Generation of DCM substitutes under two-photon excitation with a nanosecond-duration radiation of a Nd–YAG laser

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The lasing characteristics of organic dyes of dicyanomethylene-pyran (DCM) substitutes have been studied at pumping with pulsed Nd–YAG-laser radiation at 1064 nm wavelength and 15-ns duration. Cavity parameters, concentration of active molecules, and pump level have been optimized to maximize the lasing efficiency. For efficient two-photon pumped upconverted lasing, organic molecules should possess not only high two-photon absorption (TPA) cross section, but also intense fluorescence, weakly subject to the concentration quenching due to aggregation and reabsorption. In addition, original design of a laser cavity is required to obtain maximum lasing efficiency in a weakly absorbing active medium. Among the compounds studied, the maximum lasing efficiency (higher than 0.5%) was obtained with the DCM molecule.

Introduction

The intense investigations in the field of nonlinear optics of organic molecules in the recent decades have led to the development of laser technologies that employ the phenomenon of multiphoton absorption. Today some technologies associated with the multiphoton absorption have found wide application in practice. This applies, in the first turn, to two-photon confocal fluorescent microscopy[1] and micromachining: two-photon microlithography, two-photon volume polymerization, etc.[2,3]

Other interesting practical applications are now at the stage of intense development: multiphoton photodynamic therapy and other medical-biological applications, as well as 3D memory,[4] two-photon optical limiters,[5] two-photon-induced lasers.[6,7] The use of two-photon absorption (TPA) to pump dye lasers opens new promises in designing lasers, tunable in the visible spectral region and pumped by high-power short-pulse laser radiation in the red and near-IR spectral regions, in particular, semiconductor lasers, without the use of nonlinear crystals for harmonic generation and parametric frequency conversion.

For successful development of the two-photon pumped (TPP) lasers, organic materials with high TPA cross section and good emissive ability are needed. The low TPA cross section requires the use of high dye concentrations (> 10^{-2} M) and high-Q cavities to obtain acceptable lasing efficiency. The number of organic molecules, satisfying the requirements to active media of TPP lasers, is quite limited.

This paper studies the TPP lasing of two organic molecules of the dicyanomethylene-pyran (DCM and DCM-doa) series pumped by the Nd–YAG laser radiation of nanosecond duration.

Objects of the study and experimental technique

Molecules of the dicyanomethylene-pyran series form a class of organic compounds much promising for use in nonlinear optics and optoelectronics.[8,9] Earlier we studied the TPA cross section of several compounds from this class in the case of the pumping by Nd–YAG laser radiation of nanosecond duration[10] and by femtosecond pulses of Ti–sapphire lasers.[11,12] Based on these studies, as well as on the ability of some dyes to dissolve at large concentrations, we have selected two compounds (Fig. 1): DCM (Kodak) and DCM-doa (Alfa-Akonis, Dolgoprudnyi, Russia) in 1-methyl,2-pyrrolidon (MP).

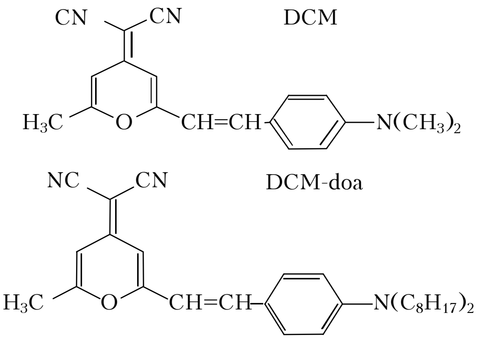

Fig. 1. Structure formulas of the studied molecules.

These dyes are efficient active media for tunable lasers; they demonstrate high quantum yield of fluorescence in MP ($\eta_{fl} \geq 0.5$) and large Stokes shift, so that the absorption and fluorescence bands almost do not overlap in contrast, for example, to xanthene dyes (Fig. 2). The latter property is very important for obtaining lasing at the end-through pumping under conditions of weak inversion, just characteristic of the TPP lasers. The long-wavelength absorption bands of these dyes in MP lie in the range of 450–520 nm (Fig. 2), which is a little bit shorter than the doubled frequency of the fundamental frequency of Nd–YAG laser radiation used for pumping. Therefore, the wavelength used for the two-photon pumping is not optimal. Nevertheless, such dyes have wide absorption bands. The TPA cross section, comparable with that of the Rhodamine 6G, at this pumping

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exceeds the TPA cross section of phenalemine 512, whose TPP lasing was obtained earlier.[13,14]

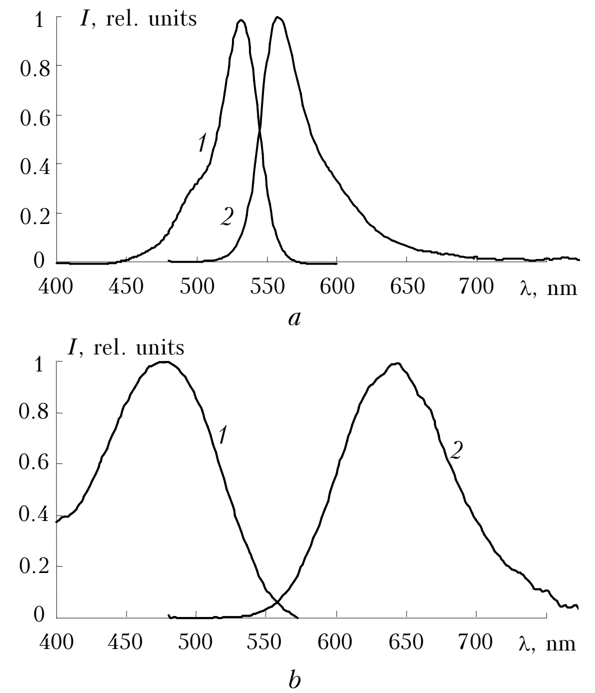

Fig. 2. Absorption (*1*) and fluorescence (*2*) spectra of Rhodamine 6G in ethanol (*a*) and DCM in MP (*b*).

The TPP lasing was studied using the end-through pump configuration (Fig. 3).

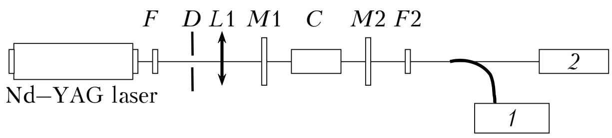

Fig. 3. Schematic of the experimental setup for the investigation of the TPP lasing: filters *F*1,2; diaphragm *D*; lens *L*1; mirrors *M*1,2; cell with the studied solution *C*; spectrum analyzer *1*; ED-100A pyroelectric detector or alignment He–Ne laser *2*.

The cavity consisted of two plane-parallel mirrors. The mirror *M*1 had the reflection coefficient of 95% at the dye lasing wavelength (600–680 nm) and 15% at the pump wavelength (1064 nm), while the mirror *M*2 had the reflection coefficients of 20 and 15%, respectively. The focusing was carried out with a short-focus spherical lens $f = 5$ cm into a cell with the studied dye solution. Cells of 0.5, 1.2, and 5 cm lengths were used. The dye concentration was 10^{-2} and $5 \cdot 10^{-2}$ M. The optimal position of the cell was determined experimentally. The cavity was aligned with the aid of a He–Ne laser. The neutral-density filter *F*1 was used to change the pump intensity, while the selective filter *F*2 was used to cut off the pump radiation when recording the TPP lasing parameters. The pump and the lasing energy were determined by a sensitive ED-100A pyroelectric detector, and the lasing spectrum was recorded using an Angström spectrum analyzer.

Results of investigation of TPP lasing

The results of investigation of the TPP lasing of DCM substitutes are tabulated below.

Characteristics of TPP lasing

Compound/ solvent	$\sigma_2\eta_{fl}$, GM*	$C \cdot 10^2$, M	L, cm	λ_{las}, nm	E_{thr}, mJ
Rhodamine 6G/ ethanol	12.4	1	2	603	28
		2		no lasing	
DCM/MP	12.4	1	2	654	26.8
		5	1	653	26.8
			2	660	2.5
			5	660	5.6
DCM-doa/MP	18.2	1	2	658	4.7
		5		668	4.1

* 1 GM (Göppert–Mayer) = 10^{-50} cm^4 · s · phot^{-1} · mol.$^{-1}$.

The Table also gives the efficiency of the TPP fluorescence, equal to the product of the TPA cross section by the quantum yield of the fluorescence $\sigma_2\eta_{fl}$. The energy thresholds of lasing E_{thr} and the lasing wavelength were determined from the experiment. The dye concentration *C* and the optical path length were changed in the experiment.

At the concentration of 10^{-2} M, all the studied compounds and the reference compound (Rhodamine 6G) are lasing, and the threshold of the TPP lasing corresponds to the efficiency of the TPP fluorescence. As the concentration increases to $2 \cdot 10^{-2}$ M or the path length *L* increased to 5 cm, the lasing in the Rhodamine 6G solution was not observed. This is connected with the increase of losses in the medium due to reabsorption and dye aggregation.

The lasing of the pyran substitutes was observed at the concentration of $5 \cdot 10^{-2}$ M and the path length from 1 to 5 cm. The best results on the DCM lasing under two-photon pumping (minimum threshold and highest efficiency) were obtained at the concentration of $5 \cdot 10^{-2}$ M and $L = 2$ cm. The increase of the threshold and the decrease of the lasing efficiency upon the increase of the path length up to 5 cm are connected mostly with the nonlinear defocusing of the pump radiation at the high-power pumping of the medium.

At the concentration of 10^{-2} M and the path length $L = 2$ cm, the lowest threshold of the TPP lasing was observed for DCM-doa, being about 4.7 mJ. At a higher concentration, the DCM lasing was characterized by the threshold of 2.5 mJ, while the DCM-doa lasing threshold at this concentration was 4.1 mJ. The most probable reason for the fact that the lasing efficiency of DCM-doa did not increase with the increasing concentration is the decrease of the quantum yield of fluorescence due to the beginning of the dye aggregation, because the reabsorption of all the studied DCM substitutes (another possible reason for the decrease of the lasing efficiency) at the lasing wavelength is low and nearly constant. The formation of weakly emitting molecular complexes (for example, dimers) in the solution decreases the efficiency of fluorescence and, consequently, of lasing.

Since it is difficult to measure correctly the quantum yield of fluorescence of concentrated solutions, we have carried out additional investigations of the lasing characteristics of DCM substitutes in MP using single-photon pumping by the second harmonic of a Nd–YAG laser radiation using the transverse pump arrangement. The investigations have shown that for DCM the transition from the concentration of 10^{-3} M to the concentration of 10^{-2} M was accompanied by the decrease in the lasing efficiency from 55 to 45%, that is, roughly 1.2 times, which can be explained mostly by the increase of the diffraction loss due to the nonoptimal geometry of the pumped volume at the increased concentration. For DCM-doa, the lasing efficiency decreased from 59 to 20%, that is, almost three times, while the peak of the lasing band in the nonselective cavity remained unchanged, which confirmed the assumption about the decrease in the lasing efficiency of the medium.

Since the TPP lasing efficiency of the studied compounds under the nanosecond-duration pump by the Nd–YAG laser radiation is low, the efficiency was estimated only for DCM, which has shown the best result of 0.5% of the total energy deposited into the cell. It should be noted that the best results on the TPP lasing efficiency at pumping by nanosecond-duration laser radiation (5–8 ns) in a plane-parallel cavity amount to 3–5% (see Ref. 6). The study of specialized cavities[7] allows the lasing efficiency to be increased up to 10%, while the application of picosecond-duration pulses for pumping increases the efficiency up to 15% and higher.

The pumping of the DCM substitutes by the radiation at 1064 nm is not optimal for obtaining the TPP lasing, because the maximum of the TPA cross section of these compounds lies in the shorter-wavelength region. Thus, at pumping by the radiation with the wavelength of 780 nm, the TPA cross section and the efficiency of TPP fluorescence of the studied compounds exceed these characteristics measured in the case of pumping at 1064 nm by more than one order of magnitude.[10,11] Thus, the use of short-wavelength (750–1000 nm) and short-pulse (0.05–1 ns) pump sources would allow the lasing efficiency of this class of compounds to be increased significantly.

Conclusions

The study of TPP lasing of the pyran substitutes has shown that the high TPA cross section and TPP fluorescence efficiency are not sufficient conditions to obtain the efficient TPP lasing. The pyran substitutes exhibit lasing upon the two-photon pumping more efficiently than Rhodamine 6G, having close value of the TPP fluorescence efficiency. The low spectrum overlap and low aggregation capability allows the dyes of the DCM series to be used for obtaining the TPP lasing at the concentrations up to $5 \cdot 10^{-2}$ M and in thick optical layers (up to 5 cm).

The use of a shorter-wavelength pump source (750–1000 nm) of the subnano- or picosecond duration would allow the TPP lasing of the pyran substitutes with higher efficiency to be obtained.

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