XXVI ENFMC - Annals of Optics Volume5 - 2003

TPPS4: Nonlinear Absorption Characteristics

P.J.Gonçalves, I. E. Borissevitch [a]

L. de Boni, N. M. Barbosa Neto, J. J. Rodrigues Jr, S. C. Zílio [b]

[a] **Av. Bandeirantes 3900, DFM, Monte Alegre, Ribeirão Preto –SP CEP 14040-901**
[b] **Instituto de Física de São Carlos**

e-mail: pablo@dfm.ffclrp.usp.br

Abstract

Porphyrins and their derivatives (PPh), which are two-dimensional molecules characterized by extend π-conjugation, possess nonlinear optical properties such as nonlinear absorption and intensity dependent refraction index. They are being considered as promising candidates for application in laser techniques, nanoelectronics, etc. Due to their spectral characteristics, phototoxicity and high affinity to tumor tissues, PPh are widely used in modern medicine as contrast agents for cancer diagnostics and as photoactive compounds in photodynamic therapy (PDT). From this point of view it is necessary to characterize their excited states. For example, for medical applications it is necessary to know the efficacy of light absorption (cross section), life times and quantum yield of fluorescence and triplets states. These characteristics depend on the PPh structure and the environment. Meso-tetra(sulfonatophenyl) porphyrin ($TPPS_4$) is a water soluble compound with well-defined structure which possesses promising characteristics for various applications. Recently $TPPS_4$ has been studied in clinics as potential photosensitizer for PDT. In this work, we present on the study of excited states characteristics of water solutions of $TPPS_4$ at pH 7.0 and 4.0 using the Z-scan techniques with a single pulse and a pulse train, in association with others complementary techniques such as UV-Vis absorption spectroscopy and time resolved fluorescence. The intensity dependence and time evolution of the nonlinear optical absorption was analyzed using the diagram with five energy levels. The values of cross sections of ground, singlet and triplet excited states, intersystem crossing constants, fluorescence lifetime and quantum yield of triplet state were obtained.

Introduction

In the last decade the interest to study nonlinear optical properties of organic materials has significantly increased since these properties are important for their application in various fields from nanoelectronics [1] to modern medicine [2]. Porphyrins (PPh) and their derivatives are two-dimensional molecules characterized by highly developed π-conjugation, which possess nonlinear optical properties, such as the intensity-dependent refraction index and various types of nonlinear absorption: excited state absorption (ESA), reverse saturable absorption (RSA) and/or saturable absorption (SA).

SA is characterized by transmittance increase with the increase of the energy input and RSA by transmittance decrease with the input increase. So, RSA occurs when the cross-section of excited states is larger than that of the ground one and results in increased absorption of the material with the increase of the exciting radiation intensity. Materials possessing RSA are of considerable interest to develop optical limiters to protect eyes and others sensors from intense laser pulses. The basic principle of the optical limiting devices is that a material transparent under normal light conditions becomes opaque rapidly under high photon flux.

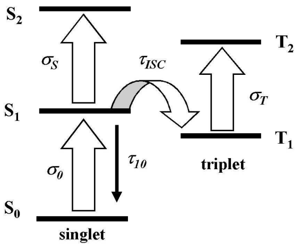

Figure 1: Five-level energy diagram.

The porphyrins posses strong triplet-triplet ($T_1 \rightarrow T_n$) absorption, they serve as one of the best optical limiting materials. The most of these materials have been studied with the help of the 5-level energy model with three singlets (ground S_0, first excited S_1 and second excited S_2) and two triplets (first excited T_1 and second excited T_2), (Figure 1). An intense laser pulse redistributes the population of molecules between the ground and excited states. This causes a transient modification in optical properties of the material. During the laser pulse absorption, molecules at S_0 can be promoted to S_1, with a cross section σ_0. In S_1 can be excited to S_2 (σ_S), and then can drop back to S_0 loosing the energy by radiation and/or radiationless, the process being characterized by constant $k_{10}=1/\tau_{10}$, or suffer intersystem crossing to the triplet state T_1 ($\kappa_{ISC}=1/\tau_{ISC}$). Then it can be excited to T_2 (σ_T). The efficiency of the T_1 formation is called quantum yield Φ_T.

PPh have rather high quantum yield of the triplet formation, and therefore, can play an important role in the triplet-assisted photochemical applications like PDT. PDT involves selective accumulation of the photosensitizer in the tumor tissue. The mechanism of the cell destruction involves the formation of the triplet excited state of the photosensitizer and the direct transfer of the absorbed energy to the target and/or the energy transfer via collision to molecular oxygen with the formation of highly active singlet oxygen. The singlet oxygen then attacks the double bonds of the cell membranes and other targets, thus killing the cell.

Meso-tetra (sulfonatophenyl) porphyrin ($TPPS_4$) was demonstrated to accumulate within the tumors, possess a high yield of singlet oxygen and be characterized by low aggregation.

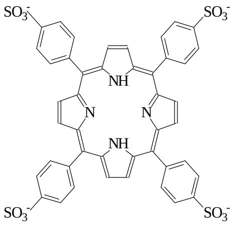

Figure 2: Chemical structure of $TPPS_4$.

$TPPS_4$ is a water-soluble tetrapyrrolic compound with a well-defined structure (Figure 2). Protonation of the porphyrin molecule can result in diverse photophysical and photochemical properties, which in turn can affect their optical nonlinearity.

In this work we present on the study of nonlinear absorption and nonlinear parameters of ground and excited singlet and triplet states of $TPPS_4$ as a function of its state of protonation, protonated at pH 4.0 and non-protonated at pH 7.0.

Experimental Setup

The TPPS4 was purchased from *Porphyrin Products Inc.* The PPh were dissolved in Milli-Q quality water. The TPPS4 concentration was controlled spectrophotometrically. Figure 3 shows typical linear absorption spectra for the protonated and non-protonated samples, pH 4.0 and 7.0. The pH changes were produced by the addition of appropriate quantities of HCl or NaOH stock solutions. All presented data are the average values of three independent experiments at different concentrations. All experiments were made at room temperature.

The UV-Vis spectra were measured on a Beckman DU 640 spectrophotometer. The fluorescence lifetimes were measured with a laser system from Spectra Physics. For Z-scan measurements [3] the pump source was a frequency-doubled, Q-switched and mode-locked Nd:YAG laser delivering ≈70 ps pulses at 532 nm, in pulse trains containing ≈20 pulses. The complete envelope of the pulses under the Q-switch can be used to investigate the time evolution of the optical nonlinearity [4] in a technique called pulse train Z-scan (PTZS). The pulses in the train are separated by 13.2 ns. A single 70 ps pulse can be extracted from the Q-switch envelope by using a Pockels cell sandwiched between two crossed polarizers. For both temporal regimes, the beam was focused onto the cuvette with a lens of the focal length f = 12 cm, resulting in a 40 mm light spot at the focal plane. A 10 Hz repetition rate was used to avoid accumulative thermal nonlinearities.

The absorption and emission dynamic experiments were analyzed with the five-level energy model (Figure 1). The singlet energy level was determined by the linear absorption and fluorescence. Then the ground state cross-section σ_0 was obtained, once the absorbance and concentration were determined. The excited singlet state cross-section σ_S can be obtained from the measurements with single pulse, by measuring several Z-scan curves at different pulse intensities. The profile of the saturation curve can inform on the excited singlet cross-section σ_S, since no appreciable population of triplet state has been created during the pulse duration. The triplet energy level was determined by use of the complete set of the pulses under the Q-switch envelope in the PTZS technique. For the pulse train measurements, the triplet state contributes with an accumulative nonlinearity because if the long duration of the Q-switch envelope (≈200 ns). Therefore, the absorption and emission dynamics is described by the triplet-triplet absorption, triplet relaxation and the singlet-singlet absorption, already determined earlier. This experimental method is very convenient to determine the triplet cross-section σ_T and the inter system crossing time τ_{ISC}.

Results and Discussions

The ground state absorption spectra of the samples studied is shown in Figure 3. The absorption spectrum of $TPPS_4$ in buffered aqueous solutions at pH 7.0 consist of four Q bands localized at 515, 550, 578 and 633 nm. One intense near UV band (Soret band) has its maximum at around 413 nm. Because of the presence of nitrogen atoms the $TPPS_4$ molecule can be protonated, which changes dramatically its spectrum. These spectral bands can be attributed to the bi-protonated state of the TPPS$_4$. The absorption spectrum of this form in the visible region is characterized by two strongest maxima at 644 and 593 nm. The Soret band shifts to 434 nm. Once the absorbance and concentration are determined, we can obtain the ground state cross-section σ_0 of the samples from the equation $\sigma_0 = \alpha / N$, where α is the linear absorption coefficient and N is the concentration.

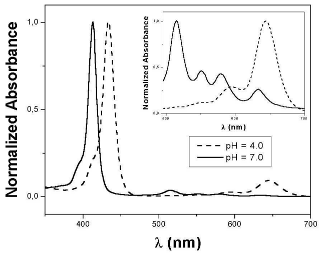

Figure 3: Linear absorption spectra for TPPS$_4$ at pH 4.0 and 7.0.

Figure 4 shows the TPPS$_4$ fluorescence decay curves. A monoexponential function was applied to fit the fluorescence decay kinetics at pH 4.0 (3.6 ns) and 7.0 (10 ns).

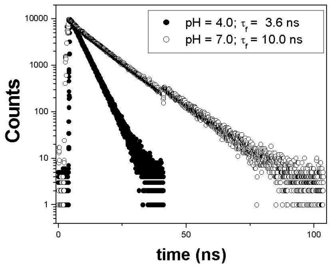

Figure 4*:*Fluorescence kinetics of TPPS$_4$. A monoexponential fit.

In order to estimate the limits for these molecules to show RSA we have recorded the Z-scan curves at different pulse intensity, with single pulse Z-scan. With a single pulse both kinds of the molecules, protonated and non-protonated, showed RSA behavior. The enhancement in the nonlinear absorption with the single pulse Z-scan and the saturation effects with pulses at higher pulse intensity were analyzed with the help of a generalized five-level model and the rate equations describing different mechanisms: the absorption from $S_0 \rightarrow S_1$, ESA from $S_1 \rightarrow S_2$, $T_1 \rightarrow T_2$ and different relaxation times. Here are the rate equations used to describe the fractions of molecules at each level (Figure 1):

$$\frac{dn_0}{dt} = -W_{01}n_0 + n_1\left(\frac{1}{\tau_f} - \frac{1}{\tau_{isc}}\right)$$

$$\frac{dn_1}{dt} = W_{01}n_0 - \frac{n_1}{\tau_{isc}}$$

$$\frac{dn_3}{dt} = \frac{n_1}{\tau_{isc}}$$

where $W_{01}=\sigma_0 I/h\nu$ is the transition rate, τ_f, and τ_{ISC} are the measured fluorescence lifetime and the intersystem crossing time, respectively, n_0, n_1, n_2 are the population fraction in the singlet levels: ground, first and second excited, n_3 and n_4 are population fraction in the triplet levels. We have used $1/\tau_f = 1/\tau_{10} + 1/\tau_{ISC}$, τ_{10} being the excited singlet state lifetime which includes radiative and radiativeless processes. The rate equations are solved numerically using respective temporal intensity patterns (Q-switched/mode-locked pulse trains or single pulse) used in the Z-scan experiments.

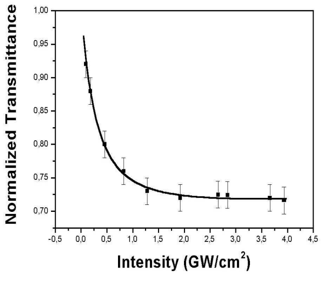

Figure 5: Normalized transmittance as a function of the pulse intensity for the TPPS$_4$.

For the single pulse experiments, the five-level model becomes a three-level one, neglecting the ISC from $S_1 \rightarrow T_1$, as the pulse duration (70 ps) is much shorter than τ_{ISC} (~ns). Moreover, in the single pulse Z-scan measurements just the singlet state is excited because there is not enough time for the triplet to be significantly populated, and so, the nonlinear absorption effect is due to the difference between the cross-sections of ground and excited singlet states. Thus, we can assume the zero triplet population ($n_4 = 0$), and have obtained from the best fit shown in Figure 5 the value of σ_S.

For the pulse train measurements, the triplet state contributes with an accumulative nonlinearity because of the long duration of the Q-switch envelope (about 200ns). With σ_0, τ_f and σ_S obtained from other measurements, we can calculate σ_T and τ_{ISC} from the best fitting of the PTZS curve. Figure 6 shows the PTZS data with the best theoretical fitting.

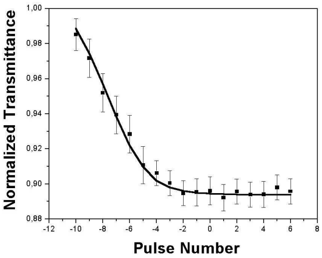

Figure 6: Pulse train Z-scan measurements

The determined parameters σ_0, σ_S, σ_T, τ_f and τ_{ISC} for $TPPS_4$ in aqueous solutions at pH 4.0 and 7.0 for λ_{ex} = 532 nm are listed in the Table-1 together with the calculated parameters: the quantum yield $\Phi_T = \tau_f / \tau_{ISC}$, the ratio of the cross sections of the singlet excited to singlet ground state σ_S/σ_0 and the ratio of the cross sections of the triplet excited to singlet ground state σ_T/σ_0.

The values of triplet quantum yield for non-protonated $TPPS_4$ (77%) obtained using the PTSZ technique is in good agree with those reported in [5] (76%) determined by the flash-photolysis technique. Thus, the Z-scan technique with pulse trains is valuable tool for obtain quantum yield.

Table 1 – Ground state σ_0, excited singlet state σ_S, excited triplet state σ_T cross sections, fluorescence lifetime and intersystem crossing time measurements and quantum yield Φ_T, the rates σ_S/σ_0 and $\sigma_{T/}\sigma_0$ calculated.

pH	**σ_0 10^{-17} cm^2**	**σ_S 10^{-17} cm^2**	**σ_T 10^{-17} cm^2**	**τ_f 10^{-9} s**	**τ_{ISC} 10^{-9} s**	**Φ_T %**	**σ_S/σ_0**	**σ_T/σ_0**
4.0	**0.8 (±0.2)**	**7.4 (±0.2)**	**7.6 (±0.2)**	**3.6 (±0.2)**	**10.0 (±1.0)**	**36 (±6)**	**9.25**	**9.50**
7.0	**2.1 (±0.2)**	**4.7 (±0.2)**	**3.3 (±0.2)**	**10.0 (±0.2)**	**13.0 (±1.0)**	**77 (±13)**	**2.15**	**1.57**

Conclusions

The singlet and triplet absorption dynamics of $TPPS_4$ in aqueous solutions at pH 4.0 and 7.0 at room temperature have been studied with the 532 nm single pulse and train pulse Z-scan. The $S_1 \rightarrow S_2$ and $T_1 \rightarrow T_2$ excited state cross-sections, intersystem crossing time, quantum yield Φ_T and the ratios σ_S/σ_0, σ_T/σ_0 were calculated. It was demonstrated that the protonation changes all characteristics of ground and excited states of $TPPS_4$, thus demonstrating changes of the electronic structure of the chromophore.

It was demonstrated that the Z-scan technique with pulse trains is valuable tool for obtain quantum yield in good agree with conventional techniques.

It was shown that the non-protonated $TPPS_4$ has high quantum yield of triplet formation, and therefore, should play an important role in triplet assisted photochemical applications like PDT. On the other hand, the protonated form of $TPPS_4$ is characterized by high (~10) ratio between the cross sections of the excited states (singlet and triplet) and that of the ground state and thus, should be considered as a perspective material for optical limiters.

Acknowledgements

The authors thank the Brazilian foundations CAPES and FAPESP for financial support.

References

[1] R.E. Araujo, G. Borissevitch and A. S. L. Gomes, *Eletronics Letters*, 36, 71 (2000).
[2] J. Mosinger, Z. Micka, *J. Photochem. and Photobiol. A: Chem* 107 (1997) 77-82.
[3] M. Sheik-Bahae, A A Said, T. Wei, D. J. Hagan, E.W. Van Stryland, *IEEE J. Quantum Electronic*. 26 (1990) 760.
[4] L. Misoguti, C.R. Mendonça, S.C. Zilio, *Appl. Phys. Lett* 74 (1999) 1531.
[5] P. Kubat, J. Mosinger, *J. Photochem. and Photobiol. A: Chem* 96 (1996) 93.