Physical-chemical properties of tetraphenylporphyrin, its octasubstituents, and complexes with metals in the ground and excited states

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The ability of limiting powerful laser radiation (up to 400 MW/cm^2) by solutions of tetraphenylporphyrin (TPP) and its derivatives, as well as spectral-luminescent and photochemical properties of these molecules at their excitation to different electronic states by radiation of different wavelength and intensity is investigated. The quantum yields of fluorescence from S_1 and S_n excited states and, in some cases, the quantum yields and features of phototransformations under exposure to powerful laser radiation have been determined.

Introduction

The study of physical-chemical properties of porphyrin molecules is one of the urgent problems in modern science, since porphyrin compounds make up the basis of many biological objects and living organisms, whose interaction with electromagnetic radiation of the UV, visible, and IR regions allows the researchers to carry out investigations into the photosynthesis, as well as to develop and improve techniques for earlier diagnostics and treatment of many diseases.[1,2] In recent years the problem of optical limitation of high-power laser pulses, that is, fast (during a laser pulse) increase of absorption of a material at its rather high initial linear transmittance (60–80%), has become increasingly important. This problem is solved both due to reverse saturable absorption (RSA) from excited states – induced absorption of complex organic molecules and due to thermo- and light-induced scattering of high-power laser radiation by the medium.[3]

Besides the requirement of intense induced absorption, one more is imposed on such compounds, namely, the absence of amplification of natural stimulated radiation under the exposure to high-power laser radiation. These requirements are met in fullerenes,[3] as well as in porphyrins and porphyrin-like compounds,[4] which are characterized by low quantum yields of fluorescence due to high rates of the internal and intercombination conversion.[1,2,4]

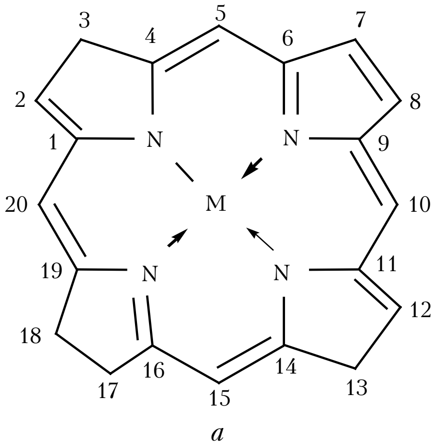
O'Flatherty et al.,[5] have analyzed the molecular structure and the absorption cross sections in excited states for a number of porphyrin-like molecules, but failed to find an unambiguous relation between variation of the absorption cross sections of the excited molecules and the capability of such molecules to optically limit high-power laser radiation in the spectral range studied. So additional information about the physical-chemical properties of molecules capable of optically limiting high-power laser radiation is needed.

By now there are rather many media for optical limitation (OL) of the visible and IR region, but the data on limitation of high-power radiation in the UV region are almost lacking. Besides, there are no data on photostability of porphyrins under the exposure to high-power laser radiation.

In this connection, the objectives of this investigation are photophysical and photochemical properties of tetraphenylporphyrin (TPP) and some its substituents at excitation into different electronic states, OL of high-power (up to 400 MW/cm^2) radiation of XeCl laser and that of the second harmonic of a Nd:YAG laser by these compounds, and discussion of the mechanisms of OL and phototransformations under these conditions.

Objects and methods of the study

As objects of study, we took some tetraphenyl-derivatives of porphyrin in complexes with different metals (MTPP, where M may be Zn, Cu, Ni, Co, Eu, In(Cl), and Al(Cl)), including metal-free base TPP, metal-free protoporphyrin IX (PP), as well as free bases of tetraphenylporphyrin octasubstituents, the technique of whose synthesis is described in Ref. 6. These compounds were selected for the study of spectral-luminescent and photochemical properties because of the practical applications of metal-porphyrins,[7] as well as the unusual structure of distorted porphyrin cycles, TPP β-octa-substituents, and their unique properties.[8] Chloroform, ethyl acetate, ethanol, and the 3-normal aqueous solution of HCl (for PP) were used as solvents. The structural formulas of the compounds under study are shown in Fig. 1*a*.



b

Fig. 1. Structural formulas (*a*): 1) tetraphenylporphyrin (TPP): 5, 10, 15, 20 – C_6H_5, M – H_2; 2) metal-tetraphenylporphyrin (MTPP): 5, 10, 15, 20 – C_6H_5, M – Zn, Ni, Co, Cu, Eu, Al(Cl), In(Cl); 3) protoporphyrin IX (PP): 2, 7, 12, 18 – CH_3, 3, 8, 13, 17 – (–CH = COOH); 4) octabrominetetraphenylporphyrin (OBrTPP): M – H_2, 2, 3, 7, 8, 12, 13, 17, 18 – Br, 5, 10, 15, 20 – C_6H_5; 5) octamethyltetraphenylporphyrin (OMeTPP): M – H_2, 2, 3, 7, 8, 12, 13, 17, 18 – CH_3, 5, 10, 15, 20 – C_6H_5; 6) indium-chlorine complex of (InClOMeTPP): M – InCl, 2, 3, 7, 8, 12, 13, 17, 18 – CH_3, 5, 10, 15, 20 – C_6H_5; 7) Dodecakis(4-phenyl)phenylporphyrin (DCPP): M – H_2, 2, 3, 5, 7, 8, 10, 12, 13, 15, 17, 18, 20 – C_6H_4 – C_6H_5; 8) Dodecaphenylporphyrin (DPP): M – H_2, 2, 3, 5, 7, 8, 10, 12, 13, 15, 17, 18, 20 – C_6H_5; and the schematic layout of the experimental setup (*b*): filters F; beam splitter BS; cylindrical lenses L1, L2; diaphragm D; cell with solution C; meters of optical energy M1, M2.

Figure 1*b* shows the schematic layout of the experimental setup. To study the limiting properties of the above compounds, two lasers were used as the excitation sources. The exciplex XeCl laser had the following parameters: wavelength λ = 308 nm, pulse energy E_p up to 40 mJ, pulse duration τ = 10 ns. The laser radiation in the form of a 1.8×0.8-cm rectangular-shaped beam was focused by two crossed cylindrical lenses, and the power density of radiation W in the focal spot was as high as 300 MW/cm^2. For radiation limitation in the visible region, radiation of the second harmonic of a Nd:YAG laser was used. This radiation had the following characteristics: wavelength λ = 532 nm, pulse energy up to 20 mJ, pulse duration τ = 6 ns, pulse power density W up to 200–300 MW/cm^2. The cell was illuminated by a converging beam, whose cross size varied from 0.5 to 1 mm and almost did not change over the cell length l = 0.5 cm. The initial transmittance T_0 of the studied solutions measured by the spectrophotometer was from 40 to 70%. At variation of the power density, the transmitted and incident energy was measured with a high-sensitive KTP-2 and a Gentec E energy meters. The error in determination of transmittance was within 6%.

The property of optical limitation of a solution was characterized by the limitation coefficient LC = T_0/T_W, that is, the ratio of the linear transmittance of the solution measured with the spectrophotometer to the transmittance at the laser radiation power density W.

In the case that the transmittance saturated with the increasing laser radiation intensity, that is, the sort of absorbing centers produced after excitation had constant transmittance and absorption coefficient K^*, the effective absorption cross section in an excited state σ^*_{532} was estimated by the technique described in Ref. 7.

The electronic absorption spectra were recorded with a Specord M-40 spectrophotometer, and the fluorescence spectra with a Hitachi-850 spectrofluorimeter.

The quantum yields of fluorescence γ_{fl} were determined by the technique described in Refs. 9 and 10. Luminophors with known quantum yields of fluorescence in the spectral regions studied were used as standards. Nile blue (NB) in ethanol (λ^{fl}_{max} = = 672 nm, γ_{fl} = 0.23) [Ref. 11] was used as a standard for determination of ordinary fluorescence, while coumarin 1 (C1) in ethanol (λ^{fl}_{max} = 450 nm, γ_{fl} = = 0.73) and coumarin 102 (C102) in ethanol (λ^{fl}_{max} = = 475 nm, γ_{fl} = 0.95) [Ref. 12] served for determination of the quantum yields of short-wave fluorescence.

The quantum yields of phototransformations were determined by a spectroscopic method[10] φ = = N_p/N_b = $[(1 - D/D_0)\ C_0 N_A V]\ h\nu/E_{tot}$, N_p and N_b are numbers of destructed and excited molecules; where D_0 and D is the optical density at a chosen wavelength before and after exposure, respectively; C_0 is the initial concentration of molecules; N_A is the Avogadro number; $h\nu$ is the energy of the exciting quantum, in J; E_{tot} is the total excitation energy, in J, absorbed by the volume V. An important aspect of this method is that it is applied to both ordinary and high-power excitation, and absorption of a photoproduct should be low in the region of absorption by the initial compound. The error in determination of the quantum yield of phototransformation was 10%.

Results and discussion

Spectral-luminescent properties. Figure 2 and Table 1 summarize the absorption characteristics of TPP and its derivatives, which indicate that as metal atoms substitute protons of pyrrole cycles, the Soret band (narrow intense band nearby 400 nm in Fig. 2) slightly shifts and its intensity increases, and only one band remains in the long-wave region. As a result of β-octa-substitution, the Soret band in metal-free porphyrins experiences a long-wave shift and decreases in intensity, and usually three rather than four peaks are observed in the visible region (Fig. 2, Table 1).

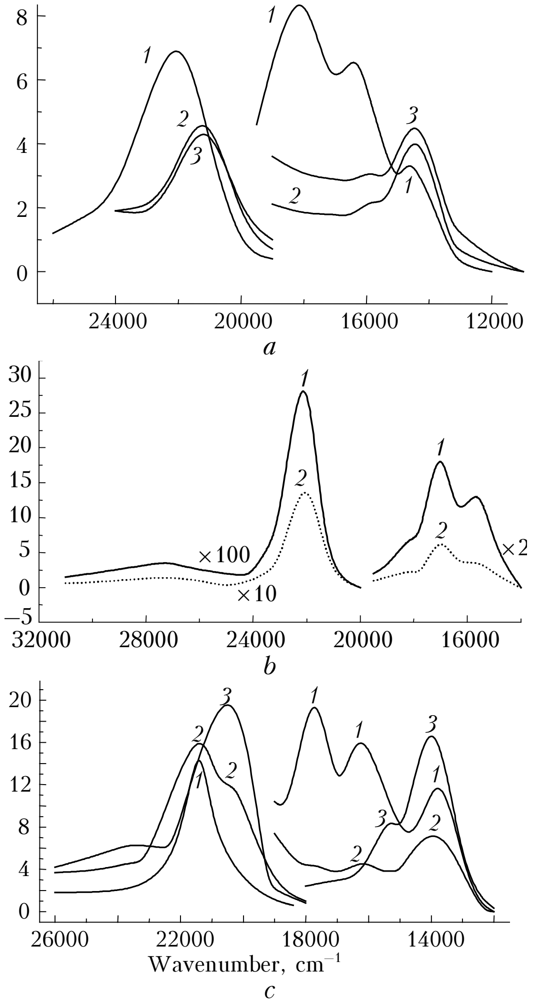


Fig. 2. Absorption spectra of chloroform solutions of OMeTPP (*a*), InClOMeTPP (*b*), and DPP (*c*); $c = 2\times10^{-4}$ mol/liter [curves *1* (*a*), *1* (*b*), *1* (*c*)], $c = 6\cdot10^{-6}$ mol/liter [*2*, *3* (*a*)], $c = 8\cdot10^{-6}$ mol/liter [*2* (*b*)], $c = 4\cdot10^{-5}$ mol/liter [*2*, *3* (*c*)]; before [*1*, *3* (*a*); *1*, *2* (*b*), *1*, *2* (*c*)] after [*2* (*b*), *3* (*c*)] exposure to XeCl laser radiation.

It was noticed that the spectral-luminescent characteristics of octasubstituted TPP in chloroform varied with variations of the concentration. Thus at the concentration $\leq 10^{-5}$ mol/liter the Soret bands in the absorption spectra shift into the long-wave region; a single band was formed in place of three peaks in the visible region (Fig. 2, cf. curves *1*, *2* (Fig. 2*a*) and *1*, *2* (Fig. 2*b*)), the fluorescence spectra changed as well (Fig. 3, curves *3* and *4*, *5* and *6*).

We believe that as the concentration of octasubstituted TPP decreases, the conditions for formation of the ionic form associated with the addition of a proton from the solution to one of the internal nitrogen atoms of pyrrolenine cycles are formed in the chloroform, because the basicity of OMeTPP, DPP, and DCPP increases significantly due to the electron-donating properties of substituents (see Fig. 1). It should be noted that the Soret bands at transition from the neutral form to the cation one shift toward longer waves, while the S_0–S_1 absorption and fluorescence bands shift to shorter waves (Table 1, Figs. 2 and 3). This is confirmed by addition of dimethylamine (DMA) to the DPP solution (Table 1)

Table 1. Spectral properties of porphyrins

Compound, solution, concentration (mol/liter)	$\nu_{\max}^{\text{abs}}$, cm^{-1}	$\varepsilon_{\max}^{\text{abs}}$, liter/mol·cm	$\Delta\nu = \nu_{\max}^{C} - \nu_{\max}^{C+1}$, cm^{-1}
TPP	24 200		
in ethylacetate	(Soret)	400 000	4700
	19 500	18 400	
	18 300	8 000	
	16 950	5 100	
	15 400	5 400	
ZnTPP	23 800		
in ethylacetate	(Soret)	472 000	5850
	17 950	15 600	
(AlCl)TPP	23 600		
in ethylacetate	(Soret)	314 000	5850
	17 750	9 400	
(InCl)TPP	23 600		
in ethylacetate	(Soret)	540 000	5800
	18 500	15 600	
CuTPP	24 200		
in ethylacetate	(Soret)	484 000	5700
	17 900	16 500	
PP in 3N HCI	24 400		
	(Soret)	278 000	6400
	17 950	13 250	
OMeTPP	22 000		
in chloroform	(Soret)	187 500	4000
$c = 2\cdot10^{-4}$	18 000	11 250	
Neutral form	16 600	8 500	
	14 400	4 750	
OMeTPP	21 100		
in chloroform	(Soret)	350 000	5300
$c = 6\cdot10^{-6}$	15 800	19 200	
Ionic form	14 500	41 700	
(InCl)OMeTPP	22 100		
in chloroform	(Soret)	194 000	5600
$c = 2\cdot10^{-4}$	17 000	9 400	
	15 600	5 300	
OBrTPP in	21 200		
chloroform	(Soret)	177 000	3800
$c = 1.5\cdot10^{-4}$	17 400	7 500	
	15 900	11 400	
DPP in chloroform	21 400		
$c = 2\cdot10^{-4}$	(Soret)	176 000	3700
Neutral form	17 700	12 000	
	16 300	10 300	
	13 800	7 900	
DPP in chloroform	20 400		
$c = 3\cdot10^{-5}$	(Soret)	174 000	6300
Ionic form	14 100	31 100	
DPP in chloroform	21 400		
$c = 2.7\cdot10^{-5}$ +	(Soret)	176 000	3700
+ 3M DMA	17 700	14 400	
Neutral form	16 300	10 650	
	13 800	6 000	
DCPP in chloroform	21 100		
$c = 10^{-4}$	(Soret)	260 000	3300
Neutral form	17700	21000	
	16 200	17 000	
	13 800	10 750	
DCPP in chloroform	19 800		
$c = 2\cdot10^{-4}$	(Soret)	230 000	6000
Ionic form	13 800	23 200	

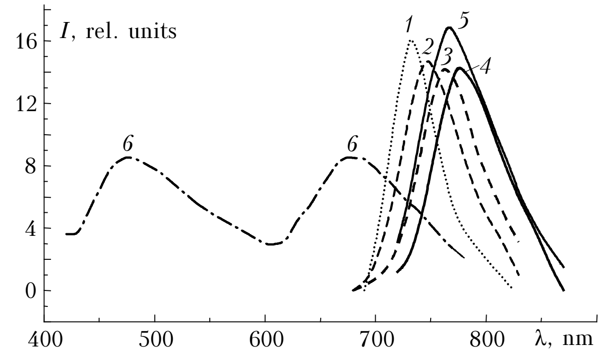


Fig. 3. Fluorescence spectra of chloroform solutions of OMeTPP (curve *1*), DPP (*2*, *3*), DCPP (*4*, *5*), InClOMeTPP (*6*); $c = 2 \cdot 10^{-6}$ (*5*), $8 \cdot 10^{-6}$ (*6*), 10^{-5} (*2*), $4 \cdot 10^{-5}$ (*3*), $8 \cdot 10^{-5}$ mol/liter (*1*, *4*); λ_{exc} = 400 (*6*), 455 (*1*), 470 (*2*, *3*), and 710 nm (*4*, *5*).

and also agrees with the results[13] for DPP and OEthTPP, where these forms were obtained in benzol (neutral form) and in methanol (cation form). As to the presence of protons in chloroform, it is known[1] that HCl traces ($\leq 10^{-3}$–10^{-4} mol/liter) can be formed in this solvent if illuminated. In the case of electron-withdrawing substitution (OBrTPP), no qualitative changes in the concentration dependence of absorption spectra were found. Fluorescence of OBrTPP is lacking, because of the high interconversion rate due to the presence of eight heavy bromine atoms.

The study of fluorescent properties of these porphyrins showed that at excitation into the Soret band many of them fluoresce not only from the lower S_1 state (red fluorescence), but also from the highly excited state S_n (blue fluorescence) (Table 2, Fig. 3).

The most intense blue fluorescence is observed for ZnTPP, which was mentioned earlier in Refs. 14 and 15, but our results showed that almost all TPPs with metals have blue fluorescence, even those of them, which do not fluoresce from the state S_1 at excitation into the S_0–S_1 band (CoTPP, CuTPP). Free bases (metal-free porphyrins) at excitation at λ_{exc} = 400 nm have only red fluorescence.

The quantum yield of red fluorescence measured at λ_{exc} = 400 nm almost in all cases (except for TPP and InClTPP) exceeds that measured at excitation into the long-wave band (λ_{exc} = 526 nm, Table 2). In the chloroform solution of OMeTPP, this difference is caused by the fact that different forms fluoresce at different excitation: the neutral form fluoresces at λ_{exc} = 526 nm with λ_{max} = 740 nm, while the ionic form fluoresces at λ_{exc} = 400 nm with λ_{max} = 715 nm, and the quantum yield of the latter is 0.018, that is, 3.6 times higher than that of the former. In the case of DPP at λ_{exc} = 526 nm, the cation fluoresces (λ^{fl}_{max} = = 750 nm), and at the short-wave excitation the neutral form can also take part in fluorescence, since the concentration in this case (to keep the same absorption at λ_{exc}) is somewhat higher ($3 \cdot 10^{-6}$ and

Table 2. Quantum yields of fluorescence

Compound	λ_{exc} = 400 nm					λ_{exc} = 526 nm	
	$\lambda^{max}_{fl,C}$, nm	γ^{C}_{fl}	$\lambda^{max*}_{fl,K}$, nm	γ^{K}_{fl}	$\gamma^{exc}_{fl} = \gamma^{C}_{fl} + \gamma^{K}_{fl}$	λ^{max*}_{fl}, nm	γ^{K}_{fl}
TPP in ethanol	no fluoresc.		653	0.063	0.063	600	0.045
TPP in ethylacetate	no fluoresc.		652	0.099	0.099	652	0.106
CuTPP in ethylacetate	440	0.004			0.004	no fluoresc.	
CoTPP in ethylacetate	460	<0.001			< 0.001	no fluoresc.	
ZnTPP in ethylacetate	465	0.024	597	0.077	0.101	600	0.056
NiTPP in ethylacetate	440	0.002	650	< 0.001	< 0.003	648	< 0.001
(AlCl)TPP in ethylacetate	430	n/d	604	0.052	0.052	604	0.036
InClTPP in ethylacetate	432	0.005	605	0.005	0.01	602	0.04
EuTPP in ethylacetate	455	0.004	648	0.041	0.081	650	0.003
PP in 3N HCl	465	< 0.001	606	0.133	0.134	n/d	n/d
DPP in chloroform	no fluoresc.		755	0.007	0.007	750	0.002
OMeTPP in chloroform	no fluoresc.		715	0.018	0.018	740	0.005
InClOMeTPP in chloroform	475	n/d	675	0.009	0.009	675	0.005

* The most intense peak is presented; n/d means not determined.

$6 \cdot 10^{-6}$ mol/liter, respectively). In the other cases, the same form fluoresces, and the differences in the quantum yields, small shifts of fluorescence peaks (2–3 nm), and intensity redistributions in them can be associated with possible manifestation of nonequilibrium processes in deactivation of the excitation energy, which result in blue fluorescence.

It should be noted that blue fluorescence occurs in the compounds, which are characterized by a rather long interval (> 5000 cm^{-1}) between the Soret band and the next long-wave band ($\Delta\nu = \nu^{C} - \nu^{C+1}$, Table 1), so that the radiative processes from the highly excited state can compete with internal conversion, for example, as in the case of azulene. If this interval is shorter than 5000 cm^{-1} (TPP, DPP, DCPP – neutral forms, and others), emission is usually observed from the S_1 state (cf. Tables 1 and 2). To explain peculiarities in the emission characteristics, in addition to the interval, it is necessary to take into account other molecular parameters. For example, Kuzmitsky,[15] in discussing the processes of emission from the highly excited state with magnesium-porphyrin (MgP), as an example, considers also the evenness of the intermediate states obtained in quantum-chemical calculations. At the rather high excitation intensity, blue fluorescence is also observed in some cases at excitation into the long-wave region (second harmonic of the Nd:YAG laser[14]) as a result of stepwise population of the highly excited S_n states or triplet-triplet annihilation.

The presence of blue fluorescence confirms that the lifetime of the S_n excited states in porphyrin compounds is of the same order of magnitude as τ_{fl}, because it is determined by the radiative processes. This means that the S_n states, along with the triplet state, can take part in the processes of saturated absorption at excitation by high-power pulses of nanosecond duration, that is, limit the optical radiation. Besides, as follows from Tables 1 and 2, DPP, DCPP, and OMeTPP in chloroform can absorb and emit in both neutral and cation forms. The shifts of the corresponding bands between the neutral and cation forms evidences that the basicity of these molecules (efficiency of proton addition from the solvent) significantly increases at excitation in the Soret band and slightly decreases at excitation into the S_1 state, which can also be a cause of variations of the absorption due to excitation by high-power radiation. The technique for estimating the basicity of organic molecules in the excited states is described in Refs. 16 and 17.

Limitation of high-power laser radiation. Optical limitation of high-power radiation manifests itself in the decrease of the initial (linear) transmittance with the increasing intensity of the incident radiation (Fig. 4).

It can be seen from Fig. 4 that the character of laser radiation attenuation (shape of the curves) depends on the molecular structure and concentration of the molecules, solvent, and its additions, as well as the laser radiation wavelength. Table 3 summarizes the characteristics of OL for high-power radiation of the XeCl laser (308 nm) and the second harmonic of Nd:YAG laser (532 nm) by solutions of octasubstituted TPP as compared with the non-substituted ones. It can be seen from Table 3 that OBrTPP limits the Nd:YAG laser radiation better than TPP does, and the increase in the concentration of molecules (that is, decrease of the initial transmittance T_0^{532}) increases the limitation coefficient: $\text{LC}_{532} = 4.6$ and 6.3 against $\text{LC}_{532} = 5$ for the TPP.

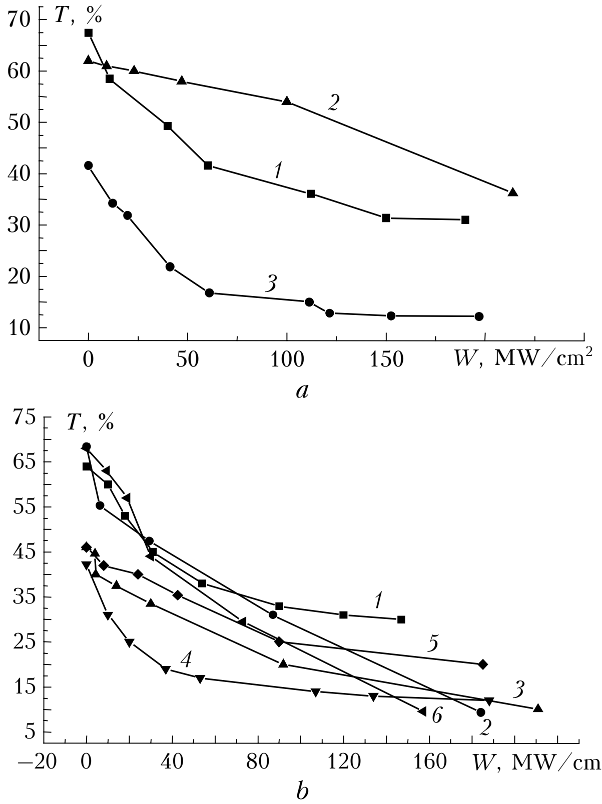


Fig. 4. Transmittance of chloroform solutions of OMeTPP (*a*) and DPP (*b*) for XeCl laser radiation [curves *3* (*a*), *1*, *2*, *5*, *6* (*b*)] and second harmonic of Nd:YAG laser [*3*, *2* (*a*), *3*, *4* (*b*)] as a function of radiation intensity. Addition: 3 mol/liter DMFA [*5*, *6* (*b*)].

These results show that the main contribution to OL of the second harmonic of Nd:YAG laser is due to the T-state of OBrTPP, having higher absorption cross section as compared to that in the ground state: $\sigma^*_{532} = 8.9 \cdot 10^{-17}$ and $\sigma_{532} = 2.8 \cdot 10^{-17}$ cm^2, respectively. The curves showing $T(W)$ for OBrTPP and OMeTPP exhibit saturation with the increasing W, that is, starting from $W \approx 50$ MW/cm^2 virtually all molecules transit into the T-state, whose yield is close to unity, as follows from the absence of fluorescence in OBrTPP.

The increase of LC_{532} with the increasing concentration is caused by the increase of the absorption coefficient for the triplet state, which is $K^* = \sigma^* N$, where N is the molecular concentration. The other compounds limit the radiation in this range worse than the TPP does, which is connected with the decrease in the yield from triplets: as follows from Ref. 13 the yield from triplets for DPP and OEthTPP is $\varphi_t^{DPP} = 0.29$, $\varphi_t^{OEthTPP} = 0.34$, and for TPP in the deoxygenated solution it is $\varphi_t = 0.84$ [Ref. 14]. On the other hand, the XeCl laser radiation is attenuated by the octasubstituted species more efficiently than by the TPP (Table 3): $LC_{308}^{DPP} = 7.1$, 6, 4.5, etc. against $LC_{308}^{TPP} = 1.2$, and the fourfold decrease in the DPP concentration leads to the increase of LC_{308}. The dependence $T(W)$ at the decreasing DPP concentration becomes linear (curves *2* and *6* in Fig. 4*b*), that is, it considerably differs from other curves.

We associate this peculiarity with the existence of ion-neutral equilibrium in these solutions: ionic form, which prevails in the DPP ground state, limits the radiation at $\lambda = 308$ nm more efficiently than the neutral form does at the decreasing DPP concentration. An addition of DMFA shifts the equilibrium toward the ionic form, as follows from the absorption and fluorescence spectra, and increases LC_{308} (from 6 to 7.1, see Table 3).

An important role in OL by these compounds is played by the shift of the ion-neutral equilibrium at excitation: the increase of the yield from the ionic form at excitation in the UV and its decrease at excitation of S_1 with respect to the ground state. This is confirmed by the recorded absorption spectra of the DPP and OMeTPP solutions after the exposure to high-power radiation of a XeCl laser (see Fig. 2).

As to the ClInOMeTPP, the presence of heavy In atoms as a coordinating metal and Cl as an axial ligand removes the possibility of changing the ion-neutral equilibrium for nitrogen atoms, but increases the probability of interconversion. This manifests itself in the increase of LC_{532} even at high initial transmittance (Table 3).

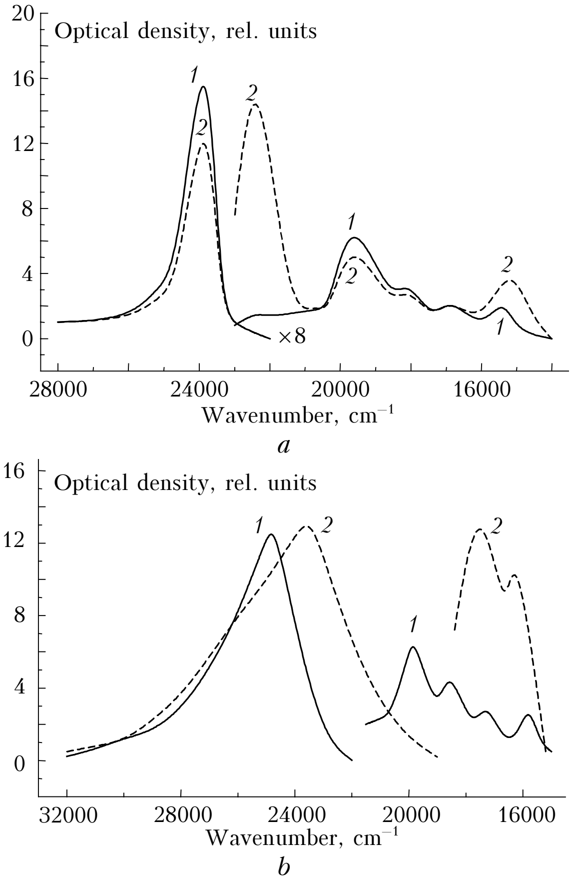
These results indicate that OL is caused both by the more intense (as compared to the initial) absorption in the channel of triplet states and by the shift of the ion-neutral equilibrium in the singlet-excited states, which lead to variation of absorption characteristics. In addition, formation of the ionic forms at excitation is promising for variation of transmittance by the scattering mechanism, which will be the subject of further studies.

Phototransformations of porphyrin compounds under high-power laser excitation. As can be seen from the absorption spectra shown in Fig. 2, the result of exposure of the DPP and OMeTPP solutions to the XeCl laser radiation is the shift of the ion-neutral equilibrium toward ions (cf. curves *2* and *3*). To obtain the more general pattern of phototransformations of porphyrins, we have studied spectral changes of nonsubstituted TPP, ZnTPP, and PP in chlorophorm and ethylacetate under the exposure to the second harmonic of a Nd:YAG laser radiation (Fig. 5).

Efficient phototransformations of the TPP and ZnTPP occur in the chloroform: the intensity of all absorption bands decreases, and new absorption bands are formed at $\lambda_{max} = 22400$ cm^{-1} (Soret band) and at $\lambda_{max} = 14000$ cm^{-1} (Fig. 5). A new absorption band with the peak at 680–690 nm arises in the fluorescence spectrum of irradiated TPP. The quantum yields of phototransformations as determined from these changes just after the exposure (for 3–5 min) are $\gamma_{TPP} = 10^{-2}$, $\gamma_{ZnTPP} = 2 \cdot 10^{-2}$. In ethylacetate the photostability of these compounds increases by more than two orders of magnitude ($\gamma < 10^{-4}$). On the other hand, PP in ethylacetate experiences significant phototransformations, but we failed to determine the quantum yield in this case, since the absorption spectra of the photoproducts overlap with the absorption spectrum of the initial compound almost everywhere (Fig. 5*b*). It can be seen from Fig. 5*b* that the absorption peaks of the photoproduct of PP in ethylacetate are close to the absorption peaks of the diprotonated form of PP obtained in 3N HCl (see Table 1). It is very interesting that all these phototransformations are reversible under the dark conditions: 2–3 h after irradiation the absorption and fluorescence spectra of the TPP,

Table 3. Optical limitation characteristics of solutions of the TPP and its substituents in chloroform

Compound, concentration (mol/liter), addition (mol/liter)	T_0^{308}, %	T_0^{532}, %	W, MW/cm^2	LC_{308}	LC_{532}	$\sigma_{01}^{532} \cdot 10^{17}$, cm^2	$\sigma_{01}^{532*} \cdot 10^{17}$, cm^2
TPP	70		170	1.2			
TPP		70	250		5	2.3	8.5
OMeTPP $2 \cdot 10^{-5}$		67	190		2.2		
OMeTPP $6 \cdot 10^{-6}$	66		230	3			
OMeTPP $8 \cdot 10^{-5}$		42	200		3.3		
(InCl)OMeTPP		85	390		4.6		
OBrTPP $2.5 \cdot 10^{-5}$		67	190		2.8		
OBrTPP $1.4 \cdot 10^{-4}$		43	190		6.3	2.8	8.9
OBrTPP 10^{-4} + DMFA 3		65	190		4.6		
OBrTPP + DMFA 3	40		195	4.5			
OBrTPP $2 \cdot 10^{-5}$ + DMFA 3	65		160	1.2			
DPP $4 \cdot 10^{-5}$	46		200	3.8		3.4	10
DPP 10^{-5}	68		190	6			
DPP $4 \cdot 10^{-5}$		46	150		2.1		
DPP $8 \cdot 10^{-5}$		42	210		3.8		
DPP + 10^{-5} + DMFA 3	68		170	7.1			
DCPP $1.4 \cdot 10^{-5}$		43	190		1.8		
DCPP $2 \cdot 10^{-4}$	64		185	1.4			



a

b

Fig. 5. Absorption spectra of the TPP in chlorophorm (*a*), PP in ethylacetate (*b*) before (curves *1*) and after (curves *2*) exposure to the second harmonic of Nd:YAG laser radiation; $c = 4.5 \cdot 10^{-5}$ (*b*) and $1 \cdot 10^{-4}$ mol/liter (*a*).

ZnTPP, and PP are recover to the initial ones almost completely. Taking into account this phenomenon, as well as the results of Ref. 18, we believe that the primary photoproducts of porphyrins under the intense laser irradiation are charged forms connected with the electron or proton transfer. Restoration of porphyrins in darkness is connected with the reverse charge transfer. The cause of this transfer and the role of dissolved oxygen in it are to be revealed in the further studies.

Conclusion

The studies performed have shown that the studied porphyrins, namely TPP octasubstituents, and complexes with metals have unique photophysical properties, which allow one to observe emission not only from S_1, but also from the high-excited state, and they are of practical interest as limiters of optical radiation by the mechanism of reverse saturable absorption. The acid-base equilibrium in the chloroform solution, characteristic of DPP, DCPP, and OMeTPP, is of interest for investigation of OL by the mechanism of light-induced scattering.

Phototransformations of porphyrins under high-power laser excitation, which were found in our experiments, are connected with the formation of charged forms and do not hamper their use as limiters of the high-power laser radiation, because charged forms also show efficient OL, and porphyrins recover after the dark period and can be used repeatedly.

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