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Photothermal effects and fluorescence spectra of tetrapyridylporphyrins

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Abstract

The generation of triplet state of tetrapyridylporphyrin and the Zn complex of this dye was established by laser induced optoacoustic spectroscopy (LIOAS). The influence of prolonged illumination by light from Soret band and Q bands regions on fluorescence spectra of dyes solutions were measured. Two concentrations of dyes in chloroform solution were investigated. The yield of fluorescence of investigated dyes was very low and the yields of singlet → triplet intersystem crossing (ISC) for higher dye concentrations were about 0.73 for both TPyP and ZnTPyP, whereas the lifetime of the triplet states for these concentrations (4×10^{-6} M for TPyP and 7×10^{-6} M for ZnTPyP) were 2.08 and 1.74 μs, respectively. At about two times lower concentrations, only weak thermal deactivation components with decay time of about 0.5 μs were observed. Probably in this case, besides these components and "prompt" thermal deactivation, some very slow decays also occur. The most other spectral properties of TPyP were similar at both concentrations, suggesting that this dye is predominantly in monomeric state. At higher concentration for ZnTPyP solution, the additional maximum fluorescence spectrum located at 631 nm is observed. It is related to $Q_x(0, 0)$ absorption band at about 625 nm. These maxima belong probably to some dimeric form of dye being much more sensitive to photodestruction than monomeric form of ZnTPyP. The appearance of various forms of dyes with different photosensitivity and various ability of triplet state generation has to be investigated in order to establish the right time of illumination of tissue stained by the dye in photodynamic treatment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorescence; Photoreaction; Tetrapyridylporphyrins; Time-resolved photothermal spectra

1. Introduction

Various porphyrin compounds play an important role in biophysics [1], conversion of light energy into electrical energy [2,3] and in photodynamic therapy (PDT) of cancer [4,5]. The efficient generation of dye triplet states facilitate the run of the photochemical reactions with high yield which is important in PDT [4,5]. The triplets are formed predominantly by intersystem crossing (ISC) from excited singlet state S_1 to triplet state T_1. The depopulation of triplet state by delayed fluorescence (DF) and phosphorescence (Ph) is less efficient than thermal deactivation (TD) from T_1 to S_0 [6–8]. Therefore, measurements of TD from triplet state enable evaluation of the efficiency of the generation of these triplet states by ISC from excited singlet S_1 to T_1.

The aggregated forms of dyes are usually less efficiently incorporated into the living cells than monomeric forms [4]. Information about dye aggregation can be drawn from absorption and fluorescence spectra [9,10]. The monomers and aggregates can undergo photoreaction with different kinetics, therefore, the measurements of the spectra after various times of illumination help to distinguish between the various forms of the dyes. In PDT, one has to know the bleaching kinetics of all forms of the dyes introduced into tissue in order to establish the right time of illumination [11]. The comparison of the locations obtained and the intensities of various absorption and emission bands of investigated dyes with the literature data which giving the results of measurements and calculations done for similar compounds [9,10,12] was also helpful in the interpretation.

In this paper, time-resolved photothermal signals, absorption, fluorescence and fluorescence excitation spectra of tetra(4-pyridyl porphine) (TPyP) and complex of this dye with zinc (ZnTPyP) in chloroform solutions at two dye concentrations were measured. Structures of dyes are shown in Fig. 1.

The yields of the triplet state generation are obtained. For ZnTPyP, the influence of illumination of the sample by light

Abbreviations: DF, delayed fluorescence; ISC, intersystem crossing; LIOAS, laser induced optoacoustic spectroscopy; PDT, photodynamic therapy; Ph, phosphorescence; TPyP, 5,10,15,20-tetra(4-pyridyl)-21*H*, 23*H*-porphine; ZnTPyP, zinc-5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine

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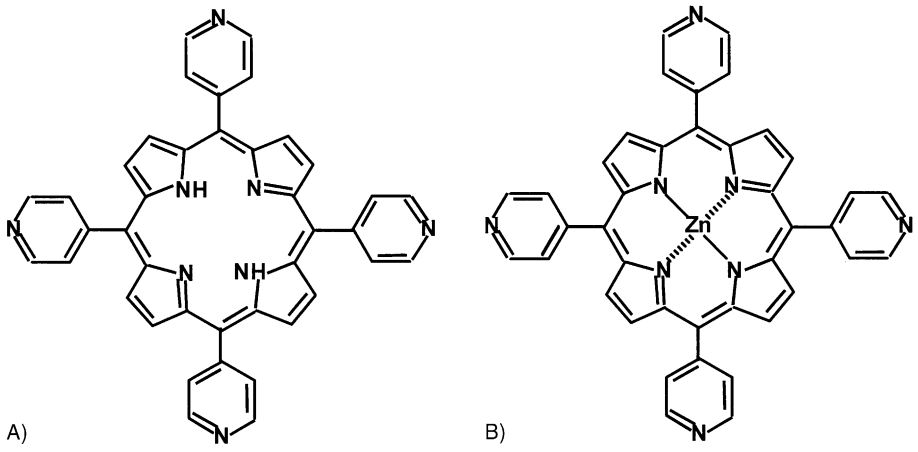

Fig. 1. Structures of investigated porphyrins: (A) 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (TPyP); (B) zinc-5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (ZnTPyP).

absorbed in Soret region and by light absorbed predominantly by $Q_x(0, 0)$ of aggregated form on the shape of fluorescence spectra were established.

2. Material and methods

The TPyP and ZnTPyP were purchased from Aldrich Chemical Co., β-carotene (used as reference in laser induced optoacoustic spectroscopy (LIOAS)) from Sigma Aldrich. All dyes were used without further purification. Chloroform used as a solvent was of spectroscopic grade from Uvasol Merck, KG&A, Darmstadt (Germany). The chloroform solutions at the following two concentrations were used for LIOAS measurements: ($C_1 = 3.8 \times 10^{-6}$ and $C_2 = 0.9 \times 10^{-6}$ M for TPyP; $C_1 = 7.4 \times 10^{-6}$ and $C_2 = 1.9 \times 10^{-6}$ M for ZnTPyP). The solutions of ZnTPyP were not stable in time, therefore, for LIOAS measurements all solutions were taken 12 h after dyes dissolution when their spectra had not changed. For other spectral investigations, freshly prepared solutions were used and their time of evolution and photosensitivity were established. The concentrations of these solutions ($C_3 = 2 \times 10^{-5}$ M) were higher than those used for LIOAS.

The arrangement used for time-resolved photothermal signal measurements was typical for LIOAS [6–8]. Such arrangement gives opportunity to distinguish between prompt effect occurring in a time shorter than time-resolution of apparatus (in our case 0.4 μs), and slow processes undergoing in longer times. The sample is illuminated by sub-nanosecond laser flash (417 nm). The dye investigated and the reference concentrations were such that both identical absorptions at 417 nm were exhibited. The waveform signal (Fig. 2) measured by piezoelectric transducer is taken for reference sample and measured solutions both in chloroforms. The β-carotene exchanges all absorbed energy into heat in time, shorter than time-resolution of apparatus. Two

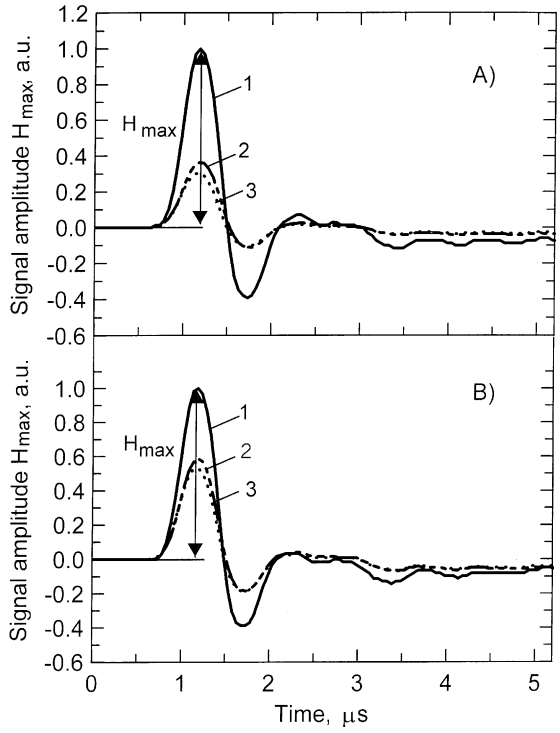

Fig. 2. Waveform photothermal signals obtained according LIOAS method [8]: (A) at lower dye concentration C_2; (B) at higher dye concentration C_1 (given in Table 1). Curve 1: β-carotene; curve 2: ZnTPyP; curve 3: TPyP.

methods of signal analysis were used: the first one proposed by Marti et al. [13] is based on the comparison of maximal amplitude (H_{max} in Fig. 2) for the sample and reference, the second one elaborated by Rudzki-Small et al. [14] gives values of decay time of TD by the deconvolution of both signals shapes. Results obtained by both methods were compared. The absorption spectra of investigated solution were taken using Specord M40 spectrometer (Carl Zeiss, Jena, Germany), while fluorescence spectra by means of a Fluorescence Spectrophotometer F 4500 (Hitachi, Japan).

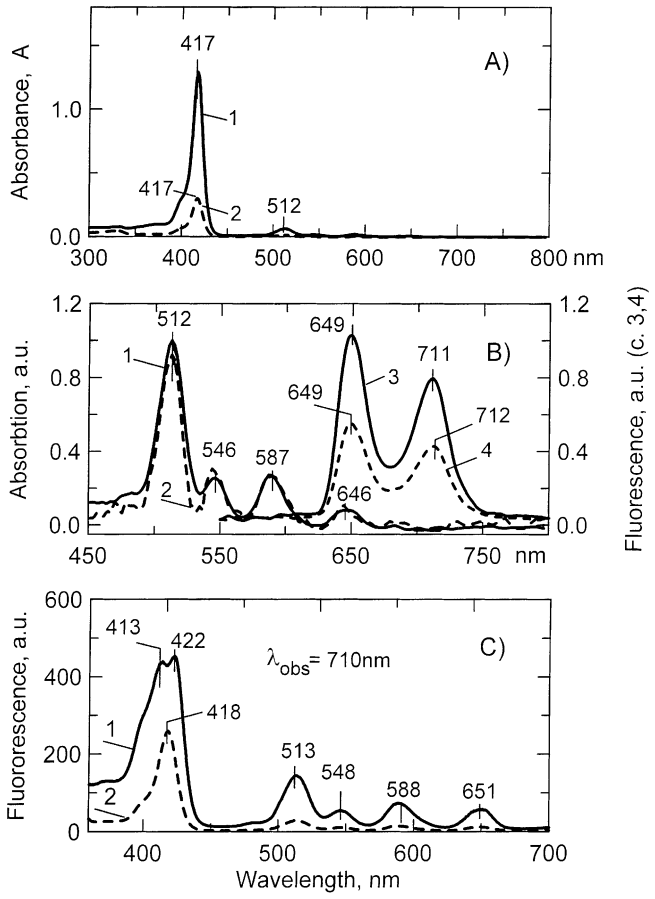

Fig. 3. Spectra of TPyP solutions in chloroform: (A) absorption; (B) enlarged long wavelength absorption (curves 1 and 2) and fluorescence (curves 3 and 4) (excited at 417 nm); (C) fluorescence excitation spectra observed at 710 nm. Curves 1 and 3: refer to the higher dye concentration C_1; curves 2 and 4: lower dye concentration C_2.

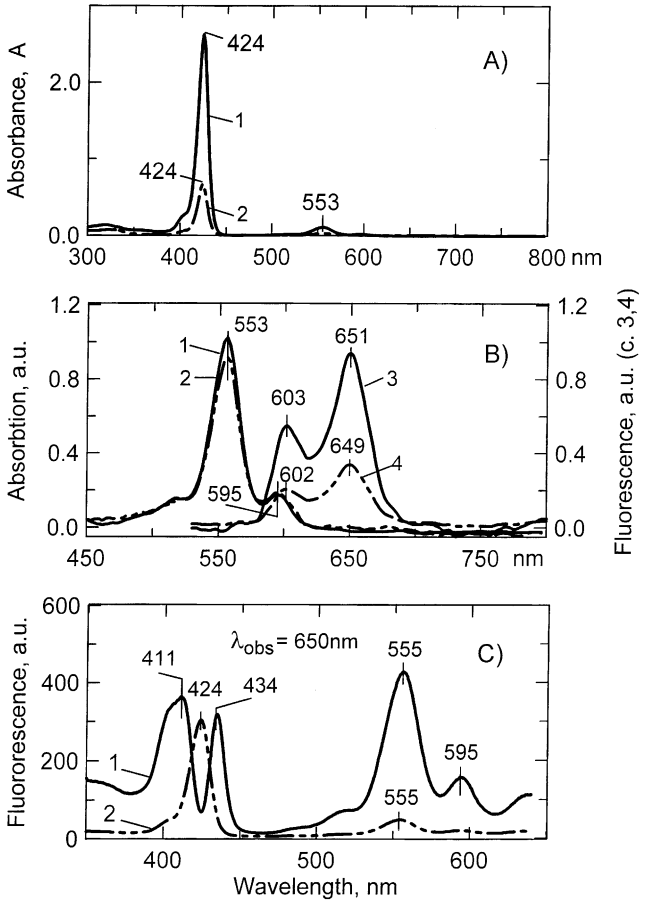

Fig. 4. Spectra of ZnTPyP in chloroform: (A) absorption; (B) enlarged long wavelength absorption (curves 1 and 2) and fluorescence (curves 3 and 4) (excited at 417 nm); (C) fluorescence excitation spectra (observed at 650 nm). Curves 1 and 3: higher dye concentration C_1; curves 2 and 4: lower dye concentration C_2 (concentrations as in Table 1).

3. Results and discussion

3.1. Absorption and fluorescence spectra

Absorption, fluorescence and fluorescence excitation spectra of TPyP at higher (C_1) and lower (C_2) concentrations are shown in Fig. 3A–C. The same results for ZnTPyP are presented in Fig. 4A–C. The positions of Soret band (B band) is not changed as a result of change in dye concentrations (Figs. 3A and 4A and Table 1). For TPyP also the Q bands in absorption and fluorescence spectra are not changed as a result of the increase in dye concentration (Table 1), but for freshly prepared ZnTPyP solution at higher concentration a new band of emission at 631 nm is

Table 1
Absorption and fluorescence maxima (nm) of dyes in chloroform[a]

Dye	C	Soret	Absorption		Fluorescence	
			Band II $Q_x(0, 1)$	Band I $Q_x(0, 0)$	Band I $Q_x(0, 0)$	Band II $Q_x(1, 0)$
TPyP	C_1	417 (413, 422)	587	646	649	711
	C_2	417 (418)	587	646	649	712
ZnTPyP monomer	C_1	424 (411, 434)	553	595	603	651
	C_2	424 (424)	553	594	602	649
ZnTPyP aggregate	C_3	424 (409, 436)	592	625	631	690

[a] For TPyP: $C_1 = 3.8 \times 10^{-6}$ M, $C_2 = 0.9 \times 10^{-6}$ M. For ZnTPyP: $C_1 = 7.4 \times 10^{-6}$ M, $C_2 = 1.9 \times 10^{-6}$ M, $C_3 = 2 \times 10^{-5}$ M. In brackets are given positions of Soret components obtained from fluorescence excitation spectra.

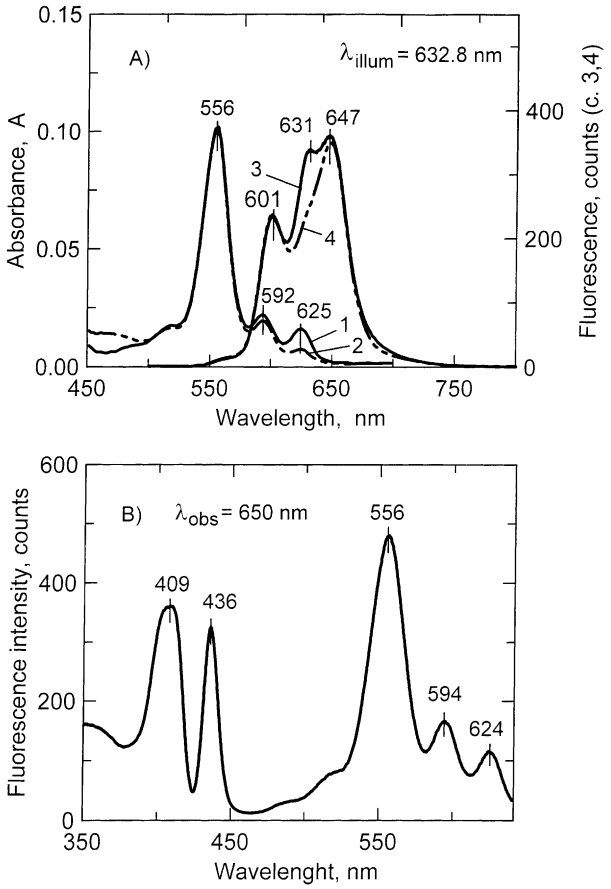

Fig. 5. Absorption, fluorescence and fluorescence excitation spectra of freshly prepared ZnTPyP solution in chloroform ($C_3 = 2 \times 10^{-5}$ M): (A) before (curves 1 and 3) and after prolonged illumination by He–Ne laser beam (632.8 nm) (curves 2 and 4); (B) florescence excitation spectrum observed at 650 nm.

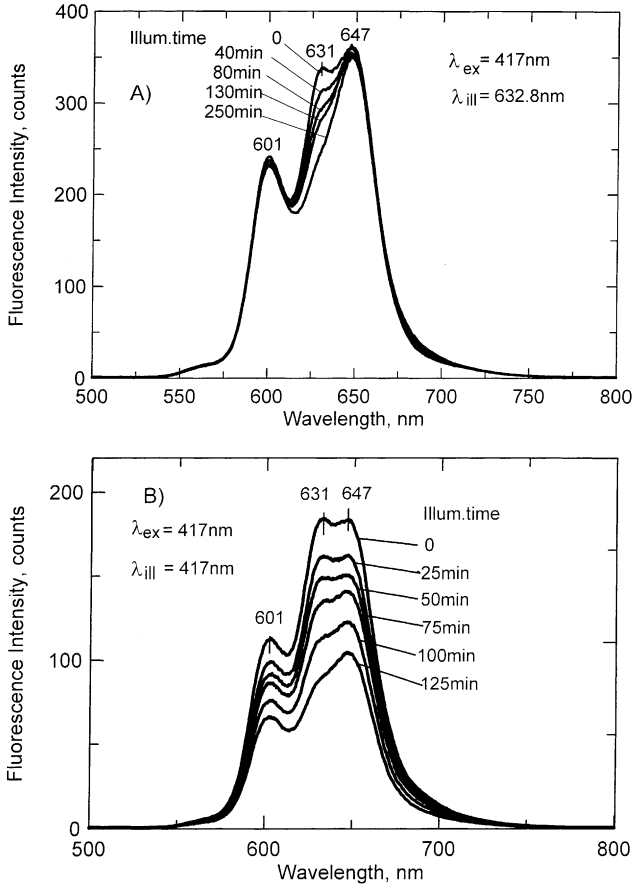

Fig. 6. The change in fluorescence spectra of freshly prepared ZnTPyP solution in chloroform ($C_3 = 2 \times 10^{-5}$ M): (A) illumination by He–Ne laser (632.8 nm, 2 mW); (B) illumination by 417 nm (2 μW/cm^2). Illumination times are given in the figure.

formed (Figs. 5 and 6) and B band is broader than for the low concentration (not shown). It is known that [12], for metal free porphyrins almost mirror symmetry between band II $Q_x(0, 1)$ and band I $Q_x(0, 0)$ and corresponding fluorescence bands is usually observed. For TPyP (Table 1), the difference in positions of absorption maxima is 59 nm, whereas between fluorescence maxima it is 63 nm. Also, characteristic for monomeric porphyrins [8–10,12], very small (3 nm) Stokes shift between band I of absorption and emission was observed. All these results suggest that predominantly the monomeric TPyP is present in solutions at both concentrations. But, the yield of fluorescence of TPyP increases slightly with increase in the dye concentration (Table 2). It is known that [10], some aggregated forms of porphyrins are fluorescent [10,15]. At higher concentration the yield of fluorescence is still low, but increases. This suggests that the aggregates fluorescence is more efficient than that of the monomers. The occurrence of some additional forms of TPyP also follows from fluorescence excitation spectra of this dye (Fig. 3C). The Soret band which exhibits in the main absorption spectra, maximum at 417 nm with only some weak shoulders besides this main peak (Fig. 3A) in fluorescence excitation spectrum (Fig. 3C and Table 1), has two well-resolved components at 413 and 422 nm. It shows that the various Soret band components excite fluorescence with various efficiency. These components could be due to B_x and B_y transitions of the same form, but in such a case, their intensity ratio and positions should be the same at various dye concentrations when fluorescence observation wavelength is the same. The results shown in Fig. 3C and Table 1 suggest that various aggregated or solvated forms can be present because the excitation spectrum depends on

Table 2
The yields of triplet state generation obtained by Marti et al. method [13][a]

Dye	C	λ_T	Φ_F	α	Φ_T
TPyP	C_1	757	0.086	0.55 ± 0.02	0.73 ± 0.15
	C_2	757	0.054	0.30 ± 0.02	1.22 ± 0.19
ZnTPyP	C_1	760	0.049	0.57 ± 0.02	0.73 ± 0.15
	C_2	760	0.029	0.34 ± 0.02	1.17 ± 0.19

[a] Parameter λ_T: wavelengths of triplet state [23]; Φ_F and Φ_T: yields of fluorescence and triplet state generation; C_1 and C_2: dye concentrations such as in Table 1; α: part of energy converted "promptly" into heat.

dye concentration. It is known that [15], aggregates of porphyrins can be red-shifted (*J* aggregates) or blue-shifted (*H* aggregates). Investigated dyes can form different types of aggregates characterized by different B band components [15].

For porphyrin complexes with metal, the distance between I and II absorption bands position is usually smaller than the distance between I and II bands of fluorescence [12]. In the case of ZnTPyP, it is also observed at both concentrations (Fig. 4 and Table 1) of the solution measured 12 h after the preparation. In the freshly prepared solutions at higher concentration, a new band in fluorescence located at 631 nm is clearly seen (Fig. 5A). The illumination by laser line 632.8 nm causes the decrease of this shoulder without the decrease in intensity of normal bands at 601 and 647 nm (Figs. 5A and 6A). The same illumination causes the decrease in 625 nm absorption (Fig. 5A). Illumination in B band (417 nm) causes the decrease of all the three bands (Fig. 6B), but the kinetic of 631 nm band decreases quicker than that of the 601 and 647 nm bands (Fig. 7A and B).

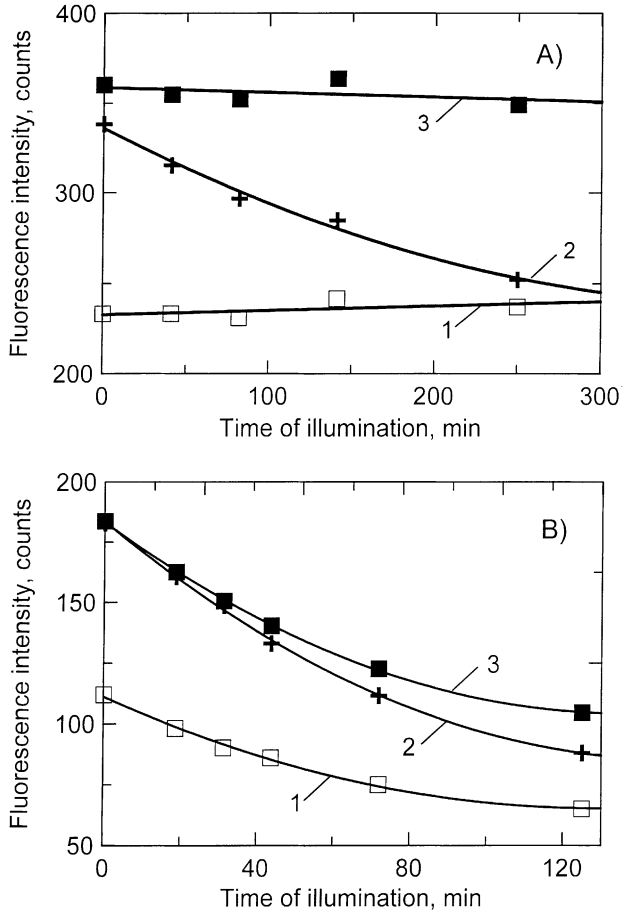

Fig. 7. Kinetics of the decrease in the dyes fluorescence obtained on the grounds of Fig. 6: (A) illumination at 632.8 nm; (B) illumination at 417 nm. Change in fluorescence — curve 1: at 601 nm, curve 2: at 631 nm, curve 3: at 647 nm.

From absorption (Fig. 5A), it seems that in Soret region, the B bands of both forms of ZnTPyP almost overlap, but in Q region they are separated (Figs. 4 and 5). On the basis of the typical TPyP Stokes shift (6 nm) and the common photodestruction with 631 nm emission, one can suppose that 625 nm is I $Q_x(0, 0)$ band of the absorption of new form of the dye related to band I of fluorescence at 631 nm. Band II of absorption should be about 590 nm, and in emission at 690 nm. The $Q_x(1, 0)$ band in emission spectra of TPyP dyes is usually low in comparison with $Q_x(0, 0)$ band [10]. The photochemical changes observed in region of band II in absorption and fluorescence spectra are low, suggesting that intensities of band II are very low in comparison with the band I.

From theoretical predictions [16], it follows that the separation between band II $Q_x(0, 1)$ and band I $Q_x(0, 0)$ varies very little between various porphyrin compounds and the intensity ratio of band I to II increases when the symmetry of molecule is destroyed by the substitution of the carbon chain. In our case, the increase in intensities of band I in absorption and emission spectra of additional form of ZnTPyP can be due to the perturbation of molecule by another one located in its close neighborhood, for example, when two molecules form a dimer. In case of the formation of the *J*-type aggregates, the spectra of porphyrins exhibit red side shift [10] as it was predicted by Kasha [17]. Yamazaki et al. [9] comparing experimental results with the result of calculations carried out for zinc porphyrin monomers, dimers and trimers have shown that most of the aggregated forms exhibit the red-shift of spectra with respect to monomers. There is only one exception — so-called *o*-dimers which have blue-shifted B band (from 412 to 410 nm) and band I Q_x (from 573 to 562 nm) in the absorption spectrum with broad spectra. Also, the fluorescence band is very diffused and shifted, as it is in our case (Table 1) to the red side. The *o*-dimer is built from two molecules with their ring planes forming small angles. Because of this proximity of planes of the rings strong interactions occur. The effects are seen in Soret band region and in Q bands range. Of course, we have different compounds, but both groups of dyes are porphyrin type Zn complexes. For TPyP without metal, additional emission and absorption bands are not observed (Figs. 3 and 4), whereas for ZnTPyP at similar concentrations they are present. It seems possible that ZnTPyP dye molecules can also form some similar bands as ZnP dimers. In order to support our supposition, we measured the fluorescence and fluorescence excitation spectra at various wavelengths of excitation and observation for the ZnTPyP solutions of various concentrations, illumination of sample at different times between sample preparation and investigation of the spectra. Examples of the results obtained by such measurements are shown in Figs. 4–6. Additional form of dye appear in freshly prepared higher concentration (C_3 solutions of ZnTPyP) and its content diminished very slowly with time. The content of this form increases with the increase in the dye concentration. Light is responsible for the bleaching of this form, but not for its

decomposition into monomers because as a result of prolonged illumination the fluorescence band at 631 nm diminished without the increase of monomer bands (Figs. 6A and 7A). On the basis of all the results, the position of absorption and fluorescence bands of dimeric form was established (Table 1). From the literature, it is known that there are several aggregated forms of porphyrin compounds exhibiting rather efficient fluorescence [10,11]. In the cells, incubated with porphyrins, several photoproducts can be formed [11]. Kinetics of the formation of these products depends on the dye concentration. They can be selectively bleached using proper color of light [11]. Modification of biomolecules which can occur in illuminated complex environments of photosensitizer located in biological systems also have an influence on the dye molecules causing their phototransformation. These complex reactions can be easily investigated, first on simple model systems such as dye solutions [18–20]. Of course, the dimeric character of ZnTPyP observed form is only a supposition. Porphyrins can occur in several forms of various character and different stability [21]. For example, it is known that under usual conditions π-electronic system of some porphyrin cannot be stable, but its singly protonated dimer can be very stable [21]. The knowledge of spectral properties of sensitizers is necessary for their right application in PDT.

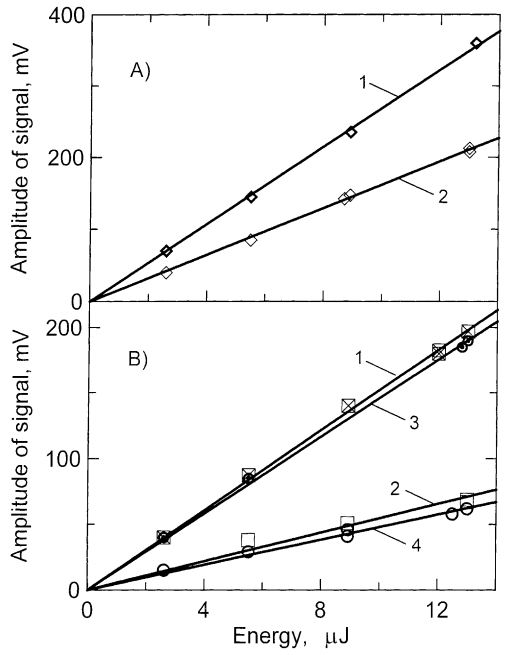

Fig. 8. First maximum of LIOAS signal (H_{max} in Fig. 2) vs. laser pulse energy: (A) β-carotene, lower concentration — curve 1, heir — curve 2; (B) ZnTPyP — curve 1 (C_1), curve 2 (C_2) and TPyP — curve 3 (C_1), curve 4 (C_2). Concentrations of all pigments are taken such that for all samples the absorbance at 417 nm at higher concentration is about $A = 1.26$ and at lower concentration is about $A = 0.29$.

4. LIOAS results

On the basis of first maximum of LIOAS (H_{max} in Fig. 2) measured for various laser pulse energy (changed by gray filters), the dependence of H_{max} on light energy was drawn (Fig. 8). The amplitude of first maximum is

$$H_{max} = k\alpha E_{las}(1 - 10^{-A}) \quad (1)$$

Where α is the part of the energy promptly deactivated into heat, E_{las} the energy of laser light, A the absorption of sample at wavelength of laser light (417 nm), k is the coefficient related to apparatus optical geometry, electronic independence and thermoelastic properties of solvent. The k-value is the same for the sample and references, α for reference is in good approximation, equal to 1. Therefore, from the measurements of the dependence of H_{max} on the intensity of laser light (changed by gray filters) — seen from the lines presented in Fig. 8, values of α for the investigated samples can be obtained and introduced into the following formula:

$$\Phi_T E_T = (1 - \alpha)E_{las} - \Phi_F E_F \quad (2)$$

where Φ_T and Φ_F are the yields of triplet and fluorescence, E_T and E_F the respective energies. E_{las} is given in kJ/mol.

The fluorescence yield of dyes at two concentrations were established according to the method described [22] using Rhodamine 6G as reference. Because of the presence of two forms of dyes, the yield of fluorescence and triplet formation were established separately for each concentration. From the slopes of the lines dH_{max}/dE versus $1–10^{-A}$ obtained from Fig. 8, only some averaged value of the yield of the triplet generation can be obtained. The Φ_T-values are gathered in Table 3. The energy of triplet state was taken from [23].

The amount of energy exchanged promptly into heat is higher for ZnTPyP than for TPyP. As a result the yield of triplet state formation is slightly higher for TPyP than for its Zn complex. Values of yields higher than unity obtained for lower concentrations are, of course, the result of experimental accuracy. Anyway, they show that at lower C_2 concentrations this yield is higher than at higher C_1 concentration. It is known that the exact value of Φ_T depends on the solvent used and the oxygen content. The yield of $^1O_2$ generation depends on yield of the formation of dye triplet. Singlet oxygen generation for various porphyrins is reported from 0.35 to 0.98 [24]. Reported yields of triplet generation are also very different [7]. It is possible to

Table 3
Results of the deconvolution of the photothermal signal done according [14][a]

Dye	C	k_1	τ_1 (μs)	k_2	τ_2 (μs)
TPyP	C_1	0.34	≤0.4	0.04	0.48
	C_2	0.53	≤0.4	0.17	2.08
ZnTPyP	C_1	0.33	≤0.4	0.12	0.53
	C_2	0.56	≤0.4	0.26	1.74

[a] Parameter k: pre-exponential factor; τ: decay time in μs; C_1 and C_2: dye concentrations such as in Table1.

compare results obtained by the same method [7]. From Table 2, it follows that ZnTPyP, because of the higher admixture of aggregated form than that in TPyP solution, exchanges more energy into heat promptly, but yields of triplet population are similar.

Table 3 shows the results of photothermal LIOAS signal deconvolution [14]. The results given were obtained supposing a "concurrent" model, this means taking into account that from excited singlet state there are two concurrent paths of deexcitation: prompt to singlet ground state and by ISC to triplet deactivated predominantly thermally by slow process. In this case, when by triplet or singlet states excitations some thermally deactivating species are produced the sequential model should be applied. Such calculations were done but the results were very similar to a concurrent model (not shown). All measurements were done in air atmosphere, therefore, triplet states were quenched by oxygen. For lower dye concentrations (for TPyP $C_2 = 0.9 \times 10^{-6}$ M, for ZnTPyP $C_2 = 1.9 \times 10^{-6}$ M) about 30% of energy was deactivated promptly (it means shorter than time-resolution of apparatus which is about 0.4 μs; some small amount in time only slightly longer which is about 0.5 μs). The rest of the energy is thermally deactivated very slowly, in times much longer than 6 μs. Such long times are not easy for observation by the applied method. Previously [7], for ZnPc in solution, in contact with the air component, time about 7 μs was obtained. In the present results for ZnTPyP and TPyP at higher concentration of dyes, 7.4 and 3.8 μs decay times were found. Probably the intermolecular interactions occurring at higher concentration causes the decrease in decay times from very long at lower concentration to much shorter at higher. But this middle component is not responsible for whole deactivation. From the data obtained by Marti et al. method ([13]; Table 2), it follows that about half of the energy is deactivated in time longer than 0.4 μs. The middle component contains only 17% of TPyP and 26% of ZnTPyP, it means that at higher concentration also at least quarter of energy is deactivated very slowly.

LIOAS signal, observed and analyzed in this study for investigated solutions in chloroform are predominantly due to the thermal effect, because the contraction effects are predominantly observed for water solutions [25]. In the case of some contributions from volume changes, these contributions are also related to the triplet state generation [25].

5. Conclusions

1. The presence of aggregated forms of dyes, influences not only the incorporation of dye into cells, as it is generally known, but also the dye photostability. Therefore, photochemical properties of dye solutions have to be established before the sensitizer application in PDT.
2. Between two investigated dyes, the TPyP is more suitable for PDT because of lower tendency to aggregate, but the efficiency of the generation of the triplet state of both dyes is similar.
3. The increase in the dyes concentration causes a decrease in the triplet lifetime for both the dyes and in the yield of triplet states generation.

Acknowledgements

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