet state found through the fitting is  $\sigma_T = (1.3 \pm 0.1) \times 10^{-17} \text{ cm}^2$ . This value is 2.6 times higher than the ground state cross-section ( $\sigma_{01} = 0.5 \times 10^{-17} \text{ cm}^2$ ). It is worth noting that  $\sigma_{1n}$  and  $\sigma_T$  exhibit similar values, indicating that both states, excited singlet and triplet, gives similar contribution to the RSA of ZnPc in DMSO.

To investigate the singlet excited absorption spectrum of Zn phthalocyanine, we employed the WLC Z-scan technique. This technique is able to obtain Z-scan signatures for each wavelength in the WLC range (5 ps chirp) at the same time. Figure 5 shows the nonlinear spectrum (normalized transmittance spectrum) of ZnPc obtained with the WLC Z-scan. Two distinct behaviors can clearly be seen: (i) a SA process that follows the Q-band, indicated by normalized transmittance values higher than 1, and



(ii) a RSA mechanism for wavelengths smaller than 600 nm (normalized transmittance values smaller than 1).

Because of the chirp in the WLC pulse, the red portion of the WLC, which is resonant with the Q-band, excites ZnPc molecules to the first excited state  $S_1$ . As the intersystem crossing time for ZnPc is in the nanosecond time scale, we do not have to consider triplet states because it is much longer than the duration of our WLC pulse. In this way, the three-energy-level diagram presented in the inset of Figure 3a can be used to establish the population dynamics to understand the data obtained through the WLC Z-scan. Molecules excited to  $S_1$  may decay to  $S_0$  with a relaxation time  $\tau_{10}$ , which is much longer than the WLC pulse duration. Again, the upper level,  $S_n$ , is assumed to be too short-lived and, therefore, does not present any appreciable population. Consequently, molecules are accumulated in the first excited state,  $S_1$ , and the absorption cross-section between states  $S_1$  and  $S_n$  can be determined. According to this energy diagram, the rate equation used to describe the change of absorption is given by

$$\frac{dn_{S_0}(t)}{dt} = -n_{S_0}(t) W_{01}(\lambda) + \frac{1 - n_{S_0}(t)}{\tau_{10}} \quad (8)$$

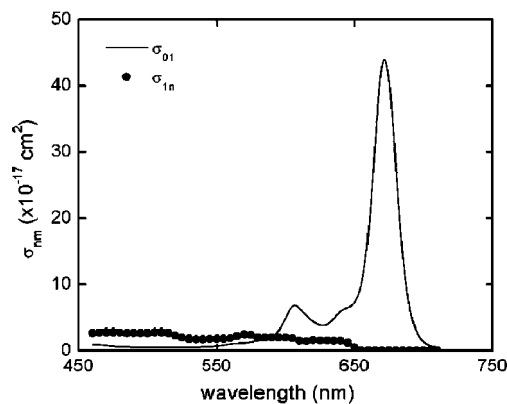
where  $n_{S_1}(t) = 1 - n_{S_0}(t)$ .  $W_{01}(\lambda) = \sigma_{01}(\lambda)I/h\nu$  is the transition rate  $S_0 \rightarrow S_1$ , and  $\sigma_{01}(\lambda)$  is the ground state cross-sections in each wavelength.  $I$  is the excitation intensity,  $n_i(t)$  are the populations fraction in each state. The nonlinear absorption,  $\alpha(\lambda, t)$ , is calculated using

$$\alpha(\lambda, t) = N[n_{S_0}(t) \sigma_{01}(\lambda) + n_{S_1}(t) \sigma_{1n}(\lambda)] \quad (9)$$

where  $N$  is the sample concentration, and  $\sigma_{1n}(\lambda)$  is the excited state cross-section correspondent to the transition  $S_1 \rightarrow S_n$ . The ground state absorption cross-section for every spectral component is determined from the linear absorption spectrum (Figure 2). In this way, the only adjustable parameter in our fitting is the excited state cross-section  $\sigma_{1n}(\lambda)$ .

To fit the data in Figure 5, we numerically solve eqs. 8 and 9 using the spectral profile of the WLC, considering it is composed of bandwidth limited pulses centered at the wavelengths comprising the WLC. As mentioned before, the red portion of the WLC (resonant with the Q-band) excites ZnPc molecules to  $S_1$ . Then, the WLC itself probes the excited state absorption, once population is accumulated in the first excited state which presents a lifetime much longer than the pulse duration.

By fitting the normalized transmittance spectrum presented in Figure 5, we are able to determine the excited state cross-sections spectrum of ZnPc,  $\sigma_{1n}(\lambda)$ , whose values are presented in Figure 6 (circles). In Figure 6, the solid line shows the ground state absorption cross-section spectrum  $\sigma_{01}(\lambda)$ . As can be seen from Figure 6,  $\sigma_{01} > \sigma_{1n}$  for wavelengths higher than 600 nm, indicating a decrease in sample absorption coefficient, characterizing a SA, as observed in the same region of Figure 5. Around 600 nm (cross-over between the solid line and open circles),  $\sigma_{01}$  and  $\sigma_{1n}$  exhibit similar values, giving rise to no appreciable change in the normalized transmittance, as shown Figure 5. It is worth noting that  $\sigma_{1n}$  values (circles in Figure 6) are zero from 650 to 710 nm, which reveals that there is no transition to a higher excited state for this range. Therefore, the SA occurs because of the ground state depletion caused by the red portion of the WLC, which is resonant with the Q-band of ZnPc. Hence, up to 650 nm the WLC pulse is populating  $S_1$ . Subsequently, this state will be probed by the rest of the WLC pulse. For wavelengths shorter than 650 nm, the nonlinear absorption



**Figure 6.** Ground state ( $\sigma_{01}$ , line) and excited state ( $\sigma_{1n}$ , circles) absorption cross-section as a function of the wavelength for ZnPc obtained with the WLC Z-scan.

spectrum of ZnPc exhibits nonzero values for  $\sigma_{1n}$  because of  $S_1 \rightarrow S_n$  transitions. For wavelengths below 580 nm, as  $\sigma_{01} < \sigma_{1n}$  the sample presents an increase in its absorption coefficient upon excitation, typical of RSA. The ratio between the excited and ground state cross-sections at 530 nm,  $\sigma_{1n}/\sigma_{01} \approx 3$ , is in agreement with single pulse Z-scan, shown in Figure 3. Similar behavior, in relation to variation of absorbance, was observed for different types of phthalocyanines.<sup>23,24</sup>

## Conclusion

We show, using single color Z-scan, that ZnPc present singlet and triplet absorption cross-sections approximately three times higher than the ground state one at 532 nm. We observed that reverse saturable absorption occurs from the triplet state, after its population by intersystem crossing with a characteristic time of 8.9 ns.

Using WLCZ-Scan, the singlet excited state cross sections were obtained for 450 nm until 710 nm. These results shown that, close to 532 nm, the ratio between the excited and ground singlet cross-sections,  $\sigma_{1n}/\sigma_{10} \approx 3$ , in agreement with the results obtained with single color Z-scan. Also in the singlet excited state spectrum, we observed two distinct nonlinear processes: (i) in the Q-band region, one present a strong saturable absorption effect; (ii) below 600 nm, it was observed reversible saturable absorption. These results indicate ZnPc for applications in photodynamic, optical limiter and optical switches.

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