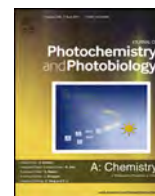




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

Invited paper

## Temperature dependent steric hindrance effects in triplet state relaxation of *meso*-phenyl-substituted Pd-octaethylporphyrins



Alexandr Gorski<sup>a</sup>, Valery Knyukshto<sup>a,b</sup>, Eduard Zenkevich<sup>c,\*</sup>, Alexander Starukhin<sup>a,b</sup>, Michał Kijak<sup>a</sup>, Jędrzej Solarski<sup>a</sup>, Alexander Semeikin<sup>d</sup>, Tatjana Lyubimova<sup>d</sup>

<sup>a</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, Poland

<sup>b</sup>B.I Stepanov Institute of Physics, National Academy of Science of Belarus, Nezavisimosti Ave., 70, 220072 Minsk, Belarus

<sup>c</sup>National Technical University of Belarus, Department of Information Technologies and Robotics, Nezavisimosti Ave., 65, Minsk 220013, Belarus

<sup>d</sup>Ivanovo State University of Chemistry and Technology, Prospect Sheremetjevskii 7, 153000 Ivanovo, Russia

### ARTICLE INFO

#### Article history:

Received 27 February 2017

Received in revised form 1 September 2017

Accepted 1 September 2017

Available online 8 September 2017

#### Keywords:

Pd-octaethylporphyrins

Singlet and triplet excited states

Phosphorescence

Arrhenius plot

Transient absorption at low temperature

Steric hindrance effects

Distortions from planarity

Radiationless transitions

### ABSTRACT

The analysis of spectral-kinetic results of transient absorption and phosphorescence experiments has been carried out in a wide temperature range (80–293 K) for a series of Pd-octaethylporphyrin derivatives (PdOEP) with increasing number of bulky *meso*-phenyl substituents. In order to elucidate the influence of steric hindrance interactions, as well as porphyrin macrocycle non-planarity on photophysical characteristics and relaxation pathways of triplet states, the following parameters were compared: i) T-state positions on the energy scale, ii) phosphorescence lifetimes and  $T_1 - T_n$  transient absorption spectra, iii) phosphorescence quantum efficiencies, iv) activation energies of temperature-dependent phosphorescence rate constants for planar PdOEP and non-planar PdOEP-*meso*(Ph)<sub>n</sub> molecules.

© 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Up-to-date, synthesis, photochemistry and supramolecular chemistry of tetrapyrrole compounds is of growing interest. It is well-known that tetrapyrroles (mostly heme and chlorophyll derivatives) are ubiquitous cofactors in nature and function in a wide range of biological processes including respiration, electron transfer, oxidation catalysis [1], photosynthesis [2,3], etc. In addition to their basic macrocycle properties, i.e., coordination and functional groups, the structural organization of tetrapyrrole complexes *in vivo*, in which chromophore molecules assume non-planar labile conformations, is a tool of subtle controlling excited-state characteristics as well as enzymatic and photocatalytic properties of natural tetrapyrrolic pigments [4,5]. Therefore, it is important to get insight into what specific factors may control photophysical properties of individual subunits.

On the other hand, a significant interest of numerous scientific groups is devoted to the design and investigation of biomimetic

models based on tetrapyrrole compounds that exhibit efficient energy transfer and charge separation [6–10]. In many cases, such synthetic multiporphyrin complexes are based on porphyrins and chlorins that are covalently linked via a *meso*-phenyl spacer [9–13]. As a rule, formation of these systems leads to steric interactions of bulky molecular fragments, which may be accompanied by static and dynamic distortions from planarity in the porphyrin macrocycle. Thus, in addition to studying photoinduced processes in these complexes, it is necessary to take into account the direct influence of bulky *meso*-phenyl substituents on the deactivation of excited electronic  $S_1$  and  $T_1$  states of tetrapyrrole macrocycles (steric factors, spatial distortions, effects of the conformational dynamics of macrocycles, etc.).

As a result, the synthesis and studies of porphyrins with non-planar macrocycle conformations have attracted considerable attention [4,5,14–16]. In most cases the so-called ‘hybrid porphyrins’ of octaethyl- (OEP) or octamethylporphyrin (OMP) type, containing bulky substituents of various nature at the *meso*-positions of the tetrapyrrole macrocycle, have been used as basic objects for the investigation of possible non-planar macrocycle conformations which may be associated with two general types of deformations, ‘saddle’ and ‘ruffle’ or their mixtures, ‘wave’ and

\* Corresponding author.

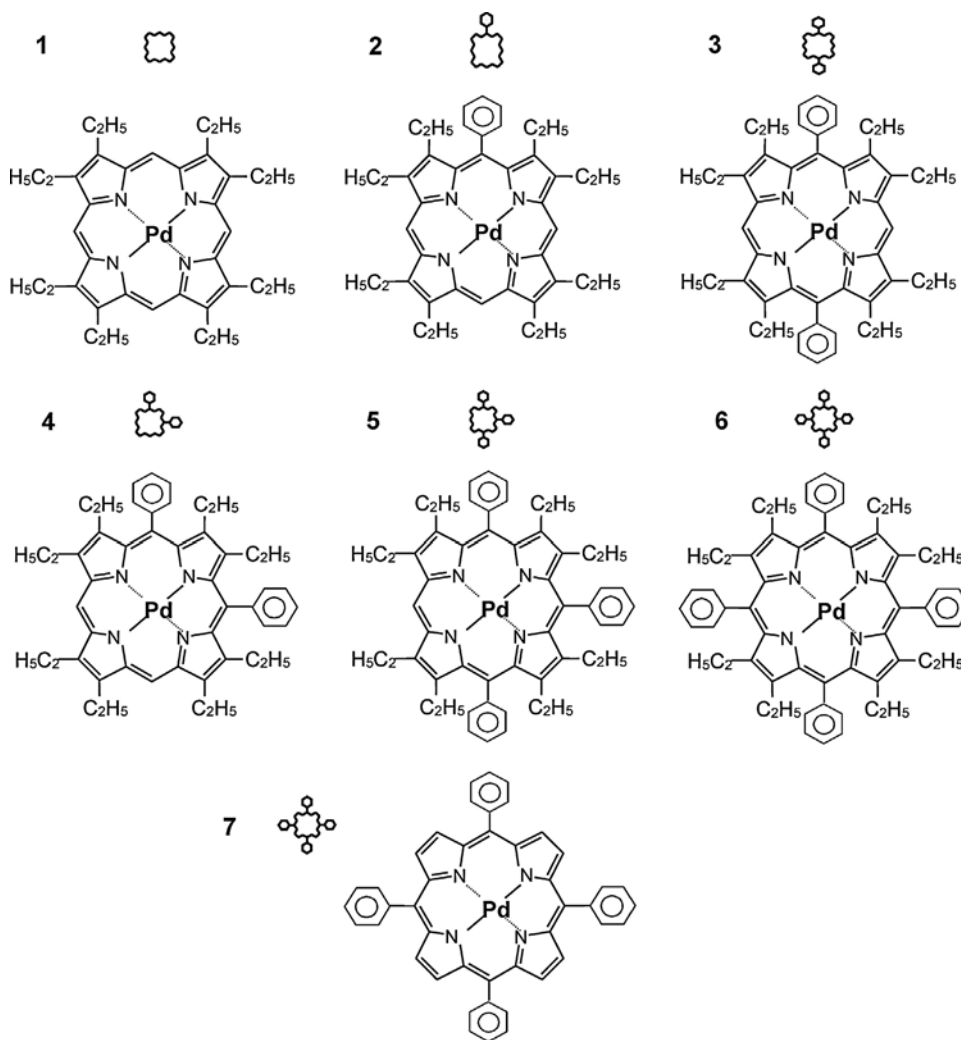
E-mail addresses: [agorski@ichf.edu.pl](mailto:agorski@ichf.edu.pl) (A. Gorski), [zenkev@tut.by](mailto:zenkev@tut.by) (E. Zenkevich), [starukhin@mail.ru](mailto:starukhin@mail.ru) (A. Starukhin), [semeikin@isuct.ru](mailto:semeikin@isuct.ru) (A. Semeikin).

'dome'. Analysis of X-ray structural data [17,18], results of time-resolved and steady state spectral investigations [18–21], various spectral information [22–26] and quantum-chemical calculations [27,28] indicate that simultaneous introduction of bulky peripheral substituents in the  $\beta$ - and *meso*-positions of the tetrapyrrole macrocycle leads to distortions from planarity even in the ground  $S_0$  state, considerably changing its geometry and electronic structure, as well as the dynamics of relaxation processes. It follows from the above references that, typically at 295 K, the conformational dynamics of a non-planar tetrapyrrole macrocycle caused by the thermal population of low-frequency out-of-plane deformation modes in the first excited singlet  $S_1$  state, would lead to the perturbation of the energy level structure and changes of deactivation channels of the excited states. This manifests itself in large bathochromic absorption and fluorescence shifts ( $\Delta\lambda \sim 1100 \text{ cm}^{-1}$ ), essential increase of the Stokes shift between  $Q(0,0)$  absorption and fluorescence bands ( $\Delta\nu_s \sim 900 \text{ cm}^{-1}$ ) and broad emission profiles in both polar and non-polar solvents, as well as in a pronounced decrease of fluorescence quantum yield and lifetime shortening. Nevertheless, important questions of

what happens with other excited states (namely,  $T_1$ ) and which states ( $S_1$  or  $T_1$ ) are more sensitive to steric interactions of bulky substituents with a tetrapyrrole macrocycle, remain to be answered. The reported spectral and kinetic parameters of  $T_1$  triplet states for sterically hindered porphyrins are not numerous and indirect in most cases [18,20,22].

It is noteworthy that, based on X-ray data [4,18], it was elucidated that in the ground  $S_0$  state mono- and di-*meso*-phenyl-substituted arylporphyrins (e.g. OEP-5Ph and OEP-5,15Ph, see structures in Fig. 1) are planar both in the crystalline form and in liquid solutions, and are characterized by a slight diamond-shaped extension along the direction in which *meso*-phenyl substituents are bonded. As a consequence of this result, it was proposed that the dynamic non-planar distortion in the  $S_1$  state for OEP-5Ph and OEP-5,15Ph molecules should be absent. Therefore it was silently assumed that the photophysics and spectral-luminescent properties of  $S_1$  and  $T_1$  states of these compounds have to be closely related to those known for usual planar porphyrins.

Nevertheless, we have found for the first time that in degassed toluene at ambient temperature, mono- and di-*meso*-phenyl



**Fig. 1.** Chemical structures, pictograms and abbreviations for a series of Pd-porphyrins and their *meso*-phenyl-substituted (Ph) derivatives. 1: Palladium octaethylporphyrin (PdOEP); 2: Palladium 5-phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (PdOEP-5Ph); 3: Palladium 5,15-diphenyl-2,3,7,8, 12,13,17,18-octaethylporphyrin (PdOEP-5,15Ph); 4: Palladium 5,10-diphenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (PdOEP-5,10Ph); 5: Palladium 5,10,15-triphenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (PdOEP-5,10,15Ph); 6: Palladium 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (PdOEP-5,10,15,20Ph); 7: Palladium tetraphenylporphyrin (PdTPP) as reference compound with planar  $\pi$ -conjugated macrocycle having four *meso*-phenyl rings and no  $\beta$ -ethyl substituents in four pyrrole rings.

substitution in octaethylporphyrin free bases (OEP) and their Zn complexes (ZnOEP), as well as the formation of octaethylporphyrin chemical dimers with the phenyl ring as a spacer, (ZnOEP)<sub>2</sub>Ph or (OEP)<sub>2</sub>Ph, leads to a drastic shortening of triplet lifetimes, from ~1.5 ms to 2–5 μs, without considerable influence on spectral-kinetic parameters of the S<sub>0</sub> and S<sub>1</sub> states [19,29,30]. Later on, the same steric effect influence was found for the triplet state deactivation in Zn(II) *meso*-diaryloctaalkylporphyrins studied in a wide temperature range [21]. In addition, the detailed experimental analysis of steric hindrance effects has been comparatively carried out by us for a series of spatially distorted *meso*-phenyl-substituted octamethyl- (OMP) and octaethylporphyrins (OEP) with an increasing number ( $n = 1 \div 4$ ) of *meso*-phenyl rings [31,32]. We have shown that for both series of OMP and OEP molecules steric porphyrin macrocycle distortion affects the triplet state properties significantly stronger than the singlet state properties. This may be explained by the decrease of the porphyrin skeleton rigidity in the excited T<sub>1</sub> state, possibly due to the π-bond alternation increase.

In this respect, studying the influence of the non-planar conformational dynamics on the non-radiative deactivation of triplet states for Pd-porphyrins is of particular interest. At ambient temperature, these complexes are characterized by a high efficiency of the intersystem transition from S<sub>1</sub> to T<sub>1</sub> and high quantum yields of phosphorescence [24,33]. The latter gives the possibility for the direct measurement of triplet state parameters (deactivation rates, spectral position, efficiencies, etc.) upon increase of steric hindrances in these molecules in a wide temperature range. Notably, such experiments for Pd-porphyrins are poorly presented in literature and are not systematic. For instance, spectral-kinetic manifestations of the conformational dynamics in the triplet state have been observed for a few Pd-complexes of sterically hindered OEP molecules at ambient temperature [34]: like for *meso*-aryl-substituted OEP molecules discussed above, the non-planar dynamic conformations of the Pd-porphyrin macrocycle in the triplet state manifest themselves in a substantial decrease of the phosphorescence quantum yield and a shorter decay time. It was shown also [24] that at 295 K in liquid solutions for Pd(II)-complexes based on OEP and TPP molecules differing by nature, number and position of peripheral substituents the splitting of low excited singlet and triplet states takes place, accompanied by the appearance of new absorption bands on the long wavelength side of the Q(0,0)-band and in the near IR region. The appearance of new bands is caused by spin-forbidden transitions from the ground S<sub>0</sub> state to a set of low excited triplet states. At last, it should be mentioned that for symmetrical and non-symmetrical Pd-porphyrins deformations from planarity may take place [34,35], which manifest themselves in the presence of two spectrally narrow different bands in the phosphorescence spectra at low temperatures in rigid glassy matrices.

The aim of this paper is a comparative description of structural dynamics and energy relaxation processes for a series of Pd-octaethylporphyrin (PdOEP) molecules with a sequential increase of the number of *meso*-phenyl rings ( $n = 1 \div 4$ , see structures 4–7 in Fig. 1). We would like to characterize systematically the observed effects for the systems under study using the whole set of experimental data (absorption, fluorescence, phosphorescence, T<sub>1</sub> – T<sub>n</sub> transient absorption, time-resolved spectroscopy) in a wide temperature range 80–295 K, in solvents that at low temperatures form glassy transparent matrices. In addition, we undertake comparative analysis of the structures of the compounds under consideration using quantum chemical calculations. Finally, we intend to analyze what happens with the efficiency of singlet oxygen generation using the sequential set of sterically hindered compounds: PdOEP-5Ph → PdOEP-5,15Ph → PdOEP-5,10Ph → PdOEP-5,10,15Ph → PdOEP-5,10,2015Ph.

## 2. Experimental

### 2.1. Objects and solvents

The structures of the compounds under study are shown in Fig. 1. Precursors, free bases of octaethylporphyrins with various number of *meso*-phenyl rings have been synthesized according to methods described in [36,37]. For TPP preparation the method developed in [38] has been used. Pd-complexes of porphyrins have been obtained according to the procedure described in [39], followed by purification and chromatography separation. Toluene (Spectroscopic Grade) was used as a basic solvent at ambient temperature. Low-temperature measurements (down to 80–77 K) were carried out in 2-methyltetrahydrofuran (Aldrich) forming an optical transparent rigid glassy matrix under these conditions. In order to diminish the T–T annihilation effect porphyrin concentrations of ~10<sup>-6</sup> M were used. Because of the significant quenching of the excited singlet and triplet states by dissolved molecular oxygen, the main part of measurements was carried out for samples degassed at the pressure down to 10<sup>-5</sup> Torr (five cycles of freeze–pump–thaw technique). All photophysical measurements were completed within a few hours after sample preparation.

### 2.2. Spectral and time-resolved measurements

Absorption spectra have been measured with a Cary 500 M double beam spectrophotometer (Varian) using 10 × 10 mm quartz cells (Type 111 QS). Luminescence emission spectra (fluorescence and phosphorescence) were measured with a home-made high-sensitive laboratory setup described in detail in our previous papers [19,24,29–32] where standard samples, necessary formulae, and experimental errors are presented.

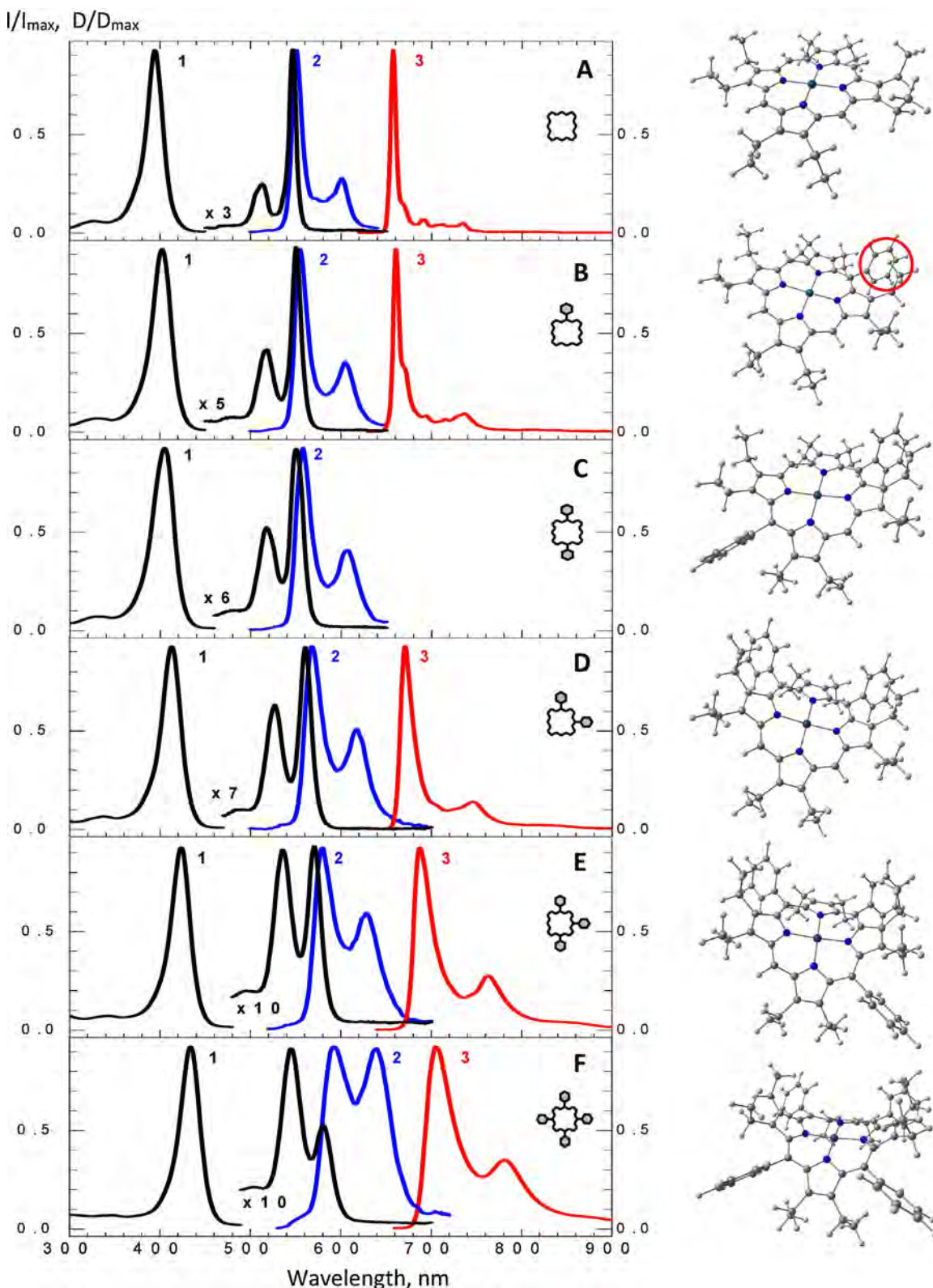
Transient triplet–triplet absorption spectra and triplet state lifetimes have been measured using a home-built laser flash photolysis setup. The pump pulses are provided by Lambda Physik FL-2002 dye laser ( $\lambda_{exc} = 545$  nm, the experimental response  $\Delta t_{1/2} = 25$  ns FWHM,  $W \approx 5$  mJ), pumped by Lambda Physik LPX100 excimer laser working at 1–25 Hz. The continuous light of laser-driven Xe lamp (Energetiq EQ-99-Plus-EU) and pump pulses of Xe flash lamp (PerkinElmer 1100 Series) have been used for kinetic and spectral data acquisitions, respectively. The setup is equipped with a two-channel CCD spectrometer (Avantes AvaSpec-ULS2048-2-USB2) for spectral measurements and allows registration of time-resolved spectra with delays from 1 μs to seconds. For kinetic measurements a home-built monochromator has been used equipped with a fast photomultiplier (Hamamatsu R5108) and oscilloscope (Tektronix TDS 3032). The samples were irradiated in 1 cm path-length quartz cell. To ensure accuracy of the obtained data upon collecting the first set of transient triplet–triplet absorption spectra and triplet state lifetimes, the solutions were diluted to half of the initial concentration and all measurements were repeated.

Measurements of quantum efficiencies ( $\gamma_{\Delta}$ ) of singlet oxygen generation (<sup>1</sup>O<sub>2</sub>, emission at  $\lambda_{max} = 1270$  nm) have been performed with a home-made highly sensitive experimental set-up described in detail in [29–32] and additionally equipped with a TE Cooled Photodiode Module (Edmund Optics, 800–1600 nm registration range). Different types of LEDs with light output of 100 – 1000 mW were used as photoexcitation sources. The efficiencies  $\gamma_{\Delta}$  were determined with respect to the well-known standard phenalenone ( $\gamma_{\Delta}^0 = 0,99$  in toluene at ambient temperature [40]). The main procedure for the measurement of quantum efficiency of singlet oxygen generation,  $\gamma_{\Delta}^x$ , is based on the comparison of emission intensity of singlet oxygen ( $\lambda_{max} = 1.27$  μm) photosensitized by a standard compound (intensity I<sub>0</sub>) and by the compound under

investigation (intensity  $I_x$ ) in the same solvent

$$\gamma_{\Delta}^x = \gamma_{\Delta}^0 \frac{I_x \times \beta_0}{I_0 \times \beta_x} \quad (1)$$

where  $\gamma_{\Delta}^0$  is the quantum efficiency of singlet oxygen generation by a standard,  $\beta_0 = (1 - 10^{-D_0})$  and  $\beta_x = (1 - 10^{-D_x})$  are fractions of exciting light absorbed by the standard and the object under study, respectively, at a given excitation wavelength. Optical density of



**Fig. 2.** Left: Normalized absorption (1, toluene at 293 K), fluorescence (2, toluene at 293 K) and phosphorescence (3, methylcyclohexane-toluene mixture 5:1 at 80–77 K) spectra of PdOEP (A), PdOEP-5Ph (B), PdOEP-5,15Ph (C), PdOEP-5,10Ph (D) and PdOEP-5,10,15,20Ph (E). Right: Optimized structures of planar and sterically hindered *meso*-phenyl substituted Pd-octaethylporphyrins in the ground  $S_0$  state.

solutions did not exceed  $OD \leq 0.05$  at optical length of  $l = 10$  mm. A relative experimental error of  $\gamma_{\Delta}^0$  measurements was estimated to be  $\pm 10\%$ .

### 2.3. Quantum-chemical calculations

Calculations were performed with Gaussian 09 (A.01) [41] and ORCA 2.9 [42] quantum-chemical software packages. In all the cases, we used the Becke–Lee–Yang–Parr exchange–correlation three-parameter functional (B3LYP). Optimization procedures of the geometry (in the  $S_0$  and  $T_1$  states) and subsequent calculation of normal coordinates were performed using the SVP basis set and applying methods of the stationary and non-stationary density functional theories (DFT, TDDFT). In this case, the TDDFT method was used at the initial steps of the geometry optimization (three–five), in order to obtain the correct electronic configuration of the excited state. Singlet electronic transitions from the ground state were calculated by the TDDFT method using the B3LYP functional and def2-SVP basis set for all atoms.

## 3. Results and discussion

### 3.1. Spectral, energetic and kinetic properties

Inspired by our earlier experience with  $\beta$ -substituted alkylporphyrin free bases having sequentially increasing number of *meso*-phenyls [31,32] we have studied the photophysical and photochemical properties for a series of *meso*-phenyl-substituted PdOEP molecules with the increasing number ( $n = 1 \div 4$ ) of *meso*-phenyl rings (structures are shown in Fig. 1) in a wide temperature range (80–293 K). Omitting the detailed analysis of all the spectral–kinetic characteristics of the compounds under study we only note the main regularities that are characteristic of the investigated series of the molecules, presented in Fig. 2 and summarized in Table 1. One can see that a sequential introduction of *meso*-phenyl rings into PdOEP molecules leads to considerable changes of their spectral–luminescent properties. Gradual bathochromic shifts are

observed for both Soret band and Q(0,0) absorption bands, as well as for fluorescence and phosphorescence spectra. In addition, one observe a considerable broadening and simultaneous change of the intensity ratio  $I_{Q(0,0)}/I_{Q(0,1)}$  for pure electronic Q(0,0) and vibronic Q(0,1) bands in absorption and fluorescence spectra. Experimental data show also that at 293 K, in the series of the investigated compounds, the Stokes shift between the absorption and fluorescence bands ( $\Delta$ ) does not remain constant but noticeably increases with an increase in the number of *meso*-phenyl substituents.

It was shown earlier [4,14,15] that mono- and symmetric di-*meso*-phenyl substituted octaalkylporphyrins (free bases, OEP-5Ph and OEP-5,15Ph) are planar. We can assume that, in liquid solutions, the planar configuration of PdOEP-5Ph and PdOEP-5,15Ph molecules in the ground  $S_0$  state is kept and, hence, the absorption and luminescence properties are close to those of ordinary planar porphyrins. Nevertheless, some shifts and spectral transformations are observed on transition from planar PdOEP to planar *meso*-phenyl substituted PdOEP-5Ph and PdOEP-5,15Ph compounds (also planar in the ground state). In this case, spectral changes are explained (as discussed in [9,20,31,32]) by the *meso*-phenyl substitution effect in the  $\pi$ -conjugated macrocycle that is a partial transition to the structure more typical of PdTPP molecule (see Fig. 1 and spectral data in Table 1 for this compound). As was discussed in [43], spectral transformations observed for a series of molecules planar in singlet states, PdOEP  $\rightarrow$  PdOEP-5Ph  $\rightarrow$  PdTPP are explained in Gouterman four-orbital model by destabilization of the HOMO  $a_{2u}$  orbital induced by the *meso*-phenyl substitution.

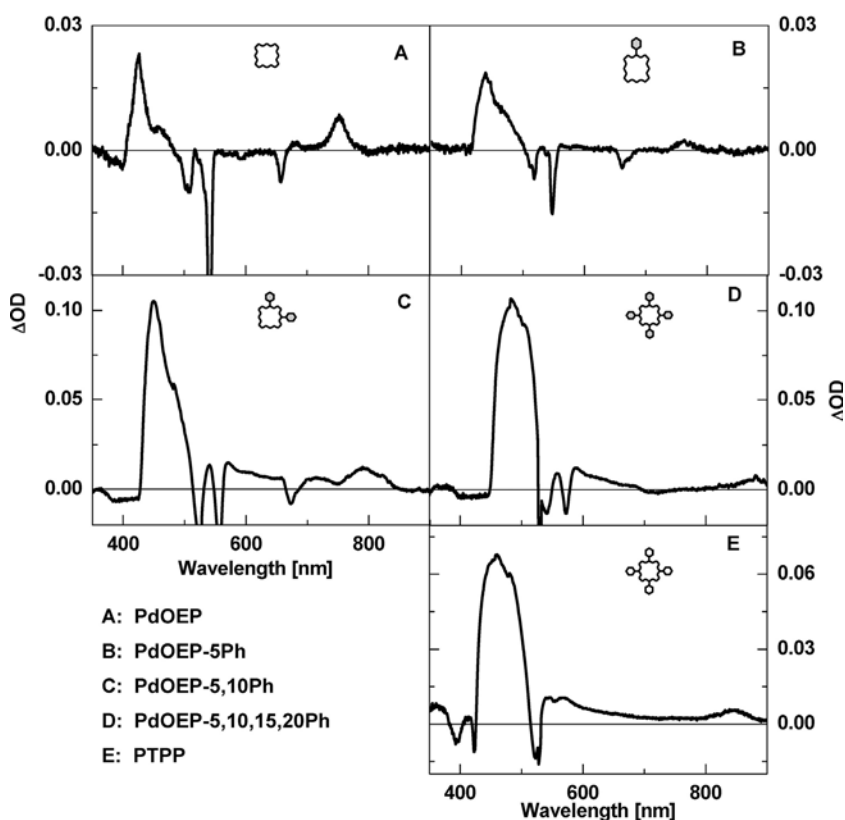
It should be added that the specific influence of *meso*-phenyl substitution is also detected upon comparison of T–T transient absorption spectra for planar macrocycles PdOEP and PdTPP (Fig. 3) in rigid glassy matrix at  $T = 80$ – $130$  K. In fact, comparative data presented in Fig. 3 show that transition from PdOEP to PdTPP (*i.e.* addition of four *meso*-phenyl rings) manifests itself in additional increase of the T–T absorption intensity in 420–500 nm and 550–700 nm spectral ranges. On the other hand, T–T absorption spectra of PdOEP and PdOEP-5Ph molecules correspond to each other in rigid glassy matrix. This result may be

**Table 1**

Spectral, luminescence, and energy parameters of singlet (293 K) and triplet (80 K) states for PdOEP and its *meso*-phenyl substituted derivatives: PdOEP-5Ph, PdOEP-5,10Ph, PdOEP-5,10,15Ph and PdOEP-5,10,15,20Ph.

Compound	Pictogram	Absorption Soret band $I_{\max}$ , nm	Absorption Q(0,0) band $I_{\max}$ , nm	Fluoresc. Q(0,0) band $I_{\max}$ , nm	Fluoresc. $j_{F1} \times 10^4$	Phosph $I_{\max}$ , nm	$DE_{S-T}$ $cm^{-1}$	Phosph $t_{ph}$ , ms	Phosph $j_{ph}$
PdOEP		394	547	551	3.1	657	3095	1.8	0.35
PdOEP-5Ph		402	550	554	2.8	660	3065	1.6	0.36
PdOEP-5,10Ph		413	561	561	2.3	671	2990	1.3	0.35
PdOEP-5,10,15Ph		424	571	579	1.9	688	3070	0.73	0.23
PdOEP-5,10,15,20Ph		434	581	592	1.6	705	3115	0.42	0.20
PdTPP		417	553	559	2.0	689	3440	1.3	0.20

Note: at 293 K toluene was used as a solvent; at 80–77 K, methylcyclohexane–toluene mixture 5:1 was used giving a glassy rigid matrix at low temperatures;  $DE_{S-T}$  is the energy separation between low-lying excited singlet and triplet states;  $\varphi_{F1}$  is fluorescence quantum yield;  $\varphi_{ph}$  is phosphorescence quantum yield;  $t_{ph}$  is phosphorescence decay time. The accuracy of emission quantum yield ( $\varphi$ ) measurements is 5–7% for  $\varphi \geq 0.1$ , and the limit of emission quantum yields measured is  $10^{-5}$ . Decay times  $t_{ph}$  were measured at 0–0 band maxima of phosphorescence spectra by the pulse method using the second harmonic of the YAG:Nd<sup>3+</sup> pulse solid laser ( $\lambda_{exc} = 532$  nm, the experimental response  $\Delta t_{1/2} = 15$  ns FWHM) [31,32,34].



**Fig. 3.** Transient T–T absorption spectra (laser excitation at 545 nm, 2-methyl-tetrahydrofuran, ambient temperature and 80–130 K) for PdOEP (A), PdOEP-5Ph (B), PdOEP-5,10Ph (C) PdOEP-5,10,15,20Ph (D) and PTPP (E) (laser excitation at 545 nm, 2-methyl-tetrahydrofuran, ambient temperature and 80–130 K).

considered as an independent proof for the planar conformation of PdOEP-5Ph molecule in the excited triplet state at 80–130 K in rigid solutions, while at ambient temperature this molecule is non-planar in the excited triplet state. Finally, specific spectral features are observed in T–T absorption spectra of PdOEP-5,10Ph and PdOEP-5,10,15,20Ph molecules, which (as was discussed above) are characterized by non-planar distortions of  $\pi$ -conjugated macrocycle in both ground and excited singlet and triplet states. Fig. 3 evidently shows that for the latter two molecules, the T–T band in the 400–500 nm range is shifted to red (compared to that for planar PdOEP and PdOEP-5Ph molecules), and additional, broad T–T absorption bands are detected in 800–850 nm spectral region. Such spectral manifestation of the non-planar effects in T–T absorption spectra of sterically hindered  $\pi$ -conjugated porphyrin macrocycles in rigid glassy solvent at low temperature has not been reported before.

Further transition to PdOEP-5,10Ph with non-symmetrical *meso*-phenyl substitution, and then to PdOEP-5,10,15Ph and PdOEP-5,10,15,20Ph is accompanied by stronger spectral changes and pronounced decrease of quantum efficiencies and decay times for both fluorescence and phosphorescence (even at 80–77 K in the latter case, see Table 1). The results of quantum-chemical calculations presented in Fig. 2 evidently show that PdOEP-5,10Ph molecule with non-symmetrical di-*meso*-phenyl substitution (structure 4 in Fig. 1) and sterically hindered porphyrins PdOEP-5,10,15Ph and PdOEP-5,10,15,20Ph (structures 5 and 6, respectively) are non-planar even in the ground singlet  $S_0$  state. In addition, it follows from the theoretical analysis that the degree of non-planarity of a  $\pi$ -conjugated macrocycle becomes more pronounced upon increasing the number of *meso*-phenyl substituents.

Taking into account previous findings obtained for various types of sterically hindered porphyrin free bases [4,5,14–18], one

should conclude the following. The non-planarity of porphyrin molecules leads to destabilization of  $\pi$ -conjugated system in the tetrapyrrole macrocycle and is accompanied by a significant increase in the energy of highest occupied molecular orbitals (HOMOs) and a slight change in the energy of the lowest unoccupied molecular orbitals (LUMOs). As the degree of non-planarity of the macrocycle increases, the energy gap between the HOMO and LUMO successively decreases. This is accompanied by the increase in the bathochromic shift of absorption and fluorescence bands, which is observed for the investigated series of *meso*-phenyl substituted PdOEP molecules. Basing on the presented results, we can state that the increase in the number of *meso*-phenyl rings in the spatially distorted PdOEP molecule leads to the situation where, in ambient temperature liquid solutions, the  $\pi$ -conjugated porphyrin macrocycle is labile in the excited  $S_1$  and  $T_1$  states and relaxes to a non-planar conformation. This non-planar conformation is most favorable energetically, and its position in the energy scale determines the spectral-kinetic characteristics of the excited states examined experimentally by us. In this low-energy conformation one should expect the increase of the rate constants ( $d$ ) of internal conversion  $S_1 \sim S_0$  and intersystem crossing  $S_1 \sim T_1$  (rate constant  $r$ ) [20,22,31,32] due to the energy-gap rule and the increase of Franck–Condon factor for non-radiative transitions [44]. Thus, upon sequential increase of the number of *meso*-phenyl rings in PdOEP molecule, a gradual enhancement of the non-radiative channels  $S_1(A) \sim S_0$  and  $S_1(A) \sim T_1$  should take place leading to additional fluorescence quenching. Experimentally, this effect is observed as a slight decrease of fluorescence quantum efficiency at 297 K in toluene (Table 1).

On the other hand, because of extremely short deactivation time of the  $S_1$  state for *meso*-phenyl substituted Pd-porphyrins ( $\tau_s = 13.6$  ps according to picosecond transient absorption data [9])

an additional decrease of  $\tau_s$  values for sterically hindered PdOEP-5,10Ph, PdOEP-5,10,15Ph and PdOEP-5,10,15,20Ph molecules are hardly to be detected. It is explained by the fact that due to two reasons (heavy atom inner effect and the influence of a non-filled  $d_{x^2-y^2}$  orbital of the Pd central ion) Pd-complexes are characterized by high efficiency of the  $S_1 \sim \sim > T_1$  intersystem crossing. These issues have been discussed by us earlier in detail [24,33]. Therefore, below we will pay more attention to deactivation of triplet states for sterically hindered *meso*-phenyl substituted PdOEP molecules.

### 3.2. Triplet state deactivation in a wide temperature range

Experimental data obtained for phosphorescence decay times of planar and non-planar Pd-porphyrins in degassed solutions upon temperature lowering from 293 K to 80 K are summarized in Table 2. It is evident that in liquid solution at ambient temperature, the most pronounced changes in the rate constants of relaxation processes are observed for the triplet states of PdOEP derivatives upon increasing the number of *meso*-phenyl substituents, while for planar PdOEP and PdTPP molecules  $\tau_T$  values are typical of various planar Pd-porphyrins studied before [9,24,33]. Two main effects are of interest upon analysis of these results: i) the influence of steric interactions of bulky side substituents (*meso*-phenyls and  $\beta$ -ethyls) and non-planarity effects in liquid solution at ambient temperature, and ii) the influence of the solvent viscosity increase when going to low temperature and formation of rigid glassy matrix.






Data collected in Table 2 reveal that in degassed liquid solution at 293 K the phosphorescence decay time for planar PdOEP molecule is at least  $\tau_T = 210.7 \mu\text{s}$  and is the same practically as for PdTPP ( $\tau_T = 208.5 \mu\text{s}$ ). Thus, the influence of *meso*-phenyl rings on deactivation of triplet states in planar Pd-porphyrin macrocycle is not manifested, while spectral properties are more sensitive to this substitution (discussed above). In contrast, one *meso*-phenyl substitution in the case of PdOEP molecule (being planar in  $S_0$  state!) leads to a drastic shortening of monoexponential  $\tau_T$  values

to  $0.2 \mu\text{s}$ . From the considerations presented above it means that the  $T_1$  state decay time strong shortening is caused by the temporal dynamics of conformational rearrangements of the macrocycle in the excited  $T_1$  state. Sequential increase of the number of *meso*-phenyl substituents (transition to PdOEP-5,10,15,20Ph molecule, which is not planar even in  $S_0$  state) are characterized by further shortening of the phosphorescence monoexponential decay time, to  $\tau_T = 0.04 \mu\text{s}$ . Such a behavior reflects the increase of the conformational dynamics in the excited triplet state which leads to the drastic increase of the non-radiative relaxation pathways of the triplet states. It should be mentioned in this respect, that the results obtained for free bases of *meso*-phenyl substituted octaethyl- or octamethylporphyrins (OEP-5,10Ph; OEP-5,15Ph; OMP-5Ph; OMP-5,10Ph; OMP-5,15Ph, OMP-5,10,15Ph [9,31] and 5,15-diaryloctaalkylporphyrins [21]) have shown biexponential decays of triplet states. This may be connected with co-existence of two different non-planar conformations in the triplet state. Therefore, for free bases of *meso*-phenyl substituted OEP molecules, it means from the photophysical point of view that, being in the long-lived triplet state in one conformation, the distorted porphyrin macrocycle can further undergo an additional structural reorganization to the other, energetically favorable non-planar conformation with a smaller energy gap  $\Delta E(T_1-S_0)$  and thus characterized by a larger rate constant of the non-radiative deactivation of its triplet state. On the other hand, in our case, for non-planar *meso*-phenyl substituted PdOEP molecules, the absence of multiexponential decay of the triplet states at low pulse excitation (thus excluding non-linear and two-photon effects) may be explained by relatively more rigid (and thus less flexible) non-planar conformation due to the presence of a central Pd ion (quantum-chemical consideration of such influence is underway in our group) or an extremely short lifetime of intermediate conformation, that is beyond the time resolution of our experimental setup.

Upon temperature lowering, a monotonous increase of measured  $\tau_T$  values is observed for all compounds (Table 2). Interestingly, at 80–100 K in a rigid glassy matrix (glass formation temperature  $T = 137\text{K}$ ) phosphorescence lifetimes  $\tau_T$  for three

**Table 2**

Temperature dependence of the phosphorescence decay time  $\tau_{\text{ph}}$  for planar and non-planar porphyrins (the corresponding structures are shown in Fig. 1) in degassed 2-methyl-tetrahydrofuran at  $\lambda_{\text{exc}} = 542 \text{ nm}$ .

	Compound Pictogram	PdOEP	PdTPP	PdOEP-5Ph	PdOEP-5,10,15,20Ph	
						
	T, K	$\tau_{\text{ph}}, \mu\text{s}$	$\tau_{\text{ph}}, \mu\text{s}$	$\tau_{\text{ph}}, \mu\text{s}$	$\tau_{\text{ph}}, \mu\text{s}$	
	Steric hindrance and non-planarity effects $\longrightarrow$					
Temperature lowering effects 	<b>293</b>	<b>210.7</b>	<b>208.5</b>	<b>0.2</b>	<b>0.04</b>	
	250	298.7	281	0.6	0.27	
	210	–	425	3.3	2.8	
	190	698.9	605	11.0	13.8	
	170	1043.6	807	53.2	55.6	
	150	1634.7	880	367.0	132.4	
	140	1695.9	928	1206.4	188.9	
		Glass transition of the solvent ( $T = 137\text{K}$ ) $\downarrow$				
	120	1830.7	1149.8	1478.6	227.5	
	100	1959.4	1399	1600.4	349.9	
79	–	1384.5	–	442.2		

*Note:* Detection conditions are the following:  $\lambda_{\text{det}} = 660 \text{ nm}$  for PdOEP,  $\lambda_{\text{det}} = 690 \text{ nm}$  for PdTPP,  $\lambda_{\text{det}} = 660 \text{ nm}$  for PdOEP-5Ph and  $\lambda_{\text{det}} = 705 \text{ nm}$  for PdOEP-5,10,15,20Ph. Decay times  $\tau_{\text{ph}}$  were measured at 0-0 band maxima of phosphorescence spectra by the pulse method using Lambda Physik FL-2002 dye laser ( $\lambda_{\text{exc}} = 542 \text{ nm}$ , the experimental response  $\Delta t_{1/2} = 25 \text{ ns}$  FWHM).

compounds PdOEP, PdTPP and PdOEP-5Ph are almost the same, in the range of  $\sim 1400\text{--}1900\ \mu\text{s}$ , while for PdOEP-5,10,15,20Ph this value is essentially shorter,  $\tau_T = 442\ \mu\text{s}$ . In order to analyze these findings with respect to various mechanisms responsible for the rise of  $\tau_T$  values upon temperature lowering, data summarized in Table 2 have been presented in Arrhenius coordinates  $\ln(k) = f(1/T)$ , and  $\ln(k) = \ln(1/\tau_T)$ , where  $k$  is the rate constant of triplet state deactivation (see Fig. 4):

$$\ln(k) = \ln(1/\tau_T) = \ln A - E_a/RT, \quad (2)$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant,  $RT$  is the average kinetic energy [43]. Since  $A$  multiplies the exponential term, its value clearly contributes to the value of the rate constant. Typically eq. (2) corresponds to a straight line whose slope is  $-E_a/R$ . This approach gives a simple way of determining the activation energy  $E_a$  from the values of  $k$  observed at different temperatures:

$$E_a = \ln\left(\frac{k_2}{k_1}\right) / \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

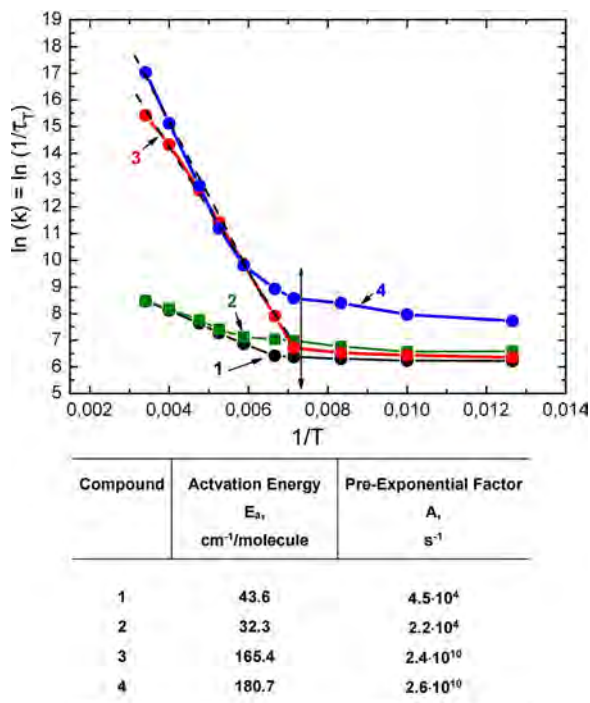
The  $E_a$  and  $A$  values calculated using this approach for compounds under study are presented in Fig. 4. It is seen from Fig. 4 that upon temperature lowering, down to the glass transition temperature of the solvent ( $T = 137\ \text{K}$ , shown by solid arrow) the Arrhenius plots are linear for all compounds. For planar PdOEP and PdTPP molecules, the slopes of these plots are practically the same, while for *meso*-phenyl substituted PdOEP-5Ph and PdOEP-5,10,15,20Ph molecules the observed slopes are essentially larger, and the largest one is obtained for the non-planar PdOEP-5,10,15,20Ph. As for planar PdOEP and PdTPP molecules, the decrease of the observed  $k$  values upon temperature lowering (that is the increase of the phosphorescence decay time  $\tau_T$ ) reflects a

well-known temperature dependence of the non-radiative rate constant for other planar free bases and metalloporphyrins (including Pd-complexes) [24,33,34]. In addition, temperature lowering leads to the suppression of the electron-phonon coupling and other non-radiative channels of the triplet state deactivation. It is seen from Fig. 4 that transition to the rigid matrix below  $T = 137\ \text{K}$  does not lead to a further decrease of  $k$  values for planar PdOEP and PdTPP molecules (as was mentioned above, phosphorescence decay times  $\tau_T$  are almost the same for these molecules in rigid degassed 2-methyl-tetrahydrofuran). It means that the increase of solvent viscosity and rigidity may also play some (minor) role in the non-radiative deactivation of triplet states of planar porphyrins. The activation energies evaluated from linear plots are  $E_a = 43.6$  and  $32.3\ \text{cm}^{-1}/\text{molecule}$  for PdOEP and PdTPP, respectively.

For PdOEP-5Ph and PdOEP-5,10,15,20Ph molecules the obtained values of the activation energy are essentially higher:  $E_a = 165.4$  and  $180.7\ \text{cm}^{-1}/\text{molecule}$ . In addition, it is seen from data summarized in Fig. 4 that in the latter case the values of the pre-exponential factor  $A$  are higher by few orders of magnitude compared to those for planar PdOEP and PdTPP molecules. These results clearly demonstrate that the rate constants of the non-radiative deactivation of triplet states for PdOEP-5Ph and PdOEP-5,10,15,20Ph are strongly temperature-dependent and this dependence is more pronounced, as compared to that for planar Pd-porphyrins in the same temperature range.

The overall interpretation of these findings should be based on the analysis of conformational dynamics of these molecules in the excited triplet as well as in the ground states in liquid solutions at ambient temperature. As was shown for the first time for free bases of *meso*-phenyl substituted OEP molecules [29,30] and mentioned above, the conformational dynamics of the porphyrin macrocycle in  $T_1$  state is governed by steric interactions of bulky  $\beta$ -alkyl substituents of  $\pi$ -conjugated macrocycle with the increasing number of *meso*-phenyl rings. According to quantum-chemical considerations [28] in the case of mono-*meso*-phenyl substituted OEP-5Ph in the triplet excited state, the barrier height of the transition into a non-planar conformation, as well as the energy of the  $T_1$  state for this form depend on the nature of the substituents on the pyrrole rings and on the initial degree of distortion of the porphyrin macrocycle. In this case the decrease in the lifetime of the  $T_1$  state is related with the enhancement of the non-radiative deactivation channel  $T_1 \sim S_0$  due to the lowering of the energy of  $T_1$  state. In addition, as was discussed in [31], the distortion of porphyrin macrocycle and the change in hybridization of atoms accompanied by activation of out-of-plane vibration modes lead to the increase of the rate constant of  $T_1 \sim S_0$  transition due to several reasons: i) the increase in contributions from one-center integrals of  $n$ -orbitals of central nitrogen atoms and  $\pi$ -orbitals of the non-planar porphyrin macrocycle, and ii) the enhancement of spin-orbit interaction matrix elements  $\langle S_1|H_{SO}|T_1 \rangle$  and  $\langle T_1|H_{SO}|S_0 \rangle$ , which activates the strictly forbidden singlet-triplet transitions [45].

We believe that in the case of OEP-5Ph both these reasons may act, also causing the decrease of phosphorescence efficiency and the drastic shortening of the triplet state decay time in liquid degassed 2-methyl-tetrahydrofuran at 293 K. Therefore, upon temperature lowering the gradual increase of solvent viscosity prevents progressively the rotational mobility of the *meso*-phenyl ring in the triplet excited OEP-5Ph molecule. In turn, this leads to a weakening of steric interactions of this ring with bulky  $\beta$ -ethyl substituents of the  $\pi$ -conjugated macrocycle. As a consequence, the conformational dynamics leading to non-planarity of the porphyrin macrocycle in  $T_1$  state becomes less probable. Fig. 4 shows that the effect of the temperature lowering on the rise of  $k$  values is significantly larger for OEP-5Ph compared to PdOEP and PdTPP molecules. Thus, it may be concluded for OEP-5Ph that upon



**Fig. 4.** Arrhenius plots of temperature dependent phosphorescence decay time for PdOEP (1,  $\lambda_{\text{det}} = 660\ \text{nm}$ ), PdTPP (2,  $\lambda_{\text{det}} = 690\ \text{nm}$ ), PdOEP-5Ph (3,  $\lambda_{\text{det}} = 660\ \text{nm}$ ) and PdOEP-5,10,15,20Ph (4,  $\lambda_{\text{det}} = 705\ \text{nm}$ ) in degassed 2-methyl-tetrahydrofuran at  $\lambda_{\text{exc}} = 542\ \text{nm}$ . Glass transition temperature for the solvent ( $T = 137\ \text{K}$ ) is shown by a thin solid arrow. Linear fits for PdOEP-5Ph (3) and PdOEP-5,10,15,20Ph (4) before the glass transition of the solvent are shown by dashed lines. Bottom: Activation energies  $E_a$  and pre-exponential factors  $A$  derived from linear fits for the compounds.



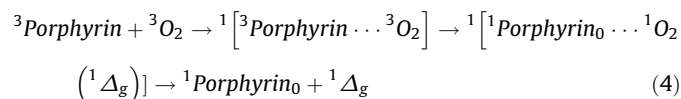
temperature changes, steric hindrance effects play a dominant role in the non-radiative relaxation of the triplet states in comparison with the electron-phonon coupling interactions. Interestingly, as we mentioned above, in rigid glassy matrix at 79–100 K the  $k$  values are practically the same for planar PdOEP, PdTPP, and PdOEP-5Ph. It means that OEP-5Ph, being planar in  $S_0$  state and non-planar in the excited triplet state at ambient temperature, undergoes the transition to the presumably planar conformation in  $T_1$  upon temperature lowering.

A comparative analysis of the temperature dependence of  $k$  values for PdOEP-5,10,15,20Ph molecule (non-planar both in ground and excited states) shows that the slope of the Arrhenius plot is a little bit larger compared to that for PdOEP-5Ph. Following the above conclusions it reflects also the dominant influence of steric hindrance effects in the non-radiative relaxation of the triplet states for the non-planar PdOEP-5,10,15,20Ph. Notably, in rigid glassy matrix at 80–100 K for the latter molecule the  $k$  value is noticeably higher compared to that found for PdOEP-5Ph (which is planar in  $T_1$  state in these conditions). It immediately leads to the conclusion that upon increase of the number of *meso*-phenyl substituents, sterically hindered PdOEP-5,10,15,20Ph molecule remains non-planar even at low temperatures in rigid matrices. Quantitative quantum-chemical description of steric hindrance effects for these compounds is underway.

### 3.3. Interaction with molecular oxygen

Interaction of tetrapyrrolic molecules (including spatially distorted  $\pi$ -conjugated macrocycles) with molecular oxygen in oxygenated liquid solutions at ambient temperature is not only of fundamental, but also of practical interest, especially in the photodynamic therapy of cancer [4,6,7]. Taking into account the experimental results and conclusions presented above, here we would like to discuss some aspects of the photosensitized singlet oxygen generation by the studied sterically hindered PdOEP molecules.

Typically in liquid solutions, the photosensitized production of active singlet oxygen ( $^1O_2$ ) in a long-living  $^1\Delta_g$  electronic state takes place via the interaction of a light-activated organic molecule (the so-called photosensitizer, Pd-porphyrins in our case) with molecular oxygen,  $O_2$ . As a result, the excited states of the porphyrin molecule, particularly the longer-lived triplet  $T_1$  state, are efficiently quenched by  $O_2$ . It is well-documented [46], that the process of  $T_1$ -states quenching by  $O_2$  occurs via non-radiative transitions between electronic states in an intermediate short-living weak collision complex formed as a result of a diffusion contact of a given excited organic molecule with an oxygen molecule. From this point of view and taking into account Wigner spin conservation rule (transitions between terms of the same multiplicity are spin-allowed) [47], the quenching of  $T_1$  state of the porphyrin molecule ( $^3\text{Porphyrin}$ ) followed by the formation of singlet oxygen,  $^1O_2$  (or  $^1\Delta_g$ ) may take place via one way:



In the case of porphyrins and chlorins as photosensitizers, the relation  $k_{\text{dis}} \approx k_S$  is used (where  $k_{\text{dis}}$  is the rate constant of the collision complex dissociation,  $k_S$  is the bimolecular rate constant of  $S_1$  state quenching by  $O_2$ ). In addition, reaction (4) of  $^1O_2$  generation corresponds to the case when  $k_T = (1/9) \cdot k_S$ , where  $k_T$  is the bimolecular rate constant of  $T_1$ -state quenching by molecular oxygen [46].

We should pay briefly the reader's attention to the following: i) what are specific differences observed between the planar and

distorted PdOEP molecule interacting with molecular oxygen, and ii) how does the number of *meso*-phenyl rings in a series of PdOEP molecules change the efficiency of singlet oxygen generation ( $\gamma_\Delta$ ). The corresponding experimental kinetic data as well as quantum yields of singlet oxygen generation by Pd-complexes measured in this study in toluene saturated with air at ambient temperature are given in Table 3. It is seen from Table that, starting from planar PdOEP, upon sequential increase in the number of *meso*-phenyl rings in PdOEP molecules, steric interactions of bulky substituents in the excited triplet states of Pd-octaethylporphyrins manifest themselves as the sequential decrease of the rate constants of non-radiative intersystem crossing  $T_1 \sim S_0$  (i.e.  $\tau_T$  decay time shortening) and the corresponding strong decrease of singlet oxygen generation quantum yield values  $\gamma_\Delta$ . In the case of the essentially non-planar PdOEP-5,10,15,20Ph the quantum yield value  $\gamma_\Delta$  is  $\sim 20$  times smaller than that measured for planar PdOEP. Comparative analysis of the data presented in Table 3 with results published in [9,19,29,31,32] shows that the same tendencies are characteristic of the sequential increase in the number of *meso*-phenyl rings in OEP molecules (free bases). The only difference is that for 5,10Ph and 5,10,15Ph substitution  $\gamma_\Delta$  values measured for Pd-complexes are noticeably higher than those found for the corresponding free bases. This difference may be explained by relatively rigid non-planar conformations for Pd-complexes compared to free bases as well as higher values of intersystem crossing  $S_1 \sim T_1$  efficiencies known for Pd-porphyrins (discussed above). In addition, it should be mentioned that our earlier results on planar and spatially distorted *meso*-phenyl substituted OEP molecules have shown [31] that the rate constants of quenching of excited singlet ( $k_S = (1.4 - 1.6) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and triplet ( $k_T = (1.0 - 1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) states are close to each other, respectively, for planar and spatially distorted octaalkylporphyrins. It means that the interaction of these free bases with molecular oxygen depends weakly on the character and degree of the non-planar distortion of *meso*-phenyl substituted tetrapyrrole macrocycle. The same situation may be extrapolated to Pd-complexes under study. Thus, the basic reason of the lowering of singlet oxygen generation quantum yields  $\gamma_\Delta$  upon sequential increase in the number of *meso*-phenyl rings both in PdOEP and OEP molecules is explained to the increase of the non-planarity effects in tetrapyrrole macrocycle, leading to the decay time drastic shortening for excited triplet states.

**Table 3**

Triplet state decay times for planar PdOEP and non-planar *meso*-phenyl substituted PdOEP molecules with sequential increase of the number of *meso*-phenyl substituents in oxygenated toluene at ambient temperature.

Compound	$\tau_T$ , ns	$g_D$
PdOEP	239.8	0.93
PdOEP- 5Ph	133.0	0.54
PdOEP- 5,15Ph	155.1	0.55
PdOEP- 5,10Ph	99.1	0.19
OEP- 5,10,15Ph	101.0	0.12
PdOEP- 5,10,15,20Ph	89.7	0.05

Note: In liquid solutions at 293 K, triplet state decays were measured using a laboratory experimental set-up, described in details in [29,30]. Samples were excited by the pulses of the second harmonic of the YAG:Nd<sup>3+</sup> pulse solid laser ( $\lambda_{\text{ex}} = 532 \text{ nm}$ , the energy density of  $E = 0.3\text{--}3.0 \text{ mJ cm}^{-2}$  with a dispersion of  $\pm 5\%$ , the pulse duration  $\Delta t_{1/2} = 15 \text{ ns FWHM}$ ). The probing of induced absorption was performed by a filament lamp of KGM type. The recording system based on a diffraction monochromator, detectors (a photomultiplier FEU-84 or germanium photodiode FD-10GA) and a digital oscilloscope S9-8 connected with a personal computer, allowed to register a transient absorption optical density down to  $\Delta D \sim 10^{-4}$  with a temporal resolution up to 50 ns in visible and near-IR (850–1660 nm) region.  $\Delta D$  values were obtained for more than 64 laser pulses and then averaged and extrapolated to the maximal pulse intensity, the relative error of  $\Delta D$  measurements did not exceed  $\pm 5\%$ .

These results should be taken into account when searching for new Pd-containing tetrapyrrolic compounds for the purposes of photodynamic therapy [48].

#### 4. Conclusions

For Pd-octaethylporphyrin molecules (PdOEP) with a sequential increase of the number of *meso*-phenyl substituents we have succeeded to carry out spectral-kinetic, pump-probe and phosphorescent measurements in a wide temperature range (80–293 K) going from liquid solutions at ambient temperature (in toluene or 2-methyl-tetrahydrofuran) to glassy rigid matrices at  $T < 137$  K (2-methyl-tetrahydrofuran). We have found also that the sequential transition from a planar PdOEP molecule to the set of sterically hindered compounds PdOEP → PdOEP-5,15Ph → PdOEP-5,10Ph → PdOEP-5,1015Ph → PdOEP-5,10,15,20Ph manifests itself in the noticeable shortening of triplet state lifetimes (from 210 ms to 0.04 ms in degassed 2-methyl-tetrahydrofuran at 293 K) and in the pronounced decrease of the efficiency of singlet oxygen generation (from 1.0 down to 0.05 in oxygenated toluene solutions). Based on the whole set of experimental data and the analysis of Arrhenius plots for rate constants for the overall deactivation of triplet state the detailed picture of steric interactions between bulky *meso*-phenyls and peripheral  $\beta$ -alkyl substituents of pyrrole ring has been elucidated and the main reasons for the essential shortening of the triplet state lifetime have been discussed for compounds under study.

#### Acknowledgements

The research has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 645628 as well from Belarussian State Program for Scientific Research "Convergence–2020 3.03" and "Convergence–2020 3.01".

#### References

- [1] S. Wörmke, S. Maćkowski, T.H.P. Brotsudarmo, C. Jung, A. Zumbusch, M. Ehrl, H. Scheer, E. Hofmann, R.G. Hiller, C. Bräuchle, Monitoring fluorescence of individual chromophores in peridinin–chlorophyll–protein complex using single molecule spectroscopy, *Biochim. Biophys. Acta–Bioenergy* 1767 (2007) 956–964.
- [2] A. Gall, C. Ilioaia, T.P.J. Kruger, V.I. Novoderezhkin, B. Robert, R. van Grondelle, Conformational switching in a light-harvesting protein as followed by single-molecule spectroscopy, *Biophys. J.* 108 (2015) 2713–2720.
- [3] Sh. Farooq, J. Chmeliov, G. Trinkunas, L. Valkunas, H. van Amerongen, Is there excitation energy transfer between different layers of stacked photosystem-II-containing thylakoid membranes? *J. Phys. Chem. Lett.* 7 (2016) 1406–1410.
- [4] M.O. Senge, Highly substituted porphyrins: synthesis and organic chemistry, in: M. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, V.1, Acad. Press, New York, 2000, pp. 240–348.
- [5] Z. Shi, R. Franco, R. Haddad, J.A. Shelnutt, G.C. Ferreira, The conserved active-site loop residues of ferrocyclase induce porphyrin conformational changes necessary for catalysis, *Biochemistry* 45 (2006) 2904–2912.
- [6] E.I. Zenkevich, C. von Borczyskowski, Formation principles and excited states relaxation in self-assembled complexes: multiporphyrin arrays and semiconductor CdSe/ZnS quantum dot-porphyrin nanocomposites, in: K. Kadish, K.M. Smith, R. Guilard (Eds.), *Handbook of Porphyrin*, V. 22, World Scientific Publishing Co. Pte. Ltd., Singapore 596224, 2012, pp. 68–159.
- [7] Y. Terazono, T.A. Moore, A.L. Moore, D. Gust, in: D. Kim (Ed.), *Light Harvesting, Excitation Energy/Electron Transfer, and Photoregulation in Artificial Photosynthetic Systems*, Pan Stanford Publishing Pte. Ltd., Singapore, 2012, pp. 349–388.
- [8] M.T. Colvin, A.B. Ricks, A.M. Scott, A.L. Smeigh, R. Carmieli, T. Miura, M.R. Wasielewski, Magnetic field-induced switching of the radical-pair intersystem crossing mechanism in a donor-bridge-acceptor molecule for artificial photosynthesis, *J. Am. Chem. Soc.* 133 (2011) 1240–1243.
- [9] E.I. Zenkevich, Deactivation of excited states in nanostructures containing Copper porphyrin subunit, *Macrocyclic Chem.* 9 (2016) 121–140.
- [10] E.I. Zenkevich, C. von Borczyskowski, Self-organization principles in the formation of multiporphyrin complexes and semiconductor quantum dot-Porphyrin nanoassemblies, *J. Porphyrins Phthalocyanines* 18 (2014) 1–19.
- [11] O. Osifeko, T. Nyokong, Photophysical behaviour of metallophthalocyanines when doped onto silica nanoparticles, *Dyes Pigm.* 131 (2016) 186–200.
- [12] M. Maiuri, J.J. Snellenburg, I.H.M. van Stokkum, S. Pillai, K. Wongcarter, D. Gust, T.A. Moore, A.L. Moore, R. van Grondelle, G. Cerullo, D. Polli, Ultrafast energy transfer and excited state coupling in an artificial photosynthetic antenna, *J. Phys. Chem. B* 117 (2013) 14183–14190.
- [13] T. Lazarides, D. Dafnomili, G. Charalambidis, G. Landrou, A. Kahnt, R.P. Sabatini, D.W. McCamant, D.T. Gryko, A.G. Coutsolelos, D.M. Guldi, Photoinduced charge transfer in porphyrin–cobaloxime and corrole–cobaloxime hybrids, *J. Phys. Chem. C* 117 (2013) 165–1647.
- [14] J.A. Shelnutt, J.-G. Ma, S.-L. Jia, W. Jentzen, C.J. Medforth, Nonplanar porphyrins and their significance in proteins, *Chem. Soc. Rev.* 27 (1998) 31–42.
- [15] Cr.J. Medforth, P.E. Berget, J.C. Fettingter, K.M. Smith, J.A. Shelnutt, Determination of the activation energies for Nd tautomerism and anion exchange in a porphyrin monocation, *J. Porphyrins Phthalocyanines* 20 (2016) 307–317.
- [16] I. Rozas, M.O. Senge, A two-pronged attack on DNA: targeting guanine quadruplexes with nonplanar porphyrins and DNA-binding small molecules, *Future Med. Chem.* 8 (2016) 609–612.
- [17] W. Jentzen, J.-G. Ma, J.A. Shelnutt, Conservation of the conformation of the porphyrin macrocycle in hemoproteins, *Biophys. J.* 74 (1998) 753–763.
- [18] M.O. Senge, C.J. Medforth, T.P. Forsyth, D.A. Lee, M.M. Olmstead, W. Jentzen, R. K. Pandey, J.A. Shelnutt, K.M. Smith, Comparative analysis of the conformations of symmetrically and asymmetrically deca- and undecasubstituted porphyrins bearing *meso*-Alkyl or -Aryl groups, *Inorg. Chem.* 36 (1997) 1149–1163.
- [19] V.N. Knyukshto, E.I. Sagun, A.M. Shulga, S.M. Bachilo, E.I. Zenkevich, Dynamic relaxation of triplet states for mono- and di-*meso*-arylsubstituted porphyrins and their chemical dimers, *J. Appl. Spectrosc.* 65 (1998) 487–491.
- [20] V.S. Chirvony, A. van Hoek, V.A. Galievsky, I.V. Sazanovich, T.J. Schaafsma, D. Holten, Comparative study of the photophysical properties of nonplanar tetraphenylporphyrin and octaethylporphyrin diacids, *J. Phys. Chem. B* 104 (2000) 9909–9917.
- [21] J. Andreasson, H. Zetterqvist, J. Kajanus, J. Martensson, B. Albinsson, Efficient non-Radiative deactivation and conformational flexibility of meso-diaryloctaalkylporphyrins in the excited triplet state, *J. Phys. Chem. A* 104 (2000) 9307–9314.
- [22] J.L. Retsek, C.J. Medforth, D.J. Nurco, S. Gentemann, V.S. Chirvony, K.M. Smith, D. Holten, Efficient non-Radiative deactivation and conformational flexibility of meso-diaryloctaalkylporphyrins in the excited triplet state, *J. Phys. Chem. B* 105 (2001) 6396–6411.
- [23] S.G. Pukhovskaya, L.S. Guseva, A.S. Semeikin, E.M. Kuvshinova, O.A. Golubchikov, Extra-coordinating properties of spatially distorted zinc porphyrins, *Zhurn. Neorg. Khimii* 50 (2005) 635–639 (in Russian).
- [24] V.N. Knyukshto, A.M. Shulga, E.I. Sagun, E.I. Zenkevich, Spectral manifestations of the splitting of the lowest triplet levels in Pd-complexes of non-symmetric porphyrins, *Opt. Spectrosc.* 101 (2006) 895–901.
- [25] S. Tewari, R. Das, A. Chakraborty, R. Bhattacharjee, Resonance Raman study on distorted symmetry of porphyrin in nickel octaethyl porphyrin, *Pramana J. Phys.* 63 (2004) 1073–1077.
- [26] L.A. Yatsunyk, F.A. Walker, NMR and EPR spectroscopic and structural studies of low-spin (dxz, dyz)<sup>4</sup>(dxy)<sup>1</sup> ground state Fe(III) bis-tert-butylisocyanide complexes of dodecasubstituted porphyrins, *Inorg. Chem.* 43 (2004) 4341–4352.
- [27] H. Wasbotten, J. Conradie, A. Ghosh, Electronic absorption and resonance raman signatures of hyperporphyrins and nonplanar porphyrins, *J. Phys. Chem. B* 107 (2003) 3613–3623.
- [28] I.V. Avilov, E.I. Zenkevich, E.I. Sagun, I.V. Filatov, Quantum-chemical investigation of the conformational dynamics of the mono-*meso*-phenyl-substituted octaalkylporphyrins in the triplet excited state, *J. Phys. Chem. A* 108 (2004) 5684–5691.
- [29] V. Knyukshto, E. Zenkevich, E. Sagun, A. Shulga, S. Bachilo, Unusual dynamic relaxation of triplet-excited meso-phenyl-substituted porphyrins and their chemical dimers at room temperatures, *Chem. Phys. Lett.* 297 (1998) 97–108.
- [30] V. Knyukshto, E. Zenkevich, E. Sagun, A. Shulga, S. Bachilo, Unusual pathways of triplet state dynamic relaxation in meso-arylsubstituted porphyrins and their dimers at 295 K, *J. of Fluorescence* 10 (2000) 55–68.
- [31] E.I. Sagun, E.I. Zenkevich, V.N. Knyukshto, A.Y. Panarin, A.S. Semeikin, T.V. Lyubimova, Relaxation processes with participation of excited S1 and T1 states of spatially distorted meso-phenyl substituted octa-methylporphyrins, *Opt. Spectrosc.* 113 (2012) 388–400.
- [32] E.I. Sagun, E.I. Zenkevich, Comparative analysis of the influence of bulky  $\beta$ -alkyl substituents on fluorescent properties of spatially distorted meso-phenyl substituted porphyrins, *Opt. Spectrosc.* 115 (2013) 727–738.
- [33] G.D. Egorova, V.N. Knyukshto, K.N. Solovjev, M.P. Tsvirko, Intramolecular spin-orbit perturbations in ortho- and meta-halogen derivatives of tetraphenylporphyrin, *Opt. Spectrosc.* 48 (1980) 1101–1109.
- [34] V.N. Knyukshto, E.I. Sagun, A.M. Shulga, D.A. Starukhin, S.M. Bachilo, E.I. Zenkevich, Manifestation of non-planarity effects and charge-transfer interactions in spectral and kinetic properties of triplet states of sterically strained octaethylporphyrins, *Opt. Spectrosc.* 90 (2001) 67–77.
- [35] A.S. Starukhin, M. Kruk, R. Czerwieńec, Observation of the distorted form of Pd-porphin in single site spectra at low temperatures, *J. Luminesc.* 128 (2008) 531–536.

- [36] A.M. Shulga, G.V. Ponomarev, Synthesis of octapropylporphyrin by method of monopyrrole cyclotetramerization of 5-carboxy-2-metoxymethyl-3, 4-dipropylpyrrole, *Khimiya Heterocyclicheskikh Soedinenii*. (in Russian) 7 (1984) 922–927.
- [37] S.A. Syrbu, T.V. Lyubimova, A.S. Semeikin, Phenyl-substituted porphyrins. 1. Synthesis of meso-phenyl-substituted porphyrins, *Chem. Heterocycl. Comp.* 40 (2004) 1262–1270.
- [38] J.S. Lindsey, I.C. Schreiman, H.C. Hsu, A.M. Marguerettaz, Rothemund and Adler-Longo reactions revisited: synthesis of tetraphenylporphyrins under equilibrium conditions, *J. Org. Chem.* 52 (1987) 827–836.
- [39] A.D. Adler, F.R. Longo, F. Kampas, J. Kim, On the preparation of metalloporphyrins, *J. Inorg. Nucl. Chem.* 32 (1970) 2443–2445.
- [40] R. Schmidt, Ch. Tanielian, R. Dunsbach, W. Chr, Phenalenone, A universal reference compound for the determination of quantum yields of singlet oxygen O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) sensitization, *J. Photochem. Photobiol. A: Chem.* 79 (1994) 11–17.
- [41] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, 2009.
- [42] U. Becker, D. Bykov, D. Ganyushin, A. Hansen, R. Izsak, D.G. Liakos, C. Kollmar, S. Kossmann, D.A. Pantazis, T. Petrenko, C. Reimann, C. Riplinger, M. Roemelt, B. Sandhofer, I. Schapiro, K. Sivalingam, B. Wezisa, Orca 2.9, Max Planck Institute for Bioinorganic Chemistry, Mulheim, 2012.
- [43] V.N. Knyukshto, A.M. Shulga, E.I. Sagun, E.I. Zenkevich, Formation of intersystem crossing transitions in Pd(II)- and Pt(II)-porphyrins: nonplanar distortions of the macrocycle and charge transfer states, *Opt. Spectrosc.* 100 (2006) 590–601.
- [44] N. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing, Menlo Park, 1978, pp. 153–198.
- [45] M.K. Bowman, Intersystem crossing in photosynthetic pigments, *Chem. Phys. Lett.* 48 (1977) 17–21.
- [46] O.L.J. Gijzeman, E. Kaufman, G. Porter, Oxygen quenching of aromatic triplet states in solution. Part 2, *J. Chem. Soc. Farad. Trans. II* 69 (1973) 721–726.
- [47] IUPAC, *Compendium of Chemical Terminology*, 2nd ed., (2017) (the Gold Book). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006) created by M. Nic, J., Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0–9678550–9–8. 10.1351/goldbook.
- [48] V.S. Tyurin, D.R. Erzina, I.A. Zamilatskov, A.Y. Chernyadyev, G.V. Ponomarev, D. V. Yashunskiy, A.V. Maksimova, K.V. Neverov, A.S. Kozlov, A.A. Krasnovsky, A.Y. Tsvadze, Palladium complexes of azomethine derivatives of porphyrins as potential photosensitizers, *Macroheterocycles* 9 (4) (2016) 462–469, doi: <http://dx.doi.org/10.6060/mhc161073k>.