Strong Enhancement of the Two-Photon Absorption of Tetrakis(4-sulfonatophenyl)porphyrin Diacid in Water upon Aggregation

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Received: September 24, 2004; In Final Form: November 8, 2004

A strong enhancement of the two-photon absorption (TPA) cross section of tetrakis(4-sulfonatophenyl)porphyrin diacid (H_4TPPS^{2-}) at various wavelengths when a J-type aggregate is formed in water with respect to the one observed for the H_4TPPS^{2-} monomer in a mixture of water, dimethyl sulfoxide (DMSO), and urea is presented. The TPA properties are characterized by the open aperture Z-scan technique and the ultrafast two-photon absorption spectroscopy with white light continuum probe (TPA-WLCP) technique. The observed enhancement is discussed in terms of possible electronic cooperative effects in the aggregate.

Introduction

The study of the two-photon absorption (TPA) properties of porphyrins has been the focus of many recent works because they are suitable candidates for a number of possible applications, such as building optical limiting devices, requiring a high TPA absorption cross section.[1,2] Furthermore, they can be of interest for the pharmaceutical industry, since their pronounced TPA in the infrared region can be exploited in the field of photodynamic therapy.[3]

Another important characteristic of porphyrins substituted with ionic groups is the capability to promote the aggregation of many monomer units when dissolved in a highly polar solvent such as water. J-aggregation is clearly observed only for the diacid form tetrakis(4-sulfonatophenyl)porphyrin diacid (H_4TPPS^{2-}) even at low concentrations. The photophysical properties of these aggregates have been thoroughly investigated by steady state absorption and emission spectroscopy, resonance Raman spectroscopy, and transient absorption experiments with ultrafast laser pulses.[4−6]

In this work, attention is placed on the influence of aggregation on the TPA properties of H_4TPPS^{2-} in water. The formation of a J-type aggregate, giving rise to delocalized excitation when light of a suitable wavelength is absorbed, should increase the nonlinear absorption properties of the system, thanks to cooperative effects. Theoretical studies predict an enhancement of the nonlinear optical response in molecular aggregates.[7,8] The aim of this work is to find experimental evidence of such behavior.

Very recently, a short communication on a covalently bound porphyrin dimer reported a very strong cooperative enhancement of the TPA cross section when this system was pumped at 780 nm.[9] In that work, the TPA cross section was measured by TPA induced fluorescence. The dimer investigated differs from the self-assembled aggregates analyzed in the present work, since the two porphyrin moieties are connected through a butadiyne

linker. Both the ground and excited state properties of the dimer are heavily affected by such a linker. By contrast, the electronic properties of a J-aggregate differ from those of the corresponding monomer just because of the spatial coherence of the excited electronic (exciton) state, so that transition energies and dipole moments still hold a clear relationship to those of the monomer.

Experimental Section

In the present work, aqueous solutions of H_4TPPS^{2-} (Porphyrin Products, Inc.) are prepared with bidistilled water acidified with HCl (37%) until a pH of ∼1.0 is reached. The analytic concentrations of the four solutions examined are 2.5×10^{-4}, 5.0×10^{-4}, 7.5×10^{-4}, and 1.0×10^{-3} M. The lowest value is imposed by the detection limits of the techniques used.

To compare the TPA cross section measured for the J-aggregates with the one of the diacid monomer, it was necessary to obtain a solution with a 1×10^{-2} M concentration, required to measure the TPA cross section with the two-photon absorption spectroscopy with white light continuum probe (TPA-WLCP) technique. Since such a concentration cannot be reached in acidified water without aggregate formation, we used as solvent a 1:1 mixture of bidistilled water/dimethyl sulfoxide (DMSO) (Sigma-Aldrich, Uvasol) with addition of urea of ∼1 g/mL (water/DMSO/urea mixture). This mixture has been chosen because both DMSO and water are highly polar solvents capable of dissolving the H_4TPPS^{2-}. Already, a mixture of 1:1 DMSO/water allows a 1×10^{-3} M solution of diacid monomer to be reached. To achieve the 1×10^{-2} M concentration of monomer, urea, a well-known antiaggregation agent for proteins and DNA strands, was also added.

Measurements of the TPA cross section at 812 nm are performed by the open aperture Z-scan technique.[10] The laser source is an amplified Ti:sapphire system delivering 160 fs long pulses centered at 812 nm. Typical pulse energies, after suitable attenuation, are in the range 0.1−0.4 μJ. The beam waist at the focus is 22 ± 5 μm. The TPA spectra are recorded with the TPA-WLCP technique. This method employs pump and probe ultrafast laser pulses which are overlapped spatially and

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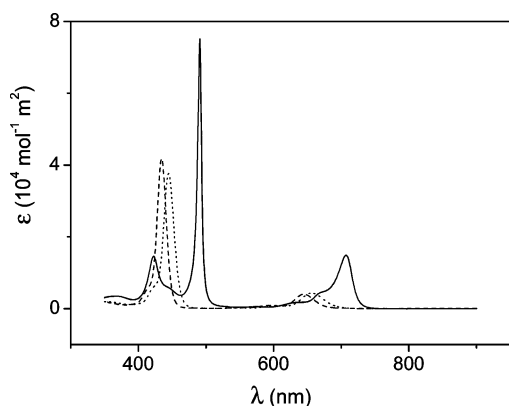
Letters

J. Phys. Chem. B, Vol. 109, No. 1, 2005 **3**

Figure 1. Absorption spectra of H_4TPPS^{2-} in acidified water at $c = 2.5 \times 10^{-4}$ M (solid line), H_4TPPS^{2-} in acidified water at $c = 1.0 \times 10^{-5}$ M (dashed line), and H_4TPPS^{2-} in a water/DMSO/urea mixture at $c = 1.0 \times 10^{-2}$ M (dotted line).

Figure 2. Z-scan of H_4TPPS^{2-} at 812 nm in water (open squares) and in water/DMSO/urea (open circles) measured under the same experimental conditions. The concentration of the monomer solution is 10 times higher than the one of the aggregate. The solid lines are a fit of experimental data.

temporally on the sample. The pump pulse has a fixed wavelength (812 nm), while the probe pulse is a white light continuum covering the range 600–1000 nm.[11] The pump pulse energy and beam waist on the sample are 40 μJ and 2 ± 0.5 mm, respectively. It is important to notice that the Z-scan is a degenerate technique for measuring a TPA cross section, since only one beam with a single wavelength is employed, while the TPA-WLCP method records a nondegenerate TPA cross section at all of the probe wavelengths but the 812 nm value.

Results and Discussion

It is well-known that porphyrins substituted with anionic groups, such as tetrakis(4-sulfonatophenyl)porphyrin, form aggregates in aqueous solutions when the concentration is above 1×10^{-5} M and the pH is less than the pK_a for the protonation of the pyrrole groups in the central ring.[4] The presence of such aggregates in all the aqueous solutions investigated is confirmed by the appearance, in the absorption spectra, of the bands typically attributed to J-aggregate formation.

Figure 1 shows the absorption spectra for a 2.5×10^{-4} M solution of H_4TPPS^{2-} in water (solid line), a 1.0×10^{-5} M solution of H_4TPPS^{2-} in water (dashed line), and a 1.0×10^{-2} M solution of H_4TPPS^{2-} in a water/DMSO/urea mixture (dotted line), all at pH $\sim$ 1.0. The ordinate scale reports absolute values of the molar extinction coefficient (ϵ). The striking differences between the two spectra of H_4TPPS^{2-} in water at pH $\sim$ 1.0 are ascribed to aggregate formation. In particular, the bands at 706 and 489 nm arise from the excitonic absorption of a J-type aggregate formed by the H_4TPPS^{2-} molecules.

The origin of the 422 nm band is still an argument of discussion, since it is blue shifted with respect to the monomer peak and therefore should be ascribed to H-aggregate formation. Chen et al.[5] propose that, instead of a real H-aggregate, this band is due to different exciton manifolds originating from the B band of the H_4TPPS^{2-} monomer. In the monomer, two degenerate transition dipole components, lying in the porphyrin plane and perpendicular to each other, contribute to the B band. When the aggregate is formed, a lifting of the degeneracy occurs and the original B band is split into the 422 nm band, which has H-exciton character, and the 489 peak, which has J-exciton character. In the present paper, we endorse such an explanation.

The absorption spectra of the monomer H_4TPPS^{2-} in the acidified water/DMSO/urea mixture and in acidified water at a 10^{-5} M concentration (Figure 1) show bands with similar shapes and relative intensities. The only difference is a slight shift of $\sim$10 nm toward higher wavelengths in the case of the mixture
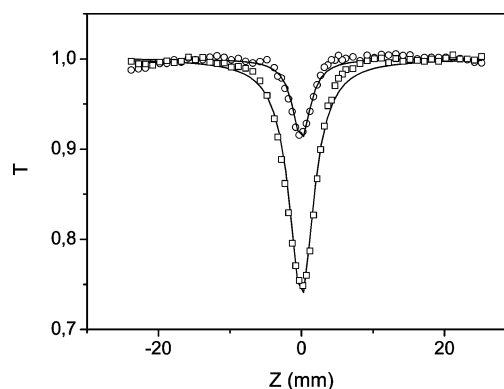
with respect to water. The absence of aggregate formation in the water/DMSO/urea solution is confirmed by the fact that, upon dilution, the bands do not change shape or shift in wavelength.

The concentrations of all the solutions investigated are analytic concentrations, since they are referred to the amount of monomer dissolved in solution. For the four solutions where the aggregate is present, an estimate of the amount of monomer still present is not trivial. On the other hand, when the absorbances of these solutions are normalized with respect to the analytic concentration of the monomer, all four spectra are superimposed within the experimental error. This implies that the monomer concentration still present in the investigated solutions should be negligible compared to the aggregate concentration. Furthermore, the coherence length of the exciton, that determines the width of the J-aggregate bands, does not vary significantly in this concentration range. The latter statement does not mean that the effective dimension of the aggregates, that is, the number of monomers forming it, is invariant in this concentration range. The absorption spectrum of an aggregate is solely influenced by the delocalization length of the effective excitation; this dimension is called the exciton coherence length and can be smaller than the real length of the aggregate.[12]

Figure 2 shows the Z-scan curves at 812 nm for the H_4TPPS^{2-} monomer in the water/DMSO/urea mixture (open circles) and for the H_4TPPS^{2-} in water (open squares), where aggregation occurs. The Z-scan curves are measured under the same experimental conditions. As can be noticed immediately, the nonlinear absorption properties of the system are strongly enhanced upon aggregation.

The TPA coefficient (β, cm/GW) is evaluated from a fit of the Z-scan curve (solid lines). Normalization with respect to the analytic concentration of the solution allows the determination of σ_{TPA}, the TPA cross section, usually expressed in Göppert–Mayer (GM) units (10^{-50} cm⁴·s·photons⁻¹·molecule⁻¹). The values obtained for β and σ_{TPA} for the four solutions in acidified water and those for the water/DMSO/urea mixture are summarized in Table 1. The error affecting β and σ_{TPA} is $\sim$20% of their absolute value. The σ_{TPA} value found for the H_4TPPS^{2-} monomer is in good agreement with the cross section measured by Rebane et al.[13,14] on porphyrins with similar structure by the two-photon excited fluorescence technique.

These data show that the value of σ_{TPA} per single molecule is approximately 30 times larger when aggregation occurs. Furthermore, in the range of concentrations investigated in the

TABLE 1: Value of β and σ_{TPA} Obtained with the Open Aperture Z-Scan Technique at 812 nm for the Four Solutions in Acidified Water Containing Aggregate and the One in an Acidified Water/DMSO/Urea Mixture Containing Monomer

	c (mol/L)	$\beta/10^{-11}$ (cm/W)	σ_{TPA} (GM)
monomer	1.0×10^{-2}	0.74	30
aggregate	2.5×10^{-4}	0.84	1.2×10^{3}
	5.0×10^{-4}	1.42	1.0×10^{3}
	7.5×10^{-4}	2.23	1.0×10^{3}
	1.0×10^{-3}	2.52	9.0×10^{2}

water solutions, there is no difference for σ_{TPA} within the experimental error.

The invariance of σ_{TPA} for all the water solutions may be taken as an indication that the energy delocalization, which can influence the TPA properties of the aggregates, is equal for all of them in this concentration range. The experimental limit of the Z-scan technique does not allow the behavior of the TPA cross section at lower concentrations to be followed.

To shed light on the origin of the enhancement observed for σ_{TPA} at 812 nm, the measure of the whole TPA spectrum in the probe range 750−950 nm is undertaken. To this end, the TPA-WLCP technique is employed. This experiment allows the determination of the variation of the transmittance of a white light continuum probe caused by a two-photon absorption process promoted by one photon of the pump pulse and one photon of the probe itself. Under suitable conditions, the transmittance of the probe beam (T_{probe}) is directly proportional to the TPA coefficient (β):[15, 16]

$$T_{probe} = 1 - \beta I_{pump} k \qquad (1)$$

where I_{pump} is the intensity of the pump beam and k is a parameter influenced by the geometry of the experiment. The σ_{TPA} values at the different probe wavelengths are obtained through normalization of the experimental data with respect to the value obtained through the Z-scan experiments at 812 nm. Obtaining absolute σ_{TPA} values from the TPA-WLCP data would yield a higher error, since it requires the measure of a number of experimental parameters larger than the one required for the Z-scan technique.

Figure 3 reports the spectra for the 1.0×10^{-3} M solution of H_4TPPS^{2-} in acid water (open circles), where aggregation occurs, and for monomers of H_4TPPS^{2-} in a water/DMSO/urea mixture (full circles), whose enlargement is shown in the inset. On the abscissa scale, the wavelength $\lambda_{pump+probe} = \lambda_{pump}\lambda_{probe}/$
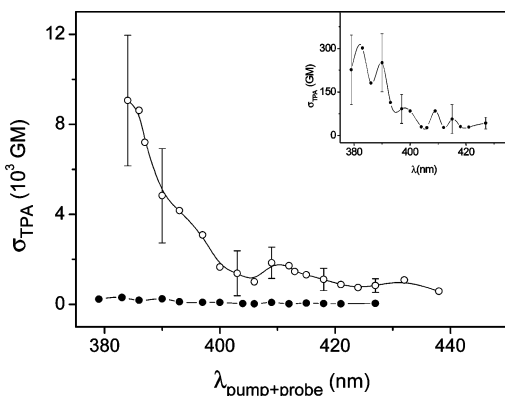

Figure 3. TPA spectra of the J-aggregate (open circles) and monomeric diacid form (filled circles) of H_4TPPS^{2-}. The inset shows an enlargement of the diacid monomer TPA spectrum. The solid lines are just a guide for the eye.

($\lambda_{pump} + \lambda_{probe}$) is used. Error bars are estimated from repeated measurements.

A closed inspection of the TPA spectra for the two systems shows the following features:

(i) σ_{TPA} increases steeply as $\lambda_{pump+probe}$ decreases in both samples.

(ii) σ_{TPA} for the aggregate is strongly enhanced in the whole spectral range investigated. In particular, above 400 nm, this enhancement is almost constant and equal to 30 ± 10.

(iii) There is a clear shoulder centered at 410 nm in the aggregate spectrum. The presence of analogous shoulders in the monomer spectrum cannot be ascertained because of the poor signal-to-noise ratio.

The monotonic increase of σ_{TPA} when $\lambda_{pump+probe}$ decreases is attributed by many authors[13,17] to the one-photon preresonant term affecting σ_{TPA}.

For a simple three-level system, the TPA cross section at the third order of the perturbative approach is given by:

$$\sigma_{TPA} \propto \frac{|\mu_{10}|^2}{(\omega_{10} - \omega_{probe})^2} \frac{|\mu_{12}|^2 \Gamma_{20}}{(\omega_{20} - \omega_{probe} - \omega_{pump})^2 + \Gamma_{20}^2} \qquad (2)$$

where the subscripts 0, 1, and 2 refer to the ground state, a one-photon allowed state (in the present work the Q-band), and a two-photon allowed state, respectively; μ_{ij}, ω_{ij}, and Γ_{ij} are the dipole moment, the frequency, and the Half Width at Half Maximum (HWHM) relative to transition between states i and j, respectively; ω_{probe} and ω_{pump} are the frequencies of the probe and pump beam. This equation can be used when $|\omega_{10} - \omega_{probe}| \gg \Gamma_{10}$ and $|\omega_{10} - \omega_{pump}| \gg |\omega_{10} - \omega_{probe}|$ and $|\omega_{10} - \omega_{pump}| \gg |\omega_{20} - (\omega_{probe} - \omega_{pump})|$.[18]

The first term accounts for the one-photon preresonance and increases monotonically as ω_{probe} approaches ω_{10}, in this case the Q-band resonance.

The enhancement observed when aggregation occurs can be attributed to the following effects: (a) the relative position and shape of the two-photon excited resonance for the aggregate may change with respect to those of the monomer, (b) the two-photon resonance with two-exciton or bi-exciton states may influence only the TPA cross section of the aggregate, and (c) the one-photon preresonance with the Q-bands can be more effective in the aggregate than in the monomer.

The first two hypotheses are connected to cooperative effects, which should enhance σ_{TPA} in the aggregate. The influence of the one-photon preresonance with the Q-bands can be roughly estimated by using the first term in eq 2.

All the parameters in it can be evaluated from the linear absorption spectrum of the samples. The ratio of the value calculated for the aggregate over that for the monomer varies from 7 to 4 in the range $\lambda_{pump+probe} = 400-440$ nm. Below 400 nm, the hypotheses on which eq 2 has been evaluated are not satisfied anymore. The preresonance effect accounts only for one-fifth of the whole enhancement observed. It is clear that the remaining enhancement is caused by the cooperative interactions, that is, the aforementioned hypotheses a and b.

The shoulder observed at 410 nm in the aggregate spectrum can be attributed to a two-photon resonance state. The nature of such a state can be a source of debate, since it can be a pure state of the monomer, a two-exciton or a bi-exciton state of the aggregate which can contribute as two-photon resonant states.[19]

Two-exciton states are excited states were two, noninteracting, delocalized excitations are simultaneously present on the same aggregate. They will absorb at transition frequencies which are more than twice the transition frequency of the one-exciton state

Letters

J. Phys. Chem. B, Vol. 109, No. 1, 2005 **5**

and therefore should lie below 350 nm. As a consequence, the shoulder at 410 nm cannot be a two-exciton state.

If one considers that, because of the centrosymmetric nature of H_4TPPS^{2-}, two-photon allowed states are characterized by a vanishing transition dipole moment, it is highly unlikely that they shift in energy upon aggregation, since the exciton splitting would also vanish in the dipole approximation. As a consequence, these states should fall at about the same wavelength in the monomer and in the aggregate. A comparison with the monomer spectrum does not provide support to this hypothesis. Literature data for *meso*-tetraphenylporphine (H_2TPP) in toluene/CH_3I show that there is a two-photon allowed state around 400−420 nm.[20] Although H_2TPP has an electronic structure similar to the one of H_4TPPS^{2-}, this cannot be considered definitive proof for attributing the shoulder at 410 nm to a two-photon allowed state, which does not change its frequency upon aggregation.

The possible assignment of the 410 nm resonance to a biexciton state (i.e., a state where two bound excitations are simultaneously present in one aggregate) is very intriguing in that it would imply an attractive interaction between two excitons in the aggregate.

Conclusions

In this paper, a 30-fold enhancement of the σ_{TPA} value of H_4TPPS^{2-} in the range 400−440 nm is reported when aggregation occurs. This enhancement is attributed to cooperative effects, which have been theoretically predicted for molecular aggregates, as well as to a preresonance effect with the Q-bands. The latter contribution has been estimated through the linear absorption spectra of the monomer and of the aggregate, and it accounts only for one-fifth of the observed enhancement.

A shoulder in the TPA spectrum of the aggregate at 410 nm is tentatively attributed either to a two-photon excited state not influenced by the intermolecular interactions present in the aggregate or to a bi-exciton state.

Supporting Information Available: Derivation of eq 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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