

Structural Dynamics and Relaxation Processes with Participation of Excited Singlet and Triplet States in Sterically Hindered Porphyrins and Their Chemical Dimers

Eduard I. Zenkevich

Dedicated to the Corresponding member of Russian Academy of Sciences Prof. Oscar Koifman on the occasion of his 70th Birthday

National Technical University of Belarus, Department of Information Technologies and Robotics, 220013 Minsk, Belarus
E-mail: zenkev@tut.by

Paper presents an overview of mutual Belarussian-Russian collaboration in the field of sterically hindered porphyrins compared with the relevant literature data. Typically, the conformational dynamics of a non-planar tetrapyrrole macrocycle at 295 K manifests itself in bathochromic absorption and fluorescence shifts ($\Delta\nu \sim 1100 \text{ cm}^{-1}$), the increase of the Stokes shift ($\Delta\nu_s \sim 900 \text{ cm}^{-1}$), broadened emission and the fluorescence strong quenching. Nevertheless, the T_1 states dynamics upon steric interactions and porphyrin non-planarity remained to be not studied yet. We found for the first time that mono- and di-meso-phenyl substitution in octaethylporphyrins led to a drastic shortening of T_1 decays ($\sim 1.5 \text{ ms} \rightarrow 2-5 \mu\text{s}$) in deaerated solutions at 295 K without considerable influence on spectral-kinetic parameters of singlet states. These effects have been systematically studied for porphyrins and their chemical dimers with a controllable structure of meso-phenyl substituents as well as for meso-phenyl-substituted octaarylporphyrins with increasing number ($n=1-4$) of meso-phenyl rings. In some cases, quantum-chemical calculations have been used to explain experimental findings. Paper contains also some recent results showing what circumstances should be taken into account when using these compounds in various areas (excited state deactivation in multiporphyrin complexes, photoinduced electron transfer, singlet oxygen generation).

Keywords: Porphyrins, porphyrin chemical dimers, singlet and triplet excited states, steric effects, non-planar distortions, non-radiative transitions, photoinduced electron transfer, singlet oxygen generation.

Структурная динамика и релаксационные процессы с участием возбужденных синглетных и триплетных состояний в стерически затрудненных порфиринах и их химических димерах

Э. И. Зенькевич

Посвящается Член-корреспонденту РАН Оскару Иосифовичу Койфману по случаю его 70-летнего юбилея

Белорусский национальный технический университет, факультет информационных технологий и робототехники, 220013 Минск, Беларусь
E-mail: zenkev@tut.by

В статье представлен обзор результатов совместного белорусско-российского сотрудничества в исследовании стерически затрудненных порфиринов с привлечением литературных данных из других источников. Как правило, конформационная динамика непланарного тетрапиррольного макроцикла при 295 К проявляется в bathochromic смещении поглощения и флуоресценции ($\Delta\nu \sim 1100 \text{ см}^{-1}$), увеличении стоковского сдвига ($\Delta\nu_s \sim 900 \text{ см}^{-1}$), уширении полос флуоресценции и сильном тушении свечения. Однако динамика триплетных состояний T_1 при стерических взаимодействиях и непланарных искажениях макроцикла оставалась не исследованной. Мы впервые показали, что моно- и ди-мезо-фенильное замещение в октаэтилпорфиринах приводит к существенному сокращению времени жизни T_1 состояний $\sim 1.5 \text{ мс} \rightarrow 2-5 \text{ мкс}$ в обескислороженных растворах при 295 К без

значительного влияния на спектрально-кинетические параметры синглетных состояний. Эти эффекты были систематически исследованы для порфиринов и их химических димеров с контролируемой структурой мезо-фенильных заместителей, а также для мезо-фенил-замещенных октаарилпорфиринов с возрастающим числом ($n=1\div 4$) мезо-фенильных колец. В некоторых случаях для объяснения экспериментальных результатов были выполнены квантово-химические расчеты.

Статья содержит также ряд последних результатов, показывающих, какие принципиальные моменты следует учитывать при использовании соединений такого рода в различных исследованиях (деактивация возбужденных состояний в мультипорфириновых комплексах, фотоиндуцированный перенос электрона, генерация синглетного кислорода).

Ключевые слова: Порфирины, химические димеры порфиринов, синглетное и триплетное возбужденные состояния, стерические эффекты, непланарные искажения, безызлучательные переходы, фотоиндуцированный электронный перенос, генерация синглетного кислорода.

Introduction

At the moment, chemistry, photophysics and supramolecular chemistry of tetrapyrrole compounds is of growing interest. Firstly, it opens the possibilities to model primary light-induced processes of natural photosynthesis^[1-5] and, secondly, is a basis for the development of functional devices in molecular electronics, nanotechnologies, sensorics and biomedicine.^[6-12] In this respect, two principal peculiarities characteristic for tetrapyrrole macrocycles should be mentioned. 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, signaling to photosynthesis, *etc.*^[13] In addition to their basic macrocycle properties, *i.e.*, coordination properties and functional groups their conformation is of significant relevance for the biological function.^[14] This is based on the hypothesis that fine-tuning of the macrocycle conformation by the protein scaffold is one way by which nature might control the physicochemical properties of the cofactors in intact tetrapyrrole-protein complexes. It means that the structural organization of tetrapyrrole complexes *in vivo*, in which chromophore molecules are in nonplanar labile conformations, is a tool of subtle controlling enzymatic and photocatalytic properties of natural porphyrins.^[14-19] Under these conditions, observed changes in spectral-luminescent properties, as well as in redox characteristics of interacting subunits, can be caused not only by purely electronic effects in natural nanoassemblies but also by changes in the spatial structure of the tetrapyrrole macrocycle itself. In fact, tetrapyrrole macrocycle conformations have been identified in porphyrin protein complexes.^[20,21]

On the other hand, the intense development of supramolecular chemistry facilitated the appearance of a large number of multiporphyrin systems of different functional purposes, which contain sterically hindered tetrapyrrole macrocycles, the properties of which can differ considerably from those of ordinary porphyrins. In a lot of cases, synthetic donor-acceptor multiporphyrin complexes developed for modeling energy transfer in light-harvesting antenna complexes and photoinduced charge separation in the reaction center *in vivo*, are based on porphyrins and chlorines that are covalently linked via the phenyl spacer.^[2,8,22-25] As a rule, formation of these systems leads to steric interactions of molecular fragments, which may be

accompanied by static and dynamic nonplanar distortions of the porphyrin macrocycle. In this case, in studying spectral-kinetic properties, as well as typical features of 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 singlet S_1 and triplet T_1 states of tetrapyrrole macrocycles (steric factors, character of spatial distortions, effects of the conformational dynamics of macrocycles, *etc.*).

As a result, porphyrins with nonplanar macrocycle conformations have attracted considerable attention.^[14,19-21,26-29] Analysis of numerous X-ray structural data,^[30-33] results of spectral-kinetic investigations,^[34-41] and quantum-chemical calculations^[42-54] indicate that simultaneous introduction of bulky peripheral substituents in β - and *meso*-positions of molecules of tetrapyrrole compounds leads to spatial distortions of the macrocycle, considerably changing its geometry and electronic structure as well as the dynamics of relaxation processes. To date, there are a lot of additional publications being devoted to the study of sterically hindered tetrapyrrole macrocycles by methods of electronic,^[55-65] vibrational,^[66-68] and NMR^[69-73] spectroscopy.

In most cases the basic objects for the investigation of possible nonplanar macrocycle conformations were the so-called 'hybrid porphyrins' of octaethyl- (OEP) or octamethylporphyrin (OMP) type, containing bulky substituents of various nature in *meso*-positions of a tetrapyrrole macrocycle. Non-planar structures of these 'hybrid porphyrins', depending on the nature and number of substituents, central metal ion and axial ligand type, are manifested in several classes of distortion modes and may be associated with two general types of deformations 'saddle' and 'ruffle' or their mixtures 'wave' and 'dome'^[14,36] which conserve both in the crystal state and in liquid solutions.^[14] A considerable body of spectral-kinetic information has accumulated for non-planar sterically hindered porphyrins. Typically, the conformational dynamics of a non-planar tetrapyrrole macrocycle at 295 K, caused by the thermal population of the low-frequency out-of-plane deformation modes in the first excited singlet S_1 state, would in and of itself perturb the mean structure and deactivation parameters of the excited state. As a result, it manifests itself in large bathochromic absorption and fluorescence shifts ($\Delta\nu \sim 1100 \text{ cm}^{-1}$), the 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 yields and lifetime shortening.^[14,34-41,55-65] Nevertheless, the important question what happens with other excited states (namely, with T_1) upon steric interactions of bulky substituents with a tetrapyrrole macrocycle, remained still to be answered.

It follows from the cited scientific literature that the basic strategy for the synthesis and investigation of spatially distorted porphyrins was based on the analysis of changes in the spectral and photophysical properties of the initial tetraphenylporphyrin (TPP) molecule under conditions of successive introduction

of bulky ethyl ($-C_2H_5$) or methyl ($-CH_3$) substituents into β -positions of pyrrole rings of the macrocycle. For instance, the enhancement of the non-radiative deactivation of S_1 and T_1 states for the tetra-*meso*-phenyl substituted arylporphyrins has been typically associated with the macrocycle non-planarity in the ground S_0 state.^[14,34-41] On the other hand, from X-ray data,^[14,36] it was known that in the ground S_0 state mono- and di-*meso*-phenyl-substituted arylporphyrins (e.g. 5-PhOEP and 5,15-PhOEP) are planar both in crystalline form and in liquid solutions and are characterized by a slight diamond-shaped extension along the direction in which *meso*-phenyl

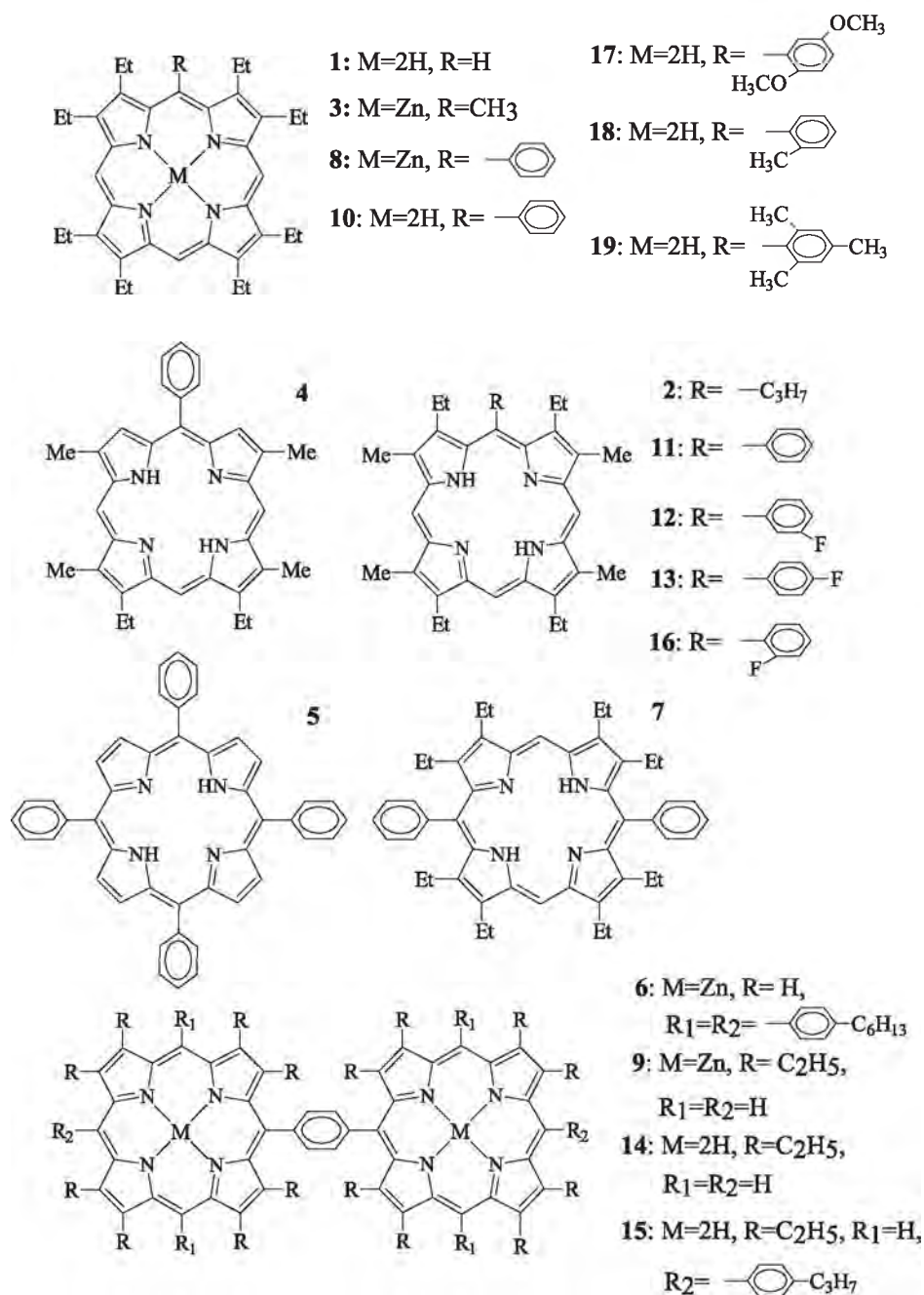


Figure 1. Chemical structures and abbreviations for a series of porphyrins and their phenyl bridged chemical dimers with a controllable structure of *meso*-phenyl substituents: **1** = octaethylporphyrin, OEP; **2** = etioporphyrin II, EPII-Pr; **3** = Zn-octaethylporphyrin, ZnOEP- CH_3 ; **4** = tetramethyldiethylporphyrin, TMDE-Ph; **5** = tetraphenylporphyrin, TPP; **6** = chemical dimer of Zn-tetra-hexylphenylporphyrin, ZnHTPP₂; **7** = 5,15-phenyl OEP, Ph-OEP-Ph; **8** = ZnOEP; **9** = chemical dimer (ZnOEP)₂-Ph; **10** = OEP-Ph; **11** = EPII-Ph; **12** = EPII-Ph(*m*-F); **13** = EPII-Ph(*p*-F); **14** = chemical dimer OEP-Ph-OEP; **15** = chemical dimer (PrPh)₂-(OEP)₂-Ph; **16** = EPII-Ph(*o*-F); **17** = OEP-Ph(OCH₃)₂; **18** = OEP-Ph(*o*-CH₃); **19** = OEP-Ph(CH₃)₃.

substituents are bonded. From this point of view, because of the dynamic distortion in the S_1 state was proposed to be absent there was no reason to study planar mono- and di-*meso*-phenyl substituted porphyrins. It was silently assumed that for later compounds the energetics and spectral-luminescent properties of S_1 and T_1 states have to be closely related to those for usual planar porphyrins. It should be noted that some attempts in this direction have been made for asymmetrically substituted porphyrins with various degrees of conformational distortion,^[74] but either related planar porphyrins were not used for the comparison or only structural data have been published without any information on the deactivation of the excited states. In fact, before our own results of 1998 in this direction the spectral-kinetic parameters of excited triplet states T_1 for some sterically hindered porphyrins were few and indirect in most cases.^[56,57] The intersystem crossing $S_1 \rightarrow T_1$ decrease and the drastic T_1 state decay shortening were found for two types of non-planar tetra-*meso*-substituted porphyrins at 295 K in deaerated solutions.^[75]

We found for the first time that mono- and di-*meso*-phenyl substitution in octaethylporphyrin free bases (OEP) and corresponding Zn complexes (ZnOEP) as well as the formation of an octaethylporphyrin chemical dimer with the phenyl ring as a spacer, (ZnOEP)₂Ph, led to a drastic shortening of triplet lifetimes at room temperature from ~1.5 ms down to 2-5 μ s in deaerated toluene solutions without considerable influence on spectral-kinetic parameters of the S_0 and S_1 states.^[38,76] Later on, our pioneer results and ideas in this direction have been reproduced in.^[41]

In order to study the observed effects more closely, at the first stage Minsk team (B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Dr. A. Shulga) has prepared a series of porphyrins and their chemical dimers with a controllable structure of *meso*-phenyl substituents and carried out a comprehensive investigation of spectral and photophysical parameters for S_0 , S_1 and T_1 of these objects in various solvents at 77-295 K.^[76-85] In addition, due to long-standing fruitful cooperation with Ivanovo team (Ivanovo State University of Chemical Technology, Russia, Prof. O. Koifman, Prof. A. Semeikin, Prof. O. Golubchikov) we have succeeded to realize the next step, that is the detailed experimental analysis of spectral-kinetic correlations for singlet and triplet states in *meso*-phenyl-substituted octaarylporphyrins with increasing number ($n = 1 \div 4$) of *meso*-phenyl rings.^[86-88] This second step has been also presented in literature by other groups

in 2000-2010.^[29,39,40,48,49] Finally, theoretical quantum-chemical calculations have been used in order to explain the conformational lability of *meso*-phenyl-substituted octaarylporphyrins leading to the enhancement of the non-radiative deactivation channels of various nature.^[44,48,89]

This paper is dedicated to the 70th anniversary of the world-known expert in tetrapyrrole chemistry and photochemistry as well as of my friend Oscar Koifman. The given material presents itself an overview of our collaboration in the field of sterically hindered porphyrin macrocycles in comparison with the relevant data from the literature as well as contains some recent results showing what circumstances should be taken into account when using these compounds in various areas (excited state deactivation in multiporphyrin complexes, photoinduced electron transfer, singlet oxygen generation).

Experimental

Synthesis, purification, and determination of the structure of *meso*-phenyl substituted octaethylporphyrin (OEP) molecules were performed by Dr. A. Shulga at B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus (Minsk) and described in details in our earlier publications.^[76,78,79] OEP chemical dimers (free bases and Zn complexes) were synthesized also in Minsk according to known methods and described in^[90,91]. The structures of this series of compounds being investigated are shown in Figure 1. *Meso*-phenyl-substituted octaarylporphyrins with increasing number ($n=1 \div 4$) of *meso*-phenyl rings were synthesized and identified by Prof. A. Semeikin at Ivanovo State University of Chemical Technology (Ivanovo, Russia) using techniques described in^[58,62,63,87]. The corresponding structures of these compounds are depicted in Figure 2.

Toluene (spectroscopic grade), glycerol and polymeric acrylic film were used as basic solvents at 295 K. Low-temperature measurements (77 K) were carried out in a mixture of methylcyclohexane-toluene (6:1, spectroscopic grade, Fluka SeccoSolv dried over a molecular sieve) forming an optical transparent rigid glass matrix at these conditions. In order to diminish the annihilation effects porphyrin concentrations of $\sim 10^{-6}$ M were used. The absorption spectra were measured on a Cary 500 M automated double beam spectrophotometer using 10×10 mm quartz cells (Type 111 QS).

For increasing solubility of the porphyrins under study, *tert*-butyl (*t*-Bu) substituents have been introduced into *meta*-positions of *meso*-phenyl rings (C).

Because of the significant quenching of the excited S_1 and T_1 states by dissolved molecular oxygen, the main part of the measurements was carried out for deaerated samples purging up to

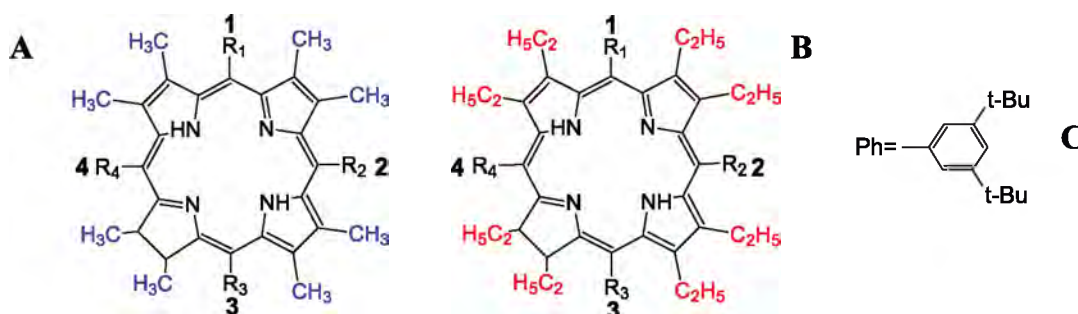


Figure 2. Chemical structures and abbreviations of octamethylporphyrin (A, OMP) and octaethylporphyrin (B, OEP) molecules and their *meso*-phenyl substituted (Ph) derivatives. OEP / OMP: $R_1=R_2=R_3=R_4=H$; 5-PhOEP / OMP: $R_1=Ph, R_2=R_3=R_4=H$; 5,15Ph-OEP / OMP: $R_1=R_3=Ph, R_2=R_4=H$; 5,10Ph-OEP / OMP: $R_1=R_2=Ph, R_3=R_4=H$; 5,10,15Ph-OEP / OMP: $R_1=R_2=R_3=Ph, R_4=H$; 5,10,15,20Ph-OEP / OMP: $R_1=R_2=R_3=R_4=Ph$.

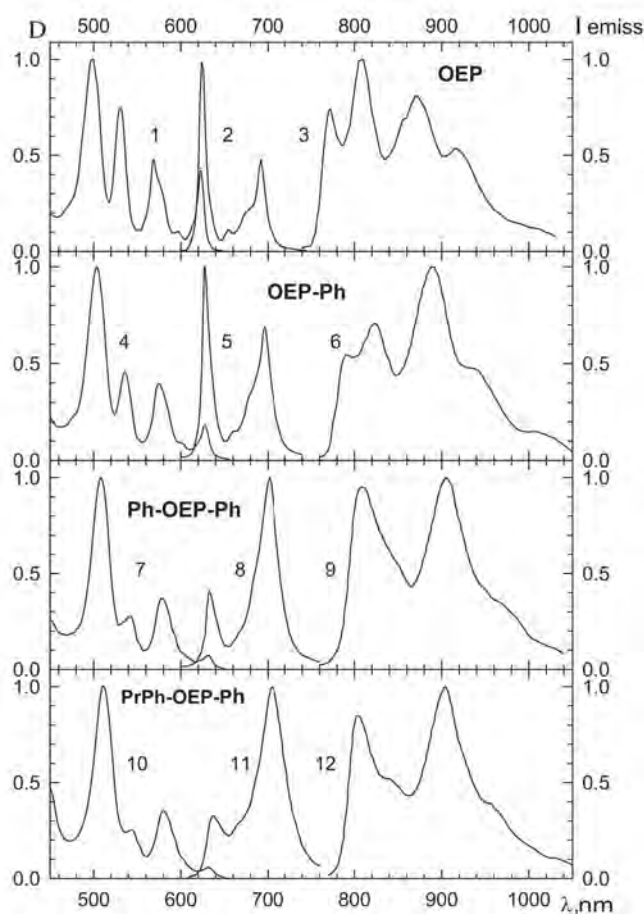


Figure 3. Absorption (1, 4, 7, 10) and fluorescence (2, 5, 8, 11) spectra in toluene at 295 K and phosphorescence spectra 3, 6, 9, 12 in methylcyclohexane-toluene mixture 6:1 at 77 K for porphyrins with mono- and di-*meso*-aryl substitution and their chemical dimer: OEP (1, 2, 3); OEP-Ph (4, 5, 6); Ph-OEP-Ph (7, 8, 9); and PrPh-OEP-Ph (10, 11, 12).

10^{-5} Torr pressure. The main spectral-luminescent experiments and emission (fluorescence and phosphorescence) decay measurements were performed on analytical instruments and high-sensitive automated laboratory setups including that for the detection of IR-emission of singlet oxygen, which were described in detail in our earlier papers,^[6,38,64,65,78-83,87] where standards, necessary equations and expressions as well as experimental errors have been also presented.

Results and Discussion

Unusual Deactivation of Triplet States in meso-Phenyl Substituted Porphyrins and Their Dimers

Spectral data show (Figure 3) that at 295 K, the absorption and fluorescence Q (0,0) bands for mono- and di-*meso*-aryl substituted OEP molecules are slightly red-shifted by ~6-9 nm, relative to the OEP molecule. In addition, the transition from OEP to *meso*-aryl substituted derivatives does not lead to Stokes shift changes which are 25-40 cm^{-1} that is typical for the majority of planar 'normal' porphyrins at 295 K.^[34,38,76]

The analysis of photophysical parameters for all compounds under study (summarized in Table 1) gives the

following conclusions. In the sequential series OEP \rightarrow OEP-Ph \rightarrow Ph-OEP-Ph, fluorescence lifetimes τ_s° and quantum yields ϕ_F decrease monotonically at 295 K. This tendency is well documented for the comparison of these parameters for a planar OEP molecule and those for a planar TPP molecule. At 77 K, τ_s° and ϕ_F values increase by 35-40 % both for OEP and its *meso*-phenyl substituted derivatives, this is obviously the typical temperature effect well known for planar 'normal' porphyrins.^[2,76-78] All these facts indicate that for mono- and di(5,15)-*meso*-aryl substituted OEP molecules the porphyrin macrocycle conformational dynamics leading to the non-radiative deactivation enhancement of the S_1 states at 295 K does not take place, in contrast to the known facts for non-planar tetra-*meso*-substituted porphyrins.^[14,34-41]

Interestingly, for chemical dimers, OEP-Ph-OEP and PrPh-OEP-PhPr, τ_s° and ϕ_F values are coincident by an order of magnitude with those for *meso*-phenyl substituted OEP derivatives. The small decrease of these values found the dimers with respect to the corresponding monomer OEP-Ph is characteristic for various porphyrin chemical dimers with a small overlapping of π -conjugated macrocycles and is connected with the manifestation of excitonic effects.^[2,8]

We have found for the first time that a principally different situation is observed when studying the deactivation of the T_1 state of the same compounds.^[38,76] Indeed, it is seen from Table 1 that in degassed toluene at 295 K for OEP, the T_1 state lifetime is measured to be $\tau_T^\circ = 1200$ ms. However, at the same experimental conditions mono- and di-*meso*-phenyl substitution in OEP and EPII molecules leads to a dramatic shortening by 300-500 times of τ_T° values (compounds 7-11, 14, 15). In addition, for OEP-Ph (10) $\tau_T^\circ = 4.0$ μs at 295 K and does not depend on the solvent viscosity (the transition from toluene to glycerol), but in polymeric acrylic film τ_T° increases up to 5000 ms. At 77 K in rigid glassy matrices for all compounds being investigated triplet lifetimes increase to tens of milliseconds and the phosphorescence quantum yields ϕ_p values are close to analogous parameters found for the planar OEP molecule and its Zn complex. It follows that in rigid media the reason leading to the dramatic shortening of τ_T° values for OEP-Ph in liquid solutions at 295 K is eliminated. Finally, data presented in Table 1 evidently show also that the dramatic shortening of τ_T° values (T_1 state quenching) is followed by the strong decrease of singlet oxygen generation efficiency for these compounds. In the later case, the quantum efficiency of the singlet oxygen generation is estimated by the value of $\delta = \gamma_\Delta / \gamma_T \approx 0.3$ whereas for 'normal' planar porphyrins $\delta \approx 1.0$.^[38,76] The strong decrease of singlet oxygen generation efficiency was found later for non-planar porphyrins with graded degree of saddle distortion.^[29]

The same τ_T° shortening as well as low temperature increase of τ_T° values from μs to ms time scale is found for OEP chemical dimers (compounds 9, 15). But in the case of chemical dimer (ZnHTPP)₂ not having bulky β -alkyl substituents these effects are absent. It should be noted in respect that the value of $\tau_T^\circ = 200$ ms in deoxygenated benzene solutions at 298 K was measured for 5-phenyl-13,17-dibutyl-2,8-diethyl-3,7,12,18-tetramethylporphyrin, while for the corresponding dimeric and trimeric porphyrin arrays with a phenyl spacer triplet lifetimes shortening of up to ~5 μs was detected.^[92] and explained by the enhancement of the non-radiative decay rates due to the excitonic interactions

Table 1. Photophysical characteristics of *meso*-aryl substituted porphyrins and their chemical dimers.

№	Compound	τ_{S_1}	$\tau_{S_2}^0$	Φ_F	$\Phi_P \times 10^4$	τ_p/τ_{TP}	τ_{TP}	τ_{TP}^0	γ_T	γ_Δ
		ns	ns							
	OEP	12.4	19.1	0.09	6,3	16/21*	330	1200	0.80	0.75
	EPII-Pr	–	–	–	–	–	260	1000	–	–
	ZnOEP-CH ₃	1.6	1.7	0.03	70	35/31*	360	1200	1.0	0.85
	TMDE-Ph	11.3	17.1	0.06	1.8	16	265	1640	0.85	0.90
	TPP	9.7	12.2	0.09	0.6	4.9/5.8*	400	1000	0.82	0.68
	(ZnHTPP) ₂	1.5	1.6	0.02	10	22.3/14.5*	605	1160	–	–
	Ph-OEP-Ph	9.9	13.0	0.05	1.0	10.3/13.5*	380	16.5	–	–
	ZnOEP-Ph	1.5	1.6	0.03	300	90/25*	355	5.8	–	–
	(ZnOEP) ₂ -Ph	1.2	1.2	0.02	50	28.5/16.6*	925	2.85	–	–
	OEP-Ph	11.2	16.0	0.05	1.9	14.5/11.1*	410	4.0	0.78	0.54
	EPII-Ph	11.0	16.5	0.06	1.3	14.3	330	5.5	–	–
	EPII-Ph(<i>m</i> -F)	10.7	15.9	0.07	1.8	14.5	390	4.2	–	–
	EPII-Ph(<i>p</i> -F)	10.8	17.0	0.07	1.5	14.2	350	6.0	–	–
	OEP-Ph-OEP	8.2	11.2	0.06	–	–	840	2.45	0.95	0.26
	(PrPh) ₂ -(OEP) ₂ -Ph	7.9	10.6	0.05	1.2	10.2	900	3.6	–	0.45
	EPII-Ph(<i>o</i> -F)	11.0	16.6	0.07	2.1	16.8	275	240	–	–
	OEP-Ph(OCH ₃) ₂	11.2	16.7	0.07	2.1	16.3	330	125	–	–
	OEP-Ph(<i>o</i> -CH ₃)	–	–	0.07	1.8	14.7	370	1000	–	–
	OEP-Ph(CH ₃) ₃	–	–	–	–	13.3	345	1490	–	–

*Triplet-triplet absorption measurements in methylcyclohexane at 77 K; phosphorescence parameters were measured in a glassy matrix of methylcyclohexane-toluene mixture 6:1 at 77 K. Meanings of all indexes are the following: τ_s and τ_s^0 are fluorescence lifetimes in normal and degassed solutions, respectively; τ_T and τ_T^0 are triplet state decays in normal and degassed solutions, respectively, measured in pump-probe experiments; τ_p is phosphorescence decay value at 77 K; Φ_F and Φ_P are fluorescence and phosphorescence quantum yields; γ_T is the intersystem crossing $S_1 \sim T_1$ quantum yield; γ_Δ is the quantum efficiency of singlet oxygen generation.

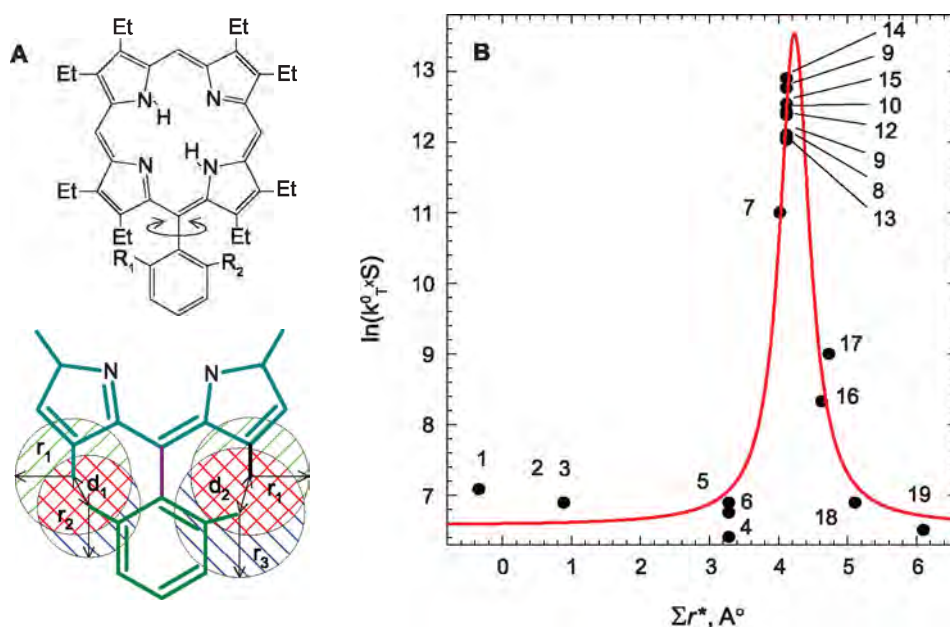


Figure 4. Schematic representation of the «apparent overlap» of interacting flanking groups in a crowded transition state (A) and the correlative dependence (B) of the triplet state deactivation rate constants k_T^0 on the overlap geometrical parameter (Σr^*), $\ln(k_T^0) = \ln(1/\tau_T^0) = f(\Sigma r^*)$, for the compounds being studied in toluene at 295 K. (A): The inset shows a schematic structural presentation of the effective Van der Waals radii (r_i) for interacting substituents, intercenter distances d_1 , d_2 and corresponding substituent bond lengths in the porphyrin macrocycle and in the *ortho*-positions of the phenyl ring solid lines for the hypothetical coplanar arrangement of the porphyrin macrocycle and the phenyl ring planes (HyperChem optimization). The contributions to Σr^* in *meso*-aryl substituted porphyrins have been calculated using equation $\Sigma r^* = (r_{X1} + r_{X2}) - d_X + (r_{Y1} + r_{Y2}) - d_Y$ (B): Numbers 1–19 correspond to compounds with the chemical structure shown in Figure 1.

within the dimers. We apt to believe that according to our experience with *meso*-phenyl bridged porphyrin dimers^[2,8,76] the excitonic coupling in these dimers is not strong enough in order to change so dramatically intersystem crossing rate constants. The other reason, namely steric interactions in *meso*-phenyl substituted OEP derivatives and their chemical dimers should be taken into account.

It is evident that steric interactions play a role in the deactivation of the excited triplet states of porphyrins bearing *meso*-phenyls and flanking bulky groups at the β -pyrrole positions (Figure 4). Thus, the phenomenological description of the unusual non-radiative deactivation of triplet excited states for OEP-Ph type molecules in liquid solutions at ambient temperature is related to the internal rotation motions (librations) and/or the possible overall tumbling of the phenyl ring about the single C–C bond and its interaction with a π -conjugated macrocycle.^[38,76] In this case, in the transition excited triplet state, when the phenyl ring is coplanar with the sterically hindered porphyrin macrocycle, deformation of the porphyrin may take place, leading to an enhancement of non-radiative deactivation of the T_1 state. Then, based on the approach developed for the semi-quantitative analysis of steric effects in the atropoisomerism in tetraarylporphyrins,^[93] we calculated the overlap geometrical parameters Σr^* . These are defined as the ‘apparent overlap’ of flanking sub-substituents at the β -pyrrolic positions of the porphyrin macrocycle with the corresponding groups in the *meso*-position of the macrocycle or in the *ortho*-position of the phenyl ring, when the porphyrin molecule is in the excited triplet transition state with a coplanar arrangement of the porphyrin and phenyl ring planes. The corresponding analysis of the experimental data is presented in Figure 4.

The overall interpretation of the correlative dependence having a pronounced maximum may be explained by the following way. It is well documented^[94] that in electronic S_0 and S_1 states porphyrins are characterized by low-frequency ($\nu \leq 80 \text{ cm}^{-1}$) torsion vibrations of *meso*-phenyl rings with high nuclear amplitudes. In fact, at 295 K for molecules of TPP type in their S_0 state within $t_{\text{rot}} \leq 10^{-3}$ - 10^{-4} s, the overall tumbling of the phenyl ring around a single C–C bond is possible with the preferable displacement of the phenyl ring at the dihedral angle of 60-90° with respect to π -conjugated porphyrin macrocycle. It means, that in the range of $\Sigma r^* < 3.4$ Å librational motions of *meso*-substituents in the conditions of the partial overlap of Van der Waals spheres even do not lead to the essential non-planar distortions of the porphyrin macrocycle and, correspondingly, do not influence on the T_1 state deactivation. On the other hand, in the range of $\Sigma r^* > 4.8$ Å the overlap of Van der Waals spheres for the corresponding *meso*- and β -substituents is so large that within the T_1 state lifetimes ($\tau_T^0 \approx 1000 \text{ }\mu\text{s}$) no rotations of the phenyl ring take place and its libration motions are essentially limited. As a result, in the latter case the porphyrin macrocycle is still planar in the T_1 state and corresponding molecules are characterized by long τ_T^0 . High values of the deactivation rate constants k_T^0 are characteristic for the middle range $3.4 \text{ Å} < \Sigma r^* < 4.8 \text{ Å}$. This may be explained by the fact that in situation torsion librations of the phenyl ring may cause the non-planar deformations of the sterically encumbered porphyrin macrocycle in the excited triplet state. The computer modeling of this situation

(HyperChem software, release 4, semiempirical AM1 and PM3 methods) shows that non-planar deformations of porphyrin macrocycle for molecules of the of porphyrin macrocycle of OEP-Ph type manifest themselves in the rotation of pyrrolic rings (flanking the phenyl ring) around the C_α - C_α axis. As a result, nitrogen atoms and β -carbons of the pyrrolic ring are on the opposite sides relative to the porphyrin plane. Calculation show also that the non-planarity of the π -conjugated porphyrin macrocycle is more pronounced in the T_1 state than the S_0 state. These facts may be connected to the decrease of the porphyrin skeleton rigidity in the excited T_1 state possibly due to the π -bond alternation increase. The co-existence of two conformers in the excited T_1 state for 5,15-diaryloctaalkylporphyrins has been found later by other group.^[41] Finally, it should be added that up to now a good theoretical explanation of the obtained dependence with the calculation of the corresponding energetic barriers is absent.

The presented results evidently show that steric hindrance effects and the dynamic non-planarity of *meso*-phenyl-substituted porphyrins and their chemical dimers with the phenyl spacer in the excited triplet state have been taken into account in the analysis of photophysical properties of locally excited states and photochemical events in systems of this type or more complex multiporphyrin arrays. Some physical reasons leading to the enhancement of the dynamic non-radiative relaxation of locally excited T_1 states of non-planar *meso*-phenyl substituted octaethylporphyrins and chemical dimer $(\text{ZnOEP})_2\text{Ph}$ in liquid solutions at 295 K should be taken into account: i) an increase of the rate constant of the non-radiative intersystem crossing $T_1 \sim S_0$ due to the decrease of the energy gap $\Delta E(T_1-S_0)$, that is the Franck-Condon factor enhancement; ii) an additional singlet and triplet state mixing facilitated by the enhancement of spin-orbit coupling due to the out-of-plane displacement of nitrogen atoms; iii) an initiation of some new types of accepting modes.^[8,95]

*Influence of Bulky β -Alkyls on S_1 and T_1 State Deactivation in a Series of Spatially Distorted *meso*-Phenyl Substituted Porphyrins*

Stimulated by experience with β -alkyl-porphyrins having two *meso*-phenyls or one phenyl ring with various bulky substituents in *ortho*-position of the phenyl we have studied the photophysical and photochemical properties for a series of *meso*-phenyl substituted octaarylporphyrins (OEP and OMP) with increasing number ($n=1\div 4$) of *meso*-phenyl rings (see Figure 2).^[86-88] One should mention, that such an approach has been also realized by two other groups for a closely related series of nonplanar porphyrins with graded degree of steric strain^[29,39,40] but differing with respect to our chemical engineering. Here, we present the whole set of experimental data on a detailed photophysical investigation of singlet and triplet parameters of the members belonging to above mentioned two series and compare our results with the relevant data known from the literature.

As an example, consider spectral-kinetic properties being obtained for a series of *meso*-phenyl substituted OMP and OEP molecules.^[87] A comprehensive analysis of these results (Figure 5 and Table 2) shows that the sequential

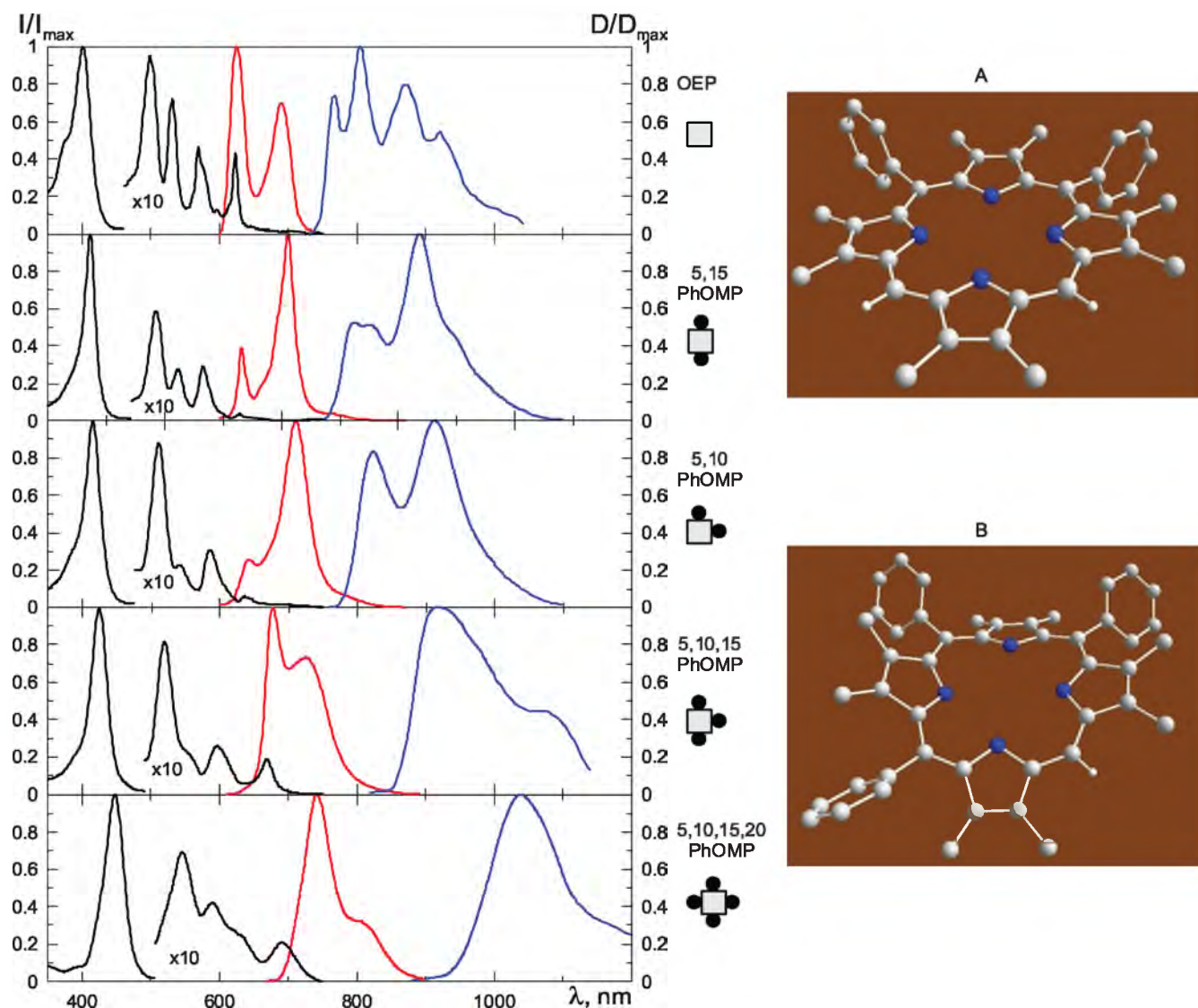


Figure 5. Normalized absorption (black), fluorescence (red) and phosphorescence (blue) spectra in toluene at ambient temperature for (from top to down) OEP; 5,15Ph-OEP; 5,10Ph-OEP; 5,10,15Ph-OEP; 5,10,15,20Ph-OEP. Pictograms on the right present structural features of the compounds under study with increasing number of *meso*-phenyl substituents, black circles indicate *meso*-phenyl rings. Right: Structures of sterically hindered *meso*-phenyl substituted 2,3,7,8,12,13,17,17-octamethylporphyrins, (A) for 5,10-diphenyl OMP and (B) for 5,10,15-triphenyl OMP, on the basis of X-Ray STOE IPDS data (friendly given by Profs. P. Stuzhin, A. Semeikin and O. Koifman).

Table 2. Spectral-luminescent and kinetic parameters for OEP and its *meso*-phenyl substituted derivatives (toluene).

Porphyrin	Abs (nm) (293K) $\lambda_{Q(0,0)}$	Fluor (nm) (293K) $\lambda_{Q(0,0)}$	Fluor (nm) (77K) $\lambda_{Q(0,0)}$	τ_S^0 (293K) ns	τ_S (293K) ns	Phos (nm) (77K) $\lambda_{Q(0,0)}$	τ_{ph} (77K) ms	τ_T^0 (293K) μ s	τ_T (293K) ns	Φ_f (293K)	$\Phi_{ph} \cdot 10^4$ (77K)	γ_Δ
OEP	622	623	620	19.1	12.4	771	16.0	1200	330	0.09	6.3	0.75
5Ph-OEP	626	628	621	16.0	11.2	790	14.5	4.0	410	0.05	1.9	0.60
5,15Ph-OEP	629	633	624	13.0	9.9	806	10.3	3.9 14.0	380	0.05	1.0	0.65
5,10Ph-OEP	643	657	641	–	1.85 4.76	853	1.3 3.5	0.35 41.4	–	0.016	0.52	0.02
5,10,15Ph-OEP	669	700	676	–	1.93	900	2.2	0.3	–	0.012	0.16	0.01
5,10,15,20Ph-OEP	698	739	732	–	1.09	1005	0.8	1.0	–	0.008	0.48	0.06

Meanings of all indexes are presented in footnotes to Table 1 and in the text.

increase of *meso*-phenyl substituents into OMP macrocycles manifests itself in considerable changes of their spectral-luminescent characteristics. Indeed, it leads to a gradual bathochromic shifts of both the Soret band and $Q_x(0,0)$ (curve 1) absorption bands as well as of the fluorescence spectra. In this case, a considerable broadening (from 300 cm^{-1} for 5Ph-OMP to $\sim 1000 \text{ cm}^{-1}$ for 5,10,15,20Ph-OMP) and a simultaneous decrease in the intensity of the long wavelength absorption band $Q_x(0,0)$ and fluorescence band with respect to corresponding vibronic bands $Q_x(0,1)$. The data presented in Figure 5 show that at 293 K, in the series of the investigated compounds, the Stokes shift between the absorption and fluorescence bands ($\Delta\nu$) does not remain constant but noticeably increases with an increase in the number of *meso*-phenyl substituents. For OMP molecules with mono-(5Ph-OMP) or symmetric di-*meso*-phenyl (*trans*-) substitution (5,15Ph-OMP), the Stokes shift is 25-50 cm^{-1} and almost coincides with the similar value for OEP, which is typical of the majority of porphyrins with the planar macrocycle. As we mentioned in previous sections, mono- and symmetric di-*meso*-phenyl substituted porphyrins are planar.^[14,36] In this respect, we can assume that, in liquid solutions, the conformational composition of mono- and symmetric di-*meso*-phenyl substituted OMP (as well as OEP) in the ground S_0 state is preserved and, correspondingly, the absorption and fluorescence properties are close to those characteristic of ordinary planar porphyrins.

At the same time, the observed pronounced broadening of absorption bands for 5,10Ph-OMP, 5,10,15Ph-OMP and 5,10,15,20Ph-OMP molecules at 293 K is indicative of more substantial deformations of the porphyrin macrocycle already in the ground S_0 state. The overall interpretation of

the above findings is that according to is well-documented results,^[14,34-41,55-59] the presence of a large number of *meso*-phenyl rings with flanking bulky β -alkyl substituents in porphyrin molecules leads to steric interactions between these molecular fragments and is accompanied by out-of-plane distortions of the π -conjugated tetrapyrrole macrocycle in the ground state. In addition, our data show that these compounds also exhibit a gradual increase (from 170 to 880 cm^{-1}) of Stokes shift $\Delta\nu_s$, which is indicative of the dynamic structural relaxation of the tetrapyrrole macrocycle at 293 K already in the excited S_1 state.

Data of Table 2 reveal that in liquid solutions at 293 K, upon a sequential increase in the number of *meso*-phenyl substituents, the fluorescence lifetime τ_s and the quantum yield ϕ_f of OEP macrocycles monotonically decrease. Furthermore, this tendency is especially clearly pronounced for compounds with a large number of *meso*-phenyl substituents. For instance, as a result of the mono- and di-*meso*-phenyl substitution, the fluorescence lifetime of the OEP molecule decreases insignificantly compared to that for OEP molecule without *meso*-phenyl rings, whereas the τ_s value for 5,10,15,20Ph-OEP molecule decreases by more than 10 times accompanied by the fluorescence quantum yield decrease by \sim one order of magnitude. These results (experimental data on Stokes shift $\Delta\nu_s$ and fluorescence quenching) indicate directly that spatially distorted OEP molecules (like OMP) having a large number of *meso*-phenyl substituents experience the dynamic relaxation to the energetically most favorable conformation in the excited S_1 state.

It is evidently seen also from Table 2 that upon increase of a number of *meso*-phenyl substituents the strong decrease of singlet oxygen generation efficiency takes place, reflecting

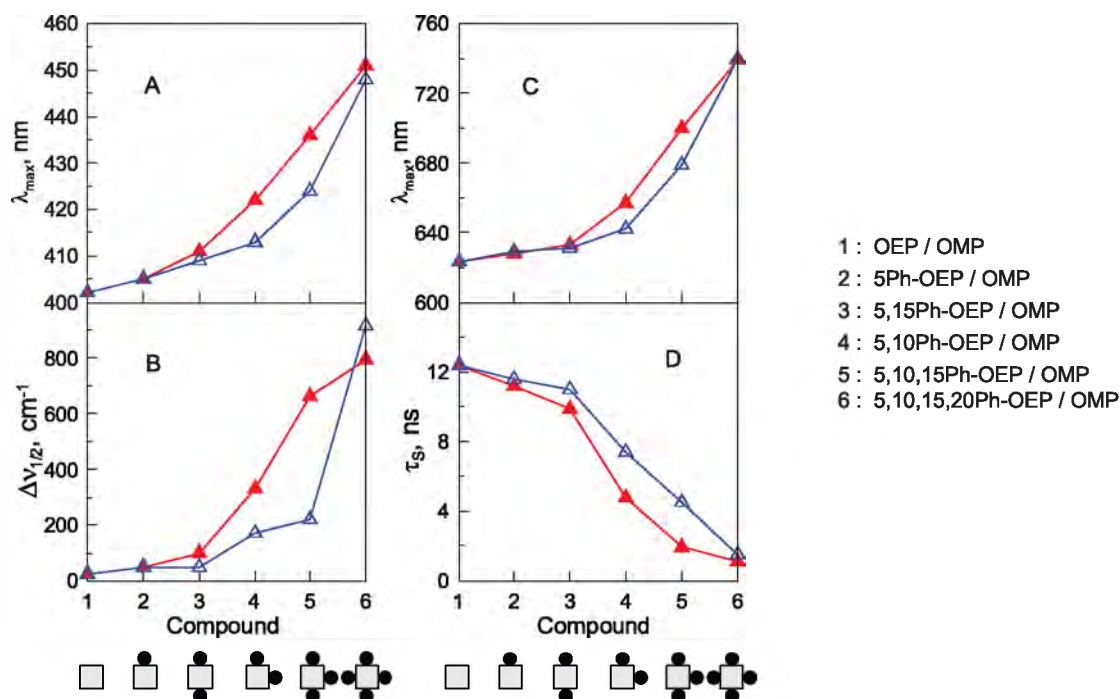


Figure 6. Correlation dependences of steric interactions for *meso*-phenyl substituted octaethylporphyrins (OEP, \blacktriangle) and octamethylporphyrins (OMP, \blacktriangle) reflecting changes of spectral-kinetic parameters upon sequential increase of number (and position) of *meso*-phenyl rings: λ_{\max} of Soret band in absorption (A); $\Delta\nu_s$, Stokes shift (B); λ_{\max} of the fluorescence band (C); fluorescence decay values τ_s in non-degassed solutions (D). Pictograms are the same as in Figure 5.

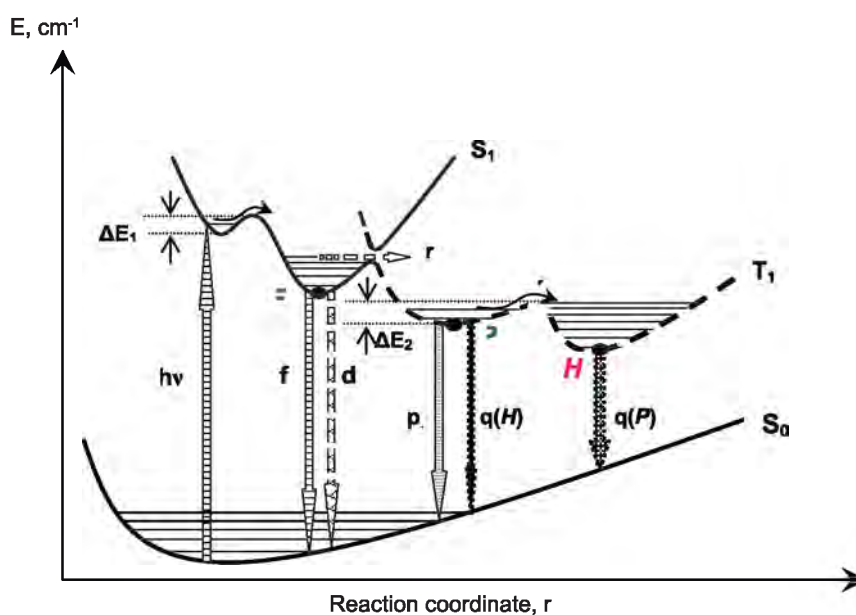


Figure 7. Energetic scheme of potential surfaces describing ground S_0 and locally excited S_1 and T_1 electronic states as well as photoinduced electronic transitions between these states for *meso*-phenyl substituted octaalkylporphyrins in liquid solutions at ambient temperature. ΔE_1 and ΔE_2 are the potential barriers for conformational rearrangements of non-planar porphyrin macrocycle. The rate constants of radiative and non-radiative transitions are denoted as follows: (f) – fluorescence $S_1 \rightarrow S_0$; (d) – internal conversion $S_1 \rightarrow S_0$; (r) – intersystem crossing $S_1 \rightarrow T_1$; (p) – phosphorescence $T_1 \rightarrow S_0$; q(H) and q(P) – intersystem crossing transitions $T_1 \rightarrow S_0$ from the triplet to the ground state for nonequilibrium (H) and equilibrium (P) conformations of the tetrapyrrole macrocycle.

τ_T° values drastic shortening. In addition, we have shown^[87] that for 5,10Ph-OMP and 5,10,15Ph-OMP molecules (non-planar in S_0 state), triplet state decay is two-exponential. These results may be considered as a direct and independent proof of the realization of non-planar conformations in the excited T_1 state for OEP molecules with a large number of *meso*-phenyl substituents. This argumentation is in line with the findings presented in.^[29]

In this respect it seems to be reasonable to compare the observed dependences of spectral-kinetic properties on the number of *meso*-phenyl rings for OMP and OEP macrocycles. Our results have shown^[86-88] that upon increase of a number of *meso*-phenyl substituents both OEP and OMP π -conjugated systems are sensitive to the steric interactions of *meso*-phenyl rings with flanking bulky β -alkyl substituents (quenching of excited states, spectral shifts and broadening). We found that for both series of OMP and OEP molecules steric porphyrin macrocycle distortion affects the triplet state properties significantly stronger than the singlet properties. The reason of that as we mentioned above may be explained by the decrease of the porphyrin skeleton rigidity in the excited T_1 state possibly due to the π -bond alternation increase. Nevertheless, the analysis of spectral-kinetic manifestations leads to the conclusion that the character of steric interactions of *meso*-phenyls with β -CH₃ substituents differ noticeably from those with β -C₂H₅ groups (Figure 6).

The observed differences may be connected with the manifestation of atropisomerism caused by different spatial arrangements of C₂H₅ groups in β -positions (in contrast to CH₃) with respect to the tetrapyrrole macrocycle. This atropisomerism can lead to “softening” of steric hindrances in 5,10,15,20Ph-OEP molecules having bulky ethyl

substituents, thus leading to the change of the character of spatial distortions for this macrocycle in comparison with 5,10,15,20Ph-OMP molecules characterizing more stronger steric interactions of closer located bulky substituents.

Finally, taken together, all experimental findings and dependencies being obtained for *meso*-phenyl substituted octaalkylporphyrins (OEP and OMP) with increasing number ($n=1-4$) of *meso*-phenyl rings give us the possibility to present the phenomenological scheme of main relaxation pathways in these molecules governed by the dynamic non-planarity of π -conjugated macrocycle in excited states (Figure 7).

It follows from Figure 7 that in liquid solution at ambient temperature, after excitation (hv) the transition to an energetically favorable conformation (the point F) is determined by the energy barrier ΔE_1 , which is governed by the character of distortion of the π -conjugated macrocycle in the excited S_1 state. For this rearranged conformation of the porphyrin macrocycle one should expect an increase in the rate constants of internal conversion $S_1 \rightarrow S_0$ (channel d, Figure 7) and intersystem crossing $S_1 \rightarrow T_1$ (channel r, Figure 7),^[34,57,59] due to the energy gap rule and the increase of Franck–Condon factor for non-radiative transitions.^[96] In this case, upon a sequential addition of a number of *meso*-phenyl substituents in octaalkylporphyrins, there occurs a gradual enhancement of the non-radiative channels $S_1(F) \rightarrow S_0$ and $S_1(F) \rightarrow T_1$, thus manifesting itself in a fluorescence noticeable quenching (decay shortening and quantum yield decrease).

One should remember 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 octaalkylporphyrins upon increase of *meso*-phenyl

rings. Data collected in Table 2 reveal that in degassed liquid solution at 293 K, the lifetime of the T_1 state for OEP molecule $\tau_T^0 = 1200 \mu\text{s}$, while for *meso*-phenyl substituted OEP molecules it is drastically shortened down to values of $\sim 0.3 \div 14.0 \mu\text{s}$. This T_1 state decay strong shortening is caused by the temporal dynamics of conformational rearrangements of the macrocycle in the excited T_1 state. As we shown for the first time^[38,76] and discussed above, this conformational dynamics of the porphyrin macrocycle in T_1 state is governed by steric interactions of bulky β -alkyl substituents of π -conjugated macrocycle with the increasing number of *meso*-phenyl rings. One should note that for 5,15Ph-OEP and 5,10Ph-OEP molecules the state T_1 decay is biexponential (Table 2). This implies that there are two different conformations of the macrocycle for these compounds in the triplet state at ambient temperature. We may suggest that after photoexcitation and subsequent intersystem crossing transition $S_1(F) \rightarrow T_1$, to the long-lived triplet excited conformation (the point H in Figure 7), the macrocycle can undergo a further structural reorganization to another, energetically more favorable conformation with a smaller value of the energy gap $\Delta E(T_1(P)-S_0)$, where the point P denotes the minimal energy for the equilibrium conformation on the potential energy surface of the triplet state. In turn, a decrease in the energy gap $\Delta E(T_1-S_0)$ leads to an increase in the probability of the non-radiative deactivation of T_1 state (the reasons of that were discussed before).

In addition, it is known that the distortion of the porphyrin macrocycle and activation of out-of-plane vibrational modes cause an increase of intersystem crossing rate constants due to an increase of the contributions from one-center overlap integrals of n-orbitals of central nitrogen atoms and π -orbitals of the macrocycle,^[97] resulting in the enhancement of matrix elements of spin-orbit interaction and the corresponding increase of rate constants for spin-forbidden transitions.^[98] In fact, the individual reason or their summary action may cause a decrease of the fluorescence quantum yield as well as the decay shortening for excited S_1 and T_1 electronic states of porphyrins.

The presented argumentation is in line from basic photophysical background with ideas discussed in^[39,40,59] earlier.

Conformational Dynamics of Mono-meso-phenyl Substituted Octaalkylporphyrins in the Excited Triplet State (Quantum-Chemical Approach)

It should be noted, that the numerous information on the nature and type of the macrocycle distortion (usually obtained by the X-ray and NMR spectroscopy) is related to the ground S_0 states. Meanwhile, the available data concerning the conformational distortions for sterically strained porphyrins in the excited states (in the triplet states, particularly) are scarce. Our kinetic data presented above have shown the existence, at least, two conformers for sterically hindered OEP and OMP molecules. Results obtained for octaethyltetraphenyl porphyrin free base by time-resolved EPR method^[99] and for Zn and free base 5,15-diaryloctaalkylporphyrins^[41] upon triplet state decay analysis have shown also the co-existence of two conformers in the

excited triplet state. Important information about spectral-kinetic properties of the T_1 state of sterically hindered porphyrins exhibiting conformational dynamics has been obtained by us from transient T_1-T_n absorption spectra^[76, 80] and will be discussed later. Here we discuss the nature of the non-planar conformations of the mono-*meso*-phenyl substituted octaethylporphyrins in the excited triplet state based on quantum-chemical calculations.^[44]

By means of molecular dynamics simulations at 300 K (PM3 method) and UB3LYP/6-31G geometry optimization in the T_1 state the unusual highly non-planar conformation was identified (see Figure 8A,B). Molecular dynamics simulations showed that during the heating step OEP-Ph and OMP-Ph molecules adopted the highly non-planar conformation. This switch from planar to non-planar conformation takes place in two steps. At the first step the single bond $C_{m1}-C_1$ went out of the porphyrin plane, the angle γ decreased to the value about 130° in the process. Then phenyl rotated about this single bond to the values of dihedral angle $\beta \sim 0^\circ$. This transition to the non-planar conformation occurred at the simulation temperature about 50–60 K.

Calculations by the density functional theory (DFT) were performed using Becke's three-parameter hybrid functional. For the triplet state calculations USCF formalism was used, while the restricted SCF version was used for the ground state calculations. DFT calculations have shown that this highly non-planar conformation is by ~ 2.2 kcal/mol more stable with respect to the planar one. The barrier height of the transition into the non-planar conformation was calculated to be ~ 6.9 kcal/mol. Results presented in Figure 8 (right, A) show that this non-planar conformation is characterized by the greatly reduced vertical energy gap $\Delta E_V(T_1-S_0)$ (0.45 eV in comparison with 1.33 eV for the planar conformation). We believe that namely the decrease of the energy gap $\Delta E_V(T_1-S_0)$ in this specific non-planar conformation is the reason for the drastic reduction of the triplet state decays for 5Ph-OEP type molecules. Since the transition into the non-planar conformation is accompanied by the shortening of the energy gap $\Delta E_V(T_1 \rightarrow S_0)$ by a factor of 3, this may lead to the considerable increase of the efficiency of the non-radiative deactivation of the triplet state causing the drastic shortening of the triplet state lifetime of 5Ph-OEP molecule ($t_T^0 = 4 \mu\text{s}$) in comparison with $\tau_T^0 = 1.2$ ms for OEP.

When replacement of β -ethyl substituents by β -methyl ones (transition to OMP-Ph molecule, Figure 8, right C), the calculated height of the barrier for conformational reorganization increases slightly in comparison with OEP-Ph (from 6.9 kcal/mol for OEP-Ph up to 7.7 kcal/mol for OMP-Ph). At the same time the total energy of OMP-Ph molecule in non-planar conformation is by ~ 0.8 kcal/mol higher than that for the planar conformation. Thus, by energy reasons, OMP-Ph molecule should spend more time in planar conformation. In its turn, it should increase the experimentally measured triplet state lifetime in comparison with OEP-Ph. Indeed, this is the case from our experimental findings in degassed toluene at 293 K: $\tau_T^0 = 4.0 \mu\text{s}$ for OEP-Ph, while $\tau_T^0 = 11.6 \div 62.5 \mu\text{s}$ for OMP-Ph).

Our experimental findings show^[76,80] that T_1-T_n absorption spectrum of OEP is characterized by the monotonic decrease of intensity in the near-IR region down to 1660 nm (Figure 9). In sterically hindered molecule OEP-

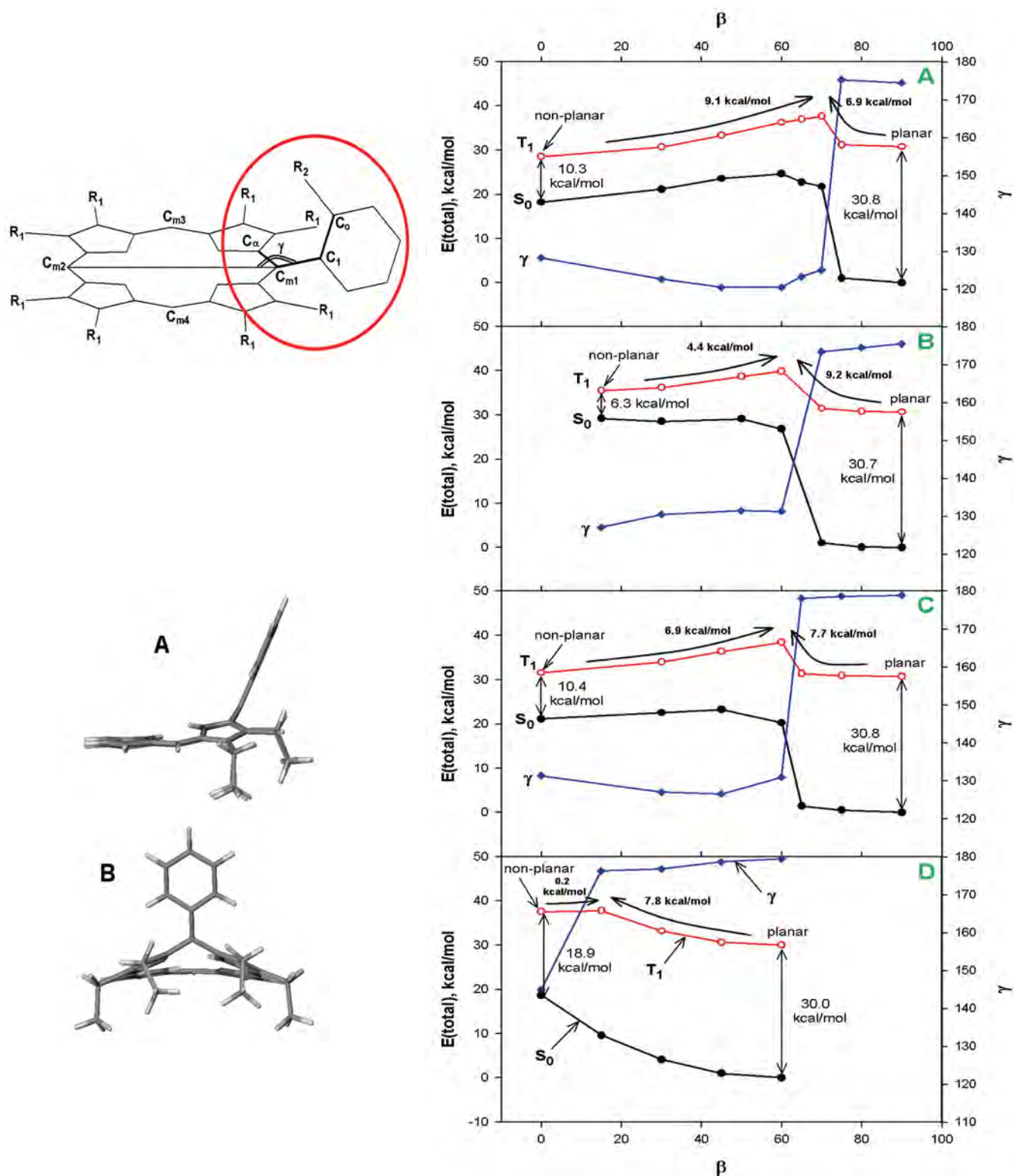


Figure 8. Left (Top): Structure elements for the compounds under consideration OEP-Ph: $R_1=C_2H_5$, $R_2=H$; OEP-Ph(*o*-CH₃): $R_1=C_2H_5$, $R_2=CH_3$. In calculations alkyl groups on the pyrroles that are far from the phenyl ring were substituted by hydrogens. Dihedral angle β is formed by the atoms $C_\alpha-C_{m1}-C_1-C_0$ (marked with bold lines). Left (A, B): The non-planar conformation of 5Ph-OEP molecule in T_1 state depicted from two different sides (A, B). This conformation corresponds to the maximal conjugation of the phenyl ring with the porphyrin macrocycle ($\beta \sim 0^\circ$). Calculations were performed for structures with alkyl groups on the pyrroles distant from the phenyl ring substituted by hydrogens. Right: Theoretical dependence of the total energies, $E(\text{total})$, for the excited T_1 (red curve, open circles) and ground S_0 (black curve, filled circles) states as well as the angle γ value (blue curve, filled diamonds) on the dihedral angle β : (A) - OEP-Ph (compound 10, Figure 1); (B) - OEP-Ph(*o*-CH₃) (compound 18, Figure 1); (C) - OMP-Ph; (D) - Porphyrin-*meso*-Ph (P-Ph). The energies of the ground S_0 state (black curves, filled circles) were calculated at the molecular geometry of the excited T_1 state. It means that the vertical energy gap $\Delta E_{\nu}(T_1-S_0)$ corresponds to the energy difference between the corresponding T_1 and S_0 curves for every compound. The total energy of the ground S_0 state for planar conformations was taken to be $E(S_0) = 0$ in all cases. The values of the $\Delta E_{\nu}(T_1-S_0)$ energy gap for planar and nonplanar conformations, as well as the heights of the barriers of conformational transformations, are shown.

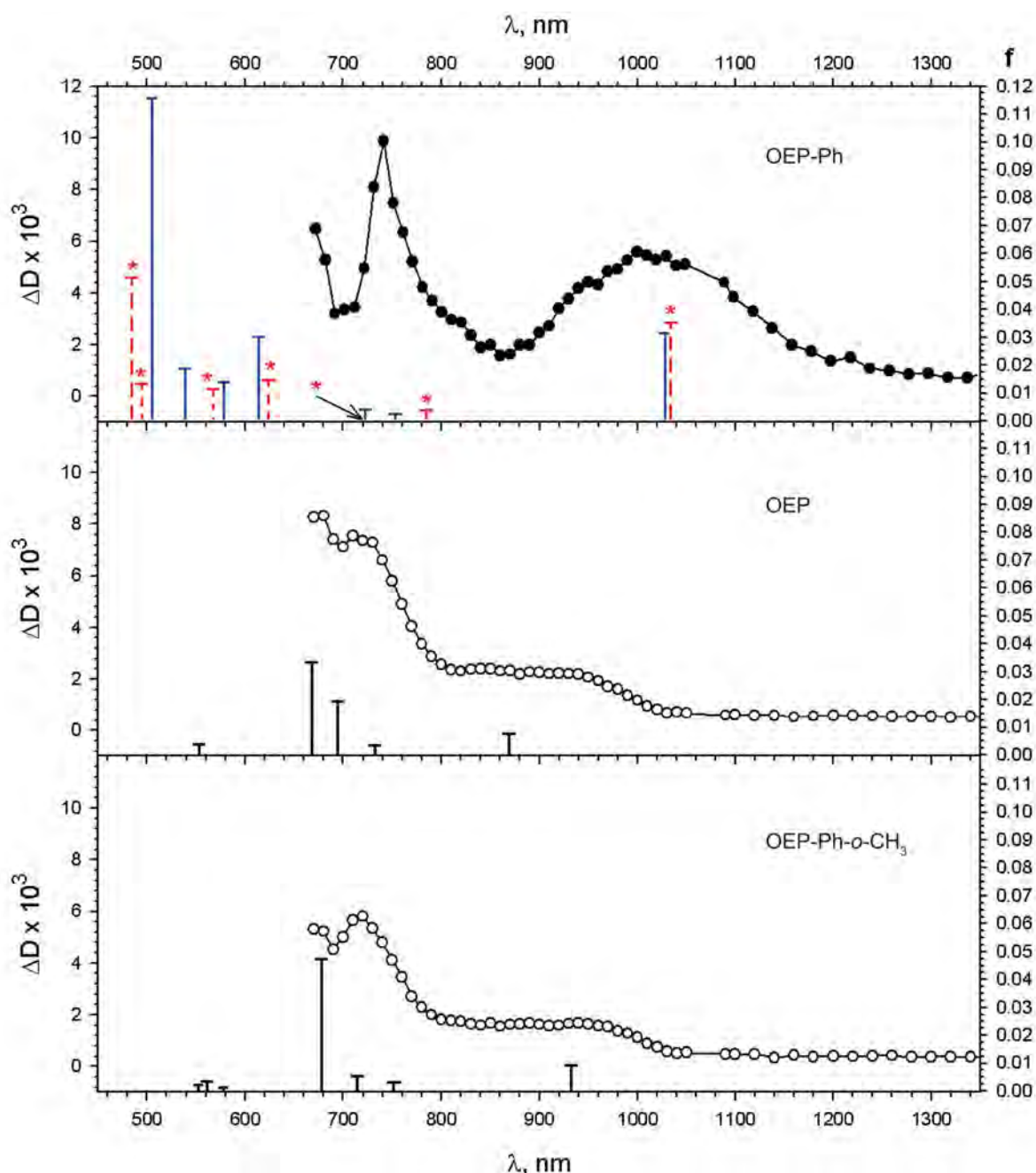


Figure 9. Experimental $T_1 \rightarrow T_n$ absorption spectra of OEP-Ph (A), OEP (B) and OEP-Ph(*o*-CH₃) (C). They are compared with the calculated $T_1 \rightarrow T_n$ absorption spectra of OEP-Ph in non-planar, planar and saddle-shaped conformation. The calculated transitions of the non-planar conformation of OEP, corresponding to the non-planar conformation of OEP-Ph, but without the phenyl are marked by asterisk. One of the transitions, calculated for this molecule, practically coincide by its energy and intensity with the corresponding transition in OEP-Ph. An arrow marks its position. Note that calculations were performed for structures without alkyl groups on the pyrroles distant from the phenyl ring.

Ph a new band with rather large half-width is found in this region with the maximum at 1000 nm. The presence of this long-wavelength band was thought to be related with the effect of dynamic non-planarity of the macrocycle, because in presumably planar molecule OEP-Ph(*o*-CH₃), this band is absent in T_1 - T_n absorption spectrum (Figure 9), as far as the conformational reorganization is hindered due to the bulky substituent in *ortho*-position of the phenyl ring.

Keeping these experimental results in mind we calculated T_1 - T_n absorption spectra for the compounds under study DFT method and 6-31G basis set implemented in

Gaussian 98. The overall conclusion is that calculated by TD-DFT method T_1 - T_n absorption spectra confirm the hypothesis of the conformational reorganization of the mono-*meso*-phenyl substituted octaethylporphyrins in the excited triplet state (Figure 9).

Data presented in Figure 9 show that for OEP-Ph molecule the distinct feature of the calculated photoinduced triplet-triplet absorption spectrum of the non-planar conformation is the intensive band red-shifted with respect to that of the lowest absorption band of the planar and "saddle" conformations. The experimental T_1 - T_n absorption spectrum

of OEP-Ph differs from those of OEP and OEP-Ph(*o*-CH₃) mostly by the presence of the intensive red-shifted band. Thus, our calculations of the T₁-T_n spectra also suggest that OEP-Ph adopt non-planar conformation in the triplet state. Another distinguishing feature of the T₁-T_n spectrum of the non-planar conformation is the presence of the intense band at 505 nm. Unfortunately, experimental T₁-T_n spectra were not recorded in this wavelengths region due to the strong S₀-S_n absorption.

Concluding, an exceptionally good agreement of experimental results and theoretical calculations of T₁-T_n absorption spectra in the red and near-IR regions provides the additional support for the conformational reorganization leading to the formation of the highly nonplanar distortion of OEP-Ph molecule in the excited triplet state. The overall interpretation of these results suggest that the conformational dynamics of this type in the T₁ state is characteristic for other "hybrid" porphyrins, which have alkyl substituents on the pyrrole rings and phenyls in *meso*-positions of the porphyrin. The barrier height of the transition into the non-planar conformation and its energy with respect to more planar conformations depend on the nature of the substituents on the pyrrole rings and on the initial degree of distortion of the porphyrin macrocycle. Really, recent theoretical revision of this problem^[89] confirmed our main ideas and showed that that a decrease in the lifetime of the T₁ state of OMP-Ph molecule is related with the enhancement of the channel of non-radiative deactivation (T₁→S₀), which occurs (i) due to the conformational lability in the T₁ state, as a result of which the energy gap ΔE_v(T₁-S₀) considerably decreases, and (ii) because of an increase in the matrix element of the spin-orbit interaction due to a change in the hybridization of atoms of the macrocycle as a consequence of its nonplanar distortion. The value of the vibronically induced matrix element of the spin-orbit interaction between the S₀ and T₁ states of OMP-Ph depends weakly on the type of the conformation and the value and the character of distortion of the porphyrin macrocycle.

Dynamics and Pathways of Relaxation Processes in *meso-ortho*-Nitrophenyl Substituted Octaethylporphyrins

In previous sections we have argued that in *meso*-phenyl substituted octaalkylporphyrins, steric interactions of *meso*-phenyls with bulky β-alkyl substituents lead to the non-planar deformations of the porphyrin macrocycle manifesting in quenching of excited states, spectral shifts and spectral broadening. Nevertheless, in some cases such interactions may play a "positive" role thus enhancing some interesting photoinduced phenomena. One of them is the photoinduced electron transfer, PET, from a donor to an acceptor D→A and is often used in supramolecular electronics and nanotechnologies.^[1,9,100]

For mono-*meso*-phenyl substituted OEP and their chemical dimers containing the NO₂ group in the *ortho*-position of the phenyl ring, the nonadiabatic PET rate constant was measured to be of $k_{\text{PET}} \sim 10^{10} \text{ s}^{-1}$ in nonpolar toluene at 295 K.^[77,78] Notably, in this *D-A* pair, steric interactions between bulky C₂H₅ substituents in β-positions of pyrrole rings and NO₂ group favor the efficient electronic interaction between the donor and the acceptor thus leading to efficient quenching of the porphyrin fluorescence due to the direct PET from the S₁ state to a low-lying charge-transfer state (CT) via "through-space" mechanism.

Here, we comparatively discuss PET in *meso-ortho*-nitrophenyl substituted Pd-octaethylporphyrins which involves donor triplet states.^[80,82] For Pd complexes, the intersystem crossing S₁→T₁ quantum yield and rate constant are $\gamma_{\text{T}} \approx 1$ and $r = 8.3 \cdot 10^{10} \text{ s}^{-1}$ correspondingly,^[101] thus providing the effective population of T₁ state even in the case of PET from S₁ state. The structures of the objects under study are presented in Figure 10. In addition, this Figure 10 collects the structures of the comparison OEP-type molecules containing electron neutral CH₃ group in *ortho*-position of the *meso*-phenyl, that is in these last objects PET is absent.

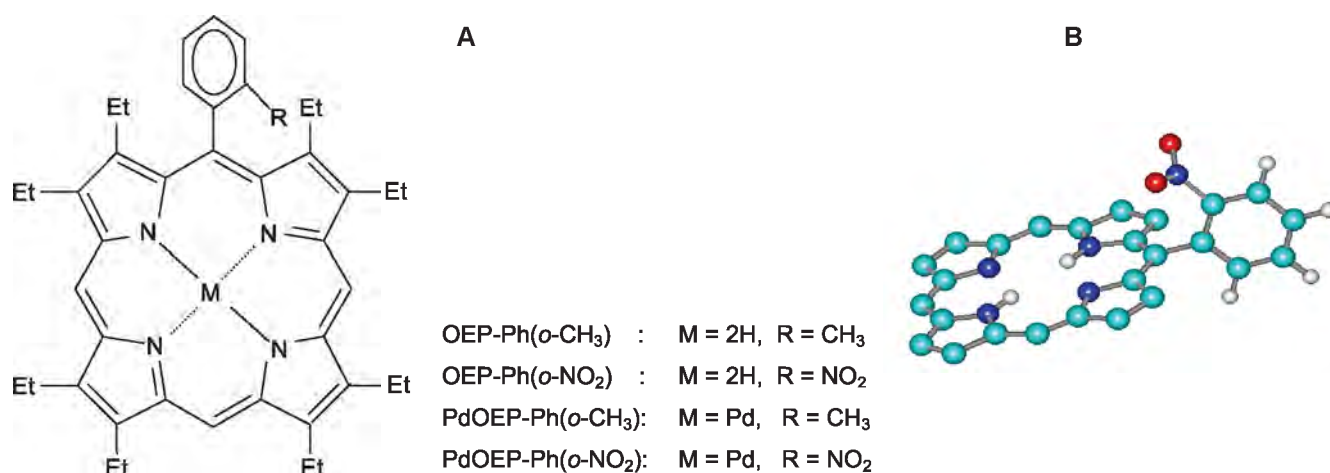


Figure 10. (A) Structural formulas of molecules studied and their abbreviations: 5-(*ortho*-methylphenyl)-2,3,7,8,12,13,17,18-OEP-Ph(*o*-CH₃); 5-(*ortho*-nitrophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin, OEP-Ph(*o*-NO₂); 5-(*ortho*-methylphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinato-Pd(II), PdOEP-Ph(*o*-CH₃); 5-(*ortho*-nitrophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinato-Pd(II), PdOEP-Ph(*o*-NO₂). (B): Optimized (HyperChem 4.0, semiempirical AM1 and PM3 methods) structure of octaethylporphyrin with NO₂ group in *ortho*-position of *meso*-phenyl. For clarity, bulky C₂H₅ substituents in the β-positions of the pyrrole rings are omitted. Synthesis, purification, and characterization of these compounds were performed by Dr. A. Shulga.^[77,78]

Table 3. Spectral and photophysical parameters of S_1 states for the compounds under study in toluene.

Compound	λ_{00}^{Abs}	λ_{00}^{Flu}	Φ_F	τ_{S_1}	τ_{S_1}
	nm	nm		ns	
	295 K	295 K	295 K	295 K	77 K
OEP-Ph(<i>o</i> -CH ₃)	627	629	0.07	11.4	21.2
OEP-Ph(<i>o</i> -NO ₂)	629 627*	634 632*	0.002 0.0003*	0.125# 0.040#*	20.2 —
PdOEP-Ph(<i>o</i> -CH ₃)	551 549*	555 554*	3.2·10 ⁻⁴ 2.8·10 ⁻⁴ *	0.0136 —	— —
PdOEP-Ph(<i>o</i> -NO ₂)	553 551*	558 557*	1.4·10 ⁻⁴ 0.5·10 ⁻⁴ *	0.007# ~0.003*†	— —

*Values were measured in polar dimethylformamide.

#Values were obtained on the basis of ps transient absorption measurements.

†Values were estimated from the decrease of fluorescence quantum yields in dimethylformamide.

Table 4. Spectral and photophysical parameters of T_1 states for the compounds under study in toluene.

Compound	λ_{00}^P	Φ_P^0	λ_{00}^P	Φ_P	τ_{TP}	τ_T^0	τ_{TP}
	nm	295 K	nm	77 K	ns	μ s	ms
	295 K	295 K	77 K	77 K	295 K	295 K	77 K**
OEP-Ph(<i>o</i> -CH ₃)	—	—	796	1.8·10 ⁻⁴	370	1000	14.7
OEP-Ph(<i>o</i> -NO ₂)	—	—	797	1.4·10 ⁻⁴	700#	0.75#	13.0
PdOEP-Ph(<i>o</i> -CH ₃)	672	0.03	661	0.46	200	85	1.9
PdOEP-Ph(<i>o</i> -NO ₂)	675 —	~10 ⁻⁵ —	665 —	0.45 —	0.046 0.020*	0.65# 0.25*#	1.6 —

Notes: λ_{00}^P are phosphorescence bands maxima, Φ_P and τ_P are phosphorescence quantum yields and decays, respectively. Values of τ_T and τ_T^0 are transient T-T absorption decays in nondegassed and degassed solutions, correspondingly.

*Values were measured in dimethylformamide.

**Values were measured in a glassy matrix of methylcyclohexane-toluene mixture (6:1).

#These values reflect the recombination of the radical ion pair.

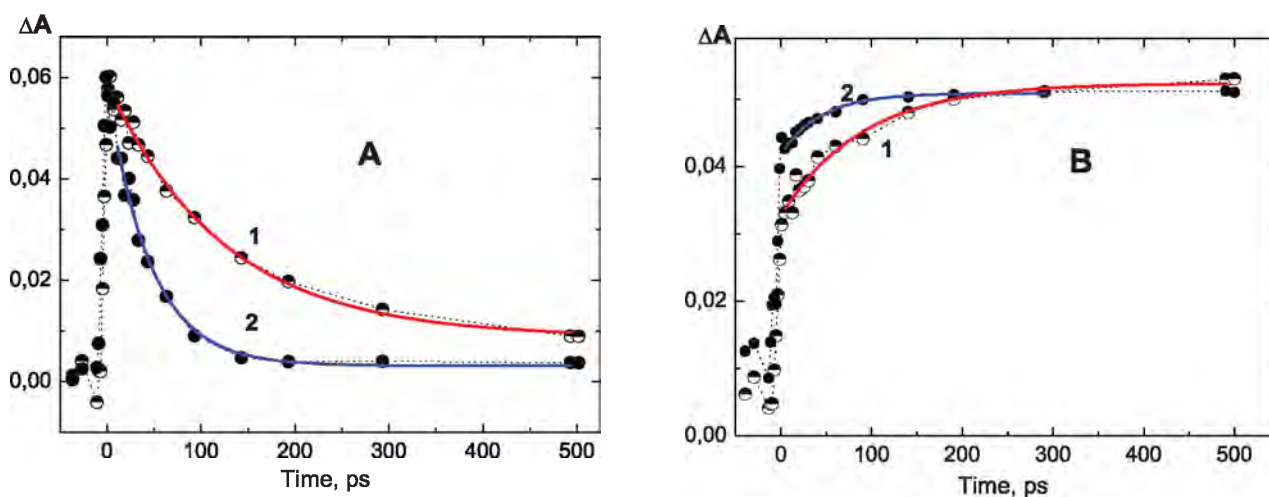


Figure 11. Kinetics of decay of transient absorption for OEP-Ph(*o*-NO₂) molecule (A, $\lambda_{reg} = 480$ nm,) and radical-ion pair absorption rise (B, $\lambda_{reg} = 800$ nm) in toluene (1) and dimethylformamide (2) at 295 K.

Experimental data (Tables 3 and 4) show that when going from OEP-Ph(*o*-CH₃) and PdOEP-Ph(*o*-CH₃) molecules containing electron neutral CH₃ group to the corresponding nitro derivatives OEP-Ph(*o*-NO₂) and PdOEP-Ph(*o*-NO₂), the bathochromic shift ($\Delta\lambda \sim 2$ –5 nm) of Q(0,0) bands in the absorption, fluorescence, and phosphorescence spectra is observed accompanied by slight broadening of these bands in toluene. In addition, the positions and intensities

of Q(0,0) bands in the absorption spectra of nitro substituted compounds depend on the solvent polarity. Quantum-chemical calculations (using the semiempirical ZINDO/S method and PM3 geometry optimization)^[102] show that the lowest unoccupied molecular orbital of the OEP-Ph(*o*-NO₂) molecule is almost completely localized at the nitro group (93.8 %) and has only a small admixture (3.3 %) of atomic orbitals of the porphyrin macrocycle. In addition, according

to these calculations, a nonzero contribution of the atomic orbitals of NO₂ group to the porphyrin e_{gx} orbital (2.7%) is typical for OEP-Ph(*o*-NO₂), which indicates a direct overlap of porphyrin π-orbitals with the lowest unoccupied molecular orbital of NO₂ group.

It follows from Table 3 that the fluorescence quantum yield of OEP-Ph(*o*-NO₂) is decreased by 35 times with respect to that for OEP-Ph(*o*-CH₃) in toluene at 295 K, and in polar dimethylformamide (DMF) this quenching is stronger. On the basis of picosecond transient absorption measurements it was shown (Figure 2) that the relaxation time of S₁ state for OEP-Ph(*o*-NO₂) molecule is equal τ_s=125 ps while for OEP-Ph(*o*-CH₃) molecule τ_s=11.4 ns in toluene at 295 K. In DMF τ_s=40 ps for OEP-Ph(*o*-NO₂) thus being shorter upon the solvent polarity increase. Picosecond transient absorption data reveal (Table 3) that S₁ state of PdOEP-Ph(*o*-CH₃) molecule decays with τ_s=13.6 ps while for PdOEP-Ph(*o*-NO₂) molecule τ_s=7.4 ps in toluene and 3 ps in DMF. For PdOEP-Ph(*o*-NO₂) S₁ state decay shortening is accompanied by the decrease of the fluorescence efficiency by 2.3 times with respect to that for PdOEP-Ph(*o*-CH₃). Finally, it should be noted that at 77 K in glassy matrixes, fluorescence lifetimes for PdOEP-Ph(*o*-CH₃) and PdOEP-Ph(*o*-NO₂) coincide practically. Taken together, all these results for OEP-Ph(*o*-NO₂) and PdOEP-Ph(*o*-NO₂) molecules demonstrate the existence of the effective PET in a picosecond time scale with participation of locally excited S₁ states.

The analysis of decay kinetics for PdOEP-Ph(*o*-NO₂) in nondegassed toluene at 295 K (λ_{reg} = 480 nm, Figure 11A) reveals that in addition to a short-living component (τ_s = 7.4 ps belonging to a quenched S₁ state) the second longer component with τ_T = 46.4 ps is detected belonging to a quenched T₁ state. In contrast, T₁ state decay kinetics for PdOEP-Ph(*o*-CH₃) is measured to be τ_T = 200 ns in these conditions (Table 4). In case of polar DMF the triplet state of PdOEP-Ph(*o*-NO₂) is characterized by a shorter decay with τ_T = 19.7 ± 1.3 ps. Thus it is reasonable to attribute the T₁ state shortening when transition from PdOEP-Ph(*o*-CH₃) to PdOEP-Ph(*o*-NO₂) as a direct manifestation of PET with participation of locally excited T₁ state.

Since the absorption spectra of nitro-phenyl substituted OEP-Ph(*o*-NO₂) and PdOEP-Ph(*o*-NO₂) molecules only slightly differ from those for OEP-Ph(*o*-CH₃) and PdOEP-Ph(*o*-CH₃) correspondingly, the rate constant k_{PET}^S of

nonadiabatic endothermic PET processes in such D-A pairs can be described in terms of the semi-classical Marcus theory^[103] developed for charge-transfer reactions in the “normal” region:

$$k_{PET} = \frac{2\pi}{\hbar} \frac{V_{12}^2}{(4\pi\lambda k_B)^{1/2}} \exp(-\Delta G^*/k_B T) \quad (1),$$

where ΔG* is activation energy, k_B is the Boltzmann constant, V₁₂ is the electronic coupling, λ = λ_m + λ_{solv} is the reorganization energy. The energy of the charge-transfer state E(CT) in a condensed phase is calculated according to E(CT) = e(E_{1/2}^{ox} - E_{1/2}^{red}) + ΔE(ε), where E_{1/2}^{ox} and E_{1/2}^{red} are the one-electron potentials of the porphyrin oxidation and nitrobenzene reduction. The correction term ΔE(ε) accounts for the Coulomb interaction between components of the radical ion pair. All these parameters have been carefully calculated using literature data on solvent properties and D-A geometric parameters.^[77,78,80,82] The final results of theoretical estimations are listed in Table 5.

It is seen from Table 5 that for OEP-Ph(*o*-NO₂) molecule the rate constant k_{PET}^S increases significantly on going from toluene to DMF. This rise reflects the increase of the electronic coupling V₁₂^S = 70 cm⁻¹ in DMF with respect to V₁₂^S = 7 cm⁻¹ in toluene due to the fast polarization-induced orientational rearrangements of the solvate shell in polar media. The same reason is responsible for the rise of V₁₂^S = 14 cm⁻¹ in toluene to V₁₂^S = 56 cm⁻¹ DMF for PdOEP-Ph(*o*-NO₂). The smaller change of V₁₂^S values upon the solvent polarity rise for PdOEP-Ph(*o*-NO₂) in comparison with OEP-Ph(*o*-NO₂) is explained by essentially shorter S₁ state decay (τ_s = 7 ps) of Pd-complex with respect to porphyrin free base (τ_s = 125 ps in toluene, Table 3).

The presented results show that the direct PET processes are responsible for the observed fluorescence quenching T₁ state shortening, and PET rate constants are in a reasonable agreement with the predictions of Marcus theory. The data of Table 5 suggest that, for PdOEP-Ph(*o*-NO₂) molecules, the rate constants of the PET involving the triplet states, k_{PET}^T are somewhat smaller than the values of k_{PET}^S. At the same time, the calculated values of the electronic factor V₁₂^T for the PET involving the triplet states in PdOEP-Ph(*o*-NO₂) molecules in both solvents are by two times larger than the values of V₁₂^S for the PET involving the singlet states. A possible

Table 5. Energies of locally excited S₁ and T₁ states and PET parameters for OEP-Ph(*o*-NO₂) and PdOEP-Ph(*o*-NO₂).

Compound	E(S ₁), eV	E(T ₁), eV	E(CT), eV	λ _{solv} , eV	λ _i , eV	ΔG ⁰ , eV		ΔG*, eV		k _{PET} ^S , s ⁻¹	k _{PET} ^T , s ⁻¹
						S ₁ →CT	T ₁ →CT	S ₁ →CT	T ₁ →CT		
Toluene (ε = 2.38), 295 K											
OEP-Ph(<i>o</i> -NO ₂)	1.96	1.54	1.78	0.03	0.23	-0.18	+0.24	0.003	—	8.0·10 ⁹	—
PdOEP-Ph(<i>o</i> -NO ₂)	2.23	1.84	1.79	0.03	0.23	-0.44	-0.05	0.05	0.035	7.0·10 ¹⁰	2.2·10 ¹⁰
Dimethylformamide (ε = 36.7), 295 K											
OEP-Ph(<i>o</i> -NO ₂)	1.97	1.54	1.75	0.45	0.65	-0.22	+0.21	0.07	—	2.5·10 ¹⁰	—
PdOEP-Ph(<i>o</i> -NO ₂)	2.24	1.85	1.76	0.45	0.65	-0.48	-0.09	0.01	0.12	2.6·10 ¹¹	5.0·10 ¹⁰

Calculations of rate constants for PET with participation of S₁ states, k_{PET}^S and T₁ states, k_{PET}^T were done according to well-known expression k_{PET}^S = 1/τ - 1/τ⁰, where τ⁰ and τ are decays of unquenched and quenched S₁ or T₁ states. Calculations of free Gibbs energy for PET were carried out using equations ΔG⁰ = E(CT) - E(S₁) and ΔG* = E(CT) - E(T₁) for S₁ and T₁ states, correspondingly.

reason of that may be connected with a different character of distribution of the local electron densities of the porphyrin macrocycle in S_1 and T_1 states leading to a distinct overlap with molecular orbitals of NO_2 group.

We like to point out again that such an overlap becomes possible exclusively for *meso-ortho*-nitrophenyl substituted octaethylporphyrins due to steric interactions between bulky C_2H_5 substituents in β -positions of pyrrole rings and NO_2 group. Indeed, it follows from available literature data that at room temperature in non-polar solvents, for octaethylporphyrins with *meso*- NO_2 groups,^[104,105] TPP,^[106] and tetraazaporphyrins^[107] with β -nitro groups, and TPP with NO_2 groups in the *ortho*- and *para*-positions of the phenyl ring^[108] PET is realized with rate constants in the range of $k_{PET}^S = (1\div 5) \cdot 10^8 \text{ s}^{-1}$. With respect to mentioned nitroporphyrins, our results for *meso-ortho*-nitrophenyl substituted octaethylporphyrins give k_{PET}^S values by 1-2 orders of magnitude higher and demonstrate that steric hindrance effects and the nature of the linkage between D and A influence on the efficiency and the mechanism of PET. Our results also show that the photophysical consequences of the dynamic non-planarity of *meso*-phenyl substituted octaethylporphyrins in the T_1 state should be included in the quantitative estimation of the quenching efficiency for the corresponding porphyrins with NO_2 groups and more complex arrays on their base.

Conclusions

We have shown for the first time that at 295 K in liquid solutions, 5- and 5,15-*meso*-phenyl substitution in octaalkylporphyrins or the formation of OEP chemical dimers with the phenyl spacer (free bases and Zn-complexes) lead to the drastic shortening of T_1 state decays by ~ 300 -1000 times without any influence on spectral-kinetic parameters of S_0 and S_1 states. This quenching is attributed to torsional librations of the phenyl ring around a single C-C bond in sterically hindered octaethylporphyrins leading to non-planar dynamic distorted conformations realized in T_1 state namely. The analysis of photophysical and photochemical properties for a series of *meso*-phenyl substituted octaethylporphyrins (OEP and OMP) with increasing number ($n=1\div 4$) of *meso*-phenyl rings has shown that T_1 states are more sensitive to the non-planar deformations of the porphyrin macrocycle in comparison with S_1 states of the same compounds. In addition, spectral-kinetic manifestations and the character of steric interactions of *meso*-phenyls with β - CH_3 substituents differ significantly from those with β - C_2H_5 . For 5,10-Ph-OMP, 5,10,15-Ph-OMP molecules (non-planar in S_0 -state), triplet state decay is two-exponential showing the dynamic conformation in the excited state.

The detailed theoretical analysis (semi-empirical PM3, DFT and TD-DFT calculations) shows that OEP-Ph molecule in the excited T_1 state may occur in the highly non-planar conformation characterized by the out-of-plane displacement of the single C_{m1} - C_1 bond and the increased overlap of the porphyrin and the *meso*-phenyl ring. For the sterically hindered porphyrins, the transition into this non-planar conformation is accompanied by the essential decrease of the vertical triplet-singlet energy gap $\Delta E_v(T_1-S_0)$ in contrast to $\Delta E_v(T_1-S_0)$ value for the planar conformation.

A good coincidence between experimental results and theoretical calculations on $T_1 \rightarrow T_n$ absorption spectra in the red and near IR region gives an additional support for the conformational reorganization leading to the formation of the highly non-planar distortion of OEP-Ph molecule in the excited T_1 state.

In contrast to PET rate constants being obtained for nitroporphyrins with other displacement of NO_2 groups, our results for *meso-ortho*-nitrophenyl substituted octaethylporphyrins give k_{PET}^S values by 1-2 orders of magnitude higher. In our case, steric interactions between bulky C_2H_5 substituents in β -positions of pyrrole rings and NO_2 group favor the efficient electronic interaction between the donor and the acceptor thus leading to the direct PET from the S_1 and T_1 states to a low-lying charge-transfer state (CT) via "through-space" mechanism.

The findings of this work on the photophysics of spatially distorted *meso*-phenyl substituted octamethylporphyrins and on the efficiency of their singlet oxygen generation should be taken into account when forming multiporphyrin structures of different types of functionality and in synthesis of sterically hindered porphyrin molecules, which are proposed as photosensitizers in photodynamic therapy. In addition, the dynamic non-planar distortion of *meso*-phenyl substituted porphyrins and their chemical dimers with the phenyl spacer in the triplet state should be taken into account upon the analysis of photophysical properties and photochemical events in the systems of this type or more complicated covalently linked arrays. Finally, the data presented here clearly show that a conformationally designed series of porphyrins with graded degree of macrocycle distortion exhibits gradually altered photophysical properties. This further indicates the possibility to use such systems for the preparation of biomimetic and catalytically active chromophores with fine-tunes photophysical parameters.

Acknowledgements. I like to thank Dr. A. Shulga (B.I. Stepanov Institute of Physics, National Academy of Sciences, Minsk, Belarus) and Prof. A. Semeikin (Ivanovo State University of Chemical Technology, Ivanovo, Russia) for synthesis and identification of all compounds being studied. Data related to spectral-kinetic characterization of porphyrins and their chemical dimers have been obtained by Drs. V. Knyukshto and A. Stupak (Institute of Physics, Minsk). I also thank Dr. Habil. E. Sagun for fruitful discussion and Dr. Avilov for quantum-chemical considerations. This work was funded by the Volkswagen Foundation (VW Grant I/79435 within the Priority Program "Physics, Chemistry and Biology with Single Molecules"), the Belorussian State Program for Scientific Research "Convergence 3.2.08 – Photophysics of Bioconjugates, Semiconductor and Metallic Nanostructures and Supramolecular Complexes and Their Biomedical Applications".

References

1. *Handbook of Molecular Self-Assembly: Principles, Fabrication and Devices* (Peinemann K.-V., Barboiu M., Eds.) Pan Stanford Publishing Co. Pte. Ltd.: Singapore, 2012.

2. Zenkevich E.I., von Borczyskowski C. Formation Principles and Excited States Relaxation in Self-Assembled Complexes: Multiporphyrin Arrays and "Semiconductor CdSe/ZnS Quantum Dot-Porphyrin" Nanocomposites. In: *Handbook of Porphyrin Science with Application to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine* (Kadish K.M., Smith K.M., Guillard R., Eds.) Singapore: World Scientific Publishing Co. Pte. Ltd, **2012**, Vol. 22, Ch. 104, pp. 68-159.
3. Yakovlev A.G., Shuvalov V.A. *J. Theor. Biol.* **2014**, *343*, 92-101.
4. Lee J.-E., Yang, J., Gunderson V.L., Wasielewski M.R., Kim D. *J. Phys. Chem. Lett.* **2010**, *1*, 284-289.
5. Chen M., Scheer H. *J. Porphyrins Phthalocyanines* **2013**, *17*, 1-15.
6. Zenkevich E.I., Gaponenko S.V., Sagun E.I., von Borczyskowski C. *Reviews in Nanoscience and Nanotechnology* **2013**, *2*, 184-207.
7. Masilela N., Antunes E., Nyokong T. *J. Porphyrins Phthalocyanines* **2013**, *17*, 417-430.
8. Zenkevich E.I., von Borczyskowski C. Photoinduced Relaxation Processes in Self-Assembled Nanostructures: Multiporphyrin Complexes and Composites "CdSe/ZnS Quantum Dot-Porphyrin". In: *Multiporphyrin Arrays: Fundamentals and Applications* (Kim D., Ed.) Singapore: Pan Stanford Publishing Pte. Ltd., **2012**, Ch. 5, 217-288.
9. Cao G., Wang Y. *Nanostructures and Nanomaterials: Synthesis, Properties and Applications*. New York: World Scientific Series in Nanoscience and Nanotechnology, **2011**, 2nd Edition, Vol. 2, 596 p.
10. Bottari G., Suanzes J.A., Trukhina O., Torres T. *Phys. Chem. Lett.* **2011**, *2*, 905-913.
11. Sakurai T., Tashiro K., Honsho Y., Saeki A., Seki S., Osuka A., Muranaka A., Uchiyama M., Kim J., Ha S., Kato K., Takata M., Aida T. *J. Am. Chem. Soc.* **2011**, *133*, 6537-6540.
12. Lee C.-H., Chitre K., Galoppini E. *J. Chin. Chem. Soc.* **2010**, *57*, 1103-1110.
13. Milgrom L.R. *The Colours of Life*, Oxford: Oxford University Press, **1987**.
14. Senge M.O. Highly Substituted Porphyrins: Synthesis and Organic Chemistry. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds) New York: Acad. Press, **2000**, Vol. 1, Ch. 6, 240-348.
15. Sener M.K., Olsen J.D., Hunter C.N., Schulten K. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 15723-15728.
16. Lindsey S., Moore A.L., Moore T.A., Gust D. *J. Phys. Chem. A* **2002**, *106*, 2036-2048.
17. Forman A., Renner M.W., Fujita E., Barkigia K.M., Evans M.C.W., Smith K.M., Fajer J. *Isr. J. Chem.* **1989**, *29*, 57-64.
18. Huber R. *Eur. J. Biochem.* **1990**, *187*, 283-305.
19. Shelnut J.A., Ma J.-G., Jia S.-L., Jentzen W., Medforth C.J. *Chem. Soc. Rev.* **1998**, *27*, 31-42.
20. Ma J.-G., Laberge M., Song X.-Z., Jentzen W., Jia S.-L., Zhang J., Vanderkooi J.M., Shelnut J.A. *Biochemistry* **1998**, *37*, 5118-5128.
21. Shi Z., Franco R., Haddad R., Shelnut J.A., Ferreira G.C. *Biochemistry* **2006**, *45*, 2904-2912.
22. Duvanel G., Grilj J., Vauthey E. *J. Phys. Chem., A* **2013**, *117*, 918-928.
23. Muraoka T., Kinbara K. *J. Photochem. Photobiol., C* **2012**, *13*, 136-147.
24. Maiuri M., Snellenburg J.J., van Stokkum I.H.M., Pillai S., Wongcarter K., Gust D., Moore T.A., Moore A.L., van Grondelle R., Cerullo G., Polli D. *J. Phys. Chem., B* **2013**, *117*, 14183-14190.
25. Peuntinger K., Lazarides T., Dafnomili D., Charalambidis G., Landrou G., Kahnt A., Sabatini R.P., McCamant D.W., Gryko D.T., Coutsolelos A.G., Guldi D.M. *J. Phys. Chem., C* **2013**, *117*, 1647-1655.
26. Bogatskii A.V., Zhilina Z.I. *Russ. Chem. Rev.* **1982**, *51*, 592-604.
27. Golder A.J., Nolan K.B., Povey D. C. *Inorg. Chim. Acta.* **1988**, *143*, 71-75.
28. Keshav K., Kumar D., Elias A.J. *Inorg. Chem.* **2013**, *52*, 12351-12366.
29. Röder B., Büchner M., Rückmann I., Senge M.O. *Photochem. Photobiol. Sci.* **2010**, *9*, 1152-1158.
30. Barkigia K.M., Berber M.D., Fajer J., Medforth C.J., Renner M., Smith K.M. *J. Am. Chem. Soc.* **1990**, *112*, 8851-8857.
31. Jentzen W., Ma J.G., Shelnut J.A. *Biophys. J.* **1998**, *74*, 753-763.
32. Senge M., Ema T., Smith K.M. *J. Chem. Soc., Chem. Commun.* **1995**, 733-734.
33. Song X.Z., Jentzen W., Jia S.L., Jaquinod L., Nurco D.J., Medforth C.J., Smith K.M., Shelnut J.A. *J. Am. Chem. Soc.* **1996**, *118*, 12975-12988.
34. Gentemann S., Medforth C.J., Ema T., Nelson N.Y., Smith K.M., Fajer J., Holten D. *Chem. Phys. Lett.* **1995**, *245*, 441-447.
35. Medforth C.J., Muzzi C.M., Shea K.M., Smith K.M., Abraham R.J., Jia S., Shelnut J.A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 833-838.
36. Senge M.O., Medforth C.J., Forsyth T.P., Lee D.A., Olmstead M.M., Jentzen W., Pandey R.K., Shelnut J.A., Smith K.M. *Inorg. Chem.* **1997**, *36*, 1149-1163.
37. Barkigia K.M., Nurco D.J., Renner M.W., Melamed D., Smith K.M., Fajer J. *J. Phys. Chem. B* **1998**, *102*, 322-326.
38. Knyuksho V.N., Sagun E.I., Shulga A.M., Bachilo S.M., Zenkevich E.I. *Zh. Prikl. Spektrosk.* **1998**, *65*, 471-475 (in Russ.).
39. Chirvony V.S., van Hoek A., Galievsky V.A., Sazanovich I.V., Schaafsma T.J., Holten D. *J. Phys. Chem. B* **2000**, *104*, 9909-9917.
40. Retsek J.L., Gentemann S., Medforth C.J., Smith K.M., Chirvony V.S., Fajer J., Holten D. *J. Phys. Chem. B* **2000**, *104*, 6690-6693.
41. Andreasson J., Zetterqvist H., Kajanus J., Martensson J., Albinsson B. *J. Phys. Chem. A* **2000**, *104*, 9307-9314.
42. Kyrychenko A., Andreasson J., Martensson J., Albinsson B. *J. Phys. Chem. B* **2001**, *105*, 12613-12622.
43. Lebedev A.Y., Filatov M.A., Cheprakov A.V., Vinogradov S.A. *J. Phys. Chem. A* **2008**, *112*, 7723-7733.
44. Avilov I.V., Zenkevich E.I., Sagun E.I., Filatov I.V. *J. Phys. Chem. A* **2004**, *108*, 5684-5691.
45. Thyagarajan S., Leiding T., Arskold P.S., Cheprakov A.V., Vinogradov S.A. *Inorg. Chem.* **2010**, *49*, 9909-9920.
46. Marques H.M., Brown K.L. *Coord. Chem. Rev.* **2002**, *225*, 123-132.
47. Chen D.M., Liu X., He T.J., Liu F.C. *Chem. Phys.* **2003**, *289*, 397-407.
48. Avilov I.V., Panarin A.Yu., Malinovskii V.L., Galievsky V.A. *Chem. Phys. Lett.* **2007**, *434*, 116-120.
49. Avilov I.V., Panarin A.Yu., Chirvony V.S. *Chem. Phys. Lett.* **2004**, *389*, 352-358.
50. Parusel A.B.J., Wondimagegn T., Ghosh A. *J. Am. Chem. Soc.* **2000**, *122*, 6371-6374.
51. Ryeng H., Ghosh A. *J. Am. Chem. Soc.* **2002**, *124*, 8099-8103.
52. Wasbotten H., Conradie J., Ghosh A. *J. Phys. Chem. B* **2003**, *107*, 3613-3623.
53. Wertsching A.K., Koch A.S., DiMaggio S.G. *J. Am. Chem. Soc.* **2001**, *123*, 3932-3937.
54. Haddad R., Gazeau S., Pecaut J., Marchon J.-C., Medforth C.J., Shelnut J.A. *J. Am. Chem. Soc.* **2003**, *125*, 1253-1268.
55. Tsuchiya S. *Chem. Phys. Lett.* **1990**, *169*, 608-610.
56. Takeda J., Ohya T., Sato M. *Chem. Phys. Lett.* **1991**, *183*, 384-386.
57. Gentemann S., Nelson N.Y., Jaquinod L., Nurco D.J., Leung S.H., Medforth C.J., Smith K.M., Fajer J., Holten D. *J. Phys. Chem., B* **1997**, *101*, 1247-1254.

58. Kuvshinova E.M., Pukhovskaya S.G., Guseva L.S., Semeikin A.S., Golubchikov O.A. *Zh. Fiz. Khim.* **1998**, *72*, 1040-1043 (in Russ.).
59. Retsek J.L., Medforth C.J., Nurco D.J., Gentemann S., Chirvony V.S., Smith K.M., Holten D. *J. Phys. Chem. B* **2001**, *105*, 6396-6411.
60. Semeikin A.S., Syrbu S.A., Lyubimova T.V. *Zh. Obshch. Khim.* **2001**, *71*, 1747-1750 (in Russ.).
61. Syrbu S., Semeikin A., Ageeva T., Kolodina E., Koifman O. *J. Porphyrins Phthalocyanines* **2006**, *10*, 885.
62. Pukhovskaya S.G., Guseva L.S., Semeikin A.S., Kumeev R.S., Golubchikov O.A. *Russ. J. Coord. Chem.* **2003**, *29*, 805-809.
63. Pukhovskaya S.G., Guseva L.S., Semeikin A.S., Kuvshinova E.M., Golubchikov O.A. *Zh. Neorg. Khim.* **2005**, *50*, 635-639 (in Russ.).
64. Knyukshto V.N., Shulga A.M., Sagun E.I., Zenkevich E.I. *Opt. Spektrosk.* **2006**, *100*, 431-443 (in Russ.).
65. Knyukshto V.N., Shulga A.M., Sagun E.I., Zenkevich E.I. *Opt. Spektrosk.* **2006**, *101*, 954-960 (in Russ.).
66. Tewari S., Das R., Chakraborty A., Bhattacharjee R. *Pramana J. Phys.* **2004**, *63*, 1073-1077.
67. Unger E., Dreybrodt W., Schweitzer-Stenner R. *J. Phys. Chem., A* **1997**, *101*, 5997-6007.
68. Sibia S.A., Hu S., Piffat C., Melamed D., Spiro T.G. *Inorg. Chem.* **1997**, *36*, 1013-1019.
69. Somma M.S., Medforth C.J., Nelson N.Y., Olmstead M.M., Khoury R.G., Smith K.M. *Chem. Commun.* **1999**, 1221-1222.
70. Fonda H.N., Gilbert J.V., Cormier R.A., Sprague J.R., Kamioka K., Connolly J.S. *J. Phys. Chem.* **1993**, *97*, 7024-7033.
71. Syrbu S.A., Semeikin A.S., Buryaeva I.V., Kumeev R.S., Alper G.A. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **2002**, *45*, 141-142 (in Russ.).
72. Noss L., Liddell P.A., Moore A.L., Moore T.A., Gust D. *J. Phys. Chem., B* **1997**, *101*, 458-465.
73. Yatsunyk L.A., Walker F.A. *Inorg. Chem.* **2004**, *43*, 4341-4352.
74. Senge M.O., Kalisch W.W. *Inorg. Chem.* **1997**, *36*, 6103-6116.
75. Charlesworth P., Truscott T.G., Kessel D., Medforth C.J., Smith K.M. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1073-1076.
76. Knyukshto V., Zenkevich E., Sagun E., Shulga A., Bachilo S. *Chem. Phys. Lett.* **1998**, *297*, 97-108.
77. Knyukshto V., Zenkevich E., Sagun E., Shulga A., Bachilo S. *Chem. Phys. Lett.* **1999**, *304*, 155-166.
78. Knyukshto V., Zenkevich E., Sagun E., Shulga A., Bachilo S. *J. Fluorescence* **2000**, *10*, 55-68.
79. Knyukshto V.N., Sagun E.I., Shulga A.M., Bachilo S.M., Zenkevich E.I. *Khim. Fiz.* **1999**, *18*, 30-39 (in Russ.).
80. Knyukshto V.N., Sagun E.I., Shulga A.M., Starukhin D.A., Bachilo S.M., Zenkevich E.I. *Opt. Spektrosk.* **2001**, *90*, 67-77 (in Russ.).
81. Knyukshto V.N., Zenkevich E.I., Sagun E.I., Shulga A.M., Starukhin D.A., Bachilo S.M. *Mol. Cryst. Liq. Cryst.* **2000**, *326*, 77-82.
82. Knyukshto V.N., Sagun E.I., Shulga A.M., Bachilo S.M., Zenkevich E.I. *Opt. Spektrosk.* **2000**, *88*, 241-254 (in Russ.).
83. Knyukshto V.N., Shulga A.M., Sagun E.I., Bachilo S.M., Zenkevich E.I. *Opt. Spektrosk.* **2002**, *92*, 59-68 (in Russ.).
84. Sagun E.I., Zenkevich E.I., Knyukshto V.N., Tikhomirov S.A., Shulga A.M. *J. Porphyrins Phthalocyanines* **2004**, *8*, 907.
85. Sagun E.I., Zenkevich E.I., Knyukshto V.N., Tikhomirov S.A., Shulga A.M. *Opt. Spektrosk.* **2006**, *100*, 431-443 (in Russ.).
86. Sagun E.I., Zenkevich E.I., Knyukshto V.N., Shulga A.M., Avilov I.V., Filatov I.V., Grubina L.A., Golubchikov O.A., Semeikin A.S. *J. Porphyrins Phthalocyanines* **2004**, *8*, 908.
87. Sagun E.I., Zenkevich E.I., Knyukshto V.N., Panarin A.Yu., Semeikin A.S., Lyubimova T.V. *Opt. Spektrosk.* **2012**, *113*, 431-443 (in Russ.).
88. Sagun E.I., Zenkevich E.I. *Opt. Spectrosc.* **2013**, *115*, 727-738.
89. Shchupak E.E., Ivashin N.V., Sagun E.I. *Opt. Spectrosc.* **2013**, *115*, 37-47.
90. Chernook A.V., Shulga A.M., Zenkevich E.I., Rempel U., von Borczyskowski C. *J. Phys. Chem.* **1996**, *100*, 1918-1926.
91. Chernook A.V., Rempel U., von Borczyskowski C., Zenkevich E.I., Shulga A. *Chem. Phys. Lett.* **1996**, *254*, 229-241.
92. Sessler J.L., Capuano V.L., Harriman A. *J. Am. Chem. Soc.* **1993**, *115*, 4618-4628.
93. Crossley M.J., Field L.D., Forster A.J., Harding M.M., Sternhell S. *J. Am. Chem. Soc.* **1987**, *109*, 341-348.
94. Solov'ev K.N., Gladkov L.L., Starukhin A.S., Shkirman S.F. *Spectroscopy of Porphyrins: Vibrational States*. Minsk: Nauka i Tekhnika, **1985**, Ch. 6, 311-316 (in Russ.) [Соловьев К.Н., Гладков Л.Л., Старухин А.С., Шкирман С.Ф. *Спектроскопия порфиринов: колебательные состояния*. Минск: Наука и техника, **1985**, гл. 6, 311-316].
95. Zenkevich E. I., von Borczyskowski C. Multiporphyrin Self-Assembled Arrays in Solutions and Films: Thermodynamics, Spectroscopy and Photochemistry. In: *Handbook of Polyelectrolytes and Their Applications* (Tripathy S.K., Kumar J., Nalwa H.S., Eds.) USA: American Scientific Publishers. **2002**, Vol. 2, Ch. 11, 301-348.
96. Turro N. *Modern Molecular Photochemistry*. Menlo Park: The Benjamin/Cummings Publishing, **1978**, 153-198.
97. Bowman M.K. *Chem. Phys. Lett.* **1977**, *48*, 17-26.
98. Perun S., Tatchen J., Marian C.M. *Chem. Phys. Chem.* **2008**, *9*, 282-292.
99. Michaeli S., Soffer S., Levanon H., Senge M. *J. Phys. Chem., A* **1999**, *103*, 1950-1957.
100. *An Introduction to Molecular Electronics* (Petty M.C., Bryce M.R., Bloor D., Eds.) London, Melbourne, Auckland: Edward Arnold, a division of Holder Headline PLC, **1995**.
101. Dzhagarov B.M., Gurinovich G.P., Novichenkov V.E., Salokhiddinov K.I., Shulga A.M., Ganzha V.A. *Khim. Fizika* **1987**, *6*, 1069-1078 (in Russ.).
102. Avilov I.V., Zenkevich E.I., Sagun E.I., Shulga A.M., Filatov I.V. *Opt. Spektrosk.* **2003**, *95*, 394-405 (in Russ.).
103. Marcus R.A., Sutin N. *Biochim. Biophys. Acta* **1985**, *811*, 265-322.

Received 04.05.2014

Accepted 20.05.2014