# Lasing in a phenalemine-512 dye laser at two-photon pumping in solutions, polymer matrices, and drops

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Two-photon pumped fluorescence (TPF) of efficient red laser dyes – phenalemines – excited by nanosecond radiation pulses of an YAG:$Nd^{3+}$ laser (1064 nm) is investigated. For phenalemine 512 with the highest TPF efficiency, two-photon pumped upconverted lasing (TPL) was excited in ethanol solutions, polymethylmethacrylate (PMMA) matrices, and propyleneglycolcarbonate drops in the spectral range of 615–652 nm.

## Introduction

The great interest in the investigation of optical materials with the large cross section of two-photon absorption (TPA) is caused by their possible application to optical limiting,[1,2] in laser spectroscopy,[3] 3D optical memory and 3D monitors,[4,5] stereo-lithography,[6] and fluorescent microscopy.[7] In some cases, the material (molecules) at such excitation have to have not only efficient two-photon absorption, while at the same time good emission properties.

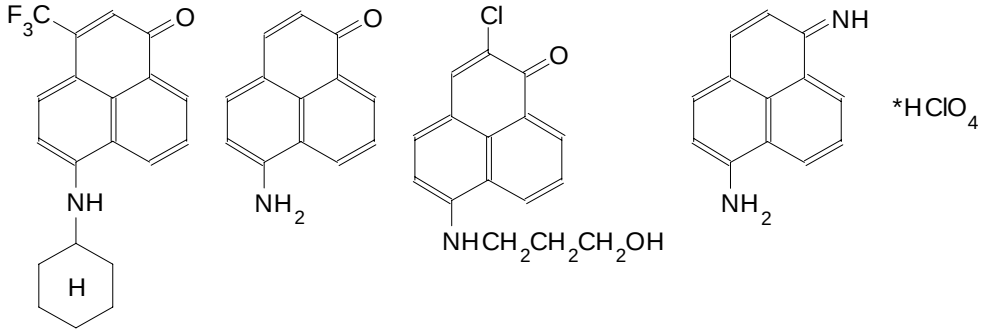
One of the most interesting nonlinear optical phenomena, which are actively studied now, is stimulated emission at two-photon excitation. Two-photon pumped lasing (TPL) opens the possibility of obtaining tunable lasing from organic compounds emitting in the visible spectral region when pumped by high-power red semiconductor lasers. In such a case, there is no need in using expensive nonlinear materials needed for second harmonic generation and parametric conversion and it becomes possible to create simple waveguide and fiber configurations of laser systems with radiation frequency conversion. In this connection, the search for new organic molecules with the large two-photon absorption cross section[8] and good lasing characteristics is nowadays being intensely carried out.

By now, two-photon pumped lasing is obtained from a limited number of organic compounds (some rhodamines, substituted pyran, stilbene, and some other molecules) in solutions, drops, and solid-state matrices.[9–12] Radiation of solid-state lasers and their harmonics, usually, of picosecond duration was used for pumping. Nanosecond pumping is used rarely, because the threshold power density, at which lasing begins, is high, which leads to damage of optical elements (lenses, mirrors, cell windows).

We have studied lasing characteristics of substituted phenylenons (phenalemines) at two-photon pumping by YAG-$Nd^{3+}$ laser radiation (1064 nm, 7 ns, 15 mJ). Stimulated emission was obtained at nanosecond pumping for phenalemine-512 in solutions, polymethylmethacrylate (PMMA) polymer matrices, and drops.

## 1. Objects under study, experiment

Phenalemines (Fig. 1) are efficient and photostable laser dyes in the red spectral region (590–660 nm), which is important for medical applications. They efficiently generate laser radiation at various pumping. The lasing efficiency when pumped by the second harmonic of the YAG-$Nd^{3+}$ laser achieves 50–56% in solutions and 30–39% in polymer matrices (see the Table), which is quite comparable with or even higher than those of xanthene dyes and pyrromethenes lasing in this spectral region.[13] These active media also show the high lasing efficiency and photostability at UV pumping (308 nm): the lasing efficiency achieves 25% in solutions and 16% in PMMA.




Phenalemine 512 Phenalemine 160 Phenalemine 510 Phenalemine 640

**Fig. 1.** Structure formulas of the molecules studied.

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**Spectral-luminescence, lasing, and nonlinear properties of organic dyes in solutions and PMMA**

| Compound* | $\lambda_{abs}$, nm | $\lambda_{fl}$, nm | $\lambda_{las}$, nm | lasing eff., % pumping | | TPF $\lambda_{fl}$, nm | Relative TPLu efficiency** |
|---|---|---|---|---|---|---|---|
| | | | | 308 nm | 532 nm | | |
| Rhodamine 6G | | | | | | | |
| ethanol | 530 | 565 | 614 | 26 | 53 | 568 | 1.00 |
| PMMA | 535 | 570 | | 18 | 50 | 573 | 0.53 ± 0.03 |
| Phenalemine 512 | | | | | | | |
| ethanol | 560 | 606 | 615 | 24 | 50 | 602 | 0.43 ± 0.03 |
| PMMA | 550 | 588 | 600 | 16 | 39 | 592 | 0.55 ± 0.03 |
| Phenalemine 160 | | | | | | | |
| ethanol | 535 | 606 | 614 | 20 | 56 | 600 | 0.15 ± 0.03 |
| Phenalemine 510 | | | | | | | |
| ethanol | 565 | 615 | 630 | 16 | 51 | 615 | 0.15 ± 0.03 |
| PMMA | 565 | 615 | 630 | 10 | 29 | 604 | 0.13 ± 0.03 |
| Phenalemine 640 | | | | | | | |
| ethanol | 590 | 630 | 643 | 25 | 56 | 630 | 0.05 ± 0.03 |
| PMMA | 590 | 630 | 643 | 14 | 38 | 630 | 0.03 ± 0.03 |

* The concentration of all the samples was $10^{-3}$ mol/l. ** As to Rhodamine 6G in ethanol; pumping wavelength $\lambda$ = 1064 nm, pumping power density $W$ = 700 MW/cm$^2$.

The dyes were received from Alfa-Akonis (Dolgoprudny, Russia); they had the quantum electronics grade purity and were used without further purification. Polymer samples were also synthesized in Alfa-Akonis. They were cut to 20×10×10 mm parallelepipeds and then polished manually. The used solvents: ethyl alcohol (ethanol) and propyleneglycolcarbonate (PGC) were of spectroscopic grade purity.

The setup used for TPLu studies is shown in Fig. 2*a*. The radiation of the first harmonic of the YAG:$Nd^{3+}$ laser (1064 nm) passed through a diaphragm 4 mm in diameter that cuts off the central, most homogeneous part of the beam and then focused with a long-focus lens with $F$ = 350 mm. The cell with the studied solution or polymer samples was set at the distance of 300 mm from the focusing lens in the converging beam. The maximum power density of the pump radiation incident on the object under study was 1 GW/cm$^2$ at this optical arrangement. Radiation was attenuated by neutral density filters. The incident and transmitted radiation was measured with the Model ED-100A pyroelectric receivers (Gentec EO). TPLu was observed with a laser spectrometer based on a linear photodiode array (Angstrem, Novosibirsk) with a fiber-optic lead-in cable (diameter of 0.3 mm) perpendicular to the direction of incidence of the pump radiation.

*a*

*b*

**Fig. 2.** Setup for investigation of TPLu (*a*) and TPL (*b*) of organic molecules: YAG:$Nd^{3+}$ laser *1*, diaphragm *2*, neutral density filters *3*, beam-splitter *4*, focusing lens *5*, sample *6*, power meters *7*, *8*, waveguide *9*, spectrometer *10*, computer *11*, selective filter *12*, photodiode *13*, oscilloscope *14*, dielectric mirrors R1 and R2 *15*, *16*, and a He–Ne-laser *17*.

To obtain lasing (in the optical arrangement with longitudinal pumping), a lens with the focal length $F = 100$ mm and a plane-parallel cavity with the base length of 80 mm, which was adjusted with a He–Ne laser (Fig. 2*b*), were used. A dielectric mirror R1 had the reflection coefficients of 0.20 at the pump wavelength and 0.30 at the lasing wavelength, while those for R2 were, respectively, 0.50 and 0.95. Thus, the lasing radiation was opposite to the pump beam. It was impossible to shorten the cavity length, because this would lead to damage of the dielectric coating by the high-power focused pump radiation ($W_{pump} > > 200$ MW/cm$^2$). The spectrum of the lasing radiation scattered by the focusing lens through a waveguide was recorded by the Angstrem-model spectrometer.

Fluorescence and stimulated emission in a drop suspended in air on a metal capillary were excited in the optical arrangement shown in Fig. 2*a*.

The time characteristics of radiation were recorded with a Model Thorlabs DET210 high-speed PIN photodiodes and a Model Tektronix TDS224 oscilloscope.

## 2. Investigation of TPLu

To assess the TPA efficiency, two-photon absorption cross section $\delta$ is used. For most organic fluorophores, this parameter ranges from $10^{-49}$ to $10^{-51}$ cm$^4 \cdot$ s $\cdot$ phot$^{-1} \cdot$ mol$^{-1}$. When the TPA cross section is determined from the secondary processes (luminescence) or when the efficiency of emission at two-photon excitation is important, the parameter equal to the product of $\delta$ by the quantum yield of fluorescence $\eta$ – TPLu efficiency – is used.

For correct measurement of $\delta$ or $\delta\eta$, it is necessary to know the square (or close to square) dependence of the TPLu intensity $I_{TPLu}$ on the pump radiation intensity $W_{pump}$. We have studied the dependence $I_{TPLu}(W_{pump})$ for Rhodamine 6G (test compound with the known TPA cross section) and phenalemine 512 at the pump intensity within 100–800 MW/cm$^2$, and it was shown that the dependences are not square ones. The tangent of the curve slope is 1.3 for Rhodamine 6G and 1.15 for phenalemine 512. These results agree with the data of Ref. 14: the square dependence $I_{TPLu}(W_{pump})$ for solutions of organic dyes at nanosecond pumping is observed only up to the pump power density of 10–30 MW/cm$^2$. As the intensity of the pump radiation increases, other nonlinear processes (for example, $S_1 \rightarrow S_n$ absorption, stimulated $S_1 \rightarrow S_0$ transitions, and others) become important, and this leads to the decrease of the TPLu efficiency. However, in this case we were interested in the relative TPLu efficiency under particular experimental conditions. The TPLu efficiency of Rhodamine 6G was taken to be unit, and the relative TPLu efficiency was estimated as:

$$(\delta\eta)_{rel} = I_x \Delta\lambda_x / I_{ref} \Delta\lambda_{ref},$$

where $I_x$, $I_{ref}$ are intensities and $\Delta\lambda_x$ and $\Delta\lambda_{ref}$ are the halfwidths of the TPF spectrum of the studied compound and the reference one (Rhodamine 6G), respectively.

The measured spectral characteristics and relative TPLu efficiency are summarized in the Table.

The laser-induced luminescence spectra at one- and two-photon pumping of phenalemines are similar: the positions of peaks and the halfwidth vary insignificant.

Phenalemine 512 has the highest TPLu efficiency among the studied phenalemines in the ethanol solution and in PMMA. In spite of the fact that its $(\delta\eta)_{ref}$ in ethanol is roughly twice as low as that of Rhodamine 6G, phenalemine 512 is promising for obtaining stimulated emission at two-photon pumping, because it is less subject to aggregation and reabsorption, which significantly decrease the emissivity at high concentrations used to get two-photon pumped lasing. For all the studied molecules, the TPLu efficiency in solutions is higher than in solid matrices. In Refs. 15 and 16, which compare the efficiency of two-photon absorption in solutions and matrices, the same regularity is observed. In our case, the only exception is phenalemine 512, for which we can see the inverse dependence – the TPLu efficiency in PMMA is higher than in ethanol. Thus, the TPLu efficiency of phenalemine 512 in PMMA exceeds that for Rhodamine 5G in the matrix.

## 3. TPL of phenalemine-512 in ethanol and PMMA

Lasing of Rhodamine 6G and phenalemine-512 in solutions and polymer matrices was studied in the longitudinal scheme of pumping on the setup shown in Fig. 2*b*.

A rectangular cell with the optical path length from 20 to 50 mm was filled with the solution of the studied dye.

For Rhodamine 6G, the lasing was obtained only in a 20-mm-long cell at the concentration of $10^{-2}$ mol/l and the threshold pump power density of $W_{thr} = 1$ GW/cm$^2$. This compound is characterized by a significant overlap of the absorption and luminescence spectra that leads to increased re-absorption and hampers obtaining generation at longitudinal excitation. The TPL wavelength $\lambda_{TPL} = 603$ nm because of re-absorption is significantly shifted to the long-wave region with respect to the peak of the fluorescence band (Fig. 3*a*). With the cell of different length or Rhodamine 6G concentration, the lasing was not observed at the pump power density up to 1 GW/cm$^2$.

For the phenalemine-512, in which the re-absorption is less significant in the ethanol solution, lasing was observed at the dye concentration of $10^{-2}$ mol/l and the cell length of 20 and 50 mm. In the former case $W_{thr}$ was roughly equal to 0.4 GW/cm$^2$, while in the second one it was ~0.8 GW/cm$^2$, and $\lambda_{TPL}$ was, respectively, 629 and 637 nm (curves *3* and *4* in Fig. 3*b*). The long wave shift of the lasing wavelength at the transition to a longer cell is connected with the re-absorption, as was mentioned above.

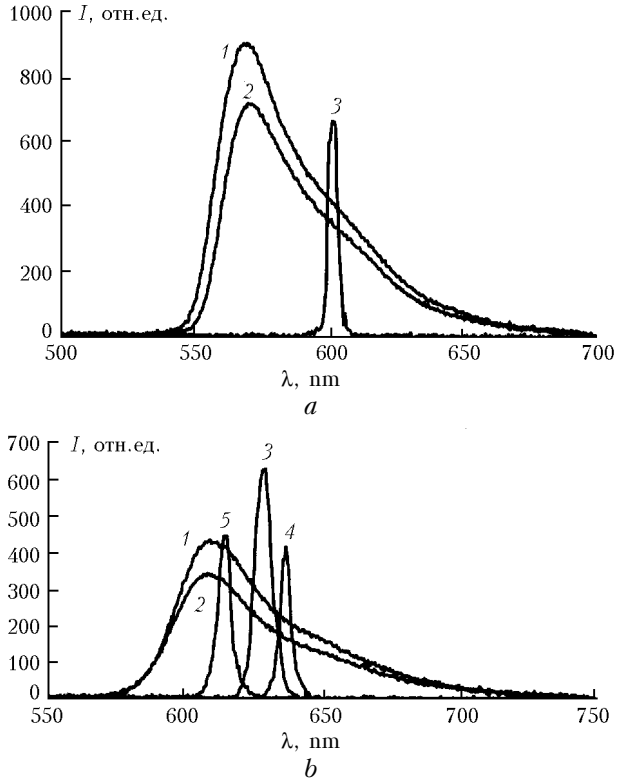


**Fig. 3.** Emission spectra of Rhodamine 6G (*a*) and phenalemine-512 (*b*) in ethanol (*1–4*) and PMMA (*5*): laser-induced fluorescence (*1*), TPLu (*2*), lasing (*3–5*).

In the polymer matrix, lasing of phenalemine-512 was obtained as well. The sample length was 17 mm at the concentration of $10^{-2}$ mol/l. In PMMA the wavelength of phenalemine-512 lasing is shorter than in the ethanol solution, $\lambda_{TPL} = 615$ nm (curve *5* in Fig. 3*b*), which is caused by the short wave shift of the fluorescence band of this dye in the PMMA. In this case, the lasing threshold is rather low: $W_{thr} \approx 0.35$ GW/cm$^2$.

## 4. TPL in a drop

The use of drops as elements of optical layout in studying nonlinear processes has some advantages:

– the liquid surface is optically smooth because of surface tension;

– whispering gallery modes with high Q arise in a spherical resonator;

– a spherical drop surface itself is a focusing element for the pump radiation;

– it is quite simple to have suspended drops.

TPLu and TPL of phenalemine-512 in drops was carried out at the same setup, as was used for studies of TPLu in solutions (Fig. 2*a*). As in solutions, the dye concentration $C$ was $10^{-2}$ mol/l during lasing studies. The PGC was used as a solvent. The emission characteristics of phenalemine-512 in PGC are almost the same as in ethanol, but PGC has the low evaporation rate, so the suspended PGC drops are stable in air for a long time. A drop was suspended at the end of a metal capillary and had the diameter from 1 to 2 mm.

In the case of pumping by radiation with the wavelength of 1064 nm, we observed intense TPLu, whose spectrum is shown in Fig. 4*a* and is almost identical to the spectrum of ordinary fluorescence and TPLu in solution. At the same time, TPLu was easily observed at irradiation by even unfocused radiation, when $W_{pump} = 20$ MW/cm$^2$, since the power density of the pump radiation inside the drop having focusing properties significantly exceeded that of the incident radiation.

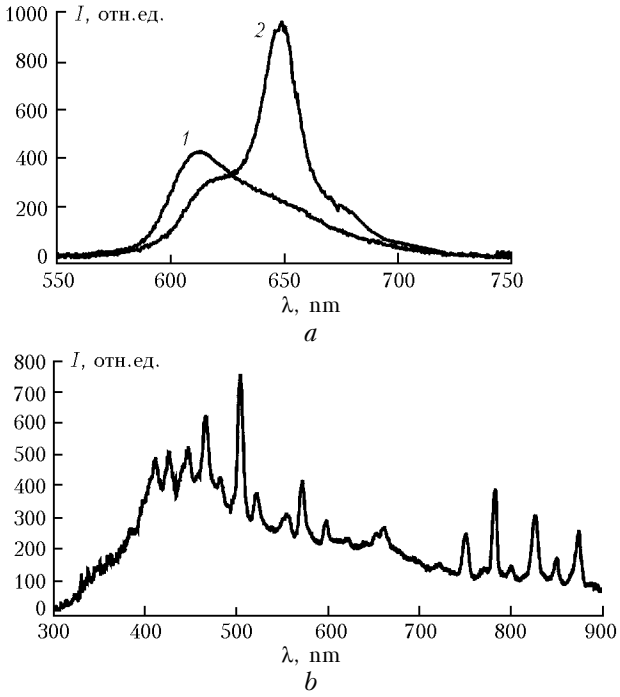


**Fig. 4.** Emission spectra of phenalemine 512 in a PGC drop (*a*) and a spark induced by the focused laser radiation in air (*b*): TPLu (*1*) and TPL (*2*).

With higher pump power density, we observed TPL. The TPL spectrum in the drop is further shifted (as compared to solutions) to the red region (Fig. 4*a*). This is connected with the presence of re-absorption in the medium and with the high Q of the whispering gallery modes in a spherical resonator. In addition, the lasing spectrum in the drop is wider as compared to TPL in the linear cavity (see Fig. 3*b*) and it is observed against the background of intense spontaneous emission. Depending on the drop radius, cross dimensions of the incident radiation, and the place of incidence of the pump radiation, the threshold level of the incident radiation, at which lasing arises, varied from 0.1 to 0.6 GW/cm$^2$. In some cases, a spark arose in air near the rear surface of the drop due to focusing of the pump radiation by the drop. In this case, lasing is induced not only by two-photon excitation directly by the laser radiation, but also by the spark radiation, whose spectrum is shown in Fig. 4*b*.

Figure 5 shows the time characteristics of the pump and lasing radiation, as well as the spark. It can be seen that the lasing is observed in the same time interval as the pump radiation. The spark radiation is longer and its peak falls on the end of the lasing pulse. Thus, in our experiments the spark was only an auxiliary factor at excitation of lasing in the drop.

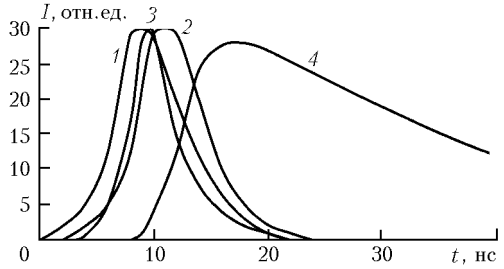


**Fig. 5.** Time characteristics of the pump radiation (*1*), TPLu (*2*), and TPL (*3*) of phenalemine 512, and spark (*4*).

Nevertheless, there is some evidence[17] that lasing in a drop was induced by the spark near its front boundary. To exclude the spark effect, the drop was decreased down to the diameter of 0.8–1.0 mm, after which it acquired the flattened (ellipsoid) shape, and the pump radiation was focused inside the drop near its rear surface. To avoid breakdown leading to destruction of the drop, the pump pulse energy was decreased to 3 mJ. Under such conditions, lasing was obtained, and the threshold value of the pump power density was 0.6 GW/cm$^2$.

An attempt was undertaken to obtain lasing with only a spark. For this purpose, a short-focus ($F$ = = 40 mm) lens was used, and the laser pulse energy was 30 mJ. A powerful spark with the length of 2–3 mm was induced in the air near the side surface of the drop. This arrangement, as compared to Ref. 17, where the spark was induced near the front surface of the drop, fully excludes irradiation of the drop with a $Nd^{3+}$–YAG laser radiation, and the spark radiation is used at maximum efficiency for excitation of the drop. In some cases, the drop was blown off the capillary by the shock wave generated by the spark, which nevertheless did not hamper recording of the time and spectral characteristics of radiation. Lasing obtained under these conditions was caused only by the radiation from the powerful spark. It should be noted that with the pump pulse energy decreased to 10 mJ, the attempts to obtain lasing in a drop with only a spark failed.

## Conclusions

Our investigations showed that phenalemine-512 is of interest as a dye for obtaining TPLu and TPL in various media. In spite of the lower efficiency of TPLu as compared to Rhodamine 6G, phenalemine-512 shows better lasing characteristics at two-photon excitation, since at the high concentrations it is less subject to the processes decreasing the emission efficiency. Thus, phenalemine-512 is promising for two-photon pumped lasers, since it generates laser radiation at nanosecond pumping with the threshold of 0.35–0.4 MW/cm$^2$, and the use of picosecond pulses for TPL excitation will allow improving the conversion efficiency.

The studies of phenalemine 512 emission in drops showed that spherical resonators are promising for TPL, because in this case the energy threshold of lasing can be decreased considerably, the pumping scheme becomes much simpler, and the size of the active element is smaller.

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