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ORIGINAL ARTICLE

Characteristics of BENZOPYRAN Laser Dyes in Annealed Silica XEROGEL

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Abstract

The spectroscopic and laser characteristics of two benzopyrane derivatives for 600–670 nm spectrum region of lasing in preliminarily annealed silica xerogel matrices in non-selective cavity under laser pumping at 551 nm have been measured and analysed. The influence of molecular structure of the dyes on their non-radiating losses has been revealed. The specific output laser energy of the studied matrices was approximately equal to the ones for corresponding methanol solutions under the same pumping conditions. The laser spectra of the matrices were displaced to the red region from the fluorescence maximum by about 1000–1500 cm^{-1} in a nonselective cavity. Such spectral displacement may improve the characteristics of biosensors made on the basis of these matrices because it shifts their emission spectrum to the range of deeper penetration into biological tissues.

Keywords Laser dye · Xerogel · SiO_2 matrix · Non-radiating losses · Specific laser energy

Introduction

Organic fluorophores and lasers on their basis are widely used for solving various scientific and applied problems [1–3] owing to their unique ability to radiate throughout the all visible region of the spectrum and the adjoining UV and IR ones. Thus authors [1] have demonstrated a series of biomedical in vitro and in vivo probes on the basis of plasmonic nanolaser – "spaser" consisting of a plasmonic Au nanoparticle surrounded by a silica nanoshell doped with various fluorescent dyes. The highly sensitive transducer of human motions based on polydimethylsiloxane optical fiber doped with Rhodamine B dye was designed and fabricated [2] for personalized health monitoring. New sensitizers for solar cells were synthesized with using the known laser dyes [4]. Like that the studies of properties of active media on the dyes are continuing at present and in this connection, coumarin derivatives (the systematic name of coumarin is 2H-1-benzopyran-2-one) attract particular attention [5–7]. At the same time solid-state matrices and films doped with the dyes [8–10] are the most convenient for practical applications.

We have earlier studded a series of silica gel matrices activated with a set of laser dyes [11]. The matrices were synthesized with low-temperature sol-gel technique by hydrolysis of alkoxysilanes in an alcoholicaqueous solution and their subsequent polycondensation [12]. In that case the temperature of synthesis, drying, and ageing of the matrices did not exceed $T_{S\text{-}G} \leq 60\ ^0C$. Among the dyes that we used [11, 12] were two benzopyrane derivatives with a condensed benzimidazole ring that are efficient and photostable dyes for the red part of the lasing spectrum both under laser pump and flashlamp one [13]. Unfortunately when they were incorporated into matrices under $T_{S\text{-}G} \leq 60\ ^0C$ the essential decolorization of these derivatives was occurred during the polycondensation process and no lasing was achieved [11] in the issue.

The aim of our present study is making laser silica gel matrices on the basis of the benzopyrane derivatives with a condensed benzimidazole ring [13] by means of activation of the preliminarily annealed xerogel with these derivatives and investigation of their spectroscopic and laser characteristics.

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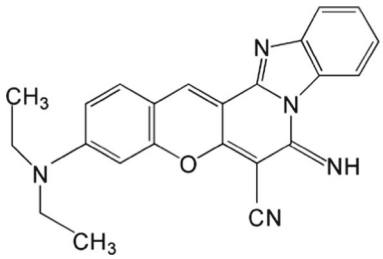
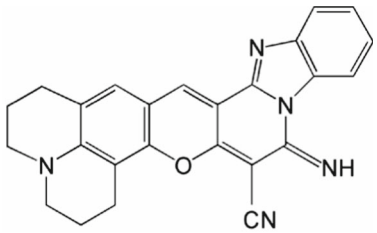
Experimental

Synthesis of silica gel matrices, preliminarily annealing of them at temperature of 700 °C, and doping with laser dyes – the benzopyrane derivatives after annealing and cooling were fulfilled like that as it was described in previous paper [14].

These derivatives were synthesized in V. N. Karazin Kharkiv National University and their structural formulas are presented below:



LD1



LD2

The impregnation of annealed matrices with the laser dyes was executed by immersing them in methanol solutions of these laser dyes [14]. The dye solutions with concentrations of $C_{LD1} = 0.16$ mmol/l and $C_{LD2} = 0.12$ mmol/l were prepared for that. These concentrations corresponded to optimal value of absorption coefficient at pumping wavelength $k_p = 8 \div 10$ cm^{-1} for used configuration of the laser in that characteristics of the dyes in methanol and in matrices were measured. For increase of solubility of LD2 dye in methanol and achievement of necessary 0.12 mmol/l concentration we used methanol with a small addition of nitric acid – 0.37 mmol/l. For measurement of absorption characteristics of the dyes the initial solutions were diluted until such concentration that corresponded to value of absorbance coefficient at the maximum $k_m \leq 1.1$ cm^{-1}. For fluorescence measurements the initial solutions were diluted until such concentrations of the ones that their optical density at the wavelength of excitation in 1 cm cuvette was smaller than $D_{ex} < 0.07$.

The absorption spectra of the samples were measured by an Optizen 3220UV (Mecasys Co. Ltd.) spectrophotometer, and the fluorescence spectra corrected for the spectral sensitivity of the analyzing monochromator and photodetector — on a FluoroMax-4 (Horiba Jobin Yuon) fluorimeter. The fluorescence of dyes was excited near their absorption band maxima. The fluorescence decay times of the dyes in the matrices and in methanol were measured on a Fluo-Time 200 (PicoQuant) picosecond spectrofluorimeter operating in photon counting mode. Results were processed by iterative convolution (FluorFit software, PicoQuant).

In determining the quantum yield of the dyes (Q) in matrices and methanol solutions we used methanol solution of LD1 dye as the references for which the value $Q_0 = 0.96$ was earlier defined [13]. Quantum yields (at room temperature) were calculated by the formula [15]:

$$Q = Q_0 \cdot \frac{1-10^{-D_0}}{1-10^{-D}} \cdot \frac{S}{S_0} \cdot \frac{n^2}{n_0^2}.$$

Where Q and Q_0 are the fluorescence quantum yields of the measured sample and the reference respectively, D and D_0 are their optical densities at the excitation wavelength, S and S_0 are the areas under their corrected fluorescence spectra, n and n_0 are the refractive indices of the matrix and methanol.

Matrices prepared by our method [14] and initial methanol solutions of the dyes were tested in laser with a square quartz cuvette of inner dimensions 10 × 10 × 40 mm. The laser cavity of length 50 mm was formed by broad-band dielectric mirrors with reflectance coefficients $R_1 \geq 95\%$ and $R_2 \approx 60\%$ in the range of lasing. The studied dyes were excited at the short-wavelength edge near the maximum of the main absorption band by transverse layout with an additional flashlamp-pumped laser on acidified ethanol solution of iminocoumarin G283 [16]. The laser on solution of G283 ($C_{G283} = 0.24$ mmol/l, $C_{HCl} = 2.1$ mmol/l) radiated light pulses of length ~ 1 μs at half-height with energies up to 150 mJ at $\lambda_p = 551$ nm and half-widths of 3.8 nm. Radiation from this laser was focused by a cylindrical quartz lens (F = 110 mm) into a horizontal band of height ~1 mm along the axis of the cavity onto the cuvette with the solution or matrix. Annealed matrices (~5 × 5 × 20 mm) were immersed into a laser cuvette filled with ethylene glycol, which did not react with the dye-activated matrix, in order to reduce optical distortions in the cavity because the matrices were not optically treated. Fig. 1 shows overall view of the laser setup for testing the synthesized matrices.

Laser energy of the tested media and pumping energies were measured using IMO-2 N instruments (Etalon). A part

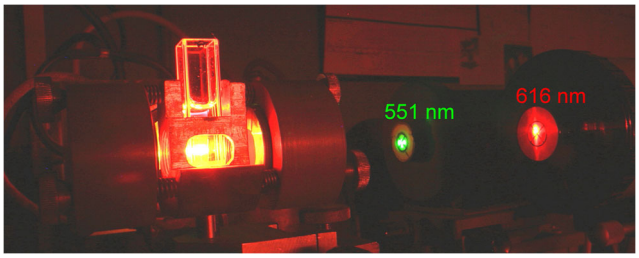


Fig. 1 Laser with non-selective wide-band cavity in moment of lasing at $\lambda_{las} = 616$ nm by the matrix doped with LD1 under pumping at $\lambda_p = 551$ nm. On the right side of the photo one can see radiation of laser dyes G283 and LD1 at entrances of the IMO–2 N instruments

of the G283 laser radiation was deflected by a plane-parallel glass plate situated in the pumping beam at an angle of ~ 45^0 onto the IMO-2 N entrance in order to measure the pumping energy. The IMO-2 N was calibrated beforehand by measuring the energy passing through this plate. Laser emission spectra were recorded in the focal plane of a spectrograph based on a UF-90 camera (LOMO) with a 1200 lines/mm diffraction grating using an EOS 400D Digital apparatus (Canon).

Results and Discussions

The main results of fulfilled measures of spectral-fluorescence and laser characteristics of studied dyes in methanol and annealed matrices are presented in Table 1. In it λ_a – maximum of long-wavelength absorption band, λ_{fl} – wavelength of fluorescence maximum, Q – fluorescence quantum yield, τ^f – its decay time, $k^r = Q/\tau^f$ and $k^{nr} = (1\text{-}Q)/\tau^f$ – rate constants of radiative and nonradiative transitions respectively, $\Delta\nu^{St}$ – Stokes shift between the maxima of the absorption and fluorescence bands, λ_{las} – central lasing wavelength, $\Delta\lambda_{las}$ – half-width of laser spectrum, $\Delta\nu^{las}$ – shift between the maxima of fluorescence band and lasing spectrum, (SiO_2 – 700 °C) – silica gel matrices annealed preliminarily at 700 °C.

Figure 2 shows the position of normalized laser emission spectra of the dyes in methanol and preliminary annealed SiO_2 matrices within the range of their fluorescence spectra under excitation with flashlamp-pumped laser on acidified ethanol solution of iminocoumarin G283 and normalized emission spectrum of this laser within the absorption bands of the dyes. For the studied laser dyes Stokes shift between absorption and fluorescence band maxima is much less (eight and more times according to our measurements [17]) than for DCM dye that is frequently used in the red spectral region. Therefore, lasing of the studied dyes was in the long-wavelength edge of their fluorescence spectra with a substantial red shift from the maximum more than 22 nm or $\Delta\nu^{las} \geq 650$ cm^{-1}.

The spectral shift of laser emission was especially large for an annealed matrix activated by LD1 dye. The value of this shift was more than 50 nm and $\Delta\nu^{las} = 1500$ cm^{-1} respectively. This effect is caused by reabsorption of laser radiation in the active medium because of considerable overlapping of absorption and fluorescence spectra (see Fig. 2) but it may be useful for fabricating biosensors operating at "whisper gallery mode" resonances because it shifts the emission spectrum into the range of deeper penetration into biological tissues [18].

Fluorescence decay curves of the dyes in studied media recorded with a Fluo-Time 200 are presented in Fig. 3. Excitation of fluorescence was carried out at $\lambda_{ex} = 531$ nm, and its registration at the fluorescence maxima of the samples. We have earlier revealed [14, 17] the stabilizing impact of the nearest neighborhood of the SiO_2 matrix on molecules of some laser dyes (DCM, Rh800, Ox170, NBA) in the higher excited state that reduced nonradiative losses in it and increased the quantum yield. A moderate buildup of specific energy of laser radiation was observed for some of these laser dyes [19]. In addition we observed that this impact was unessential for the dyes with high quantum yield Q or weak dependence of spectral-fluorescence characteristics on solvate neighborhood for example Rh6G or LD678. LD1 and LD2 dyes studied in present paper have high enough quantum yield of fluorescence in alcohols and acetonitrile approaching to one. Therefore SiO_2 matrix had not exerted a large influence upon spectroscopic characteristics of these dyes. Nevertheless we may note some peculiarities connected with their structural distinctions. The LD1 dye has a terminal diethylamino-group of the electron-donor type that may go out of the molecule flat in the excited S_1 state and in the issue the nonradiative losses in this state are increased. The structure of LD2 dye involves amino group that fixed to benzopyran moiety by two saturated six-membered rings and therefore these losses are absent [20]. These distinctions of molecular structures resulted in twice in much reduction of the rate constant of nonradiative transitions for LD1 (by 55%) than LD2 (by 24%) at the change-over from

Table 1 Spectroscopic, fluorescence, and laser characteristics of the dyes

Dye/Medium	λ_a, nm	λ_f, nm	Q	τ^f, ns	$k^r \cdot 10$, ns^{-1}	$k^{nr} \cdot 10$, ns^{-1}	$\Delta\nu^{St}$, cm^{-1}	$\lambda_{las} \pm \Delta\lambda_{las}$, nm	$\Delta\nu^{las}$, cm^{-1}
LD1/Methanol	550	571	0.96	3.98	2.41	0.100	670	593 ± 5.0	650
LD1/ SiO_2 – 700 °C	556	563	0,98	4.44	2.21	0.045	220	616 ± 6.4	1500
LD2/Methanol+H^+	567	586	0,94	4.15	2.26	0.144	570	618 ± 3.1	880
LD2/ SiO_2 – 700 °C	572	586	0,95	4.60	2.06	0.109	420	622 ± 3.7	990

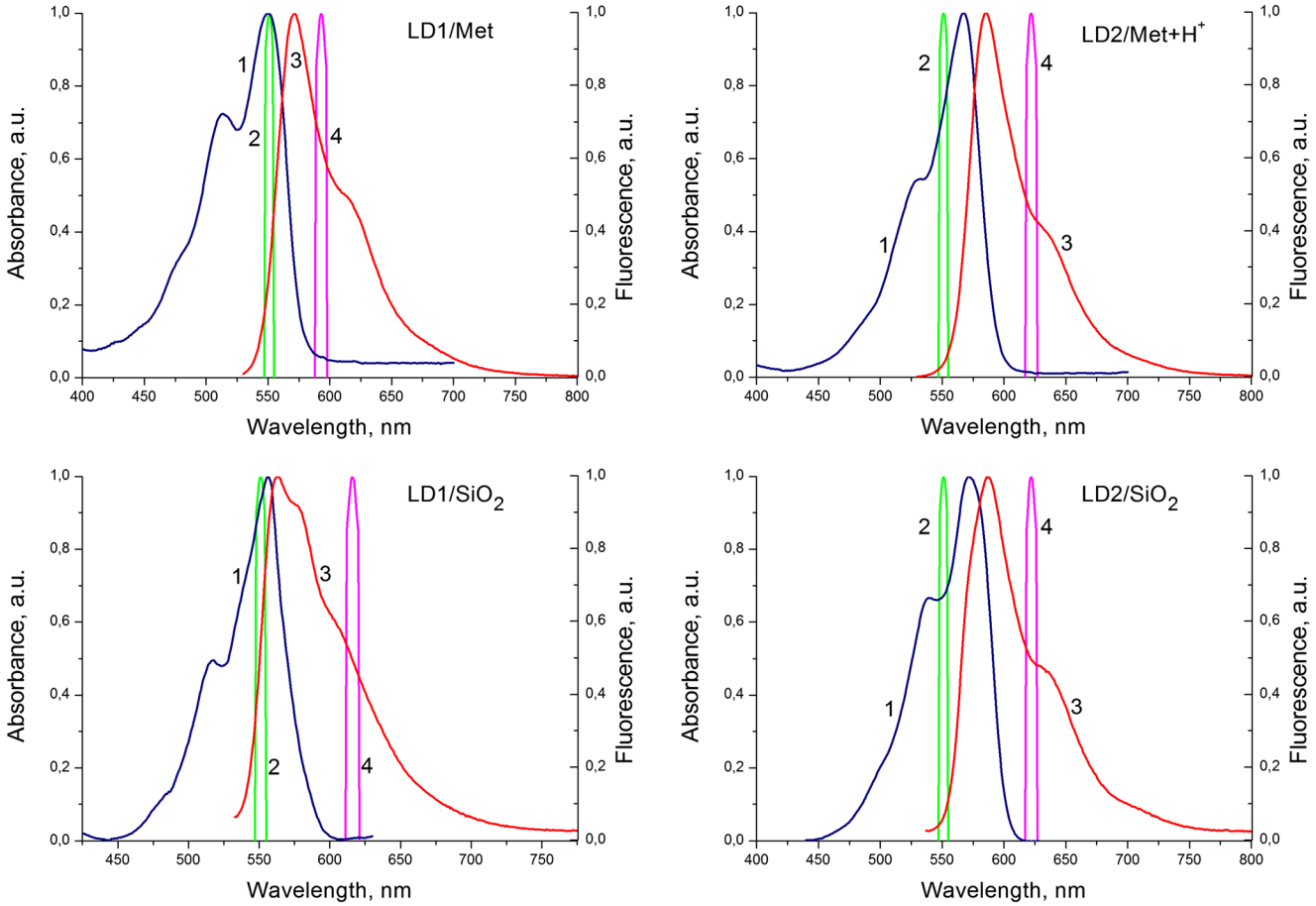


Fig. 2 Absorption (1), fluorescence (3) spectra of the dyes in methanol (Met) and lasing (4) spectra of the dyes in methanol (Met) and preliminarily annealed SiO_2 matrices. The curve 2 represent pumping spectrum of the G283 laser

methanol to the pre-annealed xerogel SiO_2 matrices. At the same time Stokes losses were reduced for the first dye about three times and for the second – by a factor of 1,4.

We have also recorded fluorescence decay curves of the dyes and measured their decay times in solutions and matrices on the fluorescence band slopes at the level of ~ $0.5I(\lambda_f)$ from the shortwave and long-wave sides of their maximum for the aim to test possible creation of "twisted" conformations of the dye molecules in the excited state. These measured have showed that the decay character and the decay times of the dyes in solutions and matrices did not practically change viz. relative changes of the last were smaller than 1.35%. This fact

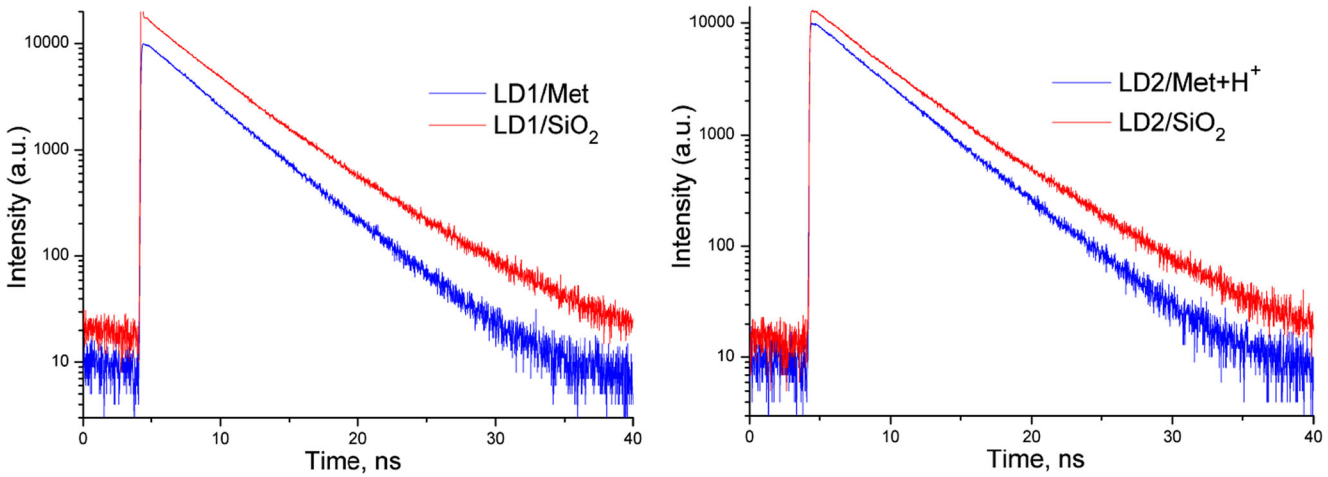


Fig. 3 Fluorescence decay of the dyes in methanol (Met) and xerogel matrices (SiO_2) annealed preliminarily

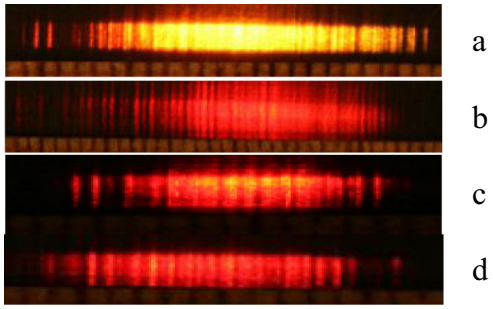


Fig. 4 Lasing spectrograms of LD1 dye (**a**, **b**) and LD2 dye (**c**, **d**) in methanol (**a**, **c**) and pre-annealed matrices (**b**, **d**). The reciprocal dispersion for spectrograms totals 0.63 nm/mm

distinguishes LD1 and LD2 dyes from NBA dye studied earlier [14] for which the "twisted" – TICT-form of the dye molecule with short lifetime was revealed in the excited state and the contribution of this form to fluorescence intensity increased monotonically with increasing its wavelength.

The laser measurements have showed the output lasing energy of studied matrices normalized to the active element length (adjusted to a length of 1 cm) or the specific energy – E_{las} under the same pumping conditions ($E_p \approx 100$ mJ) was approximately equal to ones of the corresponding methanol solutions namely for LD1 $E_{las} = 6.0$ mJ/cm and for LD2 $E_{las} = 4.5$ mJ/cm. Figure. 4 shows the lasing emission spectrograms of LD1 and LD2 dyes in methanol and pre-annealed silica xerogel matrices in non-selective wide-band cavity. The linear structure of the laser spectra of the studied matrices (submerged in the cuvette with immersion liquid) obtained at microsecond pumping duration testifies that the lifetime of photons in the resonator is sufficient to form high-quality stimulated radiation in it, and the studied matrices did not bring essential optical distortions.

Conclusions

Two benzopyrane derivatives that are efficient and photostable laser dyes for the red part of the spectrum under flashlamp and laser pumping were incorporated into pre-annealed silica xerogel matrices. Their spectroscopic, fluorescent and lasing characteristics have been measured and analyzed. The influence of structure factors of the dye molecules on their nonradiative losses in the excited state was revealed. It was ascertained the specific output laser energy of the dyes in the matrices is approximately equal to that in methanol. Laser spectra of these matrices were shifted to the red region from the fluorescence maximum by about 1000–1500 cm^{-1} in a nonselective cavity. Such a shift may improve the characteristics of biosensors made on the basis of these matrices.

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