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Yield of intersystem (singlet–triplet) crossing in phthalocyanines evaluated on the basis of a time in resolved photothermal method

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Abstract

The yields of triplet state formation for seven various phthalocyanines (Pc) unsubstituted by metal and substituted by Mg, Zn, Cu and Al in dimethyl-sulfoxide (DMSO) solutions were compared on the basis of time resolved photothermal measurements. The sample with atmospheric oxygen and bubbled by nitrogen were investigated. Absorption, fluorescence, and steady state photoacoustic spectra (PAS) of the same samples were also measured. The yields of triplet state formation for most of metal substituted dyes were higher than for investigated metal-free dyes. The triplets for various dyes were differently quenched by oxygen. The possibility of the application of investigated dyes in photodynamic therapy and diagnosis was discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorescence; Photothermal spectroscopy; Phthalocyanines; Singlet oxygen; Triplet state

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1. Introduction

The destruction of neoplastic (malignant) cells, in both mechanisms: type 1, direct interaction of sensitizer with tissue and type 2, interaction with created singlet oxygen ($^1O_2$) undergoes, through the triplet state of sensitizing dye [1–4]. Therefore, an efficient sensitizer should have a possibly high yield of triplet state formation and/or efficient creation of free radical. For a dye which is photochemically stable the yield of triplet states generation can be evaluated by the measurement of the slow component of thermal deactivation (TD) of excitation [4–6] therefore, laser induced optoacoustic spectroscopy (LIOAS) [7] can be applied. The approximated method of the evaluation of the slow component of thermal signal, proposed by Marti et al. [8,9], can be used for the evaluation of the contribution from slow component of the thermal dissipation of excitation energy.

The lifetimes of slow components of TD were obtained by the deconvolution of wave form thermal LIOAS signal [10,11].

Previous results [12] strongly suggest, on the basis of steady state photoacoustic spectra (PAS) measured at various frequencies of the light modulation [13] that the phthalocyanines (Pc) investigated have strong, slow component of TD. In most cases such component is due to TD of triplet states [6,14].

Many Pcs show very efficient photodynamic activity [1,15], therefore spectral and photochemical properties of these type of dyes are investigated in the cell as well as in various solvents [3,12,15,16,17].

2. Materials and methods

The molecular structures of dyes investigated are presented in Fig. 1. The MgPc and Solar Pc (Fig. 1a) were prepared in two stage procedure starting with $H_2Pc\ (SO_3H)_4$ and diethanol-amine according to the procedure described by Ion [18]. Other Pcs (substituted by Zn, Cu and Al) were purchased from Sigma–Aldrich and used without further purification. As a solvent dimethyl-sulfoxide (DMSO) was used.

Abbreviations: Bromophenol blue, BPB; Dimethyl sulfoxide, DMSO; Energy transfer, ET; Energy of triplet state, E_T; Fluorescence quantum yield, Φ_F; Laser induced optoacoustic spectroscopy, LIOAS; Photoacoustic signal/spectra, PAS; Photodynamic therapy, PDT; Phthalocyanines, Pc; Singlet, S; Thermal deactivation, TD; Triplet, T; Yield of triplet formation, Φ_T

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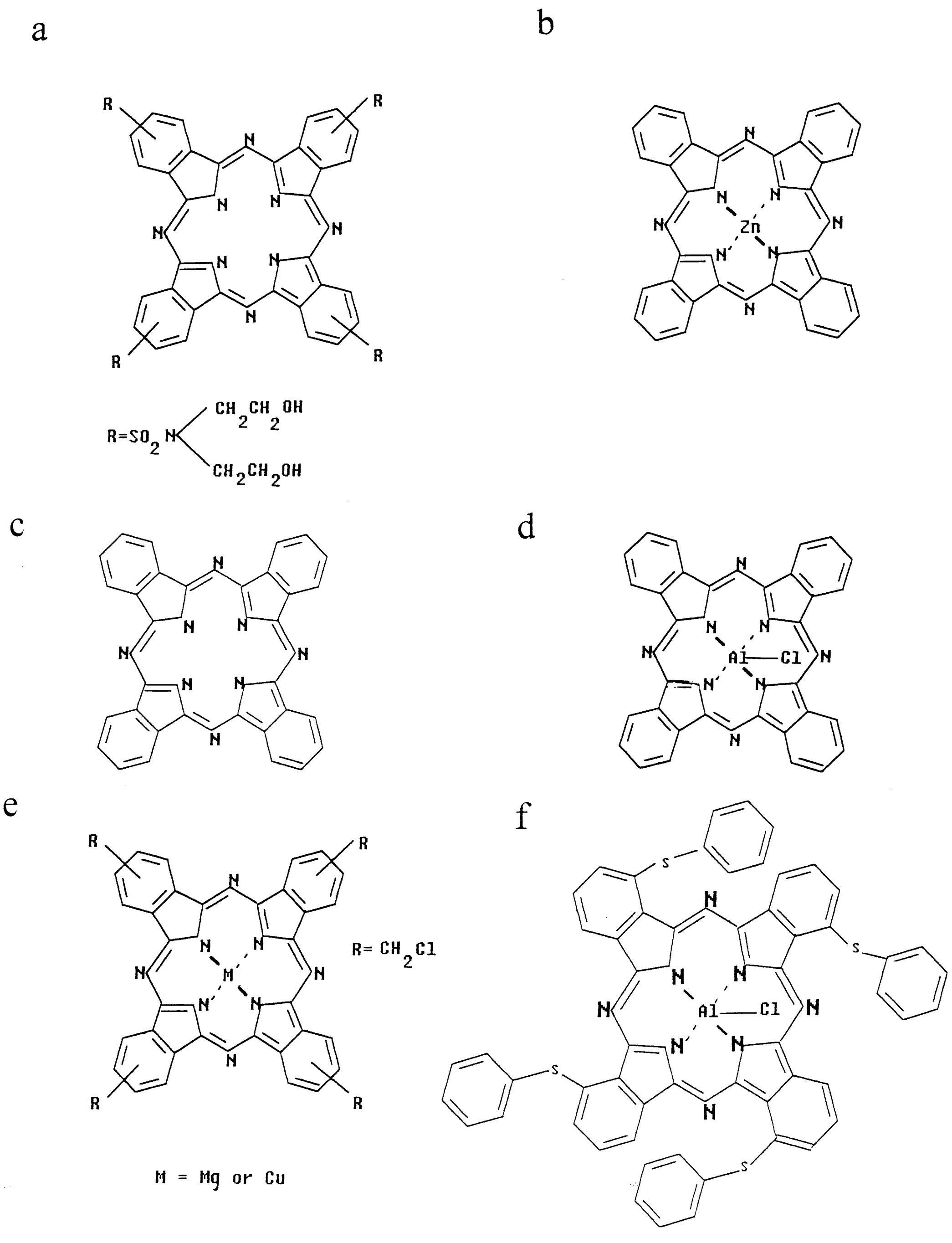

Fig. 1. Structure of investigated phthalocyanines and their notation in text. (a) Solar Pc, (b) ZnPc, (c) H_2Pc, (d) AlPcCl(I), (e) MgPc and CuPc (depending on M substitution), (f) AlPcCl(II).

The absorption spectra were measured with Specord M40 Zeiss spectrophotometer. The fluorescence spectra were measured with a home-made device in a temperature range from 18 to 40°C. The steady state PAS were measured with single beam photoacoustic spectrometer [19,20].

Scheme of the arrangement used for the measurements of the time resolved photothermal signal is shown in Fig. 2. It is an arrangement typical for LIOAS measurements [7]. The sample was illuminated by flash from dye-nitrogen laser model GL-3300/GL301 from Photon Technology Int. (Canada) with puls duration 0.2 ns. Laser light energy was measured by Laser Probe Inc. (USA) energy radiometer model Rj 7620 with Rj 736 pyrroelectric probe. The sample was located in a temperature-controlled cuvette-holder (produced by Quantum Nortwest Comp., USA). The piezoelectric transducer (Panametric, Model V1030) with 1 MHz

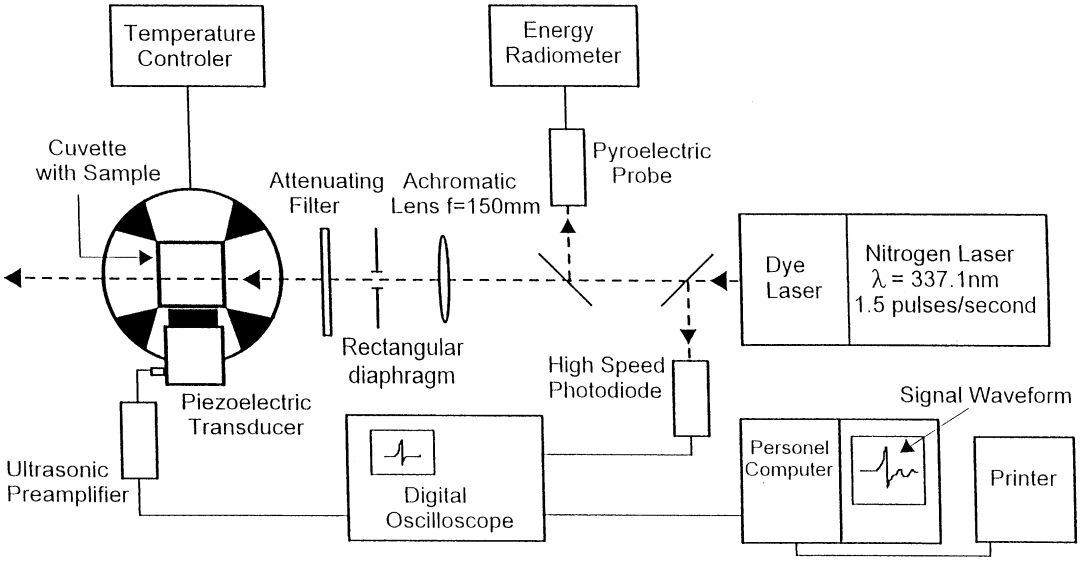

Fig. 2. Arrangement for the measurement of time resolved photothermal effects.

frequency resolution was attached to the cuvette-wall. The signal from transducer was memorized using Gold Star model 0S3060 (60 MGHz) digital oscilloscope. The wave form LIOAS signal for measured sample as well as for reference dye bromophenol blue (BPB) ($C_{21}H_{16}Br_2O_5S$) from RdH Laborchemikalien (Germany) were measured. On the basis of literature data [7] it was assumed that reference dye deactivates all excitation energy promptly, this means in the time shorter than the time resolution of the arrangement used (about 0.6 μs). The wave form signal of reference sample was compared with that of measured sample and analyzed using the method proposed by Marti et al. [8,9]. The amplitudes of first maximum of wave form signal ($H_{\max}$) obtained for the sample measured and for reference, in both cases at the same amount of absorbed quanta, are compared. Such procedure provides an opportunity to evaluate a part of the energy thermally deactivated promptly and deactivated slowly (it means in longer time than the time resolution of apparatus). This last part of energy is generated predominantly by TD of triplet states, populated by intersystem crossing from excited singlet states.

The wave form thermal signal, giving dependence of signal amplitude on time after laser flash, was deconvoluted using the program elaborated by Rudzki-Small et al. [10] and Instruction Manual Quantum Northwest [11] in order to obtain the decay times of the slow components of TD.

The LIOAS measurements were carried out in 20°C for solutions bubbled by N_2 and for the samples being in contact with atmospheric oxygen. The change in temperature can give a very slight influence on the yield of $T_1 \rightarrow S_1$ transition leading to delayed fluorescence emission, but can influence triplet lifetime, because of the increase of solvent interactions with dye molecule [21] and also the thermoelastic properties of the solvent. Therefore, only results for 20°C were discussed.

3. Results

Absorption spectra of the dyes investigated are shown in Fig. 3. As it follows from this figure absorption

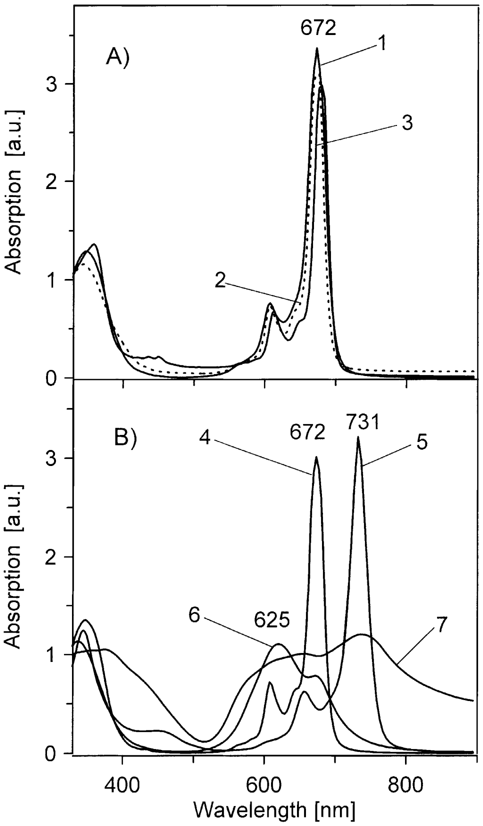

Fig. 3. Absorption spectra of investigated Pcs in DMSO (concentration about 10^{-5} M). (A) curves: 1, solar; 2, ZnPc; 3, AlPcCl(I); (B) curves: 4, MgPc; 5, AlPcCl(II); 6, CuPc; 7, H_2Pc.

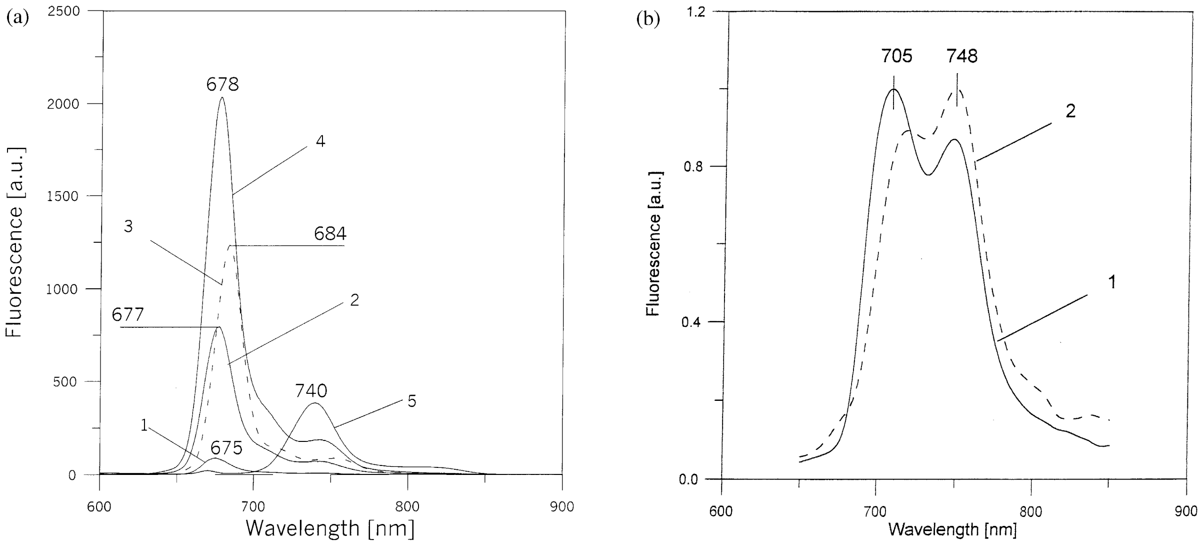

Fig. 4. (a) Fluorescence spectra. Curves: 1, solar; 2, ZnPc; 3, AlPcCl(I); 4, MgPc; 5, AlPcCl(II) (H_2Pc and CuPc fluorescence in a limit of accuracy). Dye concentrations $c = 10^{-6}$ M, $\lambda_{\mathrm{exc}} = 337$ nm. (b) Fluorescence spectra of MgPc in DMSO at two dye concentrations (curves: 1, $C_1=1\times10^{-5}$ M; 2, $C_2=2.5\times10^{-5}$ M). Both curves are normalized to one at highest maximum.

spectra of all investigated Pc dyes have a strong maximum in a 600–800 nm region. In this spectral region tissue is rather transparent [22] therefore light can reach the dye molecules embedded in the cells and can undergo the photoreaction. From this point of view all investigated dyes are suitable for PDT. The shapes of absorption spectra of various dyes are strongly different. Especially different than other Pcs derivatives are absorptions of AlPcCl(II) and H_2Pc. The photodynamic action of dye aggregates are usually less efficient than action due to monomeric forms of Pcs [17]. To establish the presence of Pcs aggregates in incubation solvent absorption spectra have to be carefully examined. As it follows from absorption spectra (Fig. 3) most of investigated dyes at used concentrations are not aggregated. Only the CuPc and H_2Pc can be partially aggregated.

The fluorescence spectra of investigated Pcs are shown in Fig. 4a. Stokes shift between absorption and fluorescence bands is for most of Pcs, very small thus the overlap of absorption and emission spectra is large [17]. Therefore, the reabsorption and secondary emission effects are very strong. To avoid these secondary effects the proper geometry of experiments [21] or correction for reabsorption [17,21] have to be applied. Otherwise the strong long wavelength fluorescence maximum, due to such secondary effects, can be interpreted as given by Pcs aggregates emission [23]. An example of such spectrum of MgPc perturbed by the reabsorption is shown in Fig. 4b. Spectrum exhibits additional maximum and long wavelength shift in comparison to that in Fig. 4a. The effect is diminished by lower concentration application (Fig. 4a). The yield of Pcs fluorescence as well as the yield of triplet state generation in Pcs molecules depends strongly on pH values [16]. In our experiments the DMSO was used, because it was a solvent applied previously [2,3] for cell incubation. Various Pcs dissolved in DMSO exhibit different pH of solution (Table 1) and therefore some of them exhibit much lower yield of fluorescence than reported in literature.

Calculated in a such way the fluorescence quantum yields of investigated dyes were rather low and strongly dependent on pH (Table 1). The CuPc and H_2Pc in DMSO emission in 600–800 nm region is very low. These dyes could be partially aggregated. Other dyes do not seem to be aggregated as follows from the comparison of their absorption and

Table 1
Yields of triplet states generation (Φ_T) for various Pcs in DMSO[a]

Dye	Results	pH	Φ_F	α	$\Phi_T E_T$	Φ_T
H_2Pc	(1)	9.2	0.00	0.83	60.4	0.56 ± 0.17
	(2)			0.87	46.2	0.43 ± 0.10
Solar Pc	(1)	9.3	0.02	0.88	37.8	0.35 ± 0.06
	(2)			0.86	47.2	0.44 ± 0.06
CuPc	(1)	8.0	0.00	0.87	46.4	0.43 ± 0.19
	(2)			0.83	59.4	0.55 ± 0.25
MgPc	(1)	8.7	0.21	0.65	88.5	0.82 ± 0.08
	(2)			0.54	127	1.18 ± 0.40
ZnPc	(1)	7.2	0.18	0.61	105.8	0.98 ± 0.18
	(2)			0.56	124.2	1.15 ± 0.11
AlPcCl(I)	(1)	6.8	0.17	0.65	94.6	0.88 ± 0.08
	(2)			0.65	94.6	0.88 ± 0.12
AlPcCl(II)	(1)	8.8	0.14	0.75	66.9	0.62 ± 0.08
	(2)			0.72	76.7	0.71 ± 0.13

[a] E_T: energy of triplet state (kJ/M), α: part of excitation exchange into heat promptly (in time shorter than time resolution of apparatus), Φ_F: yield of fluorescence. Results: (1) with atmospheric oxygen; (2) bubbled by nitrogen.

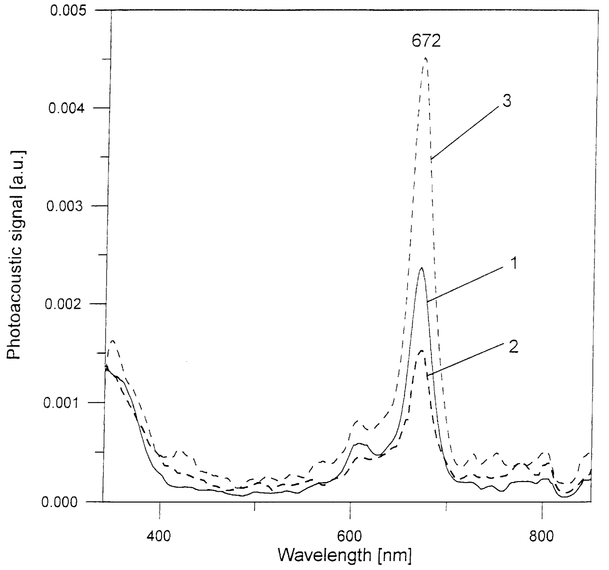

Fig. 5. Steady state photoacoustic spectra of Pcs in DMSO. Curves: 1, MgPc at light modulation frequency 10 Hz; 2, MgPc at 15 Hz; 3, AlPcCl(I) at 20 Hz; 4, ZnPc at 15 Hz.

fluorescence spectra with literature [16,17,23]. The temperature dependence (not shown) confirm such supposition, because the increasing in temperature of AlPcCl(I or II) DMSO solution from 18 to 41°C changes the shape of fluorescence spectra only slightly.

Fig. 5 presents an example of the steady state PAS for MgPc and ZnPc. The PAS of the MgPc was measured at two frequencies of light modulation. From such type of measurement it is possible to establish if components of various kinetics of TD are contributing to the PAS [13]. As it follows from Fig. 5 the ratio of maximum at about 670 nm to maxima in 700–800 nm region is changed with frequency of light modulation. It suggests that slow component of TD is present. The decrease of amplitude of PAS main maximum with frequency of light modulation occurs according to the Rosencwaig and Gersho theory [24]. The maxima in 700–800 nm region have to be related to some forms of dye very efficiently converting excitation into heat. They are not seen in absorption spectra, only in PAS. The positions of the main maxima in steady state PAS and absorption spectra are very similar, but amplitudes at the same frequency 15 Hz for ZnPc is higher than for MgPc. It is logical because the yield of fluorescence of MgPc is much higher than that of ZnPc (Table 1). From the comparison of the TD values measured at maximum 672 nm for various Pcs at the same frequency of light modulation (15 Hz) it follows that usually nonfluorescent or weakly fluorescent dyes exhibit higher TD. For example, for rather well fluorescent MgPc ratio TD(CuPc)/TD(MgPc) = 2.6 and for TD(CuPc)/TD(H_2Pc) = 1.9 (H_2Pc exhibit low yield of fluorescence (Table 1)). But there are some exceptions, for also weakly fluorescent Solar Pc the TD ratio is much higher: TD(CuPc)/TD(SolarPc) = 6.5. The exceptions are possible because to steady state TD slow and fast component of PAS contribute differently. For ZnPc the ratio TD(CuPc)/TD(ZnPc) is about 0.87. It shows that ZnPc has slightly higher TD than nonfluorescent CuPc. All steady state PAS were measured in contact with atmospheric oxygen what makes the interpretation of data complex.

On the basis of first maximum of LIOAS wave form signal (example in Fig. 6) measured for various laser pulse energy (changed by gray filters) the dependence of $H_{\max}$ on light energy was drawn. The examples of such linear dependencies are shown in Fig. 7.

The amplitude of first maximum is

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

where α is part of energy promptly deactivated into heat, E_{las} the energy of laser light, A the absorption of sample at wavelength of laser pulse (at 337 nm), k the coefficient related to apparatus optical geometry, electronic indepen-

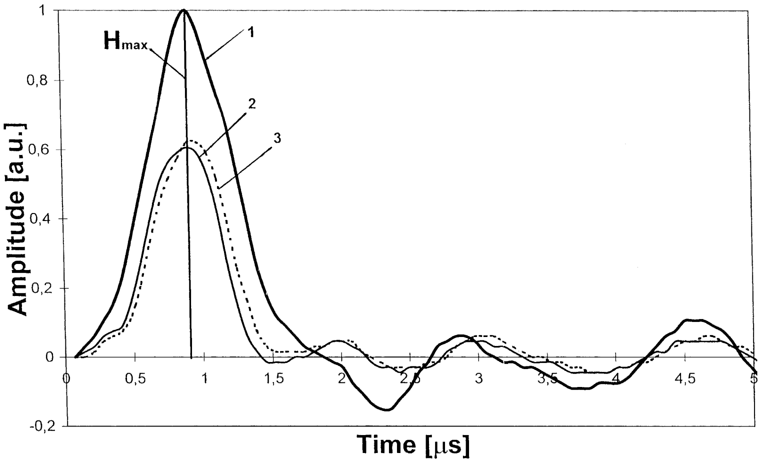

Fig. 6. Wave form LIOAS signals for reference dye (BPB) — curve: 1 analyzed sample ZnPc in DMSO; 2, with atmospheric oxygen; 3, with bubbled nitrogen.

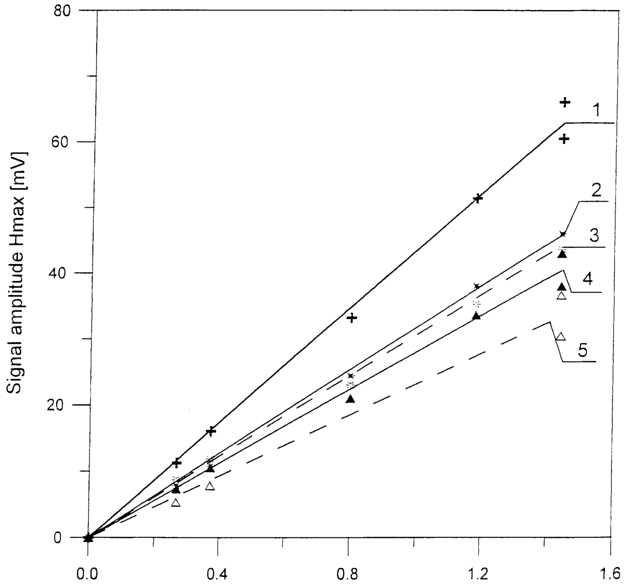

Fig. 7. The dependence of first maximum of thermal signal ($H_{\max}$ in Fig. 6) on laser pulse energy.

dence and thermoelastic properties of solvent. The k value is the same for the sample and reference, α for reference is in good approximation equal to one. Therefore, from the measurements done for the sample and reference the value of α for the sample can be obtained and introduced into formula

$$\phi_T E_T = (1-\alpha)E_{\mathrm{las}} - \phi_F E_F \tag{2}$$

where ϕ_T and ϕ_F is yield of triplet formation and yield of fluorescence, E_T and E_F, energy of triplet state and fluorescence, respectively.

Yields of the fluorescence of the dyes were established according to the method described in [21] using Rhodamine 6G as reference. The reference dye BPB was practically non fluorescent. The yields of Pcs fluorescence are given in Table 1. In literature [21] the yields of ZnPc are varied in a limit from 0.3 to 0.7 depending on substituents but our samples were measured in DMSO at rather low pH. Similar solutions used for LIOAS measurements and PDT applications exhibit rather low fluorescence yields.

E_T was evaluated on the basis of literature data [25] concerning the maximum of Pcs phosphorescence and supposition that Stokes shift between phosphorescence maximum and T_1 level energy is similar to the shift between fluorescence and singlet $S_0 \rightarrow S_1$ absorption bands. Maximum of Pc phosphorescence band is located at about 1100 nm and its position is shifted rather slightly as a result of various substitutions [25]. Because of possible error introduced by such approximation not only ϕ_T but also the values of product $\phi_T E_T$ are shown in Table 1.

4. Discussion

As it follows from Table 1 in most cases of metal substituted Pcs the decrease in the O_2 presence in the solution causes an increase of the yield of the slow TD (Φ_T). This increase is probably due to the decrease in quenching the triplet states of dyes by oxygen but, as it follows from Table 1, there are some exceptions. For AlPcCl(I) the bubbling of nitrogen practically does not change the yield of triplet TD. For metal unsubstituted dyes (H_2 Pc and Solar Pc) the oxygen effects are also in the limit of method accuracy.

For some dyes in both cases, it means for samples with and without oxygen, the yields of slow TD are very high, close to unity. All the dyes investigated exhibit low yields of fluorescence (Table 1), and high yield of triplet formation (Table 1), even higher than reported for most Pcs in literature [25–28]. Yields higher than one (Table 1) are of course the result of experimental errors.

Bishop et al. [27] reported for ZnPc in toluene with pyridine $\Phi_T = 0.58 \pm 0.08$ whereas we obtained for the same dye in DMSO a value very close to unity (Table 1). It is known [27] that the yields of singlet oxygen generation (ϕ_Δ) has a similar value (about 0.4) for DMSO and ethanol. This could suggest that the type of solvent is not a crucial factor in the triplet states generation. But values of ϕ_Δ obtained by different methods are strongly different. For example in [28] for ZnPc in DMSO it is reported $\phi_\Delta = 0.25$. It seems that in actual stage of investigation one can compare rather values of yields obtained by the same method for various dyes than the literature data gathered on the basis of various types of experiments.

The wave form thermal signals of ZnPc with oxygen and without it as well as the signal of the reference sample (Fig. 6) were used for deconvolution procedure on the sum of exponential components. Even before deconvolution it is possible to see that the amplitude of first maximum ($H_{\max}$ in Fig. 6) for reference sample is much higher than for both measured solutions. This means that in the samples less energy is thermally deactivated in short time, and more in longer time than in reference. Both samples possess similar $H_{\max}$ but that with a higher amount of oxygen has first maximum shifted towards longer times. The first maximum is due to all processes occurring in time shorter than or equal to time resolution of apparatus (0.6 μs). The shift towards longer time may suggest that there are some relatively slow processes in this region of times occurring as a result of interaction with oxygen. But this effect can be within the limit of accuracy. From the deconvolution on two exponential components follows the result shown in Table 2. About the lifetime of first component we know only that it has been no longer than time resolution of apparatus, but preexponential factor gives us information about fraction of molecules deactivated in such a short time. Second component gives information about lifetime in a measured regions of times (1–5 μs). As it follows from Table 2 this time is about 7 μs in the oxygen presence but much longer than can be reasonably

Table 2
Results of deconvolution of LIOAS signal for ZnPc (1) with oxygen and (2) without oxygen[a]

	χ_1	τ_1 (μs)	χ_2	τ_2 (μs)
(1)	0.57	<0.6	0.29	6.99
(2)	0.10	<0.6	0.99	75.74

[a] χ: preexponential factor, τ: the lifetime fitting accuracy about 0.002 μs (experimental error much higher).

measured with lower amount of O_2. The method is not able to measure very slow processes, for example, the heat generated by singlet oxygen after its time of life (about 30 μs according [29,30]). In literature lifetime of various Pcs triplet is given from 8 to 124 μs [22] or about 300 μs [26]. In paper [25] in room temperature this lifetime was in many cases shorter than 100 μs. Sumarizing both prexponential factors for sample without oxygen one obtains (Table 2) 0.86 ± 0.01 for sample with oxygen and 1.00 ± 0.01 for sample without oxygen. It seems that in the second type of sample the contributions from very slow processes, due predominantly to oxygen, are much lower than in the first one. The change in lifetime of slow component of TD due to absence of oxygen is very strong. The fraction of slow and very slow processes in comparison with quick evaluated from deconvolution is about one for sample without oxygen and 0.29 in the oxygen presence whereas from Marti et al. [8,9] approximated method (Table 1) the part of slow TD decay is similar for both types of samples, because the $(1-\alpha)$ for ZnPc is equal 0.39 (with oxygen) and 0.44 (without oxygen). Both methods are approximated, for deconvolution is taken whole wave form signal, whereas in Marti et al. [8,9] method only first maximum is taken into account. From Fig. 6 it is seen that the first maximum for sample free from oxygen is shifted towards longer times. This effect is not taken into account in this approximation. From both analysis follows that intersystem crossing in ZnPc in DMSO solution is very effective and that the oxygen quenches the dye triplets.

The ZnPc, MgPc and AlPcCl(I) among all investigated dyes are most effective in yields of triplet generation therefore in a case of incorporation into malignant cells they will act as efficient photosensitizers. In the PDT investigations carried out on the tissue in many cases Pcs solution in DMSO is applied for cell incubation [31,32,33].

5. Conclusions

1. All investigated Pcs exhibit efficient formation of triplet state therefore are suitable for the applications in PDT, but most of the metal substituted Pcs exhibit higher yields of intersystem crossing, as it follows from slow component of TD.
2. Exact values of the yields of triplet formation evaluated using different methods are different, but a set of dye can be compared when the method of measurement and calculations as well as other conditions as type of solvent, dye concentration and sample temperature are the same.

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