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Effect of protonation on the singlet–singlet excited-state absorption of *meso*-tetrakis(*p*-sulphonatophenyl) porphyrin

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ABSTRACT

This work reports on the excited singlet-state absorption cross-section spectra of both biprotonated and nonprotonated states of *meso*-tetrakis(*p*-sulphonatophenyl) porphyrin obtained by means of the Z-scan technique with white-light continuum pulses. Although our main purpose was to determine these photo-physical parameters in a wide spectral range, we also analyzed the role of accumulative effects arising as consequence of the pulse chirp caused by the group velocity dispersion. This effect leads to apparent changes in the measured excited-state absorption spectra, which can be corrected during the fitting procedure to yield meaningful absorption cross-section values.

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1. Introduction

The investigation of excited-state absorption (ESA) and emission spectra of organic molecules is important in materials characterization for both fundamental and application's point of view. Among several new organic compounds, those with macrocyclic molecules like porphyrins and phthalocyanines have attracted considerable interest because of their promising nonlinear optical characteristics [1,2]. Moreover, their chemical structures permit easy manipulation to yield desirable properties for specific applications at relatively low fabrication cost. Among porphyrins, the water-soluble *meso*-tetrakis(*p*-sulphonatophenyl) porphyrin (TPPS₄) was found to be a promising material for photonics (optical limiters) and medical (photodynamic therapy – PDT) applications [3–6]. Owing to the presence of nitrogen atoms in its structure, TPPS₄ can suffer double protonation with two nearby pK points in the vicinity of pH 5.2 [7]. This drastically changes the spectral properties and, in particular, the nonlinear optical absorption. In a recent investigation, photo-physical properties of TPPS₄ were studied at 532 nm, with special emphasis on how the protonation state modifies the excited-state lifetimes and quantum yields [4]. However, aiming at optical limiting and PDT applications, it is important to extend that investigation to characterize the material's response in a broad spectral range. Such task can be accomplished with a recently introduced version of the Z-scan technique [8,9], known as the white-light continuum (WLC) Z-scan [10,11]. This is a simple, fast and efficient tool to provide nonlinear optical characteristics, such as two-photon absorption [10,11]

and nonlinear refraction [12]. The use of a broadband light source presents advantages in comparison with single wavelength excitation, such as time saving and superior spectral resolution. The WLC Z-scan technique was already successfully applied to determine the ESA spectra of new materials [10,13,14], a task of fundamental importance for the development of broadband photonic devices [1,15]. In particular, ESA spectra of ytterbium bis-phthalocyanine [13] and chlorophyll *a* [14] were obtained. In those investigations, the existence of an accumulative effect on the excited-state population was assumed. Although this could modify the ESA spectral shape, the direct demonstration of this effect, through the comparison of the spectra obtained with the WLC with those obtained with narrower band light sources, has not yet been studied.

The present work employs the WLC Z-scan technique to provide highly resolved spectra of the singlet–singlet excited-state absorption cross-sections for both biprotonated and nonprotonated TPPS₄ samples. Although the main purpose of our investigation is to determine such parameters in a broad spectral range, it seems worthwhile to verify if their values are influenced by the particular light source employed. With this concern, we studied the influence of accumulative effects on the ESA spectra by comparing WLC results with those obtained with an optical parametric amplifier (OPA). The accumulation is strongly dependent on the sample absorption spectrum and on the WLC pulse chirp. A set of rate equations, based on a three-energy-level model, was used to find the excited singlet-state absorption cross-section in the broad spectral range investigated. Although the ESA spectra is distorted due to population build up, the use of this model allows to obtain cross-section results that agree with those of the single wavelength source.

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2. Experimental

TPPS₄ was purchased from *Porphyrin Products Inc.* and dissolved in Milli-Q quality water without further purification. The pH values were adjusted by the addition of appropriate amounts of HCl or NaOH stock solutions. At pH > 6.0, TPPS₄ is in its nonprotonated form and at pH < 4.5 it is biprotonated. In the pH region between 4.5 and 6.0, TPPS₄ in equilibrium condition presents two or three forms, simultaneously, thus excluding the possibility of measurements with only mono-protonated TPPS₄. The UV–vis spectra were measured with a Cary 17 spectrophotometer in samples with well-known concentrations to provide the spectral dependence of the ground-state absorption cross-sections. Measurements of linear and ESA spectra were carried out with the samples placed in a 2 mm-thick quartz cuvette.

Nonlinear absorption spectra were obtained with both WLC Z-scan [10,11] and conventional single wavelength Z-scan (SW Z-scan) [8,9] techniques. The later was employed to confirm that using the white-light continuum produces an accumulation on the TPPS₄ excited singlet-state population, leading to a deleterious spectral distortion of the excited-state absorption spectrum obtained in Z-scan experiments. The WLC Z-scan technique is similar to the SW Z-scan, but uses a broadband pulse instead of single wavelength. The sample is scanned along the focused Gaussian TEM₀₀ beam (z-direction) as a way to change the pulse fluence that presents its maximum value at the focal plane. In the WLC Z-scan, the light transmitted through the sample is completely focused into a portable spectrometer with a resolution of ~2 nm. The spectra are acquired for each z-position as the sample is scanned along the z-direction and then normalized to the one obtained far from the focal plane, where nonlinear effects are negligible. By selecting a particular wavelength from the complete set of measured spectra we obtain a Z-scan signature according to the nonlinear response at that wavelength.

WLC pulses spanning nearly the entire visible range were produced by focusing a pump pulse with a 10 cm focal length lens into a 4 cm-long cell containing distilled water. The pump laser producing 150 fs pulses at 775 nm is a commercial Ti:sapphire chirped pulse amplified system operating at a 1 kHz repetition rate. By using 0.3 mJ laser pulses we were able to generate about 8 μJ of WLC after a low-pass filter added before the sample to remove the strong pump pulse and the infrared portion of the WLC spectrum. The typical spectrum used in our experiments covers the range from 470 to 720 nm, as shown by the dashed line of Fig. 1, and presents a positive chirp of about 4 ps, as determined previously [10].

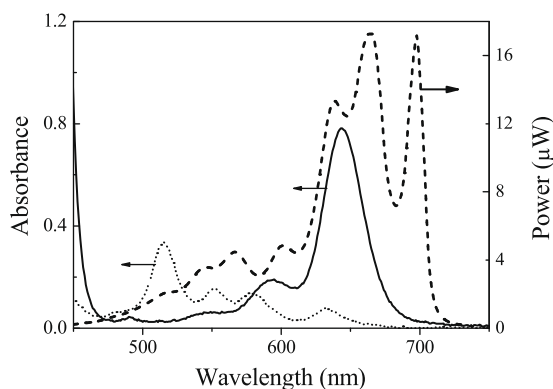


Fig. 1. Absorbance spectra ($-\log_{10}(I/I_0)$) for nonprotonated (dotted line) and the biprotonated (solid line) TPPS₄ samples. The dashed line shows the filtered WLC spectrum.

The energy of the WLC beam at a given wavelength was calculated by considering the continuum as made up of a group of nearly bandwidth-limited pulses centered at various wavelengths [10]. From the total energy and spectral distribution of the WLC pulse, the energy inside each bandwidth, which was assumed as being of the same order as those from the OPA, can be calculated. Another simplification that can be made to calculate the intensity is to consider the beam waist approximately constant for all wavelengths. This procedure simplifies the analysis and gives a fairly good agreement with the traditional discrete Z-scan method.

The light source used to perform single wavelength Z-scan measurements is a commercial OPA capable of providing 120 fs pulses tunable from 460 to 2600 nm. Conventional open aperture Z-scan measurements were carried out for each selected wavelength, using a simple silicon PIN photo-detector coupled to a lock-in amplifier instead of the spectrometer.

3. Results and discussion

Fig. 1 presents the TPPS₄ absorption spectra in its biprotonated and nonprotonated forms. The later presents four Q-bands between 480 and 650 nm, with the strongest maximum at 515 nm ($\sigma_{S_0} = 5.5 \times 10^{-17} \text{ cm}^2$). The biprotonated form also displays four Q-bands in the same region, with the strongest one centered at about 644 nm ($\sigma_{S_0} = 14.0 \times 10^{-17} \text{ cm}^2$). As we shall see later, the presence of such strong absorption shifted to the red enhances the accumulative effect. The B (Soret) bands that occur below 450 nm are not shown in the figure.

By employing the WLC Z-scan we obtain a set of normalized transmittances at the focus covering the entire 470–720 nm spectral range. When the normalized transmittance is higher than one, it indicates a saturable absorption (SA) process, while for values lower than one, reverse saturable absorption (RSA) occurs. As shown in Fig. 2a, the nonprotonated form of TPPS₄ presents RSA effect in the whole Q-band region, with higher magnitude at the blue side of the spectrum. Moreover, good agreement is found between the shapes of the NT spectra obtained with both SW and WLC Z-scans.

According to Fig. 2b, the biprotonated TPPS₄ sample presents SA in the region of the strongest linear absorption band (from 620 to 680 nm), while in the region of smaller absorption, between 470 and 620 nm, RSA is measured with both light sources. However, in this region, a great discrepancy is observed between the ESA spectra obtained in SW and WLC measurements. We attribute this discrepancy to the population that accumulates in the first excited singlet-state as consequence of the pulse chirp [13,14]. Red compo-

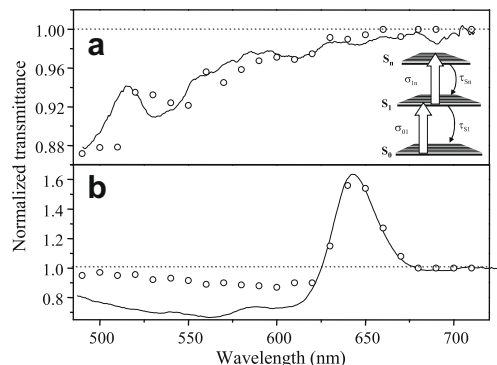


Fig. 2. Normalized transmittance versus wavelength obtained with the WLC Z-scan (solid line) and the SW Z-scan (open circles) for (a) nonprotonated and (b) biprotonated TPPS₄ samples. The inset shows the three-energy-level diagram used to obtain the absorption cross-sections.

nents of the WLC pulse are launched earlier into the sample than bluer ones. Since the spectral positions of red components coincide with the biprotonated strong Q-band absorption, they effectively populate the TPPS₄ first excited singlet-state, thus reducing the ground-state population. However, this state has a lifetime of several nanoseconds [4,5], so that bluer components find a reduced ground-state population. The extra population acquired by the excited-state enhances the RSA effect induced by the WLC pulse in the 470–620 nm range. This situation does not occur in SW Z-scan experiments because the ground-state population is the same for any exciting pulse regardless of the wavelength. The effect is not observed for the nonprotonated sample because the absorption in the red spectral region is weak, and the components of the WLC pulse at this region are not as effective to populate the first excited-state.

The excited-state absorption cross-sections can be determined with a model based on the three-energy-level diagram shown in the inset of Fig. 2. The use of such diagram is justified because the intersystem crossing time is much longer (several ns) than the pulse duration used in our experiments. According to this model, the light pulse excites molecules from the ground-state S_0 level to a vibronic Franck-Condon state in the S_1 band. From there, the molecules can be excited to a higher lying singlet-state S_n or relax back to the ground state with a time constant τ_{S_1} , corresponding to both radiative relaxation with a given fluorescence quantum yield and internal conversion. Since the molecules excited to S_n relax back to S_1 with a time constant τ_{S_n} , the population dynamics can be described by the following set of the rate equations:

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

$$\frac{dn_{S_1}}{dt} = W_{01}(\lambda)(n_{S_0} - n_{S_1}) - W_{1n}(\lambda)(n_{S_1} - n_{S_n}) - \frac{n_{S_1}}{\tau_{S_1}} + \frac{n_{S_n}}{\tau_{S_n}} \quad (2)$$

$$\frac{dn_{S_n}}{dt} = W_{1n}(\lambda)(n_{S_1} - n_{S_n}) - \frac{n_{S_n}}{\tau_{S_n}} \quad (3)$$

where n_{S_0} , n_{S_1} and n_{S_n} are respectively the population fractions in the ground (S_0), first (S_1) and higher (S_n) excited singlet-state levels, $W_{01}(\lambda, t) = \frac{\sigma_{01}(\lambda)I(t, \lambda)}{h\nu}$ and $W_{1n}(\lambda, t) = \frac{\sigma_{1n}(\lambda)I(t, \lambda)}{h\nu}$ are the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transition rates, with $\sigma_{01}(\lambda)$ and $\sigma_{1n}(\lambda)$ being the absorption cross-sections corresponding to these transitions. The time dependence introduced in the irradiance accounts for the previously determined WLC chirp. When finding the population dynamics for OPA pulses, this dependence is not necessary. Owing to the short duration of the pulses employed in our measurements when compared to the relaxation times involved, we assumed the existence of stimulated emission in our model. These equations were numerically solved using the irradiance extracted from the WLC energy at a given wavelength, which was calculated using the procedure described earlier. For the OPA, just one ~ 10 nm Gaussian pulse is considered for the irradiance determination. The calculations were carried out using $\sigma_{01}(\lambda)$ extracted from linear absorbance spectra and the S_1 state lifetime (3.6 ns for biprotonated and 10 ns for nonprotonated) taken from [4]. The higher excited-state lifetime, τ_{S_n} , was assumed to be on the order of 1 ps, in accordance with values found for similar molecules [16]. It is important to note that the fitting results are nearly independent of this value because the population of the S_n state is very small.

Considering the population re-distribution caused by strong pulse incident on the sample, the time evolution of the nonlinear absorption can be written as

$$\alpha(\lambda, t) = N[n_0(t)\sigma_{01}(\lambda) + n_1(t)\sigma_{1n}(\lambda)] \quad (4)$$

where N is the sample concentration. Here, we considered the S_n state population negligible when compared to n_{S_0} and n_{S_1} because its lifetime is very short and the population n_{S_1} , from which n_{S_n} is

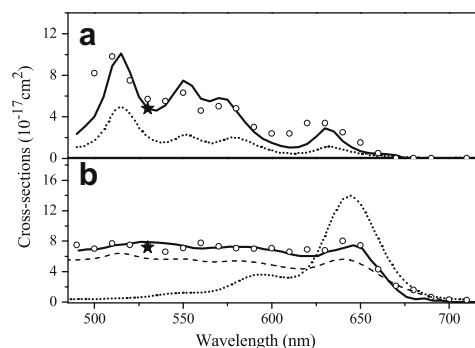


Fig. 3. First excited singlet-state spectra obtained with WLC (solid line) and SW (open circles) Z-scan techniques in (a) nonprotonated and (b) biprotonated TPPS₄ samples. The ground-state cross-section spectra are depicted by dotted lines. The solid star represents σ_{1n} obtained with 70 ps pulses at 532 nm [4]. The dashed line in (b) accounts for the ground-state cross-section spectra obtained at pH 5.4.

formed, is also relatively small. From the fitting of the NT spectra measured with the SW and WLC Z-scans using the cross-section $\sigma_{01}(\lambda)$, the S_1 lifetime and taking into account the accumulative effect, $\sigma_{1n}(\lambda)$ spectra of both TPPS₄ protonation forms were obtained, as shown in Fig. 3.

It can be seen that the S_1 cross-section of the nonprotonated sample is about twice the value of $\sigma_{01}(\lambda)$ in the entire spectral region studied. For the biprotonated TPPS₄ sample, $\sigma_{1n}(\lambda)$ is generally higher than that of the ground-state, with exception of the intense linear absorption region ($\lambda > 620$ nm). The ratio σ_{1n}/σ_{01} is approximately 10 in the 480–570 nm range, reaching 15 at 515 nm. Our results clearly show that when the chirp is considered to find the population dynamics with the three-energy-level, the cross-sections obtained with the WLC completely agree with those measured with a much narrower OPA light source. Besides, the perfect accordance with values obtained with 70 ps pulses at 532 nm [4] also demonstrates the usefulness of the WLC Z-scan method.

An interesting result that we obtained concerns to the absorption cross-sections spectral dependence. For nonprotonated TPPS₄, the profiles of $\sigma_{01}(\lambda)$ and $\sigma_{1n}(\lambda)$ spectra are similar, as seen in Fig. 3a. This fact, together with the small fluorescence Stokes shift observed previously [4,17], indicates that the TPPS₄ vibronic structure is preserved upon excitation [18,19]. In other words, the molecular structure is the same for all singlet states participating in the absorption process and the D_{2h} molecular symmetry, characteristic for the ground state other hand, the ratio $\sigma_{1n}(\lambda)/\sigma_{01}(\lambda) \approx 2$, observed in the entire Q-band region shows that the $S_1 \rightarrow S_n$ transition moment is higher than that of $S_0 \rightarrow S_1$. The transition probability between two electronic states of a molecule depends on its transition moment, which in turn depends on the dipole moment of the molecule and the electronic distributions in the initial and final transition states. The increase of the molecule dipole moment at excitation is well documented for different molecule types, including porphyrins. So, we can associate the higher $\sigma_{1n}(\lambda)$ value, as compared with σ_{01} , with the increase of the TPPS₄ dipole moment at the excitation [20–23].

For biprotonated TPPS₄, the shapes of the $\sigma_{01}(\lambda)$ and $\sigma_{1n}(\lambda)$ spectra differ significantly. The light excitation induces an absorption increase in the 500–620 nm range, similar to the nonprotonated TPPS₄ porphyrine sample, and a decrease between 620 and 700 nm. Changes in the red-ox characteristics, followed by pK shifts in organic molecules after excitation are well documented [24–27]. Based on that, we attribute the difference in the $\sigma_{01}(\lambda)$ and $\sigma_{1n}(\lambda)$ profiles to the partial TPPS₄ deprotonation that appears due to a negative pK shift at excitation. This hypothesis agrees with

the fact that at pH 5.4, where nonprotonated, mono-protonated and biprotonated TPPS₄ forms coexist in equilibrium, the absorbance spectrum shows that $\sigma_{01}(\lambda)$ has a shape similar to that of $\sigma_{1n}(\lambda)$ at pH 4.0, as shown by the dashed line in Fig. 3b.

4. Conclusions

The singlet–singlet excited-state absorption cross-sections for both biprotonated and nonprotonated TPPS₄ were measured with the white-light continuum Z-scan technique and compared to those obtained with the much narrower OPA light source. Besides providing the ESA spectrum over nearly the entire visible range, our results also validate the WLC source as an efficient tool to investigate nonlinear absorption in organic molecules. It presents clear advantages that include higher spectral resolution and the possibility of measuring the complete spectrum in a single scan. However, since the group velocity dispersion may distort the ESA spectrum due to the population build up, care must be taken to circumvent this problem when calculating the excited-state cross-section spectra, especially when the sample presents intense absorption in red region of the WLC pulse, as observed for the biprotonated TPPS₄ sample. After the fitting procedure, the cross-section spectra obtained with WLC Z-scan are in good agreement with those obtained with the conventional SW Z-scan technique. The shapes of the spectra obtained can be explained in terms of the molecular symmetry. Excitation of nonprotonated TPPS₄ increases the absorption, keeping the shapes of the ground and excited-state absorption spectra unchanged. This demonstrates that the D_{2h} molecular symmetry is preserved upon excitation. For biprotonated TPPS₄, the absorption cross-section spectral shapes are different for the ground and first excited singlet states. We associate this effect to the partial TPPS₄ deprotonation at excitation.

The corrected nonlinear absorption spectrum of the biprotonated TPPS₄ demonstrates strong reverse saturable absorption in the 450–650 nm spectral range, with a cross-section ratio $\sigma_{12}/\sigma_{01} \geq 10$. The search for new materials possessing RSA is one of the important directions in nonlinear optics, as these materials are widely applied in optical devices, such as optical light intensity limiters. Thus, we can consider the TPPS₄ porphyrin in its biprotonated form a promising material for optical applications.

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