

Photothermal methods as tools for investigation of weakly interacting non-fluorescent phthalocyanines

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Abstract

In this paper, we report the spectroscopic properties of two newly synthesized phthalocyanines when substituted with short and long alkyl chains dissolved in dimethyl sulfoxide. The dyes are non-fluorescent and show a weak tendency for dimer formation. The aggregation process is not clearly visible in the absorption spectra. Therefore, steady-state and time-resolved photothermal methods were applied to evaluate the existence of the dye aggregates and their influence on spectral parameters of the investigated dyes.

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1. Introduction

Phthalocyanines were extensively studied in the past decade for a few reasons. These dyes can find a lot of applications in some fields: as photoconverters in organic photovoltaics, as photosensitizers in photodynamic therapy (PDT) of cancer, as power and pollution indicators and also can be used in laser techniques.

In our [1,2] and other papers [3,4], we showed that phthalocyanines are very attractive candidates for light energy to electric energy conversion when used in a photoelectrochemical cell. Moreover, in PDT phthalocyanine dyes are very good photosensitizers because of the particular absorption region suitable for the human tissues and of high population of the dye triplet state.

Phthalocyanine (Pc) can be chemically very easily modified by introducing central metal ion instead of two hydrogen atoms in the main molecular macrocycle and by attaching substituents to the molecular core [2,4,5]. The differentiation in Pc molecular structure can lead to the significant changes in their photophysical behaviour. In this paper, we focus our attention on the newly synthesized metal-free phthalocyanines with the long alkyl

chains covalently linked to the isoindole units of the dyes.

It is important to consider the tendency of phthalocyanines to form aggregates since aggregation can diminish dyes photoactivity in organic photovoltaics as we showed in our previous paper [6], but it also can limit their access to cell tissues when they act as photosensitizers in PDT. In our investigation, we use dimethyl sulfoxide (DMSO) as a solvent which is very polar and thus it is able to protect some dyes against aggregation. However, in the highly concentrated samples aggregate formation is difficult to be avoided.

The investigated dye synthesis and chemical properties were described before [7,8], but a little is known about their photophysical characterization. We present herein the study of the absorption, fluorescence and photothermal properties of dyes in order to follow the radiative and non-radiative processes which can be essential for their potential applications and we pay special attention on the dye photothermal behaviour. Internal conversion leads to the relaxation of the singlet states to the ground electronic state. On the other hand, intersystem crossing transition from the singlet to triplet state can populate the latter one. The triplet state generation in the phthalocyanine dyes is essential in the processes which are important in PDT and organic photovoltaics. Particular attention is paid to interaction between the dyes which could lead to the aggregation of dyes. The triplet state population in these dyes and their aggregates has never been studied, so this study is also included in this paper. We show that the photothermal experiments (photoacoustics and laser induced

Abbreviations: BCP, bromocresol purple; LIOAS, laser induced optoacoustic spectroscopy; PAS, photoacoustic spectroscopy; Pc, phthalocyanine

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optoacoustic spectroscopy) are particularly useful in investigation of the photophysical properties of dyes and of the interaction between dyes which do not show fluorescence.

2. Materials and methods

Both phthalocyanines were prepared in a two-stage procedure starting with H_2PcSO_3H and di-ethanol-amine (PcA) or di-octane-amine (PcB) according to a similar procedure described in a literature [7,8]. The molecular structure of dyes PcA and PcB are shown in Fig. 1.

The absorption spectra were measured with the Specord M40 spectrophotometer (Carl Zeiss Jena, Germany) in the range of 300–800 nm. Fluorescence was registered with the spectrofluorimeter Hitachi F4500 (Japan) in the region of 620–900 nm (excitation wavelength was: 609 nm for both samples). The steady-state photoacoustic spectra were obtained with a single-beam photoacoustic spectrometer PAC300 (MTEC, Iowa, USA) at three light modulation frequencies: 8, 15, 30 Hz at the same phase shift: $\Phi = 20^\circ$.

The kinetics of photothermal processes and triplet state populations were studied with the laser-induced optoacoustic spectroscopy (LIOAS). In the LIOAS experiment, the resolution of the apparatus is about $0.4 \mu s$. Thus, it is possible to distinguish prompt thermal effects occurring in the time range shorter than $0.4 \mu s$ from those which occur in the time longer than $0.4 \mu s$. The pulse subnanosecond nitrogen laser was used as a light source. The solution of bromocresol purple (BCP) in DMSO was used as a standard sample on the supposition that whole energy absorbed by this dye is changed into heat in the time shorter than the resolution time of the apparatus [9]. The analysis of the photother-

mal signal was done using two methods. On the basis of the method elaborated by Rudzki-Small et al. [10], the deconvolution of the sample and reference responses for the exponential components of thermal deactivation (TD) was conducted. In the method proposed by Marti et al. [11], two waveform signals (for the dye and for a standard sample) were compared. In Marti's method, the maximal amplitude of the signal is given by:

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

where k is a factor which includes the apparatus optical geometry, the electronic impedance of the system and the thermoelastic properties of the solvent, α is a part of energy changed promptly into heat, A is absorbance of the sample and E_L is laser light energy (279.7 kJ/mol). The yield of the triplet state population (Φ_T) can be calculated from the equation:

$$\Phi_T E_T = (1 - \alpha) E_L - \Phi_F E_F \quad (2)$$

where Φ_F is fluorescence quantum yield, E_F and E_T are energies of fluorescence and of triplet state with respect to the ground state, respectively. The photoacoustic and LIOAS experiments were performed in helium and nitrogen atmosphere, respectively.

The dyes were dissolved in DMSO. The dye concentrations were: 0.01, 0.1 and 1 mM and the spectroscopic measurements were done in the 1 cm, 1 mm and $60 \mu m$ quartz cuvettes, respectively.

3. Results

3.1. The electronic absorption spectra

The electronic absorption spectra of the investigated dyes in DMSO are shown in Fig. 2 for dye concentrations in the range from 0.01 to 1 mM. The main bands arrive in the "blue" and "red" part of the visible spectral region. The bands are located at about 350 and 672 nm and they are assigned to the B (Soret band) and Q (longwavelength) states, respectively and they are characteristic for the phthalocyanine species [2,3]. On the basis of the absorption spectra of the dyes ($c = 0.01$ mM), the molar absorption coefficient were estimated (Table 1). The absorption spectroscopy showed that the Lambert–Beer law is not obey in the region of high concentrations (a broadening of the Soret band), thus a part of PcA and PcB can be in a form of a dimer or higher aggregates. Neither significant wavelength shifts nor relevant modifications in shape were observed of the band located at 672 nm for PcA. This behaviour was already observed for some Pc species in homogeneous medium [12,13]. In the absorption spectra done for PcB, the slight shortwavelength shift of the Q band is observed and it suggests the creation of some aggregated species in the sample.

Moreover, as the concentration increases the bands at 350 nm shift slightly to the shortwavelength side, broaden

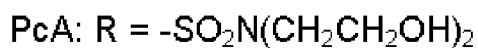
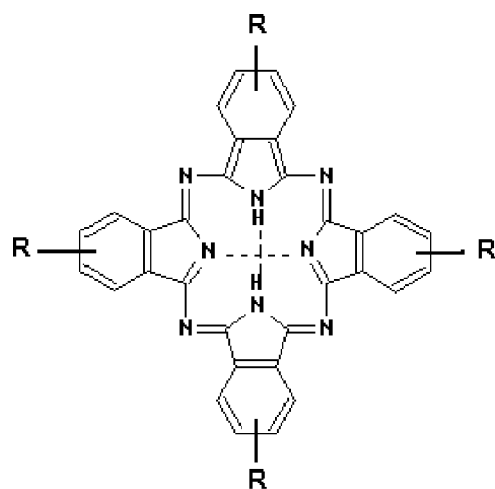


Fig. 1. The molecular structure of the investigated molecules.

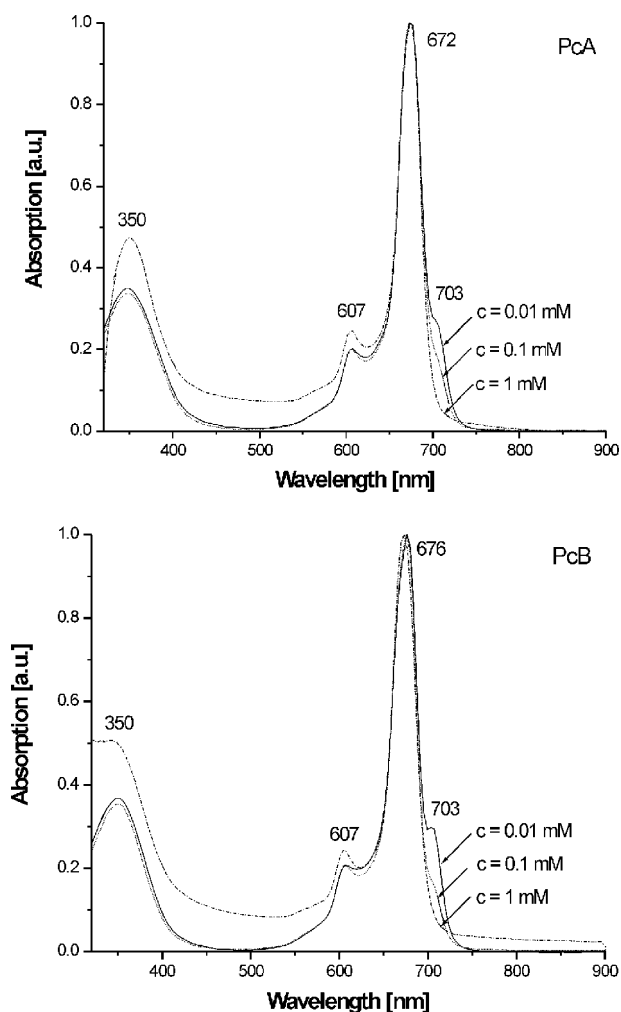


Fig. 2. The normalized absorption spectra of PcA and PcB in DMSO.

and increase in intensity both in the PcA and PcB samples. The increasing intensity is also observed for the bands peaking at about 610 nm in concentration rise. These observations are typical of the well-known effect of dimerization/aggregation of dyes, which results in shifting some bands and their broadening [1,14,15]. Since there are difficulties in judging the change of the absorption spectra in Fig. 2.

An unexpected and interesting result is the occurrence of the shoulder (PcA) or band (PcB) positioned on the long

wavelength side of the spectra in the region of about 710 nm. It is very well seen for the low concentrated samples and the shoulder/band vanishes when the dye concentrations reach 1 mM. In the literature, this band was not observed for metal-free non-substituted phthalocyanines [16]. Thus, the 710 nm band could be assigned to the existence of the alkyl chains covalently linked to the isoindole units and could be attributed to the vibrational mode of these long groups. The vibrational mode disappears when the aggregation occurs as to the 710 nm band vanishes for the highly concentrated samples of PcA and PcB.

The aggregation effect is better seen in PcB than in PcA since the clearly defined band in PcB at 710 nm instead of the shoulder in PcA is observed. Moreover, the broadening of the 350 nm band is larger for PcB than for PcA and also the blue shift of the PcB Q band (from 672 to 670 nm) together with its broadening is observed which could also confirm that aggregation in PcB is more effective than that in PcA.

3.2. Fluorescence properties

The fluorescence of PcA and PcB is very weak (not shown). The samples were excited at 609 nm. The weak fluorescence maximum is localized at about 682 nm for the two investigated dyes and is typical for the monomeric phthalocyanines [2,17]. For our metal-free alkyl-chained phthalocyanines, the fluorescence quantum yield was estimated to be less than 0.001 (Rhodamine 6G was used as a standard). Usually the low fluorescence quantum yield of metal-free non-substituted phthalocyanines in organic solvents was also observed [2,16,17]. The low fluorescence quantum yields were also found for other phthalocyanines when substituted with the long chains [2,18]. The results presented in this paper evidently show the particular influence of the long mobile groups on the fluorescence properties of the investigated dyes. The fluorescence results indicate the occurrence of other (than radiative processes) dissipative channels of deactivation of the dye excited states by non-radiative processes.

3.3. Steady-state photoacoustics

Non-radiative deactivation channels which involved internal conversion and intersystem crossing can be demonstrated by photothermal spectroscopies.

Table 1

The spectroscopic parameters of the investigated phthalocyanines in DMSO at different dye concentrations (c): absorption wavelength (λ_{\max}^A), molar absorption coefficient (ϵ), spectral width of the absorption band ($\Delta\nu_{1/2}$), thermal deactivation (TD) and correlation factors (r)

Dye	c (mM)	λ_{\max}^A (nm)	ϵ ($M^{-1} cm^{-1}$)	$\Delta\nu_{1/2} S_0 \rightarrow S_1$ (cm^{-1})	$\Delta\nu_{1/2} S_0 \rightarrow S_2$ (cm^{-1})	TD	r
PcA	0.01	673	9.2×10^4	3.1×10^5	1.2×10^5	–	–
	0.1	672	9.9×10^4	3.1×10^5	1.3×10^5	1.0	0.95
	1	672	16.1×10^4	3.4×10^5	1.7×10^5	0.9	0.92
PcB	0.01	677	12.5×10^4	3.0×10^5	1.2×10^5	–	–
	0.1	676	14.7×10^4	3.1×10^5	1.3×10^5	0.6	0.95
	1	673	12.1×10^4	3.2×10^5	1.7×10^5	1.1	0.92

$$\Delta\epsilon = \pm 0.1 \times 10^4 M^{-1} cm^{-1}; \Delta\nu_{1/2} = \pm 0.1 \times 10^5 cm^{-1}; \Delta TD = \pm 0.1; \Delta r = \pm 0.01.$$

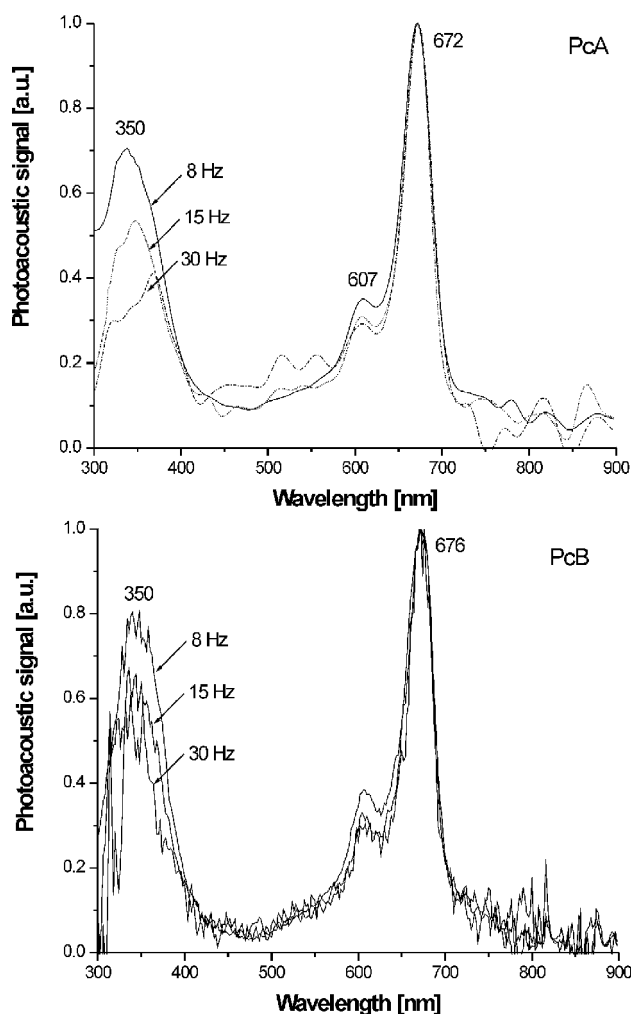


Fig. 3. The normalized photoacoustic spectra of PcA and PcB in DMSO ($c = 1$ mM).

The photoacoustic spectra (PAS) for PcA and PcB were registered at three light modulation frequencies for the samples of the 0.01, 0.1 and 1 mM concentrations. The results for the 1 mM samples are shown in Fig. 3. On the basis of the absorption spectra and PAS, it is possible to estimate a thermal deactivation (TD) parameter as a ratio of the photoacoustic signal to absorbance [19]. The TD parameters are gathered in Table 1 (for one light modulation frequency—8 Hz). From Table 1, it follows that PcA and PcB can convert absorbed energy into heat as a result of the non-radiative processes. The particular large difference in the TD parameters are seen for the low ($TD = 1.1$) and highly ($TD = 0.6$) concentrated PcB dyes. As seen in the highly concentrated samples ($c = 1$ mM), thermal dissipation is about twice effective than that in the sample of low concentration ($c = 0.01$ mM). The large alteration in the TD parameters could be assigned to the occurrence of the aggregation effect in the concentrated samples.

In accordance with Rosencwaig–Gersho theory, the PAS amplitude should linearly decrease in the increasing of light modulation frequency provide that only one spectral dye

species takes part in thermal processes (e.g. internal conversion) [19,20]. However, it is not the case for the investigated dyes—the estimated correlation factors r (see Table 1) do not reach the values of unity and they are in the range of 0.92–0.95 depending on the dye concentrations. The deviation of the correlation factors from unity indicates at least two facts: (i) the coexistence of more than one spectral species which are involved in thermal relaxation and can relax with different decay (the case of the highly concentrated samples—1 mM), (ii) not only one fast process contributes to thermal deactivation, but also slow relaxation with triplet state participation is involved in thermal deactivation to the ground state (the case of the low concentrated dyes).

For the low concentrated samples (0.01 mM) in which the domination of the monomeric species is evident, the values of the correlation factors are higher ($r = 0.95$) than those for the highly concentrated dyes of 1 mM ($r = 0.92$). This result indicates that even if monomeric dye forms are present in the sample both prompt and slow relaxation has to be considered (ii). On the other hand when the aggregates coexist together with monomers (the 1 mM sample), we have to take into account both the presence of monomeric and aggregated moieties and different relaxation decay of each (i).

3.4. LIOAS results

We can get more information on the participation of the singlet–triplet transitions in thermal deactivation from the LIOAS experiment. This experiment allows to distinguish the prompt thermal effects occurring in the time scale shorter than the apparatus resolution (in our experiment— $0.4 \mu\text{s}$) and the slow processes occurring in the time domain longer than $0.4 \mu\text{s}$. Fig. 4 shows the LIOAS data for PcA, PcB and a reference sample (BCP). Under the assumption that the k factor (Eq. (1)) is the same for the dye samples and the reference and that the whole energy absorbed by the reference sample is changed into heat, the α value for the reference

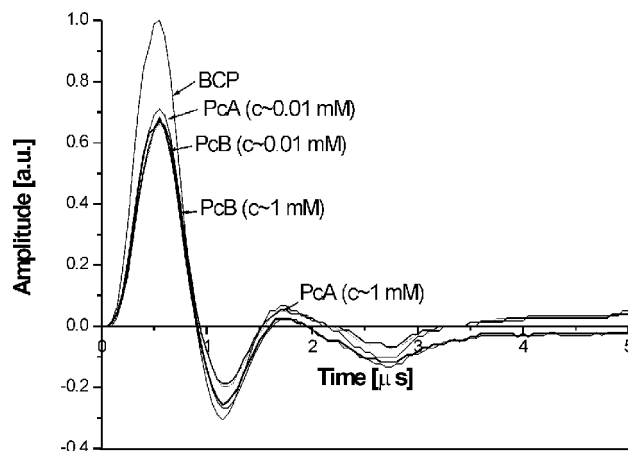


Fig. 4. The LIOAS waveform signals of BCP (reference), PcA and PcB dyes.

Table 2
Triplet state population quantum yields and the results of the deconvolution of the LIOAS signals

Dye	α	Φ_T	K_1	τ_1 (μs)	K_2	τ_2 (μs)
PcA ($c \sim 0.01$ mM)	0.71	0.76	0.75	≤ 0.4	0.09	1.28
PcA ($c \sim 1$ mM)	0.67	0.86	0.66	≤ 0.4	0.01	0.98
PcB ($c \sim 0.01$ mM)	0.68	0.84	0.71	≤ 0.4	0.09	1.18
PcB ($c \sim 1$ mM)	0.66	0.89	0.68	≤ 0.4	0.02	0.35

$\Delta\alpha = \pm 0.06$, $\Delta\Phi_T = \pm 0.10$, $\Delta K_1 = \pm 0.01$, $\Delta K_2 = \pm 0.01$, $\Delta\tau_2 = \pm 0.01$. α : The part of excited energy changed promptly into heat; Φ_T : triplet state population quantum yield; K_1 , K_2 : preexponential factors; τ_1 , τ_2 : decay times.

sample is assumed to be 1. The α values for the dyes could be estimated from the Eq. (2). The Marti et al. (α) and Rudzki-Small et al. [10] (K_1) methods give the similar results (as expected) which are comparable in the range of the experimental accuracy. The data are gathered in Table 2. The parameters in second column (α) and third column (K_1) in Table 2 give information about the contributions of the excited states which deactivate energy promptly in the time shorter than 0.4 μs . These values indicate that 0.66–0.71 of the absorbed light energy (depending on the dye molecular species) is changed into heat in the time shorter than 0.4 μs .

The dye signals shown in Fig. 4 were decomposed into exponential components which can be interpreted as deactivation of the long-lived triplet states of the monomeric and aggregated dye moieties or as heat released by other processes (e.g. singlet oxygen generation). The slow thermal transitions decay with the lifetime τ_2 ranging from 1.28 to 0.98 μs for PcA and from 1.18 to 0.35 μs for PcB. The τ_2 values depend not only on a kind of dye but also the τ_2 time is affected by the spectral dye species. We can assign the shorter relaxation time τ_2 for the samples of higher dye concentration to the aggregated dyes.

By means of Eq. (2) the yield of the triplet state population Φ_T was also estimated. In this estimation, E_T is energy of the triplet state taken from the literature for phosphorescence data typical for phthalocyanine dyes [21]. The changes of the sample volumes are rather modest for DMSO (less than 20%) [22] and were taken into account in our calculations. The Φ_T values are consistent with those presented for the porphyrin-like molecules [23] and other phthalocyanines [16,24]. The estimated Φ_T values are found to be similar for the highly concentrated samples and those for the monomeric samples.

4. Discussion

This paper deals with the basic photophysical properties of novel alkyl chained phthalocyanines and their tendency to the aggregate formation when dissolved in DMSO.

As mentioned above, DMSO is a polar solvent which protects some organic dyes against dimerization/aggregation due to the strong interaction between dye and solvent

molecules [25,26]. Thus, the aggregation of dyes in highly polar solvent is expected to be less effective than that in non-polar media, e.g. toluene or benzene [27]. Nevertheless, the interaction between dyes in a highly concentrated solution could exceed the interaction between the dye and solvent molecules and thus cannot be excluded.

In this paper, we demonstrated the creation of the aggregated species of PcA and PcB compounds by means of the absorption and photothermal experiments.

At the first point of our discussion, we consider the absorption behaviour of the investigated dyes. The arguments for the creation of the aggregated forms we found in the changes which weakly reveal in the absorption spectra of PcA and PcB. Apart from the weak blue shift of the bands observed in the Soret region (350 nm band) in PcA and PcB, and the blue shift in the Q region, increasing intensity of the band at 610 nm and its spectral broadening characteristic features for the aggregates are observed. The spectral broadening even this is not very significant, is more clearly observed in the PcB dye. The spectral width $\Delta\nu_{1/2}$ of the absorption bands of the PcA and PcB monomers are $3.1 \times 10^5 \text{ cm}^{-1}$ and $1.2 \times 10^5 \text{ cm}^{-1}$, respectively, and they are changed under high concentration regime; they are $3.4 \times 10^5 \text{ cm}^{-1}$ for aggregated PcA and $1.7 \times 10^5 \text{ cm}^{-1}$ for aggregated PcB (Table 1). The shifts of the bands and the alteration of the line width give some evidences on the creation of the dye aggregates which cannot be excluded even that polar DMSO is used as a solvent. Two general aggregation structures, namely H- and J-aggregates [12,13] can be discussed. The theory predicts [12–15] that the blue shift is expected when the H-type of the aggregates are formed. This assignment of the PcA/PcB aggregates as H-type aggregates is made on the basis of the spectral shifts observed in our experiments. In the ideal H-aggregates, the molecular frames are oriented face-to-face in which the transitions dipole moments of interacting monomer units are perpendicular to the line connecting the molecular skeleton. An angle between the transition dipole moment and the aggregates line is in the range of 54.7–90°. However, the exact molecular arrangement in the PcA and PcB aggregates is not possible to be determined at this stage of the paper.

Theoretical prediction also shows that the absorption band width of the aggregates are determined by the number of monomers which participate in the aggregation [12,13]. In our experiments, the alteration in the absorption line widths is rather hardly observed because of low tendency of the investigated dyes for aggregation creation due to protective action of DMSO solvent. Both, the spectral band shift and line widths are only slightly changed due to the small amount of created aggregates with respect to the monomers and thus is not a strong proof of the aggregate creation.

However, the luminescence studies by their greater selectivity and sensitivity are more useful to detect weak interaction between the PcA/PcB molecules, even when such interactions are not easily detectable in the low-resolution absorption experiments. Unfortunately PcA and PcB

fluoresce very weakly and their fluorescence quantum yields are extremely low due to the existence of the mobil long chains covalently linked to the isoindole units in the molecular frame. The drastic declining of the fluorescence we also observed for alkyl or alkyloxy substituted metallic phthalocyanines in DMSO [2]. Thus, the energy of the excited states of our dyes is dissipated not by the singlet–singlet radiative conversion, but by non-radiative internal conversion and/or intersystem crossing with the participation of the singlet–triplet transitions. These phenomenon we observed by the photoacoustic and LIOAS experiments which give a better insight in the triplet state formation and the triplet state behaviour in PcA and PcB monomers and aggregated species. Even if the interaction inside the PcA/PcB aggregates is not extremely strong and gives only modest changes in the absorption spectra, the sensitive LIOAS method allows us the aggregate formation to be observed. The analysis of the LIOAS data is an additional and more spectacular confirmation of the occurrence of the PcA and PcB aggregates in the homogeneous polar medium-DMSO.

As we showed the PcA/PcB monomers and aggregates participate effectively in thermal relaxation both in the prompt and slow processes. The part of the energy which is changed into heat promptly as a result of internal conversion is rather similar in monomers and aggregates, and it reaches 0.66–0.75 depending on dyes (α and K_1 parameters in Table 2). As it also is seen from Table 2, Φ_T values are similar for the dye samples at the high concentrations and for the monomeric dyes. Similar observations was done for metal-free tetraphenylporphyrins [1,23]. The Φ_T values are reported to be in the range of 0.67–0.88 [23]. For metallic Pc dyes, the yields of triplet states population are found as 0.6–0.8 [16,21]. The values got in this paper are similar when compared to other porphyrine and porphyrazine dyes.

The more spectacular alterations in PcA and PcB behaviour can be found when Φ_T , K_2 and τ_2 parameters are taken into consideration. The lack of the fluorescence in both monomers and also in aggregates indicates very effective non-radiative decay channels. In this paper, we present the occurrence of the pathways with the triplet state participation by the steady-state and time-resolved photothermal experiments. The slow thermal decay is described by K_2 factor and decay time τ_2 (Table 2). In our consideration, we have to take into account the fact that in the slow non-radiative dissipative processes more than one molecular species participate and each of them could be characterized by the different decay time. By the use of Rudzki-Small et al. [10] approach, the decay time of the triplet state of the two dyes were evaluated. The relaxation of the triplet state to the ground state occurs in times of 1.28 and 1.18 μs in monomeric PcA and PcB, respectively, which drop down to 0.92 (PcA) and 0.35 μs (PcB) in aggregated moieties of dyes. The long lifetime declining under the high concentration regime is an additional confirmation of the aggregated structures of the PcA and PcB dyes. The decay times τ_2 of the excited triplet states in aggregates are definitely shorter than those in monomers. It

evidently reveals that the depopulation of the triplet states in the aggregates *via* non-radiative processes is reduced when compared with the corresponding monomers.

As said above there are some difficulties in evaluation of the number of monomers that participate in aggregation creation since the absorption spectra are not useful for that purpose. However, apart from the changes in the absorption parameters (band shifts, alteration in the absorption line width) the number of monomers per an aggregate can be evaluated on the basis of the triplet state decays in aggregates and in monomeric moieties. In accordance with theoretical predictions [12,13], the decay time shortens with respect of that in monomers by a factor N (N is the number of monomers which create the aggregated species). For PcA, the aggregation number was evaluated to be 2, and for PcB it reaches 11. Thus, we can assume that PcB aggregate is larger in size than the PcA dimer. Thus, our assumption that the aggregation formation in the investigated compounds occurred to be more effective in PcB than in PcA, could be confirmed by the above evaluations.

In our experiment, the sum of K_1 and K_2 does not reach unity. This result can be connected with other processes in which triplet states could be involved: (i) generation of singlet oxygen, (ii) other processes occurring in the time range longer than 0.4 μs (e.g. phosphorescence or delayed luminescence), (iii) conformation changes in the dye molecular structure. Point (i) could be excluded since steady-state photoacoustics and LIOAS experiment were performed under helium and nitrogen atmosphere, respectively. The phosphorescence process under the experimental condition (room temperature, not rigid medium) can also be neglected. Moreover, the delayed luminescence can also be neglected because of the expected large energy gap between S_1 and T_1 transitions as observed for other phthalocyanines [24]. Thus, we can neglect (ii). Thus, the conformation changes of the molecular PcA and PcB structures could be the reason.

In that point of this paper, it is interesting to try to determine the reason of vanishing of the additional bands in the absorption spectrum at 710 nm under the high concentration regime. This band is most likely connected with the existence of the long alkyl chains covalently linked to the isoindole units in PcA and PcB, since no such a band appears for metal-free Pc without any substituents [16]. We assigned this band to the vibrational mode of the specific bonds of the long chains. When the dye concentration goes up, the vibrational mode could be quenched owing the aggregation creation and changes in conformations occurring in the aggregated species upon irradiation.

On the basis of our absorption, steady-state photoacoustics and time-resolved photothermal experiments we showed as follows:

- photoacoustic and LIOAS experiments are perfect tools owing their great selectivity and sensitivity and may be used to detect a weak interaction in molecular systems of non-fluorescent dyes,

- in PcA and PcB aggregate formation of the stacked H-aggregated are more favorable than J-aggregates,
- the strong quenching of the triplet state lifetimes in the investigated alkyl-chained phthalocyanines can be assigned to the aggregate formation occurring in PcA and PcB.

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