Optical limiting of high-power laser radiation by complexes of azaporphyrin and bisphtalocyanine with metals

N.S. Savenkova,[1] R.T. Kuznetsova,[1] V.A. Svetlichny,[1] G.V. Mayer,[1] S.S. Ivanova,[2] P.A. Stuzhin,[2] I.P. Kalashnikova,[3] and L.G. Tomilova[3]

[1] Tomsk State University
[2] Ivanovo State University of Chemistry and Technology
[3] Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka

Received November 2, 2005

We have studied luminescence spectra of porphin aza-derivatives as well their photochemical and nonlinear optical properties. The efficiencies of producing ionic forms of triplet molecules, their phototransformations, and ability of limiting high-power laser radiation in the UV and visible spectral regions have been determined from analysis of the luminescence spectra characteristics of these substances.

Introduction

Porphin derivatives and their complexes with different metals are of great interest due to their explicitly pronounced electrochromic and semiconductor properties as well as unique spectral characteristics in the ground and excited energy states. These features open new prospects for their application: one of them is connected with the use of such compounds as effective optical limiters of high-power laser radiation.[1–3] Useful characteristics are determined by the electronic properties of the tetrapyrrol macrocycle and by nature of the central metal. In this connection, the azaporphyrin and phtalocyanine derivatives were studied in complex with metals of the third group, specifically, indium, for which the limiting effect has been discovered.[4,5] The bisphtalocyanine complexes[6,7] synthesized in recent years are of a special interest. Their complex nonplanar structure and the properties this structure forms can be much promising for application in optical limiting (OL).

The aim of this paper was studying the luminescence spectra, nonlinear optical and photochemical properties of the hexadecasubstituted bisphtalocyanines and azaporphyrins in complex with metals at excitation to different electronic states, and investigation of OL property for high-power radiation (up to 400 MW/cm^2) of XeCl and the second harmonic of a Nd:YAG-laser.

Subjects and methods of investigation

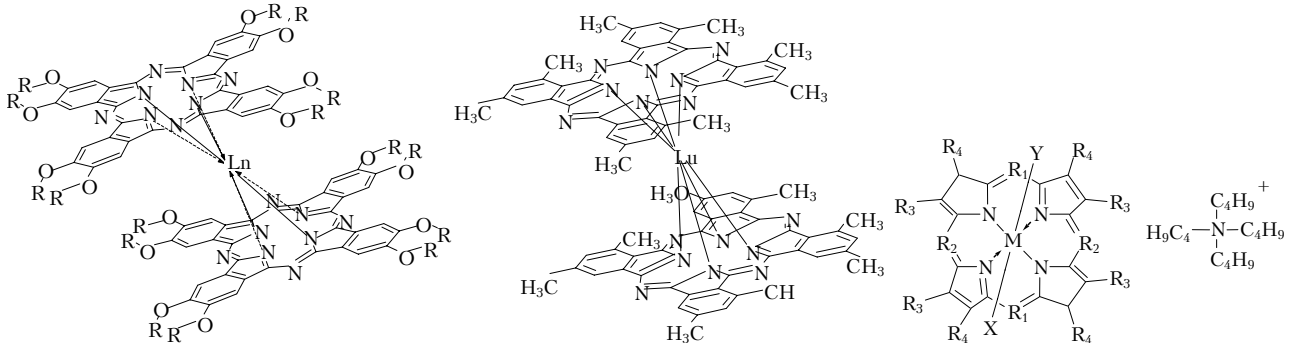
The phtalocyanine and azaporphyrin derivatives are chosen as subjects for the investigation. The choice of these compounds is connected with the presence of nitrogen mesoatoms in their structure causing interaction with solvent, i.e., enabling structure changes at production of ionic or neutral forms and thus modifying the spectral properties of such compounds depending on solvent and electronic state. The phtalocyanine derivatives are presented by bisphtalocyanine complexes of lutecium, samarium, and thulium (Figs. 1*a* and *b*).

Azaporphyrins are the complexes of diaza- and tetraazaporphyrinsubstituted with tervalent metals: indium (In), gallium (Ga), and aluminum (Al). The atoms of fluorine, chlorine, and bromine serve as extraligands (Fig. 1*c*). The synthesis procedure is described in Refs. 6–8. Chloroform and ethyl acetate were used as solvents. All solvents used were of chemically pure quality. Adding hydrochloric acid (HCl) and dimethylamine (DMA) enabled identification of the molecular form (neutral or ionic) to be done.

Electronic absorption spectra and fluorescence spectra were recorded with an SM2203 spectrometer («Solar», Byelorussia). In investigating the limiting properties of the compounds, two lasers were used as sources of exciting radiation: the exciplex XeCl-laser ($\lambda = 308$ nm, E_{pul} up to 40 mJ, $\tau = 10$ ns) and the second harmonics of a Nd:YAG-laser radiation ($\lambda = 532$ nm, $\tau = 15$ ns, E_{pul} up to 100 mJ). Initial transmission of the analyzed solutions T_0, measured with the spectrometer, was from 40 up to 70%. Spectra of short-lived induced absorption were measured using an original setup for laser photolysis.[3] Reference 3 also presents the technique of estimating the quantum yield of porphyrin molecules to the triplet state (φ_T).

Quantum yields of phototransformations were determined using a spectroscopic method.[2] To estimate the efficiency of producing ionic forms from organic compounds, the value of pK was chosen that characterizes probability of proton attachment at interaction with a proton donor solvent. The values

0235-6880/07/03 207-08 $02.00



a *b* *c*

Fig. 1. Structure formulas: (*a*) bisphtalocyanine complexes: lutecium hexadeca-propyloxybisphtalocyanine – $Lu[(OC_3H_7)_8Pc]_2$: R=C_3H_7,$^-$, Ln=Lu; thulium hexadeca-pentyloxybisphtalocyanine – $Tm[(OC_5H_{11})_8Pc]_2$: R=C_5H_{11},$^-$, Ln=Tm; samarium hexadecabenzyloxybisphtalocyanine – $Sm[(OC_6H_5CH_2)_8Pc]_2$: R=$C_6H_5CH_2$,$^-$, Ln=Sm; (*b*) lutecium hexadeca-methylbisphtalocyanine– $Lu[(CH_3)_8Pc]_2$; (*c*) azaporphyrin complexes ClInDAПMe$_4$Bu$_4$: M=In, X=Cl, Y is missing, R_1=N, R_2=CH, R_3=CH_3, R_4=C_4H_9 is the chlorindium-diazaporphyrin; ClGaDAPMe$_4$Bu$_4$: M=Ga, X=Cl, Y is missing, R_1=N, R_2=CH, R_3=CH_3, R_4=C_4H_9 is the chlorgallium-diazaporphyrin; F_2InDAPMe$_4$Bu$_4$,$^-$tba$^+$: M=In, X=Y=F, R_1=N, R_2=CH, R_3=CH_3, R_4=C_4H_9, tba$^+$=N^+ $(C_4H_9)_4$ is the tetrabutylammonium salt of difluorindium-diazaporphyrin; F_2InOPTAP$^-$tba$^+$: M=In, X=Y=F, R_1=R_2=N, R_3=R_4=C_6H_5, tba=N$(C_4H_9)_4$ is the tetrabutylammonium salt of difluorindium-diazaporphyrin; FInOPTAP: M=In, X=F, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 is the fluorindium-octaphenyltetraazaporphyrin; ClInOPTAP: M=In, X=Cl, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 is the chlorindium-octaphenyltetraazaporphyrin; ClGaOPTAP: M=Ga, X=Cl, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 is the chlorgallium-octaphenyltetraazaporphyrin BrInOPTAP: M=In, X=Br, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 is the bromindium-octaphenyltetraazaporphyrin; BrAlOPTAP: M=Al, X=Br, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 bromaluminium-octaphenyltetraazaporphyrin; PhInOPTAP: M=In, X=C_6H_5, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 is the phenylindium-octaphenyltetraazaporphyrin; CH_3COOIn(OCH_3Ph)$_8$TAP: M=In, X=CH_3COO, Y is missing, R_1=R_2=N, R_3=R_4=C_6H_5 OCH_3 is the indiumacetate-octa-*n*-oxymethyl-phenyltetraazaporphyrin.

of *pK* in the ground and excited fluorescent states are determined from the experimental titration curves plotted using data on the behavior of the absorption $pK(S_0)$ and fluorescence $pK(S_0^{fl})$ spectra, from the value of $-\log[HCl]$, at which the proton accept is half finished. The value of *pK* for the excited Franck–Condon state (pK_a,$^{f.-c}$) was determined by the shift of the $S_0 \rightarrow S_1$ band.[9]

To characterize ability of a solution to optically limiting radiation (OL) we have chosen the limitation coefficient of LC = T_0/T_W, where T_0 is the linear transmission of the solution measured by means of the spectrophotometer, T_W is its transmission at laser radiation power density equal to *W*.

Results and discussion

Stationary spectra of absorption and luminescence

Figure 2 presents the stationary absorption spectra of azaporphyrin and bisphtalocyanine derivatives showing that all complexes of the corresponding molecules in chloroform have qualitatively similar absorption spectra, which are characterized by intense bands in the range from 600 to 700 nm. The bathochromic shift of the *Q*-band increases depending on the central metal atom owing to the liganda induction effect, either electron-donor or electron-acceptor in relation to the porphyrin ring. In the short-wave region (≅ 380 nm) of electronic absorption spectra (EAS) (see Fig. 2), there is a Sore band typical for the porphyrin derivatives. Intensity and shape of the band are quite individual. For instance, the solution F_2InOPTAP$^-$tba$^+$ is distinguished among the octaphenyltetraazaporphyrins (Fig. 2*a*, curve *4*). This compound is an ion pair of the difluorinated porphyrin cycle with tetrabutylammonyl. Its absorption spectra have low intensity of the Sore band as comparison with another tetraazaporphyrins, and in the visible range have two distinct maxima at 649 and 714 nm.

In addition, PhInOPTAP (Fig. 2*b*) also essentially differs from the tetraazaporphyrins since the Sore band ($S_0 \rightarrow S_3$-transition) in neutral chloroform is found in the long-wave region (λ_{max} = 400 nm) in contrast to other OPTAP. In neutral solutions of all the rest tetraazaporphyrins: ClInOPTAP, BrInOPTAP, ClGaOPTAP, and BrAlOPTAP there is a band in the range of 380 nm. Slight acidification of the PhInOPTAP solution, for enhancing the intermolecular interactions, removes the spectral individuality, it will completely coincide with the spectra of the rest OPTAP, i.e., *Q*-band remains at its place, and the Sore band is shifted to the region of 380 nm. With the further acidification of PhInOPTAP solution, one can observe the spectral changes (see Fig. 2*b*, curve *2*), analogous to changes for other OPTAP, connected with the production of ionic forms. This difference in the position of $S_0 \rightarrow S_3$ transition can be caused by the capability of the volumetric extraligand Ph of coordinating with the localized electron density in its molecule, which is attenuated due to the intermolecular interactions.

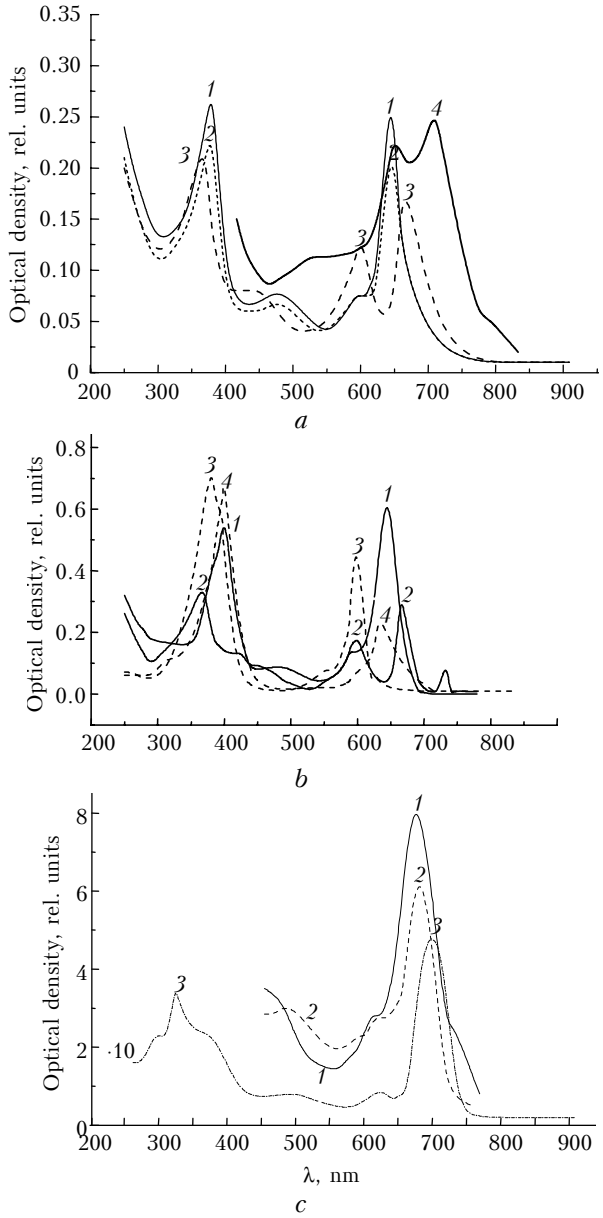


Fig. 2. Absorption spectra: (*a*) FInOPTAP in $CHCl_3$ $5\cdot10^{-6}$ mole/l (curves *1–3*), with addition of HCl: 0.005% (*2*); 0.05% (*3*); F_2InOPTAP$^-$tba$^+$ in chloroform $2.5\cdot10^{-4}$ mole/l (*4*); (*b*) solutions in chloroform $C=5\cdot10^{-6}$ mole/l; PhInOPTAP (*1*, *2*); ClInDAPMe$_4$Bu$_4$ (*3*, *4*), with addition of HCl: 0.05% (*2*); 1% (*4*); (*c*) solutions in chloroform Tm[$(OC_5H_{11}Pc]_2$ (*1*), Sm[$(OC_6H_5CH_2)_8Pc]_2$ (*2*), Lu[$(CH_3)_8Pc]_2$ (*3*); $C=6\cdot10^{-5}$ (*1*); 10^{-4} mole/l (*2*, *3*).

In absorption spectra of bisphtalocyanine complexes in the visible region, one can observe some maxima, which correspond to some forms.[7,8,10] All the complexes have the maximum in the range from 660 to 680 nm (Q-band), typical for such compounds and corresponding to the Sore band in the range of 320 nm, which conforms to absorption of the π-conjugate system. Maxima at 630 and 720 nm correspond to the reduced and oxidized forms.[7,8,10] The ratio of these forms in solution depends on the structure and can vary (Fig. 2*c*): in solution of Lu[$(CH_3)_8Pc]_2$, the neutral form dominates, in Lu[$(OC_3H_7)_8Pc]_2$ and Sm[$(OC_6H_5CH_2)_8Pc]_2$ neutral and reduced forms dominate, in Tm[$(OC_5H_{11})_8Pc]_2$ there is the dominance of the neutral and oxidized forms. Apart from the above-listed maxima, there is a maximum in the range from 460 to 480 nm in EAS of all the complexes. The unpaired electron is responsible for this maximum typical for bisphtalocyanine complexes with the rare-earth elements being the stable radicals.[10] Unfortunately, no information on the structure of the oxidized and reduced forms can be found in the literature. At this stage of the study one can assume that the oxidized form appears due to detachment of an electron or attachment of a proton to the nitrogen mesonic atom, while the reduced form appears due to the electron attachment to the electron acceptor center, apparently, to the ligand. Further investigations are needed for determining the structure of these forms.

Since the analyzed compounds have the nitrogen atoms in meso-positions, capable of localizing the electron density, in some cases the efficiency of producing the protoned molecular forms was studied by making use of these centers. Thus obtained results are presented in Table 1. As follows from the table, the protoning of azaporphyrin complexes is more efficient than that of nonmetallic azaporphyrins. It is explained by that the ligands show electron-donor properties in relation to the porphyrin cycle. According to our results, the best donors of electron density among the azaporphyrin complexes both in the excited and ground states are FIn and PhIn.

Table 1. Efficiency of proton attachment in the ground and S_1-excited states

Compound in $CHCl_3$ $5\cdot10^{-6}$ mole/l	$pK_a(S_0)$	$pK_a(S_{1,}^{f,-c})$	$pK_a(S_{1,}^{fl})$
FInOPTAP	3.1	4.1	3.25
ClGaDAPMe$_4$Bu$_4$	1.4	2.9	1.75
ClInDAPMe$_4$Bu$_4$	2.6	4.1	2.7
F_2InDAPMe$_4$Bu$_4$, $^-$tba$^+$	2.5	4.5	2.4
PhInOPTAP	3	4	3.2
ClInOPTAP	2.4	3.4	2.5
BrInOPTAP	2.1	3.1	2.65
BrAlOPTAP	1	2.8	1.2
ClGaOPTAP	<0.4	—	—

As follows from Table 1, the efficiency of proton attachment in the excited state increases due to the increase of electron density around the nitrogen mesonic atoms at $S_0 \rightarrow S_1$-transition. This means that, in the excited S_1-state, the molecule can attach a proton from the solvation sphere and thus to produce the protoned form, which can cause changes in the absorption from the excited molecular states and be the primary photoproduct at irradiation of neutral solutions.

As to the fluorescence characteristics of azaporphyrin, at excitation both into the Sore band and into the long-wave band, the fluorescence occurs with radiation maximum in the range of 600 nm for

diazaporphyrins and 660 nm for tetraazaporphyrins (Fig. 3*a*).

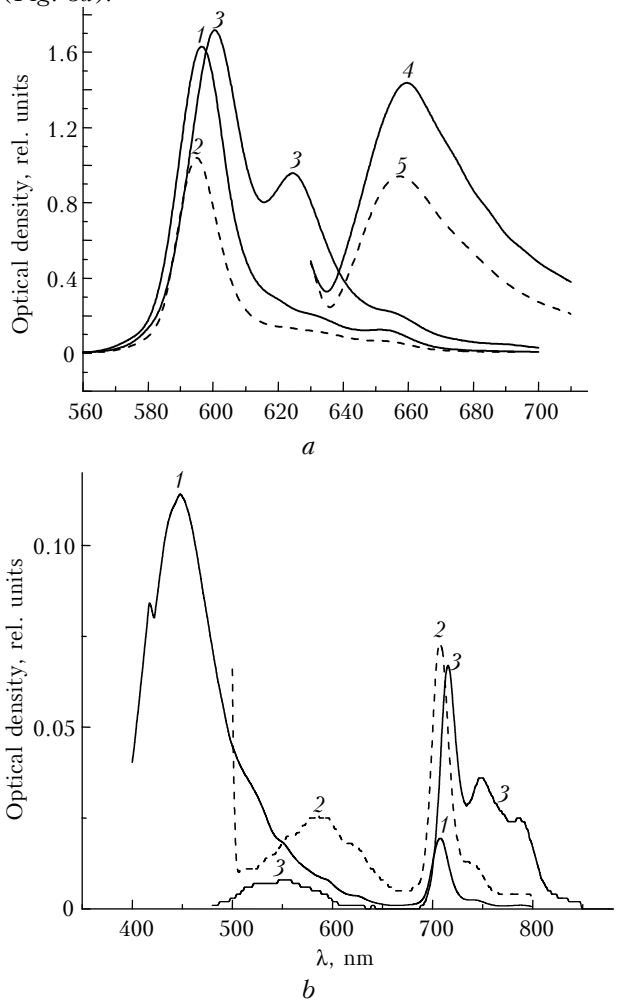


Fig. 3. Fluorescence spectra of solutions: (*a*) in chloroform $C = 5 \cdot 10^{-6}$ mole/l $ClGaDAPMe_4Bu_4$ (*1*, *2*); $ClInDAPMe_4Bu_4$ (*3*); FInOPTAP (*4*, *5*). With addition of HCl 0.05% (*2*, *3*); $\lambda_{exc} = 385$ (*1*, *2*); 400 (*3*); 625 nm (*4*, *5*). The band intensity is increased 10 times (*3*, *4*, *5*); (*b*) in chloroform $Lu[(OC_3H_7)_8Pc]_2$ (*1*, *2*), $Tm[(OC_5H_{11})_8Pc]_2$ (*3*); $\lambda_{exc} = 360$ (*1*); 495 (*2*); 470 nm (*3*).

It should be noted that neutral solutions with the central Ga-atom emit much better than azaporphyrins with the central In-atom (see Fig. 3*a*). Apparently, this is connected with a large rate value of the singlet–triplet conversion constant for $ClInDAPMe_4Bu_4$ as compared with $ClGaDAPMe_4Bu_4$ because In-atom is heavier.[12]

In analyzing the fluorescence spectra of acidified azaporphyrin solutions, one can note that the fluorescence intensity reduces at transition to the ionic form. For instance, if the acid content exceeds one or more percent in the solution of FInOPTAP, the fluorescence is completely quenched to zero. In case of diazaporphyrin complex with Ga, not only neutral but also the cationic form emits at yet longer wavelengths with $\lambda_{max} = 625$ nm (see Fig. 3*a*).

In studying the bisphtalocyanine fluorescence spectra (Fig. 3*b*), the multiple band-pass fluorescence is detected that corresponds to the multiple-center absorption of these compounds. The fluorescence with maxima at 708–710 nm can be referred to the neutral form. The oxidized form fluoresces with maxima at 740 and 788 nm. At excitation within the absorption band referred to the stable radical ($\lambda \cong 480$–500 nm, see Fig. 2*c*), one can observe fluorescence with maximum at 570–585 nm (see Fig. 3*b*) that corresponds to the fluorescence of a reduced form, which is not manifested at excitation within shorter wave bands. Besides, at excitation within the Sore-band, the short-wave bisphtalocyanine fluorescence is detected with maximum in the range from 400 to 450 nm (Fig. 3*b*).

Limiting the high-power laser radiation

It has been established that high-power laser radiation effect on solutions of the compounds causes a reduction of the linear transmission with the increase of the incident radiation intensity. The power density threshold of transmission reduction varies from 5–10 up to 150 MW/cm^2 being individual for each substance (Fig. 4).

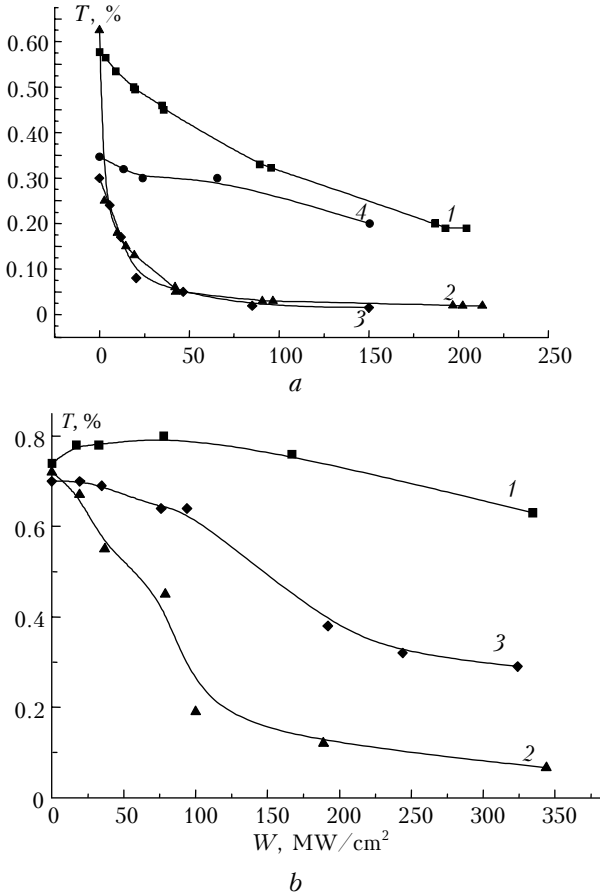


Fig. 4. Transmission dependence on the pump power density $T(W)$ of high-power radiation: (*a*) XeCl-laser: PhInOPTAP (*1*, *2*); $Sm[(O\ C_6H_5CH_2)_8Pc]_2$ (*3*); $Lu[(CH_3)_8Pc]_2$ (*4*);

addition of HCl (*2*); (*b*) the second harmonics of the Nd:YAG-laser: ClGaDAPMe$_4$Bu$_4$ (*1*); Sm[(OC$_6$H$_5$CH$_2$)$_8$Pc]$_2$ (*2*); Lu[(CH$_3$)$_8$Pc]$_2$ (*3*).

The behavior of the attenuation curves depends on molecular structure, solvent, and on the admixtures present in it, as well as on the wavelength of laser radiation. The shape of curves for the $T(W)$-dependence is different: smooth curves reflect the saturation process of transmission reduction (*1–3*, Fig. 4*a*), there are the curves with inflection points (*4*, Fig. 4*a*), and the curves, whose transmission reduction intensifies due to the increase in radiation intensity (*2*, *3*, Fig. 4*b*). Moreover, even an increase of the transmission of the acidified solution is observed, like in the case with ClGaDAPMe$_4$Bu$_4$ (*1*, Fig. 4*b*) in the power range from 20 to 70 MW/cm^2, which then is followed by its drop at the increase of power density above 100 MW/cm^2. These peculiarities specify complexity of the limiting mechanism at change of the pump power density, which can include several processes.

The summary of the results on OL is given in Table 2. It follows from these results that different initial transmission (T_0) of the compounds (30–85%) limit the high-power radiation in the visible or UV-spectral ranges. The maximum value of LF for UV- and visible regions among the bisphtalocyanine complexes is observed in Sm[(OC$_6$H$_5$CH$_2$)$_8$Pc]$_2$. In a series of azaporphyrin derivatives, the greatest values of LF in the UV are obtained for the ionic form of PhInOPTAP. It should be noted that neutral solutions of diazaporphyrins do not limit the visible radiation, acidification increases LF, and, on the contrary, the acidified solutions of diazaporphyrins hardly limit the high-power UV-radiation, compared with the corresponding neutral solutions. Thus, the OL efficiency varies at acidifying the studied solutions, since the possibility of proton attachment in the excited state can modify the limiting mechanism.

Induced absorption

The induced absorption spectrum (IA) is presented as the residual absorption by molecules in the ground state, i.e., the curve is below the abscissa axis and as the absorption by the excited molecules – the curve is above the abscissa axis (Fig. 5). Both types of absorption are typical for azaporphyrins. For instance, the IA, such as by ClGaDAPMe$_4$Bu$_4$, in the S_0-state has not only reduced intensity (λ_{max} = 595 nm), but also there is an absorption related to the ionic form (λ_{max} = 605 nm), i.e., when ClGaDAPMe$_4$Bu$_4$, in the S_1-state attaches the proton from the solvent (Fig. 5*a*).

The estimates of yields to the T-states (φ_T), presented in Table 3, well agree with the fluorescence characteristics: the least yield φ_T is obtained for ClGaDAPMe$_4$Bu$_4$, which emits more efficiently in comparison with ClInDAPMe$_4$Bu$_4$ and FInOPTAP. The protoned forms of diazaporphyrin and octaphenyltetraazaporphyrin complexes (in acidified solutions) emit less efficiently, their φ_T is higher in comparison with neutral form.

For bisphtalocyanine complexes, there is no molecular absorption in the S_0-state in the excited volume, i.e., the spectrum is recorded only above the abscissa axis (see Fig. 5). It can be caused both by full 100%-molecular transition into the T-state, and by the existence of several forms, initially, equilibrium between them can vary owing to excitation that leads to the reduction of high-power radiation transmission. The absence of explicit absorption bands in the excited state also conforms this fact – it is non-selective, as a rule (Fig. 5*b*). It should be noted that IA intensity in the visible region increases with some delay, i.e., OL for longer pulses would be even higher.

Table 2. Characteristics of OL for bisphtalocyanine and azaporphyrin complexes in chloroform

Compound in chloroform	λ_{exc} = 308 nm			λ_{exc} = 532 nm		
	T_0, %	LF	W, MW/cm^2	T_0, %	LF	W, MW/cm^2
Lu[(CH$_3$)$_8$Pc]$_2$	0.35	2	150	0.70	2.5	150
Lu[(OC$_3$H$_7$)$_8$Pc]$_2$	0.33	2.5	150	0.83	2	150
Tm[(OC$_5$H$_{11}$)$_8$Pc]$_2$	0.55 0.22	1.5 3	110 90	0.86	3	350
Sm[(O C$_6$H$_5$CH$_2$)$_8$Pc]$_2$	0.56 0.33	21 18	90 90	0.72	18	320
F$_2$InOPTAP$^-$tba$^+$	–	–	–	0.72	1.5	150
FInOPTAP	0.72 0.44	5 5	150 200	0.61	2	150
FInOPTAP + 0,1% HCl	0.51	22	200	0.88	1.4	200
BrInOPTAP	0.44	6.5	200	0.83	3	200
BrInOPTAP + 0,1% HCl	–	–	–	0.82	4.5	200
PhInOPTAP	0.58	4.5	200	0.74	4	200
PhInOPTAP + 0,1% HCl	0.63	31.5	200	–	–	–
ClInOPTAP	0.45	4.5	200	–	2.5	200
BrAlOPTAP	0.44	2.5	200	–	–	–
BrAlOPTAP + 0,1% HCl	0.46	6	200	–	–	–
ClInDAPMe$_4$Bu$_4$	0.5	10.2	150	0.81	1.05	150
ClInDAPMe$_4$Bu$_4$ + HCl	0.47	3.6	150	0.77	2	150
ClGaDAPMe$_4$Bu$_4$	0.69	3.8	150	0.86	1.1	150
ClGaDAPMe$_4$Bu$_4$ + HCl	0.73	1.7	150	0.74	1.2	150

$F_2InDAPMe_4Bu_4^-tba^+$	0.73	1.7	150	0.63	3	150	
$F_2InDAPMe_4Bu_4^-tba^+$ HCl	0.75	1.4	150	–	–	–	
$CH_3COOIn(OCH_3Ph)_8TAP$	–	–	–	0.72	1.8	150	

Thus, the OL efficiency in most cases correlates with the increase of the yield to the T-state, i.e., the OL takes place following the mechanism of reabsorption by triplet molecules. On the other hand, the OL by solutions, for instance, by diazaporphyrins in the visible region almost does not exist (see Table 3), although the IA at 532 nm is not equal to zero, that can be connected with the shift of the ion-neutral equilibrium both in singlet (see Fig. 5*a*) and triplet states.

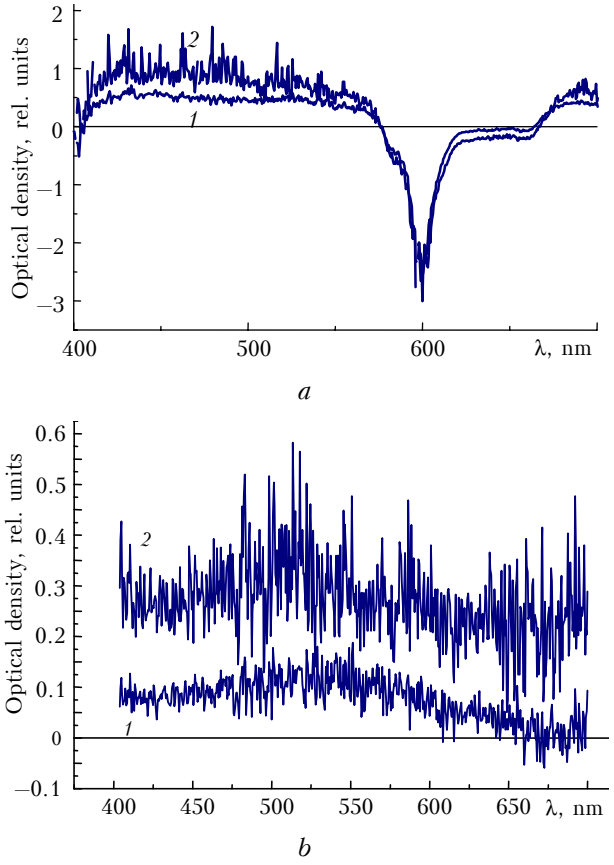


Fig. 5. The IA spectra: (*a*) $ClGaDAPMe_4Bu_4$ in $CHCl_3$, without delay (*1*); with delay ≈ 30 ns (*2*); (*b*) $Sm[(OC_6H_5CH_2)_8Pc]_2$ in $CHCl_3$, without delay (*1*); with delay ≈ 30 ns (*2*).

Table 3. Characteristics of IA and yields to *T*-states for some azaporphyrins

Compound in $CHCl_3$	φ_T	λ_{max}^{IA}, nm IA
$ClGaDAPMe_4Bu_4$	0.25	600
$ClGaDAPMe_4Bu_4$ + 1% HCl	0.44	630
$ClInDAPMe_4Bu_4$	0.60	640
$ClInDAPMe_4Bu_4$ + 0.3% HCl	0.55	645
FInOPTAP	0.5	550
FInOPTAP + HCl	≅ 1	532
$F_2InOPTAP^-tba^+$	0.8	490
BrInOPTAP	0.6	560
BrInOPTAP + 0.1 % HCl	≅ 1	555
PhInOPTAP	0.77	650
PhInOPTAP + DMA	0.58	650

Phototransformations of the investigated complexes under the action of high-power laser excitation

The investigated compounds undergo phototransformations at interaction with high-power laser radiation. Therefore, the paths of these transformations and their characteristics have been discussed in the study.

Considerable changes were observed in absorption spectra after irradiation of bisphtalocyanine complexes. Moreover, transformations are more effective at excitation by the XeCl-laser radiation. In this case, the absorption by neutral form is reduced and there occurs intensity redistribution in favor of the long-wave region, where, according to Refs. 7 and 10, the oxidized form absorbs (Fig. 6*a*).

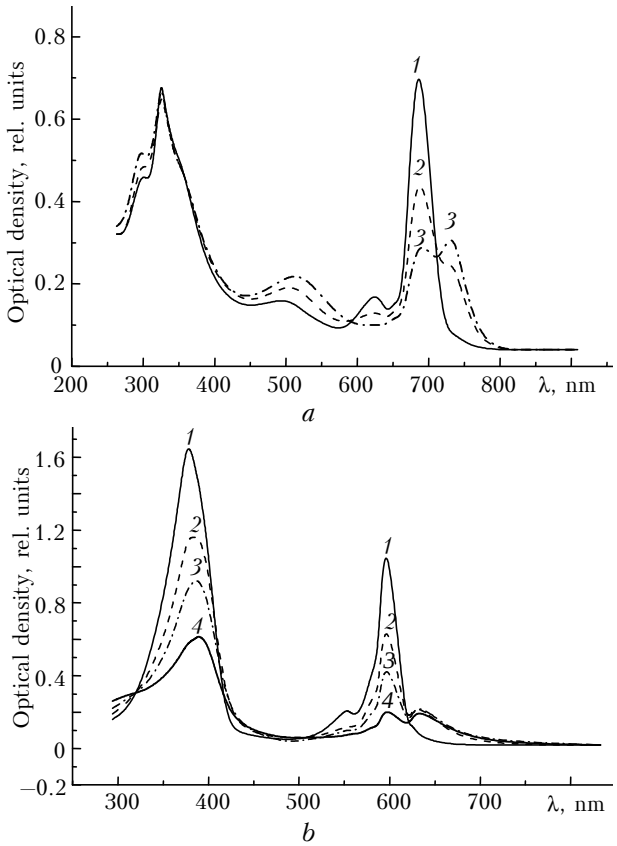


Fig. 6. Absorption spectra: (*a*) $Lu[(CH_3)_8Pc]_2$ in $CHCl_3$ before (*1*) and after (*2*, *3*) irradiation by the XeCl-laser. E_{abs} = 662 (*2*); 1600 mJ/cm^3 (*3*). $C = 10^{-4}$ mole/l; (*b*) $ClInDAPMe_4Bu_4$ in $CHCl_3$ before (*1*) and after (*2*, *3*, *4*) irradiation by the XeCl-laser (W ~45 MW/cm^2). E_{abs} = 905 (*2*); 1810 (*3*); 3320 mJ/cm^3 (*4*). $C = 5 \cdot 10^{-6}$ mole/l.

Qualitatively similar changes are observed in the diazaporphyrin derivatives, absorption and emission of neutral solutions are shifted to the cationic form due to the irradiation (Fig. 6*b*). As follows from Table 4, the neutral form experiences more effective phototransformations in comparison with the cationic one. Coincidence of quantum yields of the phototransformations of diazaporphyrin complexes with In and Ga shows that these transformations (from neutral to the cationic form) take place not in the triplet (see Table 3) but in the singlet S_1-state that is also confirmed by the IA-spectra (see Fig. 5*a*).

In studying the bisphtalocyanine complexes, it should be noted that both forms are more photostable at high-power UV-excitation ($\cong 150$ MW/cm^2) than at $W = 10$ MW/cm^2 (see Table 4). The lutecium complexes are more photostable at irradiation by the XeCl-laser in comparison with other studied compounds. Qualitatively similar phototransformations can be observed at irradiation by the second harmonic of the Nd:YAG-laser, but with lower efficiency, than at irradiation by the XeCl-laser radiation (see Table 3).

It should be noted that efficiency of phototransformations for the investigated compounds reduces at increase in the exciting radiation intensity (see Table 4). It is in a good agreement with the effect of limiting high-power laser radiation, since the excited state lifetime with possible photoreactions or phototransformations is reduced due to the high-intensity irradiation because of its depopulation through the reabsorption channel.

Table 4. Quantum yield values of phototransformations

Compound in $CHCl_3$	φ^{532}	φ^{308}
$Lu[(CH_3)_8Pc]_2$ (NF)	$2.2\cdot10^{-4}$ (300)	$2.45\cdot10^{-2}$ (150)
10^{-4} mole/l	$6.2\cdot10^{-4}$ (35)	$4.6\cdot10^{-2}$ (10)
$Lu[(CH_3)_8Pc]_2$ (IF)		$1.2\cdot10^{-2}$ (10)
10^{-4} mole/l+HCl		
$Lu[(OC_3H_7)_8Pc]_2$ (NF)		$5\cdot10^{-2}$ (150)
10^{-4} mole/l		$8.2\cdot10^{-2}$ (10)
$Lu[(OC_3H_7)_8Pc]_2$ (IF)		$1.5\cdot10^{-2}$ (150)
10^{-4} mole/l + HCl		$5.5\cdot10^{-2}$ (20)
$Sm[(O\ C_6H_5CH_2)_8Pc]_2$ (NF)	$9\cdot10^{-3}$ (330)	$5.2\cdot10^{-2}$ (100)
$5\cdot10^{-5}$ mole/l		$5.9\cdot10^{-2}$ (20)
$Tm[(OC_5H_{11})_8Pc]_2$ (NF)	$1.2\cdot10^{-3}$ (90)	$2.3\cdot10^{-2}$ (85)
$5\cdot10^{-5}$ mole/l		$2.5\cdot10^{-2}$ (15)
$F_2InOPTAP^-tba^+$(NF)	$6.5\cdot10^{-2}$ (350)	
10^{-4} mole/l	$1.6\cdot10^{-1}$ (35)	
PhInOPTAP (NF)		$5.3\cdot10^{-3}$ (150)
10^{-4} mole/l		
PhInOPTAP (IF)		$4.9\cdot10^{-3}$ (150)
10^{-4} mole/l +HCl		
$ClInDAPMe_4Bu_4$		$2.3\cdot10^{-3}$ (45)
$2\cdot10^{-4}$ mole/l		
$ClGaDAPMe_4Bu_4$		$2.5\cdot10^{-3}$ (45)
10^{-5} mole/l		
$ClInDAPMe_4Bu_4$		$9.14\cdot10^{-4}$ (45)
$5\cdot10^{-6}$ mole/l +HCl		
$ClGaDAPMe_4Bu_4$		$1.8\cdot10^{-3}$ (45)
$5\cdot10^{-6}$ mole/l +HCl		
$CH_3COOIn(OCH_3Ph)_8TAP$	$6.9\cdot10^{-5}$ (300)	
10^{-4} mole/l		

N o t e. Numbers in parenthesis denote excitation intensity, MW/cm^2.

Thus, the study of azaporphyrin solutions in chloroform have shown that the phototransformations occurring in them yield the production of ionic forms, i.e., proton attachment to the nitrogen mesonic atom owing to the increase of the basicity at excitation. The traces of HCl supplying the protons into the solution, apparently, are formed at irradiation of chloroform by laser radiation. Since the cationic forms limit the high-power laser radiation better than neutral ones, the LF of irradiated solutions, where the cations are formed, does not grow compared with the solutions that were not irradiated. On the whole, the values of the quantum yields of phototransformations have the same order of magnitude as that of the laser active media, i.e., $\cong 10^{-3}$ that makes it possible to use these compounds for limiting high-power laser radiation.

Conclusions

Thus, investigation of the spectral characteristics of luminescence of stationary and short-lived states, efficiency of producing ionic forms, as well as phototransformations of the compounds studied aimed at applying them as limiters of high-power laser radiation in the UV- and visible spectral regions have allowed us to draw the following conclusions:

1. Metals with the extraligand substituents do not directly take part in the electronic transitions in the visible and near UV-regions, however, they effect the spectral properties through the inductive effect and especially, the photophysical, nonlinear optical, and photochemical characteristics of the compounds (efficiency of proton attachment, yield of transitions to the triplet states, quantum yields of phototransformations, and LF).

2. The variety of forms has been established for solutions of bisphtalocyanine complexes both in the ground and in the excited states.

3. It is shown that production of ionic forms by attachment of a proton to one of the nitrogen mesonic atoms and of the oxidized forms in bisphtalocyanine complexes change the transmission of solutions at high-power excitation and takes part in the further irreversible phototransformations.

4. One can observe the correlation of the yield of transitions to the T-states and the OL effects for the cases of neutral and ionic forms of azaporphyrin complexes, which assume the involvement of T-states into the reabsorption of the high-power laser radiation.

5. Increase in the IA intensity in bisphtalocyanines with the increase in delay time, points to the possibility of using the compounds for

OL of not only nanosecond laser radiation, but also pulses of longer (microsecond) duration.

6. Phototransformations of the compounds do not exceed the dye phototransformations in laser active media and occur through the production of ionic forms at the first stage. Efficiency of such phototransformations reduces with the increase of the irradiation intensity and does not effect the OL efficiency.

Acknowledgements

This study was supported by the Russian Foundation for Basic Research (Grants No. 04-02-81002, 04-02-16515) and by the Federal Agency on Science (Project RI-19.0/002/064).

References

1. S.M. O'Flatherty, S.V. Hold, M.Y. Cook, et al., Adv. Mater. **15**, No. 1, 19–32 (2003).
2. R.T. Kuznetsova, N.S. Savenkova, G.V. Mayer, P.A. Shatunov, and A.S. Semeikin, Atmos. Oceanic Opt. **17**, Nos. 2–3, 149–155 (2004).
3. N.S. Savenkova, R.T. Kuznetsova, I.N. Lapin, et al., Opt. Spectrosc. **99**, No. 5, 751–758 (2005).
4. M. Hanack, T. Schneider, M. Barthel, et al., Coord. Chem. Rev. **219–221**, 235–258 (2001).
5. N.S. Savenkova, R.T. Kusnetzova, G.V. Mayer, et al., in: *Proc. the 7th Russian-Chinese Symp. of Laser Physics and Laser Technol.* (Tomsk State University, 2004), pp. 288–291.
6. I.P. Kalashnikova, I.V. Zhukov, T.V. Magdesieva, et al., Izv. Ros. Akad. Nauk, Ser. Khim., No. 7, 1238–1241 (2001).
7. I.P. Kalashnikova, I.V. Zhukov, L.G. Tomilova, and N.S. Zefirov, Izv. Ros. Akad. Nauk, Ser. Khim., No. 8, 1621–1625 (2003).
8. P.A. Stuzhin, I.S. Migalova, and H. Homborg, Rus. J. of Coordinat. Chem. **26**, No. 1, 6–11 (2000).
9. R.T. Kuznetsova, N.S. Savenkova, T.N. Kopylova, et al., Khimiya Vysokikh Energii **37**, No. 4, 287–293 (2003).
10. Y. Gorbunova, M.L. Rodriguez-Mendez, I.P. Kalashnikova, et al., Langmuir. **17**, No. 16, 5004–5010 (2001).
11. S.S. Ivanova and P.A. Stuzhin, Rus. J. of Coordinat. Chem. **30**, No. 11, 765–773 (2004).
12. S. Mac-Glinn, T. Adzumi, and M. Kinosita, *Molecular Spectroscopy of Triplet State* [Russian translation] (Mir, Moscow, 1972), 450 pp.