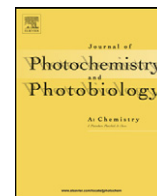




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## Femtosecond studies of the excited-state dynamics of ester-alkyloxy substituted zinc phthalocyanines

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### ABSTRACT

The ultrafast dynamics of two zinc(II) phthalocyanine derivatives with potential applications in photodynamic therapy was studied by femtosecond transient absorption spectroscopy. The kinetic features of the compounds were determined at excitation wavelengths within the Soret and the Q-bands. Three time constants revealed in time-resolved data were identified with the processes of solvent relaxation, heat transfer from the molecule to the solvent and the excited-state deactivation. The presence of long ester-alkyloxy substituents at non-peripheral positions of the molecule leads to the slow-down of the thermalization of the molecules and shortens the excited-state lifetime by a factor of approximately 3.

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### 1. Introduction

Although relatively new, its first regulatory approval dating back to 1993, the photodynamic therapy (PDT) has already become a well established technique for treatment of many cancer and some non-malignant diseases [1–3]. It involves administration of a photosensitizer (PS) which, after optical excitation, reacts with oxygen molecules either by electron transfer to form a radical (type 1 reaction) or by energy transfer leading to excitation of oxygen into its singlet state (type 2 reaction). Both oxygen radicals and singlet oxygen molecules exhibit strong toxicity, which is utilized for selective destruction of malignant cells. The selectivity of PDT is achieved in two ways: first, PS is accumulated preferentially in rapidly dividing cells; second, the excitation light is precisely directed onto the target tissues.

The key for successful PDT is PS which should fulfill simultaneously a number of conditions: absorption in the far-red part of the visible spectrum, high absorption coefficient, high quantum yield of radicals or singlet oxygen generation, low dark toxicity, rapid elimination from the body, ease of administration. Due to the last condition water solubility is advantageous, however low

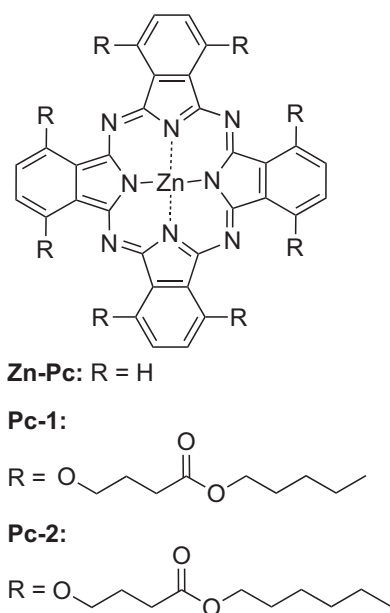
solubility in water can be overcome by application of PS in drug delivery vehicles. Additional advantage is the absorption in the blue part of the spectrum, which allows for visualization of the tissues with increased PS concentration by fluorescence excited with short-wavelength light.

So far only a few compounds have been approved for clinical use and they are still far from being ideal photosensitizers [4,5]. Therefore many research groups concentrate on studies and the understanding of the mechanism behind PDT in order to develop better photosensitizers and find optimal conditions for their use [6–8]. On the other hand, the new compounds need thorough characterization of their photochemical and photophysical parameters as well as the biological activity to test their applicability for PDT. The results of these studies should then be used as a feedback to optimize the design of future PSs.

Phthalocyanines (Pcs) are a class of promising photosensitizing agents, because they satisfy most of the above listed requirements for a successful PS. Their photochemical and photophysical properties make them very suitable for PDT and their high phototoxicity has been frequently demonstrated [9–12]. The mechanism responsible for their phototherapeutic activity is predominantly the generation of singlet oxygen through energy transfer from the triplet state of Pcs (type II) [13]. The main shortcoming of Pcs is their low solubility in water and the tendency for aggregation in tissues, which hinders the phototherapeutic activity. Nevertheless, a constant effort put in the recent years into the synthesis of novel Pc derivatives [14–25] may ultimately give birth to a family of

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**Fig. 1.** Structures of **Zn-Pc** and its ester-alkyloxy derivatives, **Pc-1** and **Pc-2**.

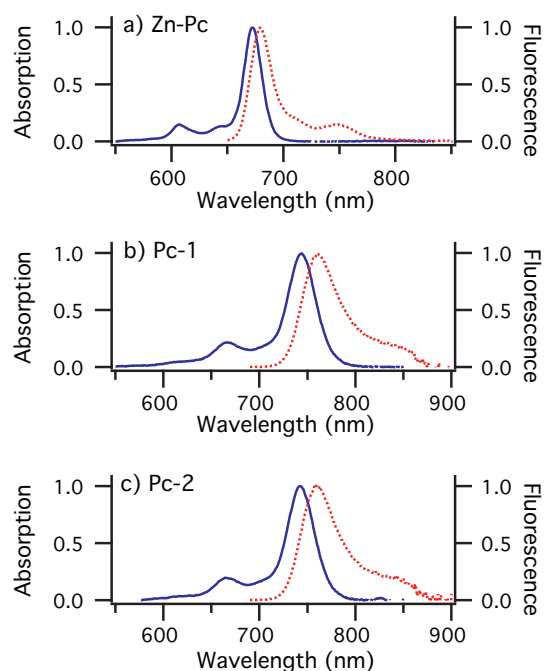
Pc-based photosensitizers free from their current drawbacks. It has been, for instance, shown that water solubility may be achieved by an appropriate substitution [22,23,26].

Recently we have described the synthesis of a series of phthalocyanine (**Zn-Pc**, Fig. 1) derivatives possessing non-peripheral ester-alkyloxy substituents [27]. Two of the compounds (Fig. 1), 1,4,8,11,15,18,22,25-octakis[3-(pentyloxy carbonyl)propyloxy]phthalocyaninato zinc(II) (**Pc-1**) and 1,4,8,11,15,18,22,25-octakis[3-(hexyloxy carbonyl)propyloxy]phthalocyaninato zinc(II) (**Pc-2**) have been the subject of photochemical and biological studies in order to understand how the substitution affects the properties relevant for PDT. It has been shown that, in spite of their favorable spectral properties and high quantum yield of the singlet oxygen generation, their biological activity was lower than that of the parent molecule. This negative effect has been attributed to the hydrophobic effect of the ester-alkyloxy substituents [27].

In this work we studied the ultrafast dynamics of optically excited **Pc-1** and **Pc-2** by femtosecond transient absorption spectroscopy and characterized their photophysics. We compared the results to the well-known dynamics of bare zinc(II) phthalocyanine (**Zn-Pc**, Fig. 1) in order to understand how the substituents affect the ultrafast processes which follow absorption of a photon. The results might be useful for the design of new compounds for PDT because the nature of these processes determines how a molecule acts as a photosensitizer.

## 2. Materials and methods

Details of the synthesis and purification of **Pc-1** and **Pc-2** have been already presented by Osmalek et al. [27]. **Zn-Pc** (Sigma Aldrich) and DMSO (Fluka, for UV spectroscopy) used as the solvent in steady-state and time-resolved measurements were used as supplied. Steady-state UV–VIS spectra were recorded using Cary Eclipse fluorescence and Cary 50 Scan absorption spectrophotometers from Varian. Fluorescence lifetime measurements were performed using the time-correlated single photon-counting technique (TCSPC). Excitation was performed at 395 nm with a laser diode (Picoquant model LDH-P-C-400B) generating 60 ps pulses at 20 MHz. The instrument response function had a full width at half-maximum (FWHM) of about 200 ps. Transient absorption



**Fig. 2.** Steady-state absorption (solid) and fluorescence (dashed) spectra of **Zn-Pc** (a), **Pc-1** (b), and **Pc-2** (c) in DMSO.

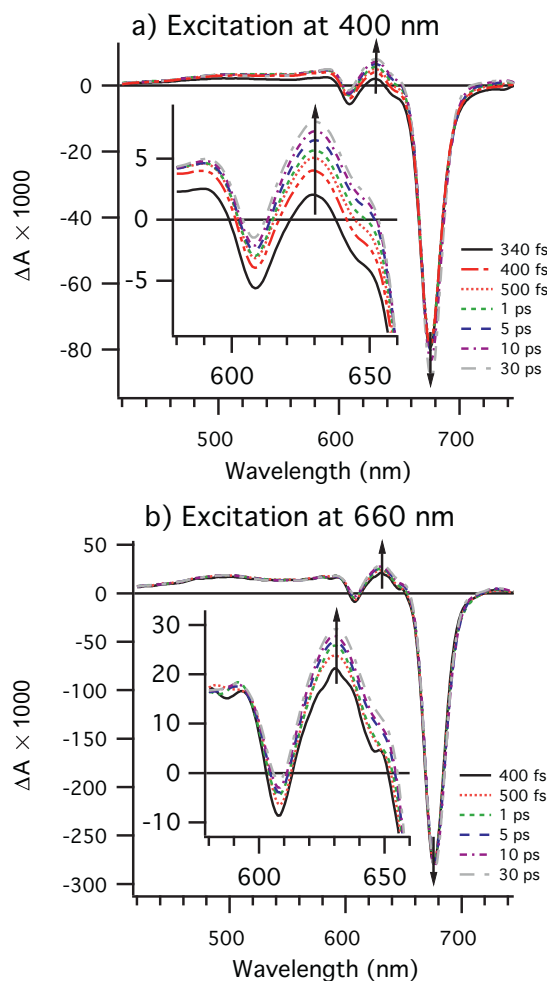
spectroscopy measurements were carried out in a setup built around a standard Ti:sapphire femtosecond amplifier system (Spitfire from Spectra Physics) working at a 1 kHz repetition rate [28]. The samples were excited either in the Q-band (at 660 nm) or in the Soret band (at 400 nm) using pulses generated by a noncollinear optical parametric amplifier (NOPA) or frequency doubled fundamental pulses, respectively. In both cases the energy of the pump pulses at the sample position was in the range of 2–3  $\mu$ J. Transient absorption was probed with white-light supercontinuum pulses generated in a 3 mm-thick CaF<sub>2</sub> plate. The useful spectral range of the supercontinuum extended from 380 to 780 nm. The polarization of the probe pulses was at the magic angle relative to that of the pump pulses. After acquisition, all spectra were corrected for the chirp of the probe pulses.

The samples (solutions in DMSO) were contained in 1 mm-thick fused silica cells and kept at room temperature. The concentration of the solutions was such that the absorbance at both excitation wavelengths was in the range of 0.15–0.2 except for unsubstituted **Zn-Pc**, for which the absorbance at 400 nm was as low as 0.03. During the measurements the samples were stirred by bubbling with nitrogen which was applied approx. 20 min before the start of the experiment so the concentration of oxygen in the solution was greatly reduced.

## 3. Results and discussion

Steady-state absorption and emission spectra of **Zn-Pc**, **Pc-1**, and **Pc-2** in DMSO are shown in Fig. 2. The spectra of all the compounds exhibit very small Stokes shift, however it is twice as big for **Zn-Pc** derivatives than for bare **Zn-Pc**. Spectra of **Pc-1** and **Pc-2** are practically identical; they are red-shifted compared to that of **Zn-Pc**. Nearly a perfect mirror-image symmetry of the absorption and emission spectra of **Zn-Pc** is slightly distorted in case of its derivatives. The fluorescence quantum yield of **Pc-1** and **Pc-2** in DMSO is approximately 3 times lower than that of **Zn-Pc** used as the quantum yield standard [27].

In order to compare the kinetic features of **Pc-1** and **Pc-2** with a well-known reference, transient absorption studies of unsubstituted **Zn-Pc** were carried out at two excitation wavelengths:



**Fig. 3.** Transient absorption spectra of **Zn-Pc** in DMSO after excitation in the Soret (a) and Q bands (b).

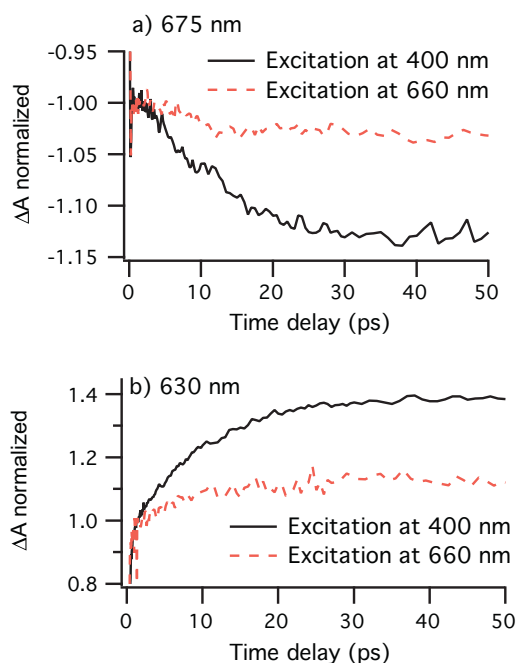
400 nm (within the Soret band) and 660 nm (within the Q band) up to the time delays between pump and probe pulses of 1.8 ns. The early evolution of the transient spectra at both wavelengths can be seen as a rise of the absorption in the range of 400–650 nm and a rise of the gain in the range of 660–720 nm, corresponding to stationary absorption (bleaching) and stimulated emission bands (Fig. 3). Global analysis of the transient absorption data performed using the matrix reconstruction algorithm [29] revealed three distinct decay times (Table 1).

Two of them ( $\tau_1$  and  $\tau_3$ ) are in a very good agreement with the values reported in the extensive study of the dynamics of **Zn-Pc** in DMSO by Savolainen et al. [30]. The longest time constant (3.3 ns) is equal to the fluorescence lifetime measured by TCSPC and can be undoubtedly ascribed to the excited-state lifetime. The 2 ps component has been previously attributed to dielectric solvation

**Table 1**

Decay times resulting from the global analysis of the transient absorption data ( $\tau_1$ ,  $\tau_2$ ,  $\tau_3$ ) and fluorescence lifetimes ( $\tau_F$ ) for **Zn-Pc** and its derivatives.

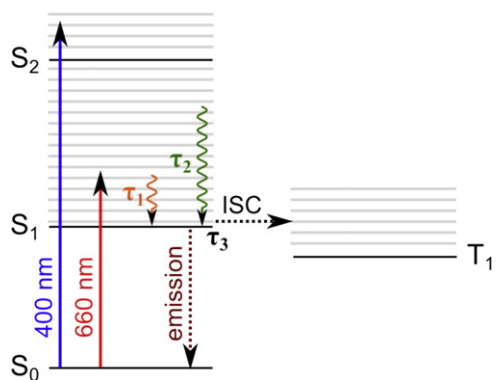
	$\lambda_{exc}$ (nm)	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ns)	$\tau_F$ (ns)
<b>Zn-Pc</b>	400	2.2	10	3.3	3.3
	660	1.7	11	3.3	
<b>Pc-1</b>	400	2.5	51	1.2	1.5
	660	2.3	28	1.2	
<b>Pc-2</b>	400	2.0	57	1.2	1.5
	660	2.8	41	1.2	



**Fig. 4.** Transient absorption kinetics recorded with **Zn-Pc** in DMSO at 675 nm (a) and 630 nm (b).

dynamics of DMSO. **Zn-Pc** has no permanent dipole moment therefore higher order (quadrupolar) electrostatic interactions must be responsible for the solvent relaxation. The intermediate decay component (10 ps) has not been reported in Ref. [30]. Comparison of the kinetics within the delays range up to 50 ps (Fig. 4) shows that this component is much more pronounced for excitation at 400 nm whereas its amplitude for excitation at 660 nm is relatively small. This might be the reason why it has not been reported by Savolainen et al. [30], because this study was done only for excitation in the Q band. The difference of the amplitudes of this decay component for the two excitation wavelengths indicates that energy dissipation must be involved in the related process.

The 10 ps component has been seen in transient absorption measurements of zinc phthalocyanine tetrasulfonate [31] and it has been ascribed to  $S_2 \rightarrow S_1$  internal conversion. Such an interpretation does not seem probable, because 10 ps is unreasonably a long time for this process and this component is also observed for excitation in the Q band. On the other hand a decay component in the range of 10–20 ps has been previously observed in various studies of porphyrins [32,33] and porphycenes [34]. Its spectro-temporal features, especially the rise of the gain in the spectral range of the bleaching and stimulated emission bands, were very similar to the evolution of **Zn-Pc** transient spectra reported here. Therefore it seems that the process associated to the 10 ps decay constant in **Zn-Pc** can be, as in the case of porphyrins and porphycenes, attributed to thermal equilibration of an excited molecule by energy exchange with the solvent. The processes attributed to the observed evolution of transient absorption spectra of **Zn-Pc** are shown schematically on a simplified diagram in Fig. 5. Temporal evolution of the transient absorption spectra for excitation in the Soret band does not exhibit any features that could be unequivocally attributed to the  $S_2 \rightarrow S_1$  internal conversion. In particular,  $\tau_1$  cannot be assigned to this process, because its value and the amplitude of the corresponding decay are very similar for excitation to  $S_1$  (660 nm) and  $S_2$  (400 nm) states. Therefore  $S_2 \rightarrow S_1$  internal conversion must be hidden within the observed spectral evolution which results mainly from energy relaxation processes. Further studies,



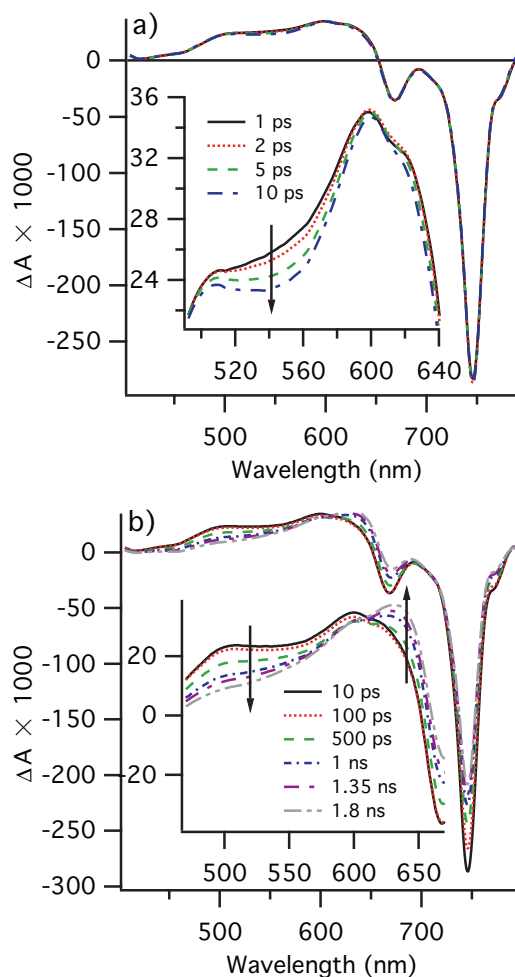
**Fig. 5.** Attribution of three time constants determined by transient absorption spectroscopy of phthalocyanines.  $\tau_1$  describes the dielectric solvent relaxation and  $\tau_2$  is ascribed to vibrational relaxation through energy exchange with the solvent. Excited-state lifetime  $\tau_3$  results from intersystem crossing (ISC) as well as radiative and non-radiative transitions to the ground state (position of energy levels on the simplified diagram does not reflect their real energy).

presumably by femtosecond time-resolved fluorescence spectroscopy, are required to determine the  $S_2$  state lifetime.

It can be observed that no spectral changes due to the triplet state population can be directly seen in the spectral evolution, although the triplet state is populated with a high yield, as indicated by the single oxygen quantum yield measurements [27]. This is due to the overlap of the triplet state absorption with the strong bleaching band which masks the former entirely [30].

The shape of transient absorption spectra of **Pc-1** and **Pc-2** recorded in the same conditions as for **Zn-Pc** is similar to that of their parent molecule: the excited-state absorption band occupies the shorter wavelengths region and is limited on the red edge by strong bleaching and stimulated emission bands (Figs. 6 and 7). The temporal evolution is however significantly different (Fig. 8; compare the insets in Figs. 3, 6, and 7). Spectral changes at early delays are very small and can be seen only around 550 nm, 650 nm and in the stimulated emission region (around 750 nm). The amplitude of the changes is much smaller than in the case of **Zn-Pc**. For longer delays the situation is reversed, and starting from 100 ps a clear spectral evolution exhibiting an isosbestic point at 600 nm can be observed (panel b in Figs. 6 and 7).

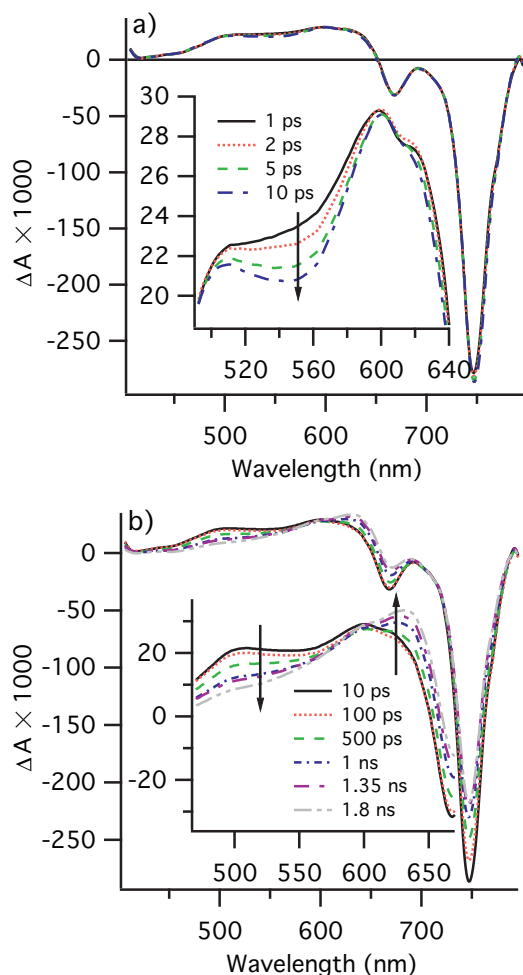
As in the case of **Zn-Pc**, three-exponential decay is required to globally fit the transient absorption data of **Pc-1** and **Pc-2**. The corresponding time constants are very similar for both compounds (Table 1). The shortest decay time,  $\tau_1$ , for all studied compounds is close to 2 ps, which again justifies its attribution to the dielectric solvent relaxation. Similar to the case of **Zn-Pc** the 2 ps decay is very similar after excitation to  $S_1$  and  $S_2$  states which prevents its attribution to  $S_2 \rightarrow S_1$  internal conversion. There is no evidence of spectral evolution in the data recorded with 400 nm excitation, which could be identified with the internal conversion process. The amplitude of the absorption changes related to the intermediate decay time,  $\tau_2$ , depends on the excitation wavelength and, as for **Zn-Pc**, is bigger for higher excitation energy (Fig. 8c).  $\tau_2$  for **Pc-1** and **Pc-2** is, however, several times longer than for **Zn-Pc** and its value depends on the excitation wavelength, being shorter for lower excitation energy. This difference indicates that the ester-alkoxy substituents play a role in the thermalization of the molecule and the energy exchange with the solvent. This observation is not surprising, because the excess of the excitation energy in the case of substituted phthalocyanines spreads over the core molecule and long chains of the substituents before it is released to the environment. It cannot be excluded that a large amplitude motion of the substituents is involved in the deactivation and due to their length their motions are significantly hindered by interaction with



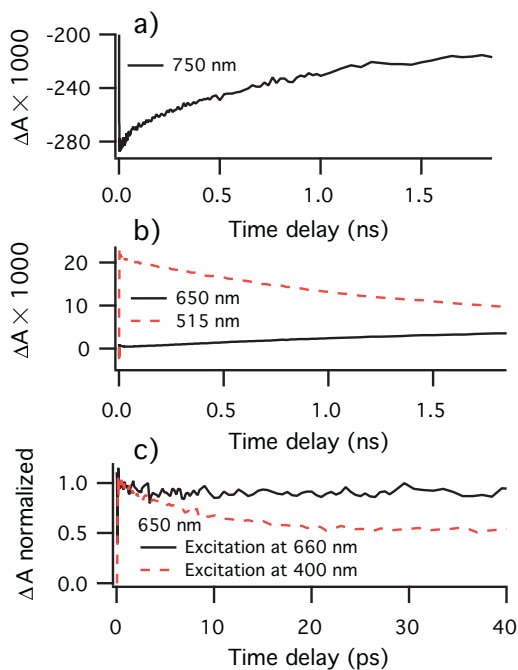
**Fig. 6.** Transient absorption spectra of **Pc-1** in DMSO at short (a) and long (b) pump-probe delays for excitation in the Soret band.

the solvent. Slightly longer thermalization time observed for **Pc-2** which has longer substituent chains than **Pc-1** seems to confirm that the ester-alkoxy groups act as “heat conductors” or “heat tank” through which the excess of vibrational energy is transferred from the core molecule to the solvent. Smaller value of  $\tau_2$  after excitation in the Q-band compared to the excitation in the Soret band can be explained by lower amount of the energy to be transferred to the surrounding thermal bath in the former case. Similar behaviour has been observed for free-base porphycene, where it also took more time for a molecule to thermalize with the environment when it was excited with a higher energy excess [34]. The slowest process observed in the transient absorption data for **Pc-1** and **Pc-2** is accompanied by large spectral changes, namely the decay of the absorption in the broad band around 500 nm and the rise of absorption at around 650 nm. At the same time, the gain due to overlapped bleaching and stimulated emission bands around 750 nm decays. The time constant of this process,  $\tau_3 = 1.2$  ns is very close to the fluorescence lifetime measured by TCSPC (1.5 ns) and can be identified with the excited-state lifetime. Precursor–successor behaviour expressed by the presence of the isosbestic point can be thus interpreted as the decay of the singlet excited state and population of the triplet state. The absorption band of the triplet state is red-shifted with respect to the absorption of the  $S_1$  state and is partially obscured by the bleaching and stimulated emission bands, but, contrary to the case of **Zn-Pc**, the absorption from the triplet state can be clearly seen in the transient spectra of **Pc-1** and **Pc-2**. The interpretation of the three decay times observed in the transient





**Fig. 7.** Transient absorption spectra of **Pc-2** in DMSO at short (a) and long (b) pump-probe delays for excitation in the Soret band.



**Fig. 8.** Transient absorption kinetics of **Pc-2** in DMSO for the excitation at 400 nm recorded at 750 nm (a), and 515 and 650 nm (b); comparison of early kinetics recorded at 650 nm for the excitation in the Soret and Q bands (c).

**Table 2**

Radiative excited-state decay constants  $k_r$  for **Zn-Pc** and its derivatives calculated using the Strickler–Berg formula.

Compound	$k_r$ ( $10^8 \text{ s}^{-1}$ )	$k_r^{-1}$ (ns)
<b>Zn-Pc</b>	$1.8 \pm 0.2$	$5.5 \pm 0.6$
<b>Pc-1</b>	$1.5 \pm 0.2$	$6.8 \pm 0.9$
<b>Pc-2</b>	$1.6 \pm 0.2$	$6.3 \pm 0.8$

absorption data of **Pc-1** and **Pc-2** is therefore the same as for parent **Zn-Pc** (Fig. 5). The ratio of the excited-state lifetimes for **Zn-Pc** and its substituted derivatives (approx. 2.8) is close to the ratio of the respective fluorescence quantum yields (approx. 3 [27]), which means that the radiative constants are similar for all three compounds, whereas non-radiative processes are more efficient in **Pc-1** and **Pc-2** than in the parent molecule. This result becomes consistent with the radiative rate constants calculated from the absorption spectra using the Strickler–Berg formula [35] (Table 2). It is worth pointing out that although the excited-state lifetime for **Pc-1** and **Pc-2** is almost 3 times lower than for **Zn-Pc**, the singlet oxygen quantum yield for them is 25% lower than for **Zn-Pc** in DMSO solution [27]. If we assumed that the shortening of the  $S_1$  lifetime was only due to higher intersystem crossing rate ( $S_1 \rightsquigarrow T_1$ ), the yield of the triplet formation should increase (not, as observed, decrease) in the derivatives compared to **Zn-Pc**. The lack of the subsequent increase of the singlet oxygen formation yield indicates one of the following effects: (1) the rates of both nonradiative processes,  $S_1 \rightsquigarrow S_0$  and  $S_1 \rightsquigarrow T_1$  are proportionally higher in the derivatives or (2) only the  $S_1 \rightsquigarrow T_1$  rate is significantly higher in the derivatives but the crossreaction for the interaction with oxygen is much lower for **Pc-1** and **Pc-2** than for **Zn-Pc**. On the other hand, if the intersystem crossing rate did not change upon substitution, the singlet oxygen quantum yield should decrease by a factor much higher than 25% due to stronger competition of the internal conversion ( $S_1 \rightsquigarrow S_0$ ) with the triplet state formation. The increase of the intersystem crossing rate is desirable for PDT, but the increase of the  $S_1 \rightsquigarrow S_0$  nonradiative relaxation rate and decrease of the crossreaction for interaction with oxygen molecules are highly unwanted. Further studies are needed to determine to what extent these effects take place after ester-alkoxy substitution of **Zn-Pc**.

#### 4. Conclusions

We studied ultrafast dynamics of two ester-alkoxy substituted zinc phthalocyanine derivatives with potential application for photodynamic therapy and compared them to the parent molecule. In all cases three decay times are required to fit the transient absorption data recorded with a femtosecond temporal resolution. The associated processes were identified as the dielectric solvation, heat transfer from the molecule to the solvent and the excited-state lifetime. It was shown that the presence of long ester-alkoxy groups leads to the increase of the time needed for the redistribution of the excitation energy excess (from 10 ps to 30–50 ps) and shortens the excited-state lifetime by a factor of approx. 3 (from 3.3 ns to 1.2 ns). The intersystem crossing rate increases after the ester-alkoxy substitution of **Zn-Pc** but this increase is accompanied by other effects which lead to the degradation of the photodynamic activity of the derivatives. The direction of this research will be continued and reported in the due course.

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