Excitation relaxation and structure of TPPS$_4$ J-aggregates

L. Kelbauskas$^{a,b,*}$, S. Bagdonas$^a$, W. Dietel$^b$, R. Rotomskis$^a$

$^a$Vilnius University Laser Research Center, 2040 Vilnius, Lithuania
$^b$Laser Research Center, Institute of Optics and Quantum Electronics, Jena University, Max-Wien-Platz 1, 07743 Jena, Germany

Received 30 March 2002; received in revised form 5 August 2002; accepted 1 October 2002

Abstract

The energy relaxation kinetics and the structure of the J-aggregates of water-soluble porphyrin 5,10,15,20-tetrasulphonatophenyl porphine (TPPS$_4$) were investigated in aqueous medium by means of time-resolved fluorescence spectroscopy and confocal laser-scanning fluorescence microscopy. The excitation of the J-aggregates, at excitation intensities higher than $\sim 10^{15}$ photons/cm$^2$ per pulse, results in a remarkable decrease of the fluorescence quantum yield and in the appearance of an additional, non-exponential energy relaxation channel with a decay constant that depends on the excitation intensity. This relaxation mechanism was attributed to the exciton single–singlet annihilation. The exciton lifetime in the absence of the annihilation was calculated to be $\sim 150$ ps. Using exciton annihilation theory, the exciton migration within the J-aggregates could be characterized by determining the exciton diffusion constant $(1.8 \pm 0.9) \times 10^{-3}$ cm$^2$/s and the hopping time $(1.2 \pm 0.6)$ ps. Using the experimental data, the size of the J-aggregate could be evaluated and was seen to yield at least 20 TPPS$_4$ molecules per aggregate. It was shown by means of confocal fluorescence laser scanning microscopy that TPPS$_4$ does self-associate in polyvinyl alcohol (PVA) at acidic pH forming molecular macro-assemblies on a scale of $\sim 1$ $\mu$m in PVA matrices.

$\copyright$ 2002 Elsevier Science B.V. All rights reserved.

PACS: 71.35; 87.15.Nn; 31.70.Hq

Keywords: J-aggregates; Excited state lifetime; Exciton dynamics; Exciton annihilation

1. Introduction

In recent years, many efforts have been made to investigate the aggregation process and the aggregate structure of diverse dye molecules due to their unique properties. Molecular aggregates of chlorophyll have been found to mediate the primary light-harvesting and charge-transfer processes in the photosynthetic complex [1–3]. Molecular dye aggregates also play an important role in many technological applications and have been employed as potential organic photoconductors [4], as markers for biological and artificial membrane systems [5], as materials with enhanced non-linear optical properties [6,7] for use in non-linear optics devices [8–10] and for information processing and storage [11]. Moreover, there has been renewed interest in molecular aggregates because their properties are suitable for superconductivity. The aggregation of biomolecules is interesting in many biological respects as well, since it may have a

*Corresponding author. Laser Research Center, Jena University, Max-Wien-Platz 1, Jena D 07743, Germany. Tel.: +49-3641-947229; fax: +49-3641-947202.
E-mail address: p6kela@rz.uni-jena.de (L. Kelbauskas).
strong effect on their cellular uptake and cellular metabolic processes. In particular, the aggregation of the photosensitizers used in the photodynamic therapy of tumors has been shown to be important for the photosensitizers’ photodynamic activity due to the uptake and intracellular distribution that is different in comparison with monomeric species [12–15].

Meso-5,10,15,20-sulfonatophenyl porphine (TPPS₄) is a water-soluble tetrapyrrolic dye of well-defined chemical structure (Fig. 1). It has been shown that TPPS₄ can self-associate to form H- and J-aggregates depending on the dye concentration, pH and ionic strength [16–18]. The formation of J-aggregates is indicated by the appearance of a sharp intense absorption band that is shifted to the red with respect to the monomeric Soret band. The aggregation often results in the delocalization of the excitation energy over a number of the aggregated molecules due to the intermolecular interaction within aggregated domains. Additional energy relaxation processes, and exciton–exciton annihilation in particular, may appear [19–22]. Despite the number of relevant studies conducted, the structure of J-aggregates formed by TPPS₄ is as yet uncertain. Measurements of the excitation relaxation kinetics in TPPS₄ reported by other authors show relatively large discrepancies [23–26] making a generalization of the reported results rather difficult.

In this study it has been attempted to elucidate some aspects of the excitation relaxation kinetics in the J-aggregates of TPPS₄ and to gain some insight into their structure on the basis of the singlet–singlet annihilation process. The exciton–exciton annihilation kinetics within the aggregate was investigated by means of time-correlated single-photon counting. In addition, the macro-structure of J-aggregates was studied employing confocal laser-scanning fluorescence microscopy.

2. Experimental

2.1. Chemicals

The TPPS₄ was purchased from Porphyrin Products Inc. of Logan, Utah, and used without further purification. The stock solution of TPPS₄ was prepared in 0.02 M phosphate buffered saline (PBS) at pH 7, at a concentration of $9 \times 10^{-3}$ M. The TPPS₄ solutions used in the experiments were prepared by diluting the stock solution to a concentration of $5 \times 10^{-5}$ M. Only freshly prepared TPPS₄ solutions were used. The J-aggregates were obtained through the lowering of pH down to 2 upon addition of HCl to the solution.

The polyvinyl alcohol (PVA) solution was prepared by dissolving 100 mg of crystalline PVA in 1 ml 0.1 M HCl solution at pH 1. The stock solution of TPPS₄ in polyvinyl alcohol (PVA) was prepared by dissolving TPPS₄ in PVA solution until saturation. The films at five different TPPS₄ concentrations (100%, 50%, 33%, 20% and 10%) were obtained by diluting the stock solution with PVA solution and further applying 1 drop (appr. 1 ml) of the PVA solution onto the 2 cm² area of the microscope cover glasses. The samples were dried on a flat surface at room temperature for 24 h.

2.2. Steady-state spectroscopy

Absorption spectra of the sensitizer were recorded using a two-channel spectrophotometer (SPECORD M 400, Carl Zeiss Jena, Germany).
2.3. Time-resolved fluorescence spectroscopy

All fluorescence kinetics measurements were conducted with TPps4 in PBS at a concentration of \(5 \times 10^{-3}\) M with the pH value adjusted to 2.2. The fluorescence kinetic spectroscopy equipment is shown in Fig. 2. A Kerr-lens mode-locked titanium:sapphire laser (Mira 900, Coherent Inc., Santa Clara, CA, USA) pumped by an Ar+ ion laser was used as an excitation source. The laser was operated at a central wavelength of 860 nm, the average power of \(\sim 500\) mW and at pulse duration of 140 fs. The 76 MHz pulse repetition rate of the laser was reduced to 4.75 MHz (average power 11 mW) by using a Bragg diffraction crystal. The second harmonics of the 860 nm irradiation were generated in a lithium-niobate (LiNbO3) crystal (thickness 2.5 mm) of type I (oo-e) yielding the average power of approx. 1 mW. The output was utilized as the excitation source for the experiments using time-correlated single photon counting (TCSPC). The excitation light was focused onto a cuvette containing TPps4 solution using one of three microscope objectives with different magnifications and numerical apertures (10×, 63×; both water immersion, and 100×; oil immersion, with NA = 0.45, 1.3, 1.4, respectively). These focusing optics and continuously adjustable neutral density filters allowed to vary the excitation intensity over 6 orders of magnitude (\(\sim 10^{16}\)–\(10^{10}\) photons/cm² pulse). The fluorescence was collected by the same microscope objective and directed onto the entrance slit of a monochromator via an optical fiber. The entrance and output slits of the monochromator were set to 2 mm, resulting in a full spectral width at half maxima (FWHM) of 8 nm.

A micro-channel plate photomultiplier (R3809U-50, Hamamatsu Photonics K.K., Hamamatsu, Japan) with an instrument response of 25 ps at FWHM was employed in counting fluorescence photons. A time-correlated single photon-counting unit and the corresponding software (SPC-430, Becker & Hickl, Berlin, Germany) were used in the acquisition of fluorescence kinetic data. The data was analysed using fluorescence decay data analysis software (FluoFit, Picoquant, Berlin, Germany), which permits the deconvolution of measured data with the instrument response function. The time resolution attained with this system was approx. 20 ps. For the calculation of annihilation parameters, an

![Fig. 2. Experimental setup for the time-resolved fluorescence measurements. F—filters, TD—trigger diode, DM—dichroic mirror, M—monochromator, MCP—multichannel-plate photomultiplier, PC—computer with acquisition card.](image-url)
additional program was written based on the LabView (National Instruments, TX, USA) software package.

The signal collection factor $G$, which accounts for both the geometry of the detecting system and for its spectral properties (monochromator spectral transparency, photomultiplier quantum efficiency, etc.), expresses the ratio between the fluorescence photons emitted from the excitation volume and those detected by the photomultiplier. It was determined by measuring the integral fluorescence intensity of rhodamine 6G dye, which was used as a reference substance, over a certain period of time. Since the absorption and emission properties of this dye are well known, the number of photons emitted from the excitation volume could be calculated. The factor $G$ was evaluated according to the ratio between the detected and anticipated number of emitted photons per time unit.

All measurements of the fluorescence kinetics were performed under the condition that the probability for detecting one fluorescence photon per excitation pulse was between 0.01 and 0.1.

2.4. Confocal fluorescence microscopy

The microscopy experiments were conducted with a confocal laser-scanning fluorescence microscope (LSM 510 Axiovert, Carl Zeiss, Jena, Germany) using one of Ar$^+$ ion laser lines for excitation. The fluorescence was detected at >685 nm using an appropriate filter set.

3. Results and discussion

Fig. 3 shows the ground state absorption spectra of TPP$\text{S}_4$ in an aqueous solution at pH 6.9, 5.15 and 2.2. The absorption spectrum of TPP$\text{S}_4$ in a buffered aqueous solution at pH 6.9 is characteristic for free-base etio-type porphyrins consisting of four Q bands located at 515, 550, 578 and 631 nm. One intense near-UV band (Soret band) has its absorption maximum at around 414 nm. The absorption spectrum in the visible spectral region changes to a five-band spectrum at an acidic pH of around 5.15. These spectral bands can be attributed to the neutral, diprotonated ionic species and J-aggregates of TPP$\text{S}_4$ [27]. A further lowering of the solution pH to 2.2 results in an increase in the intensity of the absorption bands at 490 and 706 nm, and in the diminution of the absorption bands related to the neutral and diprotonated species of TPP$\text{S}_4$. On the other hand, the Soret band is slightly broadened, reduced in intensity and shifted to the red. These changes in the absorption spectra have been attributed to the formation of the J-aggregates [16,28].

The fluorescence spectrum of TPP$\text{S}_4$ in an aqueous solution (pH = 2, excitation at 490 nm) exhibits a distinctive peak at around 720 nm which is attributed to the fluorescence of J-aggregates [27,17]. Fig. 4 shows the fluorescence decay curves measured at the fluorescence maximum of J-aggregates of TPP$\text{S}_4$. A biexponential decay law was applied for fitting of fluorescence kinetics measured at different excitation intensities (Fig. 4a–c). As is seen from the figure, the two-exponential approximation of the fluorescence decay was unsuccessful, when the excitation was performed using high photon flux densities (Fig. 4a and b), especially for the short-living component. A non-exponential fluorescence decay character persists for excitation intensities down to $\sim 10^{14}$ photons/cm$^2$ pulse, changing into a biexponential process with time constants of $\sim 150$ ps and
3 ns at even lower intensities. The decay time values obtained from the biexponential fit are summarized in Table 1. The decay time of the short-lived component increases from 63 to 150 ps when the excitation intensity decreases, whereas the long-lived component remains nearly constant (≈3 ns) for all excitation intensities used.

To clarify the origin of the long-lived component, the fluorescence relaxation of TPPS\textsubscript{4} was measured in H\textsubscript{2}SO\textsubscript{4} (Fig. 5). Since the J-aggregates break up at pH ≈1 due to the protonation of the sulfonato groups, only the dimeric diprotonated form of TPPS\textsubscript{4} remains under such severe conditions [29]. The fit of the fluorescence decay yields a monoexponential relaxation with a time constant of 3 ns (Fig. 5). Furthermore, the fluorescence kinetics measured in aqueous solutions with pH 2–2.5 at low TPPS\textsubscript{4} concentrations, where the diprotonated form of TPPS\textsubscript{4} dominates and nearly no J-aggregates are present, shows also a monoexponential decay character with a time constant of ≈3 ns (data not shown). Therefore, taking into account the findings mentioned above, the long-lived component of ≈3 ns measured in aqueous solution at pH 2.2 can also be attributed to the diprotonated species of TPPS\textsubscript{4} remaining in the solution.

The measurements of the fluorescence quantum yield as a function of the excitation intensity revealed (Fig. 6) a remarkable decrease in the fluorescence quantum yield for excitation intensities higher than $10^{15}$ photons/cm\textsuperscript{2} per pulse. Such intensity-dependent fluorescence behaviour suggests that, in addition to the exponential energy relaxation in diprotonated species of TPPS\textsubscript{4} with a time-constant 3 ns, other non-exponential decay of the excitation energy occur at high excitation intensities. A similar dependence of fluorescence relaxation characteristics on the excitation intensity has been reported for other organic molecules, such as 1,1-diethyl-N,N'-quinocyanin (PIC) [21,30], thiacyanine [22], TTBC [19] and phthalocyanine films [31] and has been explained by the exciton singlet–singlet annihilation within aggregated domains. Moreover, several recent studies carried out on TPPS\textsubscript{4} and other porphyrin-based molecules revealed the presence of exciton annihilation at sufficiently high excitation intensities [26,32]. Therefore, it is reasonable to expect that

<table>
<thead>
<tr>
<th>Excitation intensity photons/cm\textsuperscript{2} per pulse</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.9 \times 10^{16}$</td>
<td>3.2</td>
<td>0.16</td>
<td>0.06</td>
<td>0.84</td>
</tr>
<tr>
<td>$1.5 \times 10^{15}$</td>
<td>3.1</td>
<td>0.15</td>
<td>0.07</td>
<td>0.85</td>
</tr>
<tr>
<td>$4.4 \times 10^{13}$</td>
<td>3.6</td>
<td>0.26</td>
<td>0.15</td>
<td>0.74</td>
</tr>
</tbody>
</table>

### Table 1

<table>
<thead>
<tr>
<th>Excitation intensity photons/cm\textsuperscript{2} per pulse</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.9 \times 10^{16}$</td>
<td>3.2</td>
<td>0.16</td>
<td>0.06</td>
<td>0.84</td>
</tr>
<tr>
<td>$1.5 \times 10^{15}$</td>
<td>3.1</td>
<td>0.15</td>
<td>0.07</td>
<td>0.85</td>
</tr>
<tr>
<td>$4.4 \times 10^{13}$</td>
<td>3.6</td>
<td>0.26</td>
<td>0.15</td>
<td>0.74</td>
</tr>
</tbody>
</table>
the intensity-dependent behaviour of the fluorescence relaxation of the J-aggregates at high excitation intensities might be caused by the exciton–exciton annihilation as well. At low excitation intensities, when only one exciton per domain is created, the excitation energy decays through monomolecular relaxation processes, which reflect the natural excited state lifetime (150 ps) in J-aggregates. When high excitation intensities are used, more than one exciton can be created simultaneously on a molecular aggregate (domain), and bimolecular exciton–exciton annihilation may occur resulting in a decrease of the detected excitation lifetime.

It has been suggested that when pico- and subpicosecond laser pulses are used for excitation, the singlet–singlet exciton annihilation is the major bimolecular deactivation process [33] and that the singlet–triplet annihilation may be neglected [34]. Here, the singlet–singlet exciton annihilation can be expressed as the following process:

\[ S_1 + S_1 \rightarrow S_1 + S_0 + \text{heat}. \]  

This means that the interaction between two excitons (due to its low probability, the simultaneous multiple exciton annihilation is not considered here) of the first excited singlet state \( S_1 \) in a domain leads to the disappearance of one exciton. There are several theoretical approaches that have been proposed to describe singlet–singlet annihilation [35,36,20]. For exciton dynamics calculations, we applied the theory of binary
collisions, which has been successfully employed for the exciton annihilation processes within PIC aggregates in aqueous solution [36]. It assumes that, firstly, the domain size over which excitons migrate is sufficiently large for the exciton density to be considered as a continuous variable and, secondly, that the exciton migration is faster than the monomolecular exciton decay. The latter assumption means that the excitons are statistically distributed over the domain. Taking all this into consideration, the exciton decay dynamics can be described by the following equation:

\[
\frac{\partial n}{\partial t} = -kn - \frac{1}{2}\gamma n^2,
\]  

(2)

where \( n \) is the exciton population density, \( k \) is the single exciton decay rate, and \( \gamma \) is the exciton annihilation rate. The coefficient \( \frac{1}{2} \) arises because two excitons are necessary for an annihilation event to produce a single exciton. Since a linear structure of the aggregates has been proposed for the diprotonated H_4TPPS_4^2− [16,37–40], cases of domains with reduced dimensions (i.e. the exciton migration in the domain is confined to certain directions) have to be considered, in which the exciton annihilation rate \( \gamma \) becomes time dependent. It has been shown that, under assumption of dipole–dipole interaction between molecules, the time dependence can be asymptotically expressed as [20,41]:

\[
\gamma(t) = \gamma_0 t^{-h},
\]  

(3)

where \( h \) is a parameter related to the spectral dimension of the domain. The spectral dimension \( d_s \) describes the probability \( P_a \) for an exciton to decay after an excitation event within a time \( t \) in cases when annihilation occurs:

\[
P_a \sim t^{-d_s/2}.
\]  

(4)

In the theory of exciton annihilation, two different exciton interaction mechanisms are distinguished: static and diffusion-limited. The annihilation is considered to be static when the correlation distances of excitons are smaller than the reaction radius \( R \), which, in the case of long-range Förster dipole–dipole interaction, is determined as

\[
R = (R_A/R_M)^{3/2}a,
\]  

(5)

where \( R_A \) and \( R_M \) are the Förster radii of exciton annihilation and migration, respectively, and \( a \) is the distance between the nearest neighboring molecules. When the correlation distances are larger than the reaction radius, diffusion-limited exciton annihilation takes place. The parameter \( h \) is related to the spectral dimension \( d_s \) as

\[
h = 1 - d_s/6 \quad \text{static annihilation,}
\]  

\[
h = 1 - d_s/2 \quad \text{diffusion-limited annihilation.}
\]  

(6)

Inserting Eq. (3) into Eq. (2), one obtains:

\[
\frac{dn}{dt} = -kn - \gamma_0 t^{-h} n^2.
\]  

(7)

Taking into account the shortening of the short-lived fluorescence decay compound measured upon increasing excitation intensity (Fig. 4a–c), it can be assumed that the exciton annihilation is fast as compared with the monomolecular exciton relaxation. A similar result has recently been reported for aggregated TPPS_4 using transient absorption measurements [32]. Therefore, the term \( kn \) on the right side in Eq. (6) may be neglected. Under this assumption, the solution of Eq. (7) is

\[
n = \frac{N_0}{N_0\gamma_0 1/(1-h)t^{1-h} + 1},
\]  

(8)

where \( N_0 \) is the exciton density at \( t = 0 \).

The parameters \( \gamma_0, N_0, h \) can be evaluated by fitting Eq. (8) to experimental data. When their values are known, several parameters of the exciton motion within the domain can be determined. As mentioned above, the exciton migration can be described in terms of the theory of one-dimensional diffusion-limited motion. According to the theory, the exciton diffusion coefficient \( D \) in the domain can be expressed as

\[
D = \frac{\pi d N_0 \gamma_0^2}{16},
\]  

(9)

where \( d \) is the distance between the molecules and \( N_0 \) is the initial exciton density. The characteristic exciton hopping time can then be evaluated by using

\[
\tau_h = \frac{d^2}{2D}.
\]  

(10)

The fluorescence decay data were fitted using Eq. (8). In order to obtain an absolute scale of
fluorescence intensity, the number of measured integrated fluorescence photons (counts) was divided by the excitation volume (in cm³) and multiplied with the geometrical factor \( G \). The iterative reconvolution method based on the non-linear Levenberg–Marquardt algorithm was employed for the fitting procedure. For excitation intensities from \( 5.9 \times 10^{16} \) down to \( 4.4 \times 10^{15} \) photons/cm² pulse, the best-fit results were obtained with \( h = 0.5 \). At lower excitations the experimental data deviated from the annihilation law. Using Eqs. (9) and (10), the exciton motion parameters—such as the diffusion coefficient \( D \) and the hopping time \( \tau_h \)—were evaluated as \( (1.8 \pm 0.9) \times 10^{-3} \) cm²/s and \( (1.2 \pm 0.6) \) ps, respectively. Similar results were obtained for TPPS₄ when the transient absorption kinetics were measured by means of the pump-and-probe technique [32].

As seen in Fig. 6, the fluorescence quantum yield starts to decrease when the excitation intensity reaches \( \sim 1.5 \times 10^{15} \) photons/cm² pulse. This point marks the onset of the annihilation process and corresponds to a threshold value of excitation intensity when only one exciton per domain exists. The mean number of molecules within one domain can then be calculated dividing the number of the molecules within the excitation volume by the number of absorbed photons, if the concentration of the TPPS₄ molecules and the excitation volume in the sample are known. We found that the domain of the TPPS₄ J-aggregate consists of at least \( \sim 20 \) molecules.

It must be noted, however, that depending on the exciton motion characteristics and lifetime, this value may reflect either the physical size of the aggregate or the number of the molecules that an exciton visits within its lifetime in the absence of annihilation. Thus, if the diffusion length of the exciton is shorter than the length of the aggregate, exciton collisions are confined to distances of \( \sim 2\sigma_{\text{diff}} = \sqrt{8\tau_{\text{exc}} D} \). The annihilation process stops when the exciton density within the aggregate decreases to a value where the excitons do not collide as the distances between them are too large, even though more than one exciton does exist within the aggregate. It is thus obvious that only the exciton diffusion-limited size but not the physical size of the aggregate can be determined. With exciton motion parameters \( D, \tau_h \), and the exciton intrinsic lifetime all being known in the absence of annihilation, it is possible to determine which of the above mentioned cases occurs. The number of molecules visited by one exciton within its lifetime can be evaluated by calculating the distance that the exciton migrates during its lifetime in the absence of annihilation. This can be done using the following equation:

\[
d_{\text{migr}} = \sqrt{2\tau_{\text{exc}} D},
\]

where \( \tau_{\text{exc}} \) is the exciton lifetime in the absence of annihilation and \( D \) is the diffusion coefficient. \( \tau_{\text{exc}} \) was determined by fitting the fluorescence decay when low excitation intensities were used and no annihilation occurred (Fig. 4c, Table 1). Thus, we attribute the short-lived component of \( \sim 150 \) ps to the natural exciton lifetime within the aggregate in the absence of annihilation. Using this value and the previously determined diffusion coefficient, we found that the migration distance \( d_{\text{migr}} \) equals \( \sim 7 \times 10^{-7} \) cm. Assuming that the distance between molecules is \( \sim 5 \) Å, the aggregate length can be calculated to be \( \sim 10^{-6} \) cm, showing that the exciton diffusion length is shorter than the aggregate length. This result suggests that the determined number of molecules per aggregate represents the physical size of the aggregate. The number of coherently excited molecules obtained in this work is in fairly good agreement with previous findings on the aggregation number of TPPS₄ obtained from UV/VIS absorption spectroscopy (\( N = 11 \)) [17], fluorescence anisotropy lifetime measurements (\( N = 22 \)) [24] and dynamic light scattering experiments (\( N = 6–32 \)) [38]. On the other hand, it has been proposed that TPPS₄ J-aggregates tend to form large fractal-like structures or macroaggregates in organic solvents. Therefore, additional measurements of TPPS₄ embedded in polyvinyl alcohol (PVA) films were conducted by means of confocal laser-scanning microscopy. Fig. 7a shows a typical image of TPPS₄ fluorescence in a PVA film at acidic pH. Fig. 7b represents the fluorescence image of TPPS₄ in PVA at neutral pH. The fluorescence was excited at several wavelengths (488, 512, 633 nm) and detected using an appropriate filter set within
the wavelength region of >650 nm. No differences were observed in the fluorescence pattern when different excitation wavelengths were used. As can be seen, large structures on the scale of \(B1\) \(m\) are formed at acidic pH, whereas diffuse fluorescence pattern was observed in the case of neutral pH (Fig. 7b). The presence of large aggregates has been also reported by others [42] using dynamic resonance light scattering.

4. Conclusions

The energy relaxation dynamics within the J-aggregates of TPPS\(_4\) were investigated. The experimental data presented here lets us conclude that the appearance of the new, non-exponential decay process within the J-aggregates formed by the diprotonated monomers of TPPS\(_4\) can be described by the theory of exciton singlet–singlet annihilation in restricted domains. The exciton migration parameters, diffusion length \(D\) and the hopping time \(\tau_h\) were determined. The intrinsic exciton lifetime, i.e. the exciton lifetime in the absence of annihilation, was measured to be \(\sim 150\) ps and the mean physical size of the J-aggregate domain was determined to be \(\sim 20\) molecules per domain. The experiments conducted on TPPS\(_4\) embedded in PVA films showed that the J-aggregates do not decompose in PVA matrices, but form large molecular assemblies on a scale of \(\sim 1\) \(\mu\)m.

Acknowledgements

This work was supported in part by the Lithuanian State Science and Studies Foundation.

References

[34] N.E. Geacintov, J. Breton, Biophys. J. 17 (1977) 1.