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Effect of the central ion of metals on the luminescent and photophysical parameters of metallophthalocyanines

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Based on the data on the spectral and photophysical parameters of the metal complexes of tetraazaporphyrins and phthalocyanines, the effect of the central metal ion on the manifestation of spin-orbit interaction is considered. For complexes of phthalocyanines with Mg(II), Zn(II), Pd(II), and Pt(II) ions, the absorption spectra, luminescence spectra, and luminescence excitation spectra were measured, and the lifetimes and quantum yields of luminescence were determined. It was shown that metal phthalocyanines with Mg(II) and Zn(II) ions, as well as Mg-tetaraazaporphyrin, exhibit intense fluorescence with high quantum yields. For single molecules of Mg-tetaraazaporphyrin in a polymer film at $T = 6\,\text{K}$, the fluorescence excitation spectra consisting both exclusively of zero-phonon lines and containing phonon wings were measured. A wide distribution of the measured zero-phonon line widths was observed. It is demonstrated, that the introduction of Pd(II) and Pt(II) ions into the center of phthalocyanine macrocycles leads to a decrease in fluorescence and the appearance of intense phosphorescence even at room temperature. Based on measurements of quantum yields of photosensitized generation of singlet molecular oxygen, the quantum yield of interconversion into triplet states for the compounds under study was defined. Deactivation of the lower triplet state of phthalocyanines with Pd(II) and Pt(II) ions indicates the influence of the internal heavy atom effect on the rate of triplet state deactivation at room temperature and at 77 K.

Keywords: phthalocyanines with Mg(II), Zn(II), Pd(II) and Pt(II) ions, Mg-tetaraazaporphyrin, single molecule luminescence, photophysical parameters of singlet and triplet state deactivation, quantum yield of singlet oxygen generation.

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Introduction

Phthalocyanines and tetraazaporphyrins are planar aromatic π-compounds with wide opportunities of directed changes in their properties by varying the structure of the organic ligand (for example, introducing various substituents on phenyl rings), as well as by the type of metal in the center of the conjugated phthalocyanine macrocycle [1–3]. Free base and metal complexes of phthalocyanines usually have high photostability in various organic solvents, as well as in solid solutions. Such chemical and physical properties of phthalocyanine compounds, as well as the relatively low cost of their synthesis, allow these compounds to be widely used in various fields of science, technology, and medicine. Phthalocyanines are used for the development of effective photoconversion devices and optoelectronic devices (liquid crystal displays, photoconductors in laser printers, solar cells, etc.) [4–6], as well as photosensitizers in photodynamic therapy and antibacterial therapy [7–10]. The detection of single oxygen upon photoexcitation is of great importance for the quantitative determination of the generation efficiency of this photochemically active reagent. Such information is required for the evaluation of photosensitizer efficiency in photodynamic therapy, as well as in the systems of microorganisms inactivation.

Interest in the molecules of metal complexes of tetraazaporphyrins and phthalocyanines is due to the possibility of luminescence detection at the level of single molecules (SM) for these compounds. Previously, it was shown that Mg-tetraazaporphyrin (Mg-TAP) molecules in polymer matrices can be considered as effective nanoprobes for obtaining information on vibrational and tunneling excitations existing in solids, in particular, in glasses [11,12]. Such information is of undoubted interest both from the point of view of developing fundamental concepts of the vibrational and tunneling dynamics of solids [13–17], and from the point of view of developing more advanced devices for optoelectronics and quantum computing [18].

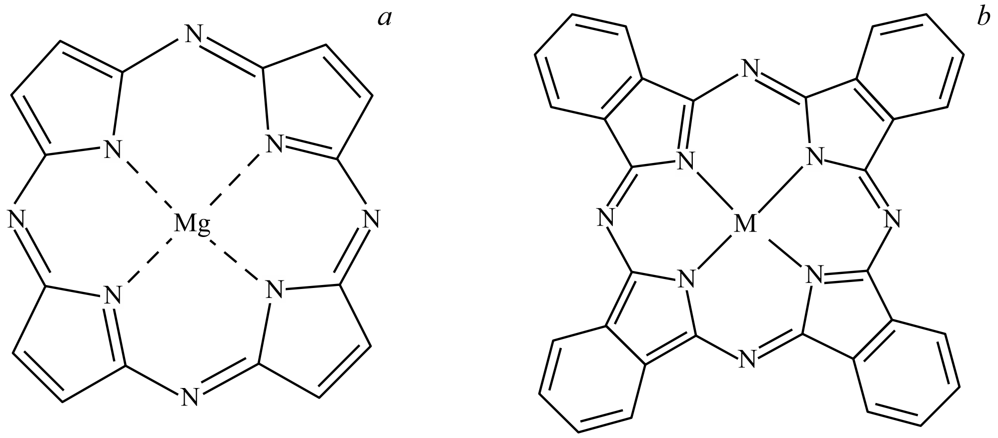

Figure 1. Structure formulas of Mg-TAP (*a*) and M-Pc (*b*); M = H_2, Mg, Zn, Pd and Pt.

This paper is devoted to the study of the spectral and photophysical properties of metal complexes of phthalocyanines and tetraazaporphyrins with various metal ions in the center of the organic ligand. The influence of the central metal ion on the spectral and photophysical parameters of a set of metal phthalocyanines is studied in detail for molecular ensembles in solutions. The paper presents the fluorescence excitation spectra of SM Mg-TAP in polymer films of polyisobutylene (PIB) at temperature of 6 K, revealing zero-phonon lines (ZPLs). It is shown that, in addition to the ZPL, some spectra contain phonon wings (PWs). A wide distribution of ZPL widths is presented, presumably indicating that fast spectral diffusion (SD) — stochastic jumps of the ZPL spectral position takes place in the host/guest system under study. The influence of the internal heavy atom effect on the photophysical parameters of triplet and singlet states for a set of phthalocyanines from free base to complexes with metal ions in the series from Mg(II) to Pt(II) is also studied. Change in the mass of metal ions in the center of the phthalocyanine macrocycle leads to an increase in the spin-orbit interaction (SOI) due to the presence of the internal heavy atom effect. As was previously shown in [19] for metalloporphyrins, the enhancement of SOI with the participance of singlet and triplet states leads to significant changes in the efficiency of singlet oxygen generation. Measurements of the intensity of this emission allows to define the quantum yield of generation of singlet oxygen (Φ_Δ), which is the main quantitative indicator of the efficiency of that process [20–22]. To study the dynamics of the SOI of phthalocyanine complexes, the quantum yields of singlet oxygen generation were used as an effective probe.

Experimental

Mg-5,10,15,20-tetraazaporphyrin (Mg-TAP), 29H, 31H-tetrabenzo[b,g,l,q]-5,10,15,20-tetraazaporphyrin (H_2-Pc) and its metal complexes synthesized by modified methods [23–25] were used in the experiments.. Structural formulae of the studied compounds are shown in Fig. 1. Phthalocyanine metal complexes were synthesized by the template method from phthalonitrile at high temperature. The synthesis of metal phthalocyanines with Mg(II), Zn(II), Pd(II), and Pt(II) ions was carried out by fusing the calculated amounts of acetates or dichlorides of the corresponding metals with phthalodinitrile according to the procedure described in [24]. All compounds were chromatographically purified and their structures were confirmed by the electronic absorption and luminescence spectra [23,24].

The absorption spectra were measured by means of a Shimadzu UV-3600 Plus double-beam spectrophotometer by using quartz cells of 1 cm. Detection of the singlet oxygen luminescence spectra, as well as of the spectra of fluorescence and fluorescence excitation for the studied compounds was performed by means of a Fluorolog-3 spectrofluorometer made by HORIBA Scientific, USA. Continuous radiation of a Ushio UXL-450SO xenon lamp with the power of 450 W, passing through a monochromator 180DF double monochromator, was used for photoexcitation of samples. Luminescence of singlet oxygen was detected by using a spectrograph with the spectral sensitivity in the range from 800 to 1700 nm. The iHR 320 spectrograph (HORIBA Scientific) was equipped with a Symphony II InGaAs CCD-array detector (HORIBA Scientific) cooled by liquid nitrogen down to 100 K. The spectra were corrected for the change of intensity of photoexcitation (lamp, monochromator and lattice), as well as for the spectral sensitivity of the detection system (spectrograph and detector). The singlet oxygen luminescence was detected directly during the measurement of luminescence in the spectral range near 1275 nm for the studied compounds in toluene and tetrahydrofuran. The singlet oxygen luminescence quantum yield (Φ_Δ) for the studied phthalocyanines was measured by the relative method using solutions of phenalenone in the same solvents as a standard sample. The Φ_Δ value for phenalenone in toluene is 0.99 [26]. For more details on the technique of spectral and kinetic measurements, see [19].

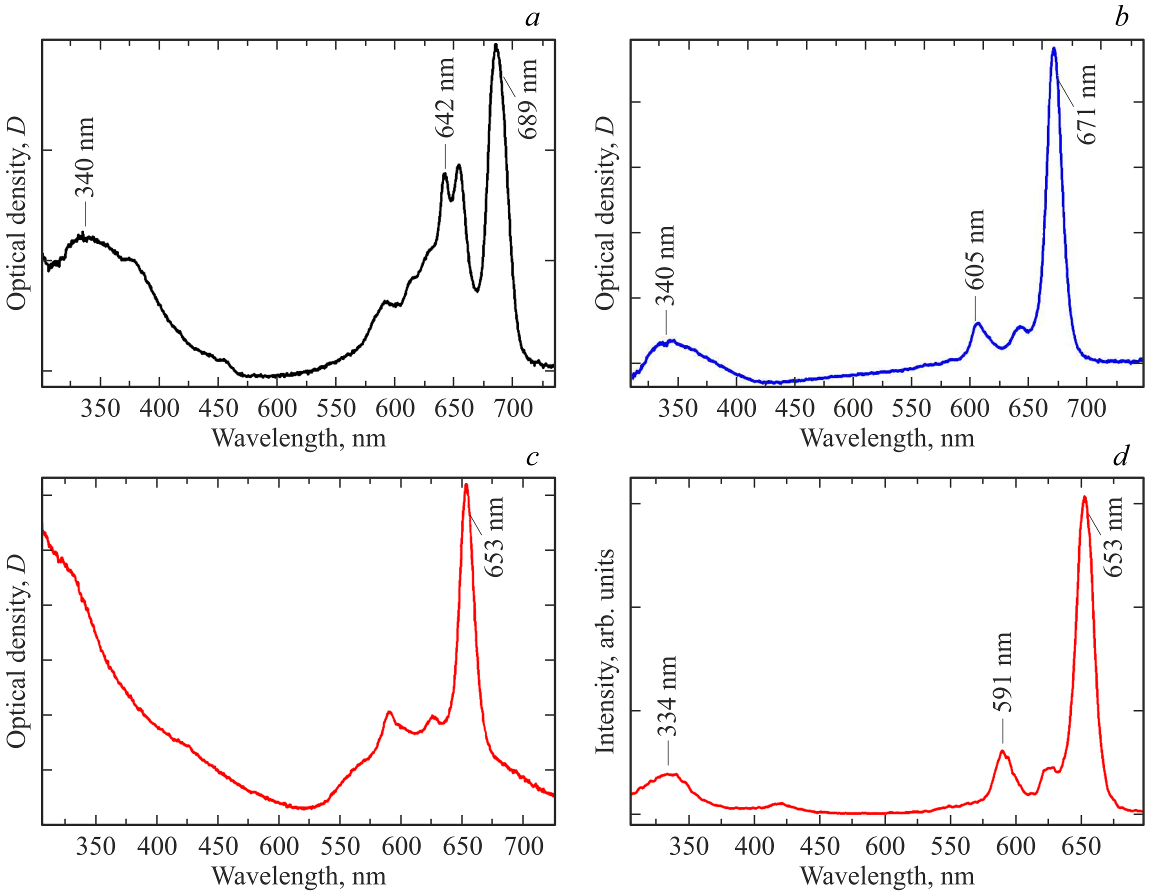

Figure 2. The absorption spectra of H_2-Pc (*a*), Zn-Pc (*b*), Pd-Pc (*c*) and the fluorescence excitation spectrum ($\lambda_{\text{det}} = 725$ nm) for Pd-Pc (*d*) in toluene at 293 K and atmospheric oxygen concentration.

The preparation of polymer films with Mg-TAP impurity molecules was carried out by spin-coating of a mixture of polymer/dye molecules/solvent onto a thin glass substrate. This approach allows to obtain polymer films with thicknesses in the range of 200-500 nm (according to atomic force microscopy data) containing impurity molecules in a predetermined concentration.

Detection of the luminescence of Mg-TAP SM was performed on a unique multifunctional luminescent nanoscope (see detailed description in [27]), which allows to detect fluorescent images and fluorescence excitation spectra simultaneously from all SMs in the field of view of a cryogenic epi-luminescent microscope ($30 \times 30\,\mu$m). In the experiments, the sample under study was mounted on a specially designed stage and placed in the focal plane of a high-aperture microobjective (Melles Griot,40×, 0.65 N.A.) and then loaded into the shaft of a temperature-regulated cryostat (RTI) where it was cooled by a flow of gaseous helium to the required temperature. Fluorescence images and fluorescence excitation spectra were recorded using synchronous frequency detuning of the exciting laser (Coherent CR-599, linewidth 8.3 GHz) in the spectral range 575–595 nm within 2000 GHz (~ 2 nm) with a step of 5 GHz and detection with a highly sensitive CCD camera (Andor iXon Ultra) of the Stokes component of SM fluorescence. The laser radiation power during the experiments was kept within 10–20 W/cm^2. Scattered laser radiation was preliminarily cut off using interference filters (Semrock, Thorlabs). The concentration of Mg-TAP molecules in the polymer film was chosen to observe only a small number (within a few tens) of emitting molecules in the field of view of the luminescent microscope for the entire laser scanning range at a given temperature.

Results and discussion

Figures 2 and 3 show the absorption, fluorescence and phosphorescence spectra, as well as the fluorescence excitation spectra for a set of phthalocyanines from free base (H_2-Pc) to complexes with metal ions in the series from Mg(II) to Pt(II). Data on the spectral and photophysical characteristics of the studied compounds are presented in Tables 1 and 2.

Figure 2 shows the absorption spectra for H_2-Pc (Fig. 2,*a*) and Zn-Pc (Fig. 2,*b*) in toluene at 293 K. In case of H_2-Pc, in the region of the long-wavelength

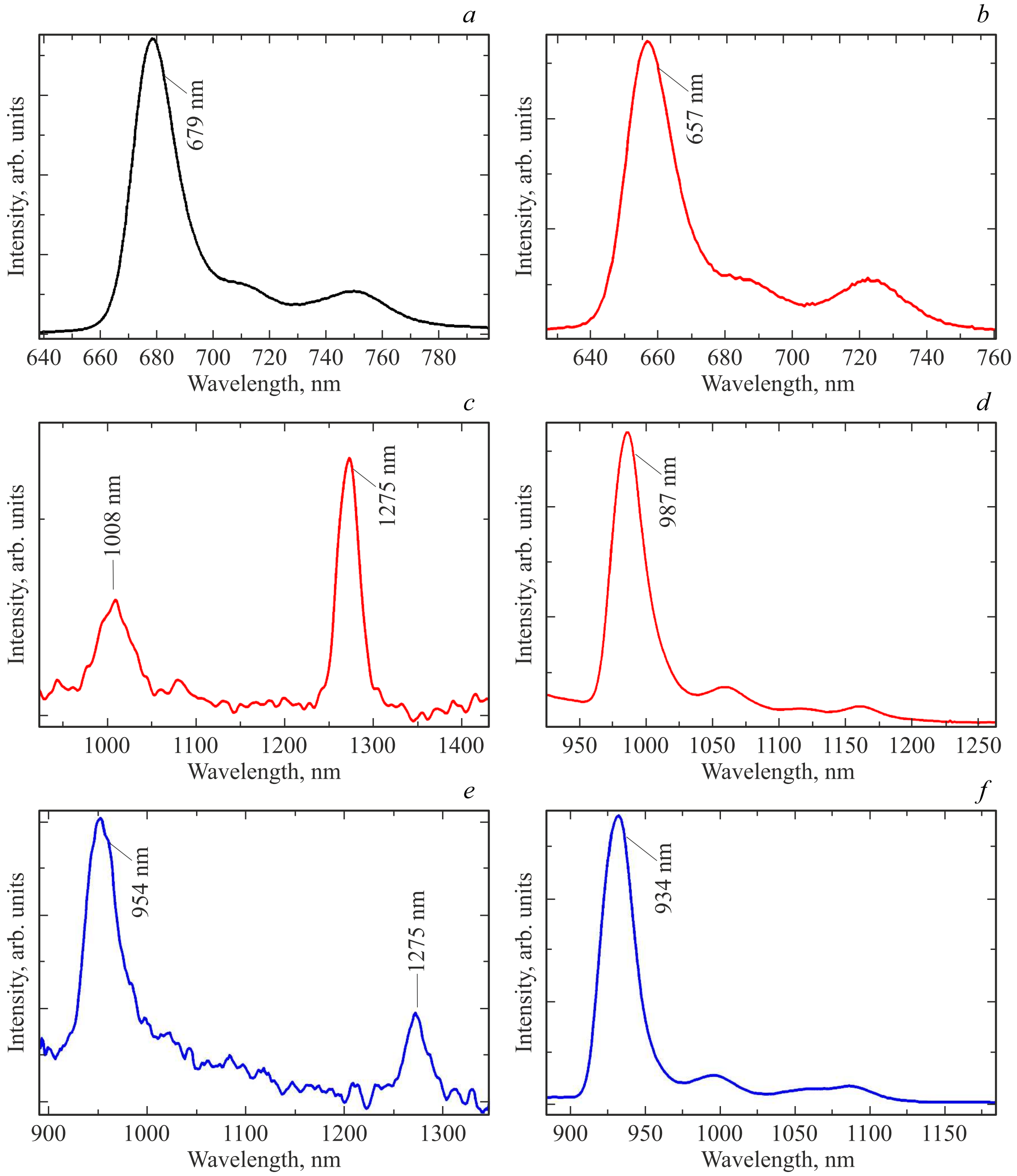

Figure 3. Fluorescence spectra of Mg-Pc (*a*) and Pd-Pc (*b*), phosphorescence spectra of Pd-Pc (*c*) and Pt-Pc (*e*) at 293 K phosphorescence spectra of Pd-Pc (*d*) and Pt-Pc (*f*) at 77 K in toluene and $\lambda_{\text{exc}} = 340$ nm.

band the removal of the two-fold degeneracy (bands 689 and 650 nm) is observed, while for Zn-Pc, a single band near 671 nm, corresponding to the superposition of two electronic transitions, is observed. One should note that Pd-Pc and Pt-Pc are extremely poorly soluble in most organic solvents. Fig. 2, *c* shows the absorption spectrum of Pd-Pc, where it is rather difficult to determine the intensities of a number of bands, which is necessary for calculating the fluorescence quantum yield and the quantum yield of singlet oxygen generation. The insufficient resolution in this spectrum is due to the poor solubility of Pd-Pc in toluene, which leads to the formation of various aggregated forms. In order to circumvent this problem, in this work we additionally measured fluorescence excitation spectra for all studied phthalocyanine compounds as such spectra are similar absorption ones for luminescent compounds when using samples with an optical density in absorption bands less than 0.1. Fig. 2, *d* shows the excitation spectrum for Pd-Pc, which allows to unambiguously determine the intensities of individual bands in the spectrum with good spectral

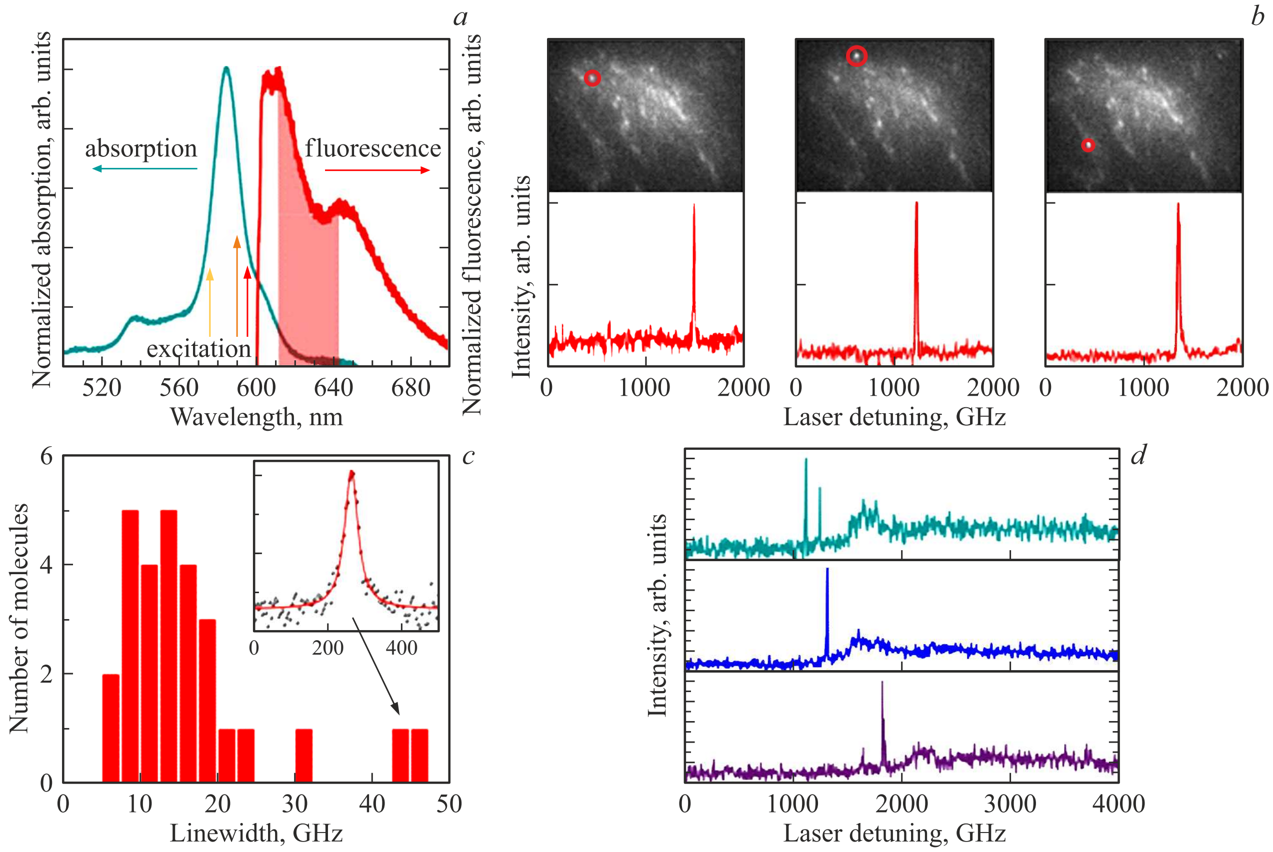

Figure 4. (*a*) Absorption and fluorescence spectra of Mg-TAP in PIB films at 293K. (*b*) Fluorescence images (top) and fluorescence excitation spectra (bottom) of three Mg-TAP SM in a PIB film at $T = 6$ K. (*c*) ZPL width distribution for 28 SM of Mg-TAP at $T = 6$ K. On insert — an example of an anomalously wide (43.3 ± 5.2 GHz) spectral line. (*d*) Successively recorded fluorescence excitation spectra for the same SM revealing PW.

Table 1. Spectral and energy characteristics at temperatures of 293 and 77 K, the values of quantum yields of singlet oxygen generation (Φ_Δ) for the studied compounds at atmospheric oxygen concentration

Compound	Fluorescence λ_{0-0}, nm 293 K	Phosphorescence λ_{0-0}, nm 77 K	$\Delta E_{\mathrm{S-T}}$ cm^{-1}	$\Delta E_{\mathrm{T-SO}}$ cm^{-1}	Φ_Δ
Mg-TPP	604	737	2990	5750	0.65
Mg-TAP	589	904	5300	3240	0.1
H_2-Pc	695	1220	6190	360	0.37
Mg-Pc	681	1084	5460	1406	0.41
Zn-Pc	681	1020	4880	1990	0.7
Pd-Pc	654	989	5180	2290	0.92
Pt-Pc	643	937	4880	2850	0.95

Note: $\Delta E_{\mathrm{S\text{-}T}}$ — energy gap between positions S_1 and T_1 of electronic levels of compounds under study; Mg-TPP — Mg-5,10,15,20-tetraphenylporphyrin; $\Delta E_{\mathrm{T-SO}}$ — energy gap between the position of the compound electronic level T_1 and the position of the singlet oxygen level $^1O_2$; Φ_Δ — quantum yield of singlet oxygen generation, Φ_Δ values were determined with an error of no more than ±0.05.

resolution. Then, based on a comparison with the absorption spectra, it is possible to obtain reliable information for calculating the photophysical characteristics.

In the fluorescence spectra for ensembles of molecules of phthalocyanines H_2-Pc and compounds with light metal ions of Mg(II) (Fig. 3, *a*) and Zn(II), as well as for Mg-TAP, an intense fluorescence with high quantum yields is observed (for example, for Mg-Pc — 0.78). Fluorescence quantum yields for all the studied compounds were measured by using the relative method. Solution of Zn-TPP in toluene with the quantum yield of 0.03 was used as the reference sample [28]. For the Pd-Pc molecule, weak fluorescence is

Table 2. Photophysical characteristics of singlet and triplet states for Mg-TPP, Mg-TAP, free base and metallic complexes of Pc in toluene at 293 K

Compound	$\tau_{\rm Fl}$, ns	$\Phi_{\rm Fl}$	$K_{\rm Fl}$, $\mu{\rm s}^{-1}$	$K_{\rm isc}$, $\mu{\rm s}^{-1}$	$\Phi_{\rm isc} = \Phi_\Delta$	$\Phi_{\rm ic}$	$\tau_{\rm Ph}$, μs	$\Phi_{\rm Ph}$	$K_{\rm Ph} \cdot 10^3$, ${\rm ms}^{-1}$
Mg-TPP	8.6	0.146	16.9	39	0.65	0.23	85000	$5 \cdot 10^{-5}$	0.9
Mg-TAP	4.5	0.55	122.2	100	0.1	0.35	10000	$4 \cdot 10^{-5}$	4
H_2-Pc	6.5	0.54	82	70.1	0.37	0.08	–	–	–
Mg-Pc	7.2	0.78	92.3	30.5	0.41	~ 0	1000	$5 \cdot 10^{-6}$	$5 \cdot 10^{-3}$
Zn-Pc	3.8	0.32	84.2	179	0.7	~ 0	1100	10^{-4}	$9 \cdot 10^{-2}$
Pd-Pc	< 1.15	$6 \cdot 10^{-4}$	0/055	~ 870	0.92	0.08	25	$3 \cdot 10^{-3}$	120
Pt-Pc	–	–	–	~ 1000	0.95	0.05	7	$1 \cdot 10^{-2}$	1400

Note: $\tau_{\rm Fl}$ — the lifetime of the first excited singlet state; $\Phi_{\rm Fl}$ — fluorescence quantum yield; $K_{\rm isc}$ — probability of nonradiative intercombination $S_1 \rightsquigarrow T_1$-transition; $\Phi_{\rm isc}$ — quantum yield of a nonradiative intercombination $S_1 \rightsquigarrow T_1$ transition; Φ_Δ — quantum yield of singlet oxygen generation; $K_{\rm Fl}$ — probability of radiative $S_1 \rightarrow S_0$-transition at 293 K; $\Phi_{\rm Ph}$ — quantum yield of phosphorescence at 77 K; $\tau_{\rm Ph}$ — phosphorescence lifetime; $\Phi_{\rm Ph}$ and $\tau_{\rm Ph}$ at 77 K were obtained by the authors and partially taken from the paper [43]; $K_{\rm Ph}$ — probability of radiative $T_1 \rightarrow S_0$-transition at 77 K.

detected (Fig. 3, *b*) with a low value of the quantum yield. Phosphorescence for these compounds is practically absent even at low temperatures.

Mg-TAP molecules can be used for luminescence detection at the level of single emitters due to the unique spectral and photophysical parameters of this compound. Generally, to date, it has turned out to be possible to observe SM luminescence at ultralow temperatures only for a fairly small set of conjugated organic macroheterocycles [29,30]. At the same time, for Mg-TAP in solid matrices of inert gases, detection of SM luminescence at 2 K was successfully implemented [31]. A direct comparison of the ZPL parameters of Mg-TAP SM embedded into matrices of frozen inert gases at $T = 2$ K and terrylene embedded into saturated hydrocarbons [30] showed that the ZPL widths of these compounds are comparable and amount to tens of MHz, i.e. are actually determined by the lifetime of their excited electronic states.

As follows from Table 2, among the porphyrins, tetraazaporphyrins, and phthalocyanines, it is Mg-TAP that stands out with the highest probability of the radiative $S_1 \rightarrow S_0$ transition ($K_{\rm Fl}$ constant), which, moreover, increases by almost 2 times (fluorescence quantum yield — 0.9) as the temperature decreases to 77 K [29]. Similar behavior is also characteristic of terrilene molecules, when the rate constant of the transition $S_1 \rightarrow T_1$ [32,33] at 300 K is $42 \cdot 10^3\,{\rm s}^{-1}$. At a temperature of 5 K, this constant only has a value of $0.4 \cdot 10^3\,{\rm s}^{-1}$, which indicates a significant drop in the probability of a transition to the triplet state and an increase in the probability of an emission transition in $S_1 \rightarrow S_0$. The issue of the triplet state population behavior for terrylene is considered in more detail in [34].

Fig. 4 shows the absorption and fluorescence spectra for Mg-TAP in a polyisobutylene (PIB) polymer film at 293 K. The arrows here show the excitation wavelengths $\lambda_{\rm exc}$, and the dashed lines show the stokes luminescence band used to record fluorescence images and fluorescence excitation spectra for Mg-TAP SM in PIB thin films at $T = 6$ K. Fig. 4 *b* shows the spectra of three SM consisting only of ZPLs. Fig. 4, *c* shows the ZPL width distribution of 28 SM Mg-TAP obtained by approximating the measured spectra with the Lorentz function. The given values are averages over 20 spectra measured for each SM. The averaging was carried out in order to level out the contribution from the rare SD of ZPLs due to the interaction of SM with tunneling two-level systems (TLSs) [35]. Spectral diffusion manifests itself in the form of stochastic jumps in the ZPL position in a wide range up to 1000 GHz, which, apparently, in addition to interaction with TLS, can be due to conformational changes in the Mg-TAP/polymer matrix system [11].

The presented results look somewhat unexpected. Although there are no data on the homogeneous ZPL broadening for Mg-TAP molecules in PIB in the literature, a comparison of the results of experiments on photon echo of structurally related Zn-tetraphenylporphine complexes in poly(methyl methacrylate) with the results for terrylene in the same matrix shows that the value of homogeneous broadening of ZPL for these molecules is comparable [36]. Based on this, one can assume that the true ZPL width of the Mg-TAP SM at a temperature of 6 K should be approximately within the limits 2–3 GHz [37], and the width of the laser line — in the limits of 11–12 GHz. However, as follows from Fig. 4, *c*, this condition is satisfied only for 11 out of 28 studied molecules.

The most rational explanation of the observed phenomenon is the presence in the Mg-TAP/PIB system of a fast SD that proceeds with characteristic times less than the time of one laser frequency detuning step ($t_{\rm exp} = 0.3$ s) and is masked by the shape of the measured spectral line $I(\omega, t_{\rm exp})$. The general form of the latter can be represented as [38]

$$I(\omega, t_{\rm exp}) = \int P(\omega, t_{\rm exp}) I_{\rm Voight}(\omega - \omega')\,d\omega',$$

where $I_{\rm Voight}$ corresponds to the Voigt profile resulting from the convolution of the Gaussian laser line profile and the Lorentz contour of the homogeneous broadened ZPL, $P(\omega, t_{\rm exp})$ — the probability of the molecule excitation at the frequency ω, depending on the parameters of the TLS interacting with the molecule and the characteristic times of the experiment t_{exp}. Although the shape of $I(\omega, t_{\text{exp}})$ can be quite complex, all recorded ZPL had a symmetrical bell shape, which indicates that the characteristic SD times in this experiment are much less than 0.3 s.

Generally speaking, the contribution of SD to the observed ZPL broadening is usually underestimated. Thus, for instance, in one of the first papers where SD was observed for SM in polymer films, it was shown that in a number of cases their ZPL cannot be considered to be broadened exclusively homogeneously even at 1.7 K, apparently, just because of fast, spectrally unsolvable SD [39]. An even more illustrative case is considered in Ref. [38], where the energy transitions in a huge number of TLS at 1.5 K are so fast that during the spectrum measurement they form an almost continuous spectral line with a width of about 15 GHz. Apparently that a similar phenomenon takes place in our case, and one may consider that it can also have a light-induced origin [14].

An example of PW in the spectra of the same Mg-TAP SM is shown in Fig. 4, *d*. Contrary to the previously shown PW of a pronounced Lorentzian shape [12], these spectra reveals PWs with an extended high-frequency „tail“. Moreover, the PW shape clearly changes from spectrum to spectrum. Based on the fact that the ZPL of the observed SM demonstrates a well-resolved SD, it is not obvious that the observed effect is a consequence of only a change in the true shape of the PW, and is not related to the behavior of the $P(\omega, t_{\text{exp}})$ function at t_{exp} on the order of units to hundreds of seconds (the recording time of one spectrum in Fig. 4, *d* is equal to 240 s). In the same time, it is known that, due to the quadratic electron-phonon (EP) interaction, the PW shape contains information on the vibrational states density (vDOS) $D(\omega)$ of the local environment of SM [40]. Generally, the shape of the PW can be described with sufficient accuracy using only single-phonon functions $\upsilon_1(\omega)$, which, with a moderate strength of the electron-phonon coupling, are related to $D(\omega)$ as follows [40]: $\upsilon_1(\omega) \sim \omega^2 D(\omega)$. It cannot be ruled out that, due to energy transitions in the TLS, the potential energy surface of the local environment of the investigated SM undergoes a continuous transformation, which, in turn, affects the shape of $D(\omega)$ and the EP coupling parameters. However, the opposite effect is also possible: the probability of tunneling transitions increases due to a change in the local vDOS. As shown in [41], a change in the phonon states of the system affects the probabilities of optical transitions in the impurity SM, which means that it can be assumed that tunneling transitions in the matrix, leading to the transformation of the vDOS, can ultimately cause light-induced SD.

The above examples show that Mg-TAP is an extremely promising candidate for impurity center spectroscopy, capable of demonstrating experimental effects at the SM level that were not previously observed for compounds of other classes.

Fig. 3 shows the fluorescence spectra for Mg-Pc (Fig. 3, *a*) and Pd-Pc (Fig. 3, *b*) in toluene at 293 K. To record the fluorescence spectra, the samples with an optical density in the range from 0.07 to 0.09 in the most intense long-wavelength band of the absorption spectrum were used, that allowed us to completely eliminate the effect of reabsorption on the fluorescence spectra.

The data in Table 2 demonstrate that Mg-Pc exhibit an intense fluorescence with a high quantum yield of 0.78 (similar to the data in [42]) and the second highest (the highest one is for Mg-TAP) probability of an radiative fluorescent $S_1 \rightarrow S_0$ transition ($K_{\text{Fl}} = 92.3\,\mu\text{s}^{-1}$). However, the constant of the radiative phosphorescent $T_1 \rightarrow S_0$ transition (K_{Ph}) for this compound has one of the smallest values in Table 2. For the Pd-Pc molecule, weak fluorescence is observed (Fig. 3, *b*) with the quantum yield value of $6 \cdot 10^{-4}$ and $K_{\text{Fl}} = 0.055\,\mu\text{s}^{-1}$. For the Pd-Pc complex, there is phosphorescence simultaneously with fluorescence (Fig. 3, *c*) with a maximum of about 1000 nm with a quantum yield of approximately $5 \cdot 10^{-5}$ [43] even in solutions with the presence of oxygen. Let us note that the obtained results basically coincide with the data for analogous compounds given in [43] (differences up to 12 nm), and such a scatter may be due to the errors in the spectrometer calibrations. The positions of the bands in the fluorescence spectra, as well as the energy gap between the electronic states of S_1 and T_1 ($\Delta E_{\text{S-T}}$) are given in Table 1.

Differences in the photophysical and spectral characteristics of phthalocyanine metal complexes are determined to a decisive extent by the influence of SOI. The effect of the internal heavy atom leads to the greatest increase in the SOI [44,45]. An increase in the mass of the central ion from Mg(II) to Pd(II) and Pt(II) has the greatest effect on the spectral and photophysical parameters of metal phthalocyanines. Previously, a similar manifestation of the effect of the internal heavy atom was observed for metalloporphyrins [19]. For H_2-Pc and complexes with light metals (Mg-Pc, Zn-Pc), intense fluorescence is observed, while phosphorescence is practically absent.

At room temperature, for all the studied metal complexes of porphyrazines and phthalocyanines, the spectra show a band at about 1270 nm, which corresponds to the luminescence of singlet oxygen. Using the quantitative measurements of the quantum yield of singlet oxygen generation under photoexcitation is of a great importance for evaluating the SOI effect and determining the deactivation channels for lower excited electronic states. The quantum yields of singlet oxygen generation for Mg-TAP, H_2-Pc, Mg-Pc, Zn-Pc, Pd-Pc and Pt-Pc were measured in toluene solutions at 293 K according to the method described in detail in [19]. Data on the values of the quantum yield of singlet oxygen generation are also given in Table 1.

In the spectral measurements performed, the photoexcitation of phthalocyanine macrocycles was carried out in the 320−370 nm range, which corresponds to absorption at the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions for these molecules. Deactivation of high-energy electronic states S_2, S_3 and S_4

occurs at a high rate (10^{-12}–$10^{-13}\,\mathrm{s}^{-1}$) due to nonradiative transitions [42,46]. Further, photophysical processes occur with the participance of only the S_1 and T_1 states.

All transitions between singlet and triplet states are forbidden by the intercombination prohibition, which is removed under the effect of SOI. The reason for SOI for porphyrines and phthalocyanines is interaction with participation of non-planar vibrations in singlet and triplet states for intense electron-vibrational transitions, which are manifested in the Soret band. Spin-orbit coupling is also due to the interaction between the orbitals of the organic ligand and metal atoms [47,48]. In addition to fluorescence in the $S_1 \rightarrow S_0$ transition, the nonradiative ones are possible for $S_1 \rightsquigarrow T_1$ and $T_1 \rightsquigarrow S_0$ Phosphorescence can be observed in the $T_1 \rightarrow S_0$, which is usually detected at a low temperature or in deoxygenated solutions. The probability of emissionless transition $S_1 \rightsquigarrow T_1$ is several orders less, than the probability of internal conversion, but the presence of SOI leads to efficient population of the triplet state T_1. For metal phthalocyanines and metal porphyrins, it was previously experimentally established that the internal conversion of $S_1 \rightsquigarrow S_0$ is insignificant in the presence of SOI.

Table 1 presents the results of estimating the energy gap between the electronic states S_1 and T_1 ($\Delta E_{\text{S-T}}$). The highest value of this parameter is observed for Mg-TAP, H_2-Pc and Mg-Pc (over $5000\,\mathrm{cm}^{-1}$), which largely explains the high values of the fluorescence quantum yield along with other factors. The energy gap between the triplet states ($\Delta E_{\text{T-SO}}$) and the singlet oxygen level do not reach $2000\,\mathrm{cm}^{-1}$ and do not exceed $3000\,\mathrm{cm}^{-1}$ for most phthalocyanine complexes.

The results of the measurements of Φ_Δ for the above listed compounds in toluene solutions are also given in Table 1. In particular, the smallest value of Φ_Δ is only 0.1 for Mg-TAP, which correlates well with the high fluorescence quantum yield for this compound. Similar values of Φ_Δ for H_2-Pc and Mg-Pc in toluene are close to 0.4. The Φ_Δ values for other metal phthalocyanines are — 0.7 for Zn-Pc and reach values of 0.92 for Pd-Pc and 0.95 for Pt-Pc. The data in Table 1 demonstrate the maximum values of Φ_Δ for the compounds with heavy ions of Pd(II) and Pt(II), which is due to the significant influence of the internal heavy atom effect.

Table 2 provides data on photophysical parameters of the studied porphyrine complexes in the states S_1 and T_1. Fluorescence with a lifetime of several nanoseconds is observed for most of the studied compounds. For H_2-Pc this value is 6.5 ns and is decreased down to the value below 1.0 ns for Pd-Pc. Note that there is no fluorescence of Pt-Pc at all, but rather significant phosphorescence is observed, which is due to highly efficient interconversion from singlet to triplet states. Let us also note that the triplet states of all the studied compounds are effectively quenched by molecular oxygen [49,50].

Experimentally obtained values of the lifetimes of states S_1 and T_1 (τ_{Fl}, τ_{Ph}), as well as measured values of quantum yields of fluorescence (Φ_{Fl}) and singlet oxygen generation yields (Φ_Δ) allowed to determine a number of photophysical parameters. We determined the probabilities of radiative and nonradiative transitions for the studied molecules. The probabilities were calculated based on the photophysical data given in Table 2, by using the formulae, which were earlier used in [51,52]. In the calculations we assumed that the sum of $\Phi_{\text{Fl}} + \Phi_{\text{isc}} = 1$ is in accordance with the results of [42,46]. Correctness of this equation for phthalocyanines and porphyrines is proven in numerous papers, i.e. energy relaxation of S_1 state occurs into the triplet state, and the probability of internal conversion $S_1 \rightsquigarrow S_0$ is negligible.

The quantum yield of interconversion into triplet states was determined by using the data on photosensitized generation of singlet molecular oxygen. The quantum yield Φ_{isc} is equal to the quantum yield of generation of singlet molecular oxygen Φ_Δ if the probability of energy transfer from the photosensitizer lower triplet state T_1 to the ground state of singlet oxygen is 100%. In case of phthalocyanines and porphyrines [22,51] singlet oxygen is generated with a high probability, thus, we can conclude that $\Phi_{\text{ics}} = \Phi_\Delta$ with good accuracy. The photosensitizer concentration in experiments was approximately 10^{-7} M/l, and the concentration of molecular oxygen was more than 10^{-3} M/l for toluene, which provided almost the 100%-probability of generation of singlet oxygen in the collisions of photosensitizer molecules with molecular oxygen.

The interconversion yield from the T_1 state is defined as $\Phi_{\text{ic}} = 1 - \Phi_{\text{isc}} - \Phi_{\text{Fl}} - \Phi_{\text{Ph}}$. The values of Φ_{ic} are also given in Table 2. For free base compounds and complexes with light metals Mg(II) and Zn(II) there is no phosphorescence at room temperature in solutions with oxygen [53]. Therefore, for these compounds, the values of $\Phi_{\text{Ph}} = 0$ and the values given in Table 2 correspond to the measurements of Φ_{Ph} at 77 K. We were unable to measure the quantum yields and lifetimes for phthalocyanine compounds at room temperature in solutions with oxygen.

The phosphorescence spectra for most of the phthalocyanine complexes were measured at 77 K, when there is no oxygen diffusion. Data on lifetimes and quantum yields are given in Table 2. At 77 K, the is no quenching of the triplet state by oxygen, and this leads to a sharp increase in the quantum yield by more than two orders of magnitude of the phosphorescence yield and to an increase in the phosphorescence lifetime. Fig. 3, *d* and 3, *f* show the phosphorescence spectra of Pd-Pc and Pt-Pc in toluene at 77 K. It follows from the data in Table 2 that the probability of a radiative $T_1 \rightarrow S_0$ transition (K_{Ph}) for Pd-Pc is $120 \cdot 10^3\,\mathrm{ms}^{-1}$ (based on formulae from [51]), while for Pt-Pc the similar value is already $1400 \cdot 10^3\,\mathrm{ms}^{-1}$. A similar constant for the other studied compounds is only $4 \cdot 10^3\,\mathrm{ms}^{-1}$ for Mg-TAP and less than $10^3\,\mathrm{ms}^{-1}$ for other compounds, which indicates an insignificant probability of radiative processes even at low temperatures. The presented data indicate a significant influence of the heavy atom effect (increase in SOI value and decrease in the influence of intercombination prohibition) on the rate of radiative deactivation of the T_1 state. It should be noted that the quantum yield of the nonradiative deactivation of the triplet state for Pd-Pc and Pt-Pc at 77 K is very significant according to the data in Table 2.

The presented data on the deactivation of the lower triplet state for the studied compounds demonstrate various regularities in the effect of SOI on the deactivation rate of the triplet state in solid solutions at 77 K.

Conclusion

Spectroscopic study of the efficiency of generation of singlet oxygen for free base H_2-Pc as well as for their metallic complexes with ions Mg(II), Zn(II), Pd(II) and Pt(II) was performed. Quantum yields of the singlet oxygen generation were measured. It was determined that the maximum values of Φ_Δ are typical for the compounds with ions Pd(II) and Pt(II), which is due to the influence of the internal heavy atom effect on the efficiency of intercombination conversion. For the free base phthalocyanine, there is no intrinsic heavy atom effect, but the presence of a significant SOI leads to high Φ_Δ values for this compound. The quantum yield of interconversion into triplet states was determined based on the data on photosensitized generation of singlet molecular oxygen for the studied compounds. The radiative deactivation of the lower triplet state for phthalocyanines with various ions demonstrates the peculiarities of the influence of the internal heavy atom effect on the deactivation rates of the triplet state at 77 K.

The paper also demonstrates the captured fluorescence images and fluorescence excitation spectra for SMs of Mg-TAP in polymer films of PIB at a temperature of 6 K. The measured spectra consist both exclusively of narrow ZPLs and, in addition to them, broad PWs are detected. The paper shows the presence of a wide distribution of ZPL widths, which, apparently, indicates the presence of a fast (compared to the temporal resolution of the experimental setup) SD in the matrix/impurity system under study.

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Conflict of interest

The authors declare that they have no conflict of interest.

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