

# Photonics of laser-excited symmetric cationic polymethine dyes

V.A. Svetlichnyi, T.N. Kopylova, G.V. Mayer, I.N. Lapin, N.A. Derevyanko, A.A. Ishchenko

**Abstract.** Efficient lasing is obtained in the visible and near-IR spectral regions in solutions of symmetric polymethine dyes of the indolenine series (indocyanines) pumped by the second harmonic of a  $\text{Nd}^{3+}$ : YAG laser at 532 nm and an exciplex  $\text{XeCl}^*$  laser at 308 nm into the first (long-wavelength) and higher-lying electronic absorption bands. The quantum lasing efficiency upon UV excitation achieves 37%. It is shown that these dyes can also limit the radiation power of these lasers. Polymethine dyes limit especially efficiently the second-harmonic power, their attenuation factor for the radiation power density of  $100 \text{ MW cm}^{-2}$  achieving 14. The nanosecond flash-photolysis study of transient absorption spectra showed that the radiation power is limited by the mechanism of reverse saturated singlet–singlet absorption. It is established that the limiting ability of polymethines strongly depends on their structure.

**Keywords:** laser excitation, polymethine dyes, photoprocesses.

## 1. Introduction

Polymethine dyes attract interest for the fundamental studies of photoprocesses proceeding in these molecules and for the development of active media for tunable near-IR lasers [1–3], passive laser  $Q$ -switches, and other devices in quantum electronics [4] and optoelectronics [5].

It has been shown that some compounds of this class have strong transient-state absorption (TSA) in the visible spectral region with the cross section  $\sim 7 \times 10^{-16} \text{ cm}^2$ , which is comparable to the ground-state absorption cross section [6–9]. As a result, some polymethine dyes can be used as optical radiation limiters based on the mechanism of

reverse saturated absorption (RSA). In this case, the TSA cross section of molecules exceeds their ground-state absorption cross section.

The aim of this paper is to study photoprocesses proceeding in a series of laser-excited symmetric cationic polymethine dyes. The structural formulas of dyes 1–5 investigated in the paper are presented in Fig. 1. Molecules 1–3 are denoted HIC, HIDC, and HITC, respectively, in laser dye catalogues.

The absorption spectra of dyes 1–5 exhibit weak UV absorption bands and strong bands in the visible or near-IR region. They are related to different electronic transitions. The first electronic  $S_0 \rightarrow S_1$  transition is polarised along the long axis of a molecule and corresponds the long-wavelength absorption band. The second electronic transition and other  $S_0 \rightarrow S_n$  transitions to higher excited states [7] have different polarisations depending on the dye structure and are located in the UV spectral region. Despite the fact that most of these transitions, as the  $S_0 \rightarrow S_1$  transition, belong to the  $\pi - \pi^*$  type, their probability is one–two orders of magnitude lower than that of the first singlet transition [7]. Figure 2 shows the absorption spectra of dyes 1–3, which illustrate aforesaid.

The absorption and luminescence parameters of the  $S_0 \rightarrow S_1$  transition can be changed in a broad range by varying the chemical composition of the chromophore of symmetric cationic dyes [7, 10]. For example, the elongation of the polymethine chain by one vinylene group in the series of dyes 1–3 results in the regular bathochromic (blue) shifts of absorption and luminescence bands by 100 nm (Fig. 2, [7]). Bathochromic shifts are also observed upon cyclisation of the polymethine chain with a carcass methylene bridge (by 36 nm on passing from dye 3 to 4) and upon benzylation of the end heterocyclic groups (by 40 nm on passing from dye 2 to dye 5). On the one hand, this effect can be used if it is desirable to shift lasing to the red, but on the other hand, in this case the absorption band of a dye moves away from the wavelength of the second harmonic of a  $\text{Nd}^{3+}$ : YAG laser, which is widely and efficiently used for pumping. In this connection it is convenient that a change in the structure of the chromophore of dyes 1–5 weakly affects the position and intensity of the  $S_0 \rightarrow S_n$  transitions (Fig. 2). Because the emission of a  $\text{XeCl}^*$  laser falls in the region of these transitions, it is important to elucidate whether it is possible to populate efficiently the  $S_1$  state due to relaxation  $S_n \rightarrow S_1$  processes by pumping dyes at 308 nm. For this purpose, we studied in this paper photophysical processes in molecular dyes 1–5 involving their higher electronic states.

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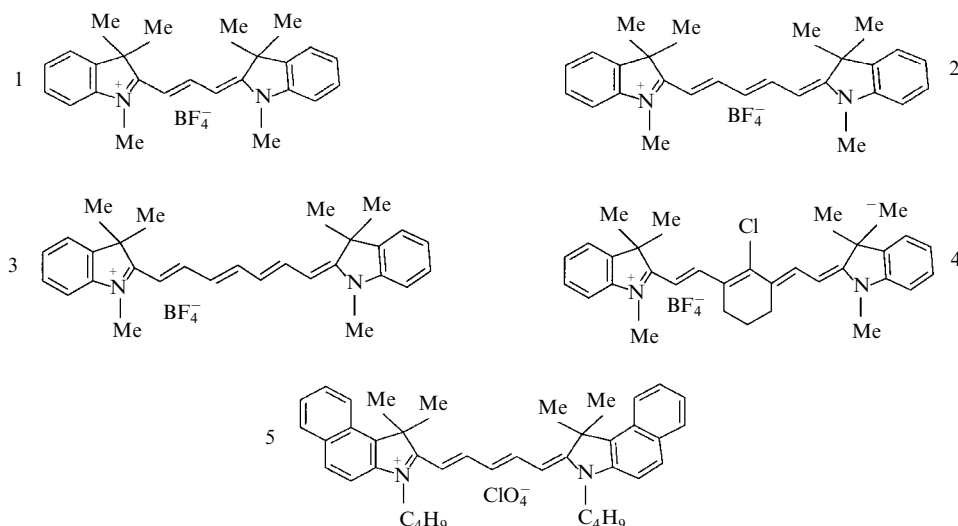
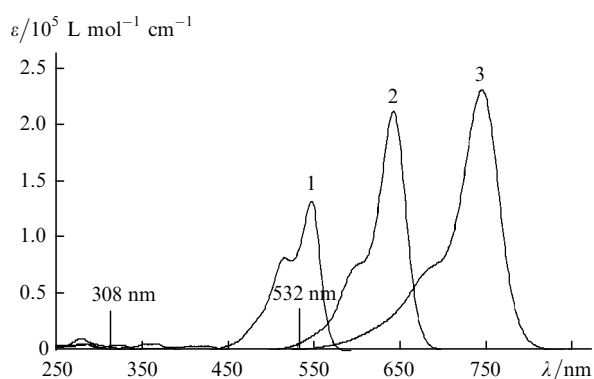
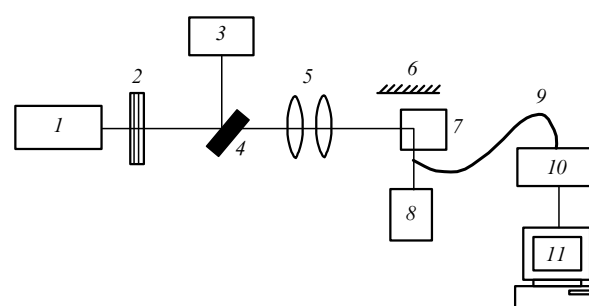
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**Figure 1.** Structural formulas of dyes.

**Figure 2.** Absorption spectra of dyes 1–3 (indicated are pump laser wavelengths used in experiments);  $\epsilon$  is the molar extinction coefficient.

**Figure 3.** Experimental setup for studying the absorption, luminescence, and lasing properties of organic dyes: (1) XeCl<sup>\*</sup> or Nd<sup>3+</sup>:YAG laser; (2) set of broadband optical filters; (3) KTP-2 calorimeter; (4) beamsplitter; (5) set of lenses; (6) aluminium mirror; (7) cell with a dye solution; (8) IMO-2N calorimeter; (9) optical fibre; (10) spectrometer; (11) personal computer.

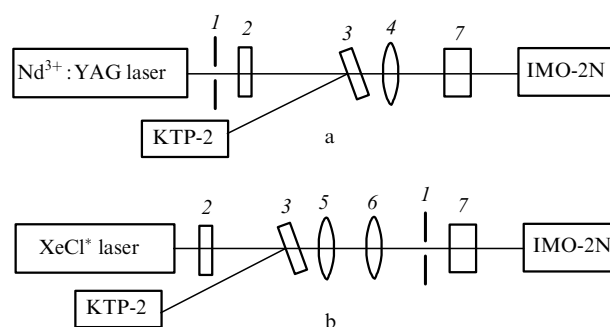
## 2. Experimental

We studied the absorption, luminescence, and lasing properties of dyes 1–5 in different solvents and their nonlinear optical properties upon excitation by a XeCl<sup>\*</sup> laser and the second harmonic of a Nd<sup>3+</sup>:YAG laser.

The scheme of the experimental setup for studying the lasing properties of dye solutions is presented in Fig. 3. Transverse pumping was used, and the resonator was formed by a highly-reflecting mirror and the facet of a cell. The cell and resonator lengths were 1 and 1.5 cm, respectively. The concentration of all the dyes in lasing experiments was 10<sup>−3</sup> M. Pump laser radiation was focused on the front face of the cell, the pump beam cross section was a rectangle of size 0.1 × 1 cm, and the pump power density was 25–30 MW cm<sup>−2</sup>. Pumping was performed by 308-nm, 12-ns, 30-mJ pulses from a XeCl<sup>\*</sup> laser with a repetition rate of 1–4 Hz or by 532-nm, 15-ns, 30-mJ pulses from a Nd<sup>3+</sup>:YAG laser with a repetition rate of 1–4 Hz.

The nonlinear optical properties of dyes were analysed by studying the dependence of the transmission of their solutions on the pump power density. Figure 4 shows the schemes of experimental setups.

The required pump power density was produced by focusing a laser beam by long-focus lenses (two crossed cylindrical lenses with  $F_5 = 600$  mm and  $F_6 = 250$  mm upon


**Figure 4.** Scheme of the experimental setup for studying nonlinear absorption in molecules excited by the second harmonic of a Nd<sup>3+</sup>:YAG laser (a) and by a XeCl<sup>\*</sup> laser (b): (1) aperture; (2) broadband optical filters; (3) beamsplitter; (4) spherical lens with  $F = 600$  mm; (5, 6) cylindrical lenses with  $F_5 = 600$  mm and  $F_6 = 250$  mm; (7) cell with a dye solution; KTP-2 and IMO-2N are calorimeters.

pumping by the XeCl<sup>\*</sup> laser or by a spherical lens with  $F = 600$  mm upon pumping by the Nd<sup>3+</sup>:YAG laser) to the centre of a 5-mm-thick quartz cell with solutions under study. The cell was placed in the converging laser beam, the incident beam diameter was about 1 mm and changed by no more than 10% over the cell length. To improve the

**Table 1.** Absorption, luminescence, and lasing properties of polymethine dyes.

Dye	Solvent	$\lambda_a/\text{nm}$ $\varepsilon/\text{L mol}^{-1} \text{cm}^{-1}$	$\lambda_{\text{fl}}/\text{nm}$ $\varphi_{\text{fl}}$	$\lambda_{\text{fl1}}/\text{nm}$	$\lambda_{\text{fl2}}/\text{nm}$	$\lambda_{\text{ex}} = 308 \text{ nm}$					$\lambda_{\text{ex}} = 532 \text{ nm}$			
						$k/\text{cm}^{-1}$	$\lambda_{\text{las}}/\text{nm}$	$\eta$ (%)	$\eta_q$ (%)	$P_{0.5}/\text{J cm}^{-2}$	$k/\text{cm}^{-1}$	$\lambda_{\text{las}}/\text{nm}$	$\eta$ (%)	$\eta_q$ (%)
1	ethanol	545 134000	565 0.03	609	609	6.9	608	1.9	4	–	187.4	608	20	23
2	aceto- nitrile	638 211000	661 0.28	715	687	7.8	721	13	30	32	14.3	721	18	24
3	PC	744 217000	784 0.28	841	806	15.9	848	12	33	68	4.2	845	3.5	5.7
4	PC	780 250000	812	865	831	16.8	875	13	37	86	2.4	870	1.2	1.9
5	PC	678 180000	710 0.15	765	725	15	779	10	25	72	7	777	3.5	5.1

Note:  $\lambda_{\text{fl1}}$  and  $\lambda_{\text{fl2}}$  are the wavelengths of maxima of laser-induced fluorescence bands detected perpendicular to and along the exciting laser beam, respectively;  $k$  is the absorption coefficient at the excitation wavelength;  $\eta$  and  $\eta_q$  are the energy and quantum lasing efficiency, respectively;  $P_{0.5}$  is the operation resource of the active medium (integral pump energy per unit volume reducing the lasing efficiency by half); dye 5, studied in detail earlier [9], is presented for comparison; PC: propylene carbonate.

homogeneity of the incident radiation distribution, the laser beam was diaphragmed to produce the bell-shaped beam profile. The initial transmission of the dye solutions at the pump wavelength was 70 %. The pump radiation intensity was varied from 2–5 to 200 MW cm<sup>-2</sup> with neutral filters. Upon high-power UV excitation by the XeCl\* laser, the nonlinear absorption in a solvent was taken into account and subtracted from the total absorption of the solution.

The radiation energy was measured with IMO-2N and KTP-2 calorimeters, the transmission measurement error being no more than 10 %.

Nonlinear absorption in dyes was measured from the attenuation coefficient  $K_W$ , which was calculated from the relation

$$K_W = T_0/T_W, \quad (1)$$

where  $T_0$  is the linear transmission of a dye at the excitation wavelength measured with a spectrophotometer; and  $T_W$  is the transmission at the pump power  $W$ .

In addition, we studied the transient TSA spectra of polymethine dyes by the method of nanosecond flash photolysis [11]. The solutions of polymethine dyes were excited by pulsed radiation from the exciplex XeCl\* laser focused by cylindrical lenses to produce the power density of 20 MW cm<sup>-2</sup> providing the efficient population of excited states of the dyes. The fluorescence of solutions of a number of organic fluorophores was used as probe radiation. Fluorescence was excited by the same exciplex XeCl\* laser. Thus, there was no need to synchronise the pump and probe beams. An optical delay line (1–40 ns) was used to separate short-lived  $S_1 \rightarrow S_n$  absorption, existing only during the pump pulse, from long-lived absorption (for example, the  $T_1 \rightarrow T_n$  absorption). The probe pulse energy density did not exceed 1  $\mu\text{J cm}^{-2}$ . The spectra were recorded in the spectral range from 350 to 650 nm with a laser spectrometer ('Angström', Novosibirsk) equipped with a CCD linear array coupled with a PC.

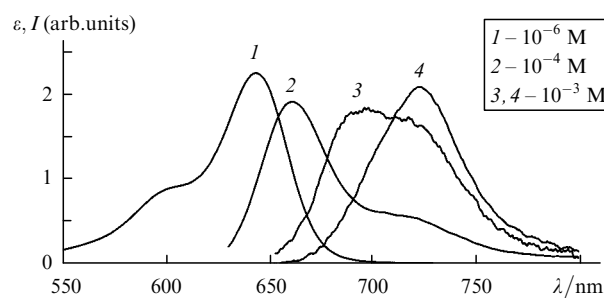
Transient absorption at a certain wavelength  $D(\lambda)$  was estimated from the optical density

$$D(\lambda) = \lg \frac{I_{\text{nex}}(\lambda)}{I_{\text{ex}}(\lambda)}, \quad (2)$$

where  $I_{\text{nex}}(\lambda)$  and  $I_{\text{ex}}(\lambda)$  are the intensities of probe radiation at the wavelength  $\lambda$  transmitted through unexcited and excited samples.

### 3. Results and discussion

The experimental results obtained in our study are presented in Tables 1 and 2 and Figs 5–7. Note first of all that polymethine dyes investigated here are multifunctional: they generate laser radiation upon pumping by UV and near-IR radiation and also can limit the high-power radiation of the XeCl\* laser and the second harmonic of the Nd<sup>3+</sup>:YAG laser. The efficiency of these processes, as expected, depends to a considerable extent on the dye structure and excitation conditions.



**Figure 5.** Absorption (1) and fluorescence (2–4) spectra of polymethine dye 2 in polypropylene carbonate at different concentrations; fluorescence upon linear excitation on a SM2203 spectrofluorimeter (2) and fluorescence excited by a XeCl\* laser [frontal detection (3) and detection perpendicular to the laser beam (4)].

#### 3.1 Absorption, luminescence, and lasing properties of polymethine dyes

One can see from Table 1 and Fig. 2 that symmetric cationic polymethine dyes strongly absorb light (the molar extinction coefficient  $\varepsilon$  is of the order of 10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) in the spectral range 545–780 nm. The dyes fluoresce in the region between 565 and 812 nm, with the quantum yield  $\varphi_{\text{fl}}$  varying in the range from 0.03 to 0.30. The Stokes shift for symmetric dye molecules is small (500–700 cm<sup>-1</sup>), which

results in a considerable overlap of their absorption and fluorescence spectra, especially in concentrated solutions. This is illustrated in Fig. 5 by the example of the absorption and luminescence spectra of polymethine dye 2. As the dye concentration was increased from  $10^{-6}$  to  $10^{-3}$  M, the maxima of fluorescence bands shift to the red, the absorption spectra being invariable. Therefore, concentration effects observed in luminescence spectra are not related to the association of dye molecules. Excimers also are not formed under our experimental conditions. This is confirmed by the absence of broad structureless luminescence bands with a large Stokes shift. Therefore, it is most likely that concentration effects are caused by reabsorption. Reabsorption for indocyanines 1–5 is pronounced because of small Stokes shifts due to close electronic energy diagrams of symmetric dyes in the ground and excited states. Reabsorption is manifested not only in the red shift of the fluorescence spectrum but also in the change in its shape (Fig. 5).

The shift of fluorescence bands depends on the excitation geometry and can exceed 50 nm. Thus, the wavelength  $\lambda_{fl}$  of the fluorescence band maximum for dye 2 (Fig. 5) at the dye concentration  $10^{-6}$  M is 661 nm and is independent of the fluorescence excitation and collection geometry. As the dye concentration is increased up to  $10^{-3}$  M, fluorescence spectra shift considerably to the red. In this case, the shape of the spectra and their red shift strongly depend on the fluorescence detection geometry. When fluorescence is detected perpendicular to the excitation beam, the red shift has the greatest value ( $\lambda_{fl1} = 715$  nm). Upon frontal detection (detection in reflected light), the red shift is smaller because fluorescence is detected mainly from the front layer of excited dye molecules in a cell ( $\lambda_{fl2} = 687$  nm).

The large spectral shifts of fluorescence and lasing bands caused by reabsorption have been studied in most detail for rhodamine solutions. Thus, it has been found in [12] that the superfluorescence spectra of rhodamine 6G strongly depend on the dye concentration and excitation geometry due to reabsorption. Reabsorption effects in polymethine dyes 1–5 are manifested even stronger, which can be explained by their higher absorption cross sections and smaller Stokes shifts compared to those for rhodamines.

All the polymethine dyes studied in the paper exhibit laser action upon pumping by the second harmonic of the  $\text{Nd}^{3+}$ : YAG laser or by the  $\text{XeCl}^*$  laser. In the first case, pumping is performed into the first singlet–singlet  $S_0 \rightarrow S_1$  absorption band, while in the second one, depending on the dye structure, into the second or higher singlet states of the dye ( $S_0 \rightarrow S_n$ ) [7]. The laser emission of polymethine dyes of this series lies in the region 608–870 nm (depending on their structure), the energy conversion efficiency for the 308-nm pump radiation for dyes 2–4 is 12%–13% and the quantum yield is 30%–37%. This indicates that the rapid internal  $S_n \rightarrow S_1$  conversion favours lasing from the  $S_1$  state upon UV laser pumping and provides efficient lasing of dyes 1–5 in the near-IR range, i.e. with a large Stokes shift with respect to the pump wavelength, despite the fact that the positions of the long-wavelength absorption bands of these dyes strongly differ.

The operation resource (the integrated pump energy per unit volume resulting in the lasing efficiency decrease by half) upon UV radiation pumping is 30–86  $\text{J cm}^{-3}$ . For dyes with a flexible polymethine chromophore (the most photosensitive part of a dye) emitting in the IR region upon

pumping by UV radiation, this is good photostability [4], which opens up new possibilities for practical applications of dyes as active laser media (for comparison, the operation resource of the active medium based on one of the most photochemically stable laser dyes with a rigidly fixed chromophore, rhodamine 6G, which is widely used in tunable lasers, is 100  $\text{J cm}^{-3}$  upon UV excitation).

The lasing efficiencies of dyes 2, 3, and 4 pumped by the second harmonic of the  $\text{Nd}^{3+}$ : YAG laser were 18, 3.5, and 1.2%, respectively. Note that dyes 3 and 4 exhibit laser action despite their low long-wavelength absorption cross sections at the pump wavelength, which correspond to the absorption coefficient  $k$  of 2–4  $\text{cm}^{-1}$  only, whereas this coefficient should be 10–15  $\text{cm}^{-1}$  to obtain efficient lasing.

Of special interest is dye 1. Having the quantum yield of fluorescence as low as  $\sim 0.03$ , it exhibits lasing at 608 nm upon pumping by the 308-nm  $\text{XeCl}^*$  laser or by the 532-nm second harmonic of the  $\text{Nd}^{3+}$ : YAG laser. In the first case, the lasing efficiency is 1.9% (obviously because of a low absorption coefficient  $k = 6.9 \text{ cm}^{-1}$ ) and in the second case, the lasing efficiency is 20%. The 532-nm pump radiation falls to the maximum of the absorption band of dye 1, providing efficient lasing despite a low quantum yield of fluorescence. A similar situation was observed for stilbene molecules, which generated radiation upon pumping at 308 nm into the maximum of the long-wavelength absorption band although the quantum yield of fluorescence was only 0.03 [13].

A specific feature of symmetric indocyanines is the red shift of their lasing band with respect to the fluorescence band of their diluted solutions caused by reabsorption due to a strong overlap of absorption and fluorescence spectra. Lasing appears near the maximum of the fluorescence band of the concentrated solution of the dye measured upon transverse excitation (see Table 1).

The presence of a strong overlap of the absorption and fluorescence bands does not allow us to increase the concentration of dyes 3 and 4 because the intensity of their emission strongly decreases due to reabsorption and other possible mechanisms of concentration quenching [7]; the discussion of these mechanisms is beyond the scope of this paper.

Thus, polymethine dyes studied here can be used as active media in near-IR lasers pumped both by visible and UV radiation and employed for various technological and medical applications [14]. We suppose that it is necessary to study the lasing properties of these dyes in solid matrices for the development of new active solid media.

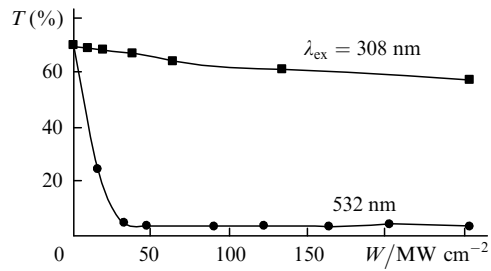
### 3.2 Nonlinear optical properties of polymethine dyes

Table 2 and Fig. 6 present the nonlinear optical properties of polymethine dyes obtained in our study, which

**Table 2.** Nonlinear optical properties of solutions of polymethine dyes in propylene carbonate.

Dye	$K_W$	
	$\lambda_{\text{ex}} = 308 \text{ nm}$	$\lambda_{\text{ex}} = 532 \text{ nm}$
1	1.20	> 1
2	1.21	2
3	1.18	14
4	1.12	10
5	1.38	10

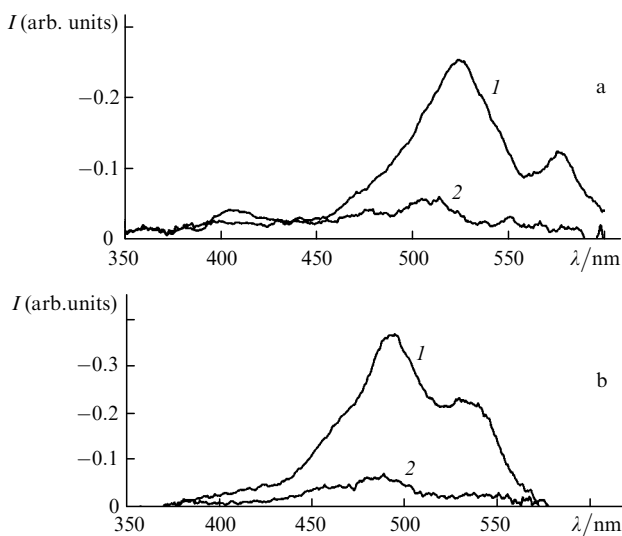
Note: the linear transmission of solutions is  $T_0 = 70\%$ ,  $W = 100 \text{ MW cm}^{-2}$ .



**Figure 6.** Dependences of the transmission  $T$  of the dye 4 solution in polypropylene carbonate on the pump power density  $W$  at 308 and 532 nm for the linear transmission of solutions equal to 70%.

characterise the possibility of limiting high-power UV and visible laser radiation. One can see that dyes 3 and 4 can limit the second-harmonic power of the  $\text{Nd}^{3+} : \text{YAG}$  laser with the attenuation coefficient  $K_W$  achieving 10–14 for the excitation power density of  $100 \text{ MW cm}^{-2}$ , which is good characteristic for organic limiters (the attenuation coefficient for fullerene  $\text{C}_{60}$  widely used for this purpose is 10 [15]).

The attenuation coefficient for dye 2 is considerably smaller ( $K_W = 2$ ). To determine the mechanism of nonlinear attenuation of the laser radiation power and the influence of the structure of molecules on their nonlinear properties, we studied absorption induced in dyes 3 and 4 by high-power laser radiation. The results are presented in Fig. 7. One can see that rather strong transient absorption is observed in the spectral range from 400 to 600 nm. Because this absorption virtually disappears after 30 ns, i.e. is short-lived, it is probably related to singlet–singlet absorption or absorption by short-lived radicals. Our experimental and quantum-chemical study of transient absorption for dye 5 and other dyes of this class confirms that singlet–singlet absorption is most probable in this spectral range [9]. These data are also confirmed by experimental studies of transient absorption for similar polymethine dyes in femtosecond, picosecond, and nanosecond ranges performed in [3, 16]. Therefore, the



**Figure 7.** Transient absorption spectra of polymethine dyes 4 (a) and 3 (b) during the excitation pulse (1) and within 30 ns after its end (2).

532-nm radiation is probably limited due to singlet–singlet RSA, i.e. the ratio of cross sections for excited- and ground-state absorption at a wavelength of 532 nm exceeds unity, resulting in the limitation effect.

Dye 2 absorbs and emits at shorter wavelengths (638 and 661 nm, respectively) than dyes 3 and 4 (744, 780 nm and 784, 812 nm, respectively). Therefore, it is possible that the transient singlet–singlet absorption spectra of dye 2 lie in the region shorter than 532 nm, which can explain a weak attenuation of the second harmonic of the  $\text{Nd}^{3+} : \text{YAG}$  by this dye. The experimental study of transient absorption in dye 2 will be performed later.

To achieve the efficient limitation of nanosecond laser radiation in a dye, the following conditions should be fulfilled:

- (i) Weak linear absorption at the required wavelength;
- (ii) rapid relaxation of dye molecules to the lower excited state from which transient absorption occurs; and
- (iii) strong transient absorption at the required wavelength, which exceeds the ground-state absorption.

These conditions are fulfilled for dyes 3–5 excited by the second harmonic of the  $\text{Nd}^{3+} : \text{YAG}$  laser. A weak limitation of the second-harmonic power of the  $\text{Nd}^{3+} : \text{YAG}$  laser by dyes 1 and 2 and UV radiation by polymethine dyes 1–5 is most likely explained by insufficient transient absorption at the second-harmonic wavelength compared to linear absorption. This is most pronounced for dye 1 excited by the second harmonic of the  $\text{Nd}^{3+} : \text{YAG}$  laser whose wavelength lies near the maximum of the long-wavelength absorption band of this dye. As a result, we observe the reverse bleaching of the solution of dye 1 upon high-power laser excitation at 532 nm.

The excitation wavelength 308 nm falls into the region of the  $S_0 \rightarrow S_n$  transitions whose probability, as mentioned above, is one–two orders of magnitude lower than that of the  $S_0 \rightarrow S_1$  transition. Then, dye molecules rapidly relax due to internal conversion to the  $S_1$  state. Therefore, the first two conditions, required for the efficient limitation of the laser radiation power, are fulfilled. In this case, weak limitation is most likely caused by a low probability of transient absorption at a wavelength of 308 nm.

At the same time, rapid internal conversion from high-lying singlet states to the  $S_1$  state plays a positive role, providing population inversion and lasing from the  $S_1$  state. As a result, dyes 1–5 exhibit efficient lasing in the near-IR region upon excitation by the UV laser, i.e. the red shift of laser emission with respect to the pump wavelength is large, which is important for practical applications.

A strong change in the position of long-wavelength absorption bands in the series of dyes 1–5 noticeably affects the value of the ground-state absorption cross section at the second-harmonic wavelength of the  $\text{Nd}^{3+} : \text{YAG}$  laser. As a result, the degree of limitation of this radiation strongly depends on the structure of dyes 1–5. The absorption bands corresponding to the  $S_0 \rightarrow S_n$  and  $S_1 \rightarrow S_n$  transitions are considerably less sensitive to variations in the polymethine chain length and its cyclisation because they are related to the end chromophore groups. Therefore, to obtain the efficient transient absorption in dyes, it is necessary to change the chemical structure of these parts of molecules.

To understand the relation between the absorption, luminescence, lasing, and nonlinear optical properties of dyes 1–5, it is necessary to perform the quantum-chemical study of electronic-energy deactivation processes in these

molecules (the complex approach to such studies was developed in [17]), which will allow us to give recommendations concerning the synthesis of dyes with the specified properties.

#### 4. Conclusions

We have shown that symmetric cationic polymethine dyes are polyfunctional and can be used to:

(i) generate near-IR radiation in tunable lasers pumped by UV and visible radiation;

(ii) limit high-power second-harmonic radiation from a  $\text{Nd}^{3+}$ : YAG laser by the mechanism of singlet–singlet reverse saturated absorption; and

(iii) limit the UV radiation of an exciplex laser, although to a much lower degree than the second-harmonic of the  $\text{Nd}^{3+}$ : YAG laser, this effect being less sensitive to the polymethine chain length in the case of UV excitation.

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