

## Fluorescence properties of dyes for 570–800 nm lasing region in sol-gel silica

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The spectral-fluorescence characteristics of the dyes for 570–800 nm lasing region: Rh6G, DCM, LD678, and Rh800 were studied with the purpose to clarify an influence of intermolecular interactions in SiO<sub>2</sub> matrix on processes of the excitation energy decay of the laser dyes in S<sub>1</sub> state. Their quantum yields Q<sub>fl</sub> and decay times τ<sub>fl</sub> of fluorescence, radiative k<sup>r</sup> and non-radiative k<sup>nr</sup> rate constants for solvents and matrices were measured and calculated. It was shown for the dyes with small solvent effect (Rh6G, LD678) that incorporation of them into the matrix did not cause the appreciable changes of Q<sub>fl</sub> and τ<sub>fl</sub> values. While for the dyes with strong solvent effect (DCM and Rh800) — SiO<sub>2</sub> matrix takes the stabilizing influence upon their molecules in S<sub>1</sub> state and as a result their non-radiative losses were diminished and quantum yield was increased.

**Keywords:** laser dye, sol-gel silica, matrix, fluorescence, quantum yield, decay time, non-radiative losses.

С целью выяснения влияния межмолекулярных взаимодействий в SiO<sub>2</sub> матрице на процессы затухания энергии возбуждения лазерных красителей в S<sub>1</sub> состоянии исследованы спектрально-флуоресцентные характеристики красителей для области генерации 570–800 нм: Rh6G, DCM, LD678 и Rh800. Измерены и рассчитаны их квантовые выходы Q<sub>fl</sub> и время затухания τ<sub>fl</sub> флуоресценции, а также константы скорости излучательных k<sup>r</sup> и безызлучательных k<sup>nr</sup> переходов как в растворах, так и в матрицах. Показано, что для красителей, на которые слабо влияет сольватное окружение (Rh6G и LD678), переход к матрице не вызывает заметных изменений величин Q<sub>fl</sub> и τ<sub>fl</sub>. В то же время для красителей, флуоресценция которых сильно зависит от растворителя (DCM и Rh800) — SiO<sub>2</sub> матрица оказывает стабилизирующее воздействие на их молекулы в S<sub>1</sub> состоянии, и в результате их безызлучательные потери уменьшаются, а квантовый выход возрастает.

**Флуоресцентні властивості барвників для лазерного діапазону 570–800 нм в силікагелі.** *О.М.Безкровна, В.В.Маслов, І.М.Притула, А.Г.Плаксій, Ю.О.Гуркаленко, О.В.Лопін, М.В.Переверзєв.*

З метою з'ясування впливу міжмолекулярних взаємодій в SiO<sub>2</sub> матриці на процеси затухання енергії збудження лазерних барвників в стані S<sub>1</sub> досліджено спектрально-флуоресцентні характеристики барвників для області генератії 570–800 нм: Rh6G,

DCM, LD678 і Rh800. Виміряно та розраховано їх квантові виходи  $Q_{fl}$  і час затухання  $\tau_{fl}$  флуоресценції, а також константи швидкості випромінювальних  $k^r$  і безвипромінювальних  $k^{nr}$  переходів як в розчинах, так і в матрицях. Показано, що для барвників, на які слабо впливає сольватне оточення (Rh6G і LD678), перехід до матриці не викликає помітних змін величин  $Q_{fl}$  і  $\tau_{fl}$ . В той же час для барвників, флуоресценція яких сильно залежить від розчинника (DCM і Rh800) —  $\text{SiO}_2$  матриця чинить стабілізуючу дію на їх молекули в  $S_1$  стані, і як результат, їх безвипромінювальні втрати зменшуються, а квантовий вихід зростає.

## 1. Introduction

Fluorescence materials, synthesized by sol-gel method [1], keep on being actively investigated and developed [2]. They find the wide application as laser media [3, 4], elements of photonics [5, 6], photosensors for biomedical diagnostics [7], and sensitizers for photodynamic therapy [8]. Furthermore lively investigations are currently fulfilled that directed at creation of visible and NIR lasers on the basis of combining the diode lasers and solid-state matrices and films doped with the laser dyes [9–11]. As a result of these investigations laser emissions from 540 nm to 660 nm with a peak power 3.5 W and slope efficiency of 11 % were obtained [11].

There is a need to know spectral-fluorescence parameters of the dyes in the medium of matrix, when new photosensors, sensitizers, elements of photonics, and solid-state laser elements doped with dyes are developed on their basis. It is particularly important when the power characteristics of pump system for the hybrid lasers on the basis of the laser diodes and solid-state dye lasers are calculated [12].

We earlier synthesized and studied [13] the matrices activated with series of the dyes lasing efficiently in alcohol solutions. The goal of the present research is measuring-in and analysis of fluorescence characteristics of these matrices and comparison of them with the same ones of the alcohol solutions for clearing up the processes of energy decay of the dye molecules in the matrices.

## 2. Experimental

The matrices were synthesized by means of hydrolysis of alkoxy-silanes in aqueous-alcoholic solution as was described in [14]. We used tetraethoxy- and tetramethoxy-silane (TEOS and TMOS, respectively; Aldrich), ethanol, methanol, formamide, twice-distilled water, and laser dyes: Rh6G, DCM, Rh800 (Aldrich) and LD678 (MKhTI) too. For making matrices doped with DCM and LD678 dyes some amount of pyridine

was added into the mixture to reduce the acidity in sol synthesis process.

Absorption spectra of the samples were measured by spectrophotometer Lambda 35 (Perkin-Elmer, USA) and the fluorescence ones — by fluorimeter FluoroMax-4 (Horiba Jobin Yuon, USA). The last allowed to record corrected spectra taking into account corrections for spectral sensibility of analyzing monochromator and photodetector that was important for determining fluorescence quantum yield of the dyes  $Q$ . Fluorescence decay times of the dyes in the matrices and solvents were measured by picoseconds spectrofluorimeter Fluo-Time 200 (PicoQuant, Germany) operating at single photon counter mode and with treatment of the results by method of iteration convolution (FluorFit software, PicoQuant, Germany). The fluorescence of the dyes was excited near their absorption band maxima.

For the measurement of absorption characteristics of the dyes we prepared the samples with optical density at the maximum of absorption band  $D_{max} \approx 0.7\text{--}1.0$  and for the fluorescence ones — with optical density at the excitation wavelength  $D_{ex} \leq 0.07$ . That was conformed to concentrations of 10–20  $\mu\text{mol/l}$  in the first case and 0.7–5  $\mu\text{mol/l}$  in the second one. For determination of  $Q$  — quantum yields of the dyes in the matrices we used alcohol solutions of the same dyes as references, for which the value of  $Q_0$  was earlier defined [12, 15–17]. The quantum yields were calculated by formula [18]:

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

Here  $Q$  and  $Q_0$  — quantum yields of the measured sample and the reference respectively;  $D$  and  $D_0$  — their optical densities at the wavelength of extinction;  $S^{fl}$  and  $S_0^{fl}$  — areas under curve of corrected fluorescent spectra;  $n$  and  $n_0$  — refraction coefficients of matrix and solvent (subscript "0" relates to reference, absence of index — to the measured sample).

### 3. Results and discussion

The main results of the fulfilled measurements of spectral characteristics of the studied dyes in different media and parameters calculated on their basis are presented in the Table. The absorption and fluorescence spectra of two laser dyes DCM and Rh800 in SiO<sub>2</sub> matrices and methanol are shown in Fig. 1 and Fig. 2. The first of them — DCM with the most short-wavelength band of absorption spectrum has the largest Stokes shift of fluorescence band that indicates the appreciable increase of dipole moment of the dye molecule under S<sub>0</sub> → S<sub>1</sub> transition. The second dye — Rh800 is the most long-wavelength of all studied in the present paper. Here the Stokes losses for it are less by order of magnitude than for DCM and overlap of the absorption and fluorescence spectra is considerable. Therefore DCM produced laser emission near maximum of the fluorescence spectrum and Rh800 — at its long-wavelength slope [13].

It is known, the solvent surroundings of DCM molecule exerts considerable influences upon its spectral properties [13]. Degree of this influence is determined by electric parameters of the solvent: dipole moment of the solvent molecule and its permittivity. The short-wavelength shift of the absorption maximum of DCM  $\lambda_a = 3$  nm

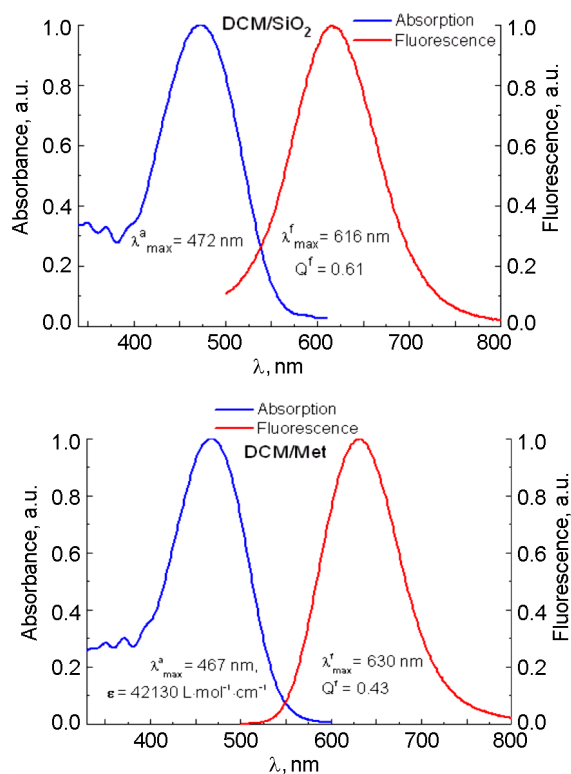


Fig. 1. Absorption and fluorescence spectra of DCM dye in SiO<sub>2</sub> matrix and methanol.

as well as the fluorescence one  $\lambda_{fl} = 14$  nm is observed when methanol is changed with SiO<sub>2</sub> matrix. Here the Stokes shift is some

Table. Spectral parameters\* of the dyes

Dye	Medium	$\lambda_a$ , nm	$\epsilon_m \cdot 10^{-3}$ , l·mol <sup>-1</sup> ·cm <sup>-1</sup>	$\lambda_{fl}$ , nm	$Q_{fl}$ **	$\tau_{fl}$ , ns	$k^r \cdot 10$ , (ns) <sup>-1</sup>	$k^{nr} \cdot 10$ , (ns) <sup>-1</sup>	$\Delta\nu^{St}$ , cm <sup>-1</sup>
Rh6G	Ethanol	530	106	552	0.95	4.30	2.21	0.116	750
Rh6G	DMSO	539	100	564	0.97	3.63	2.67	0.083	820
Rh6G	SiO <sub>2</sub> matrix	530	92	555	0.94 <sup>±0.1</sup>	3.78	2.49	0.159	850
DCM	Methanol	472	43	630	0.43	1.31	3.28	4.35	5280
DCM	DMSO	480	45	643	0.50	2.16	2.31	2.31	5280
DCM	SiO <sub>2</sub> matrix	469	—	616	0.61 <sup>±0.06</sup>	2.06	2.96	1.89	5100
LD678	Methanol	605	110	619	0.67	3.34	2.01	0.99	370
LD678	SiO <sub>2</sub> matrix	608	57	620	0.68 <sup>±0.01</sup>	3.64	1.87	0.879	320
Rh800	Methanol	680	90	701	0.086	1.74	0.494	5.25	440
Rh800	SiO <sub>2</sub> matrix	691	65	709	0.14 <sup>±0.01</sup>	1.73	0.809	4.97	370

\*  $\lambda_m^a$  — maximum of long-wavelength absorption band;  $\epsilon_m$  — molar decadic extinction coefficient at  $\lambda_m^a$ ;  $\lambda_m^f$  — wavelength of fluorescence maximum;  $Q_{fl}$  — fluorescence quantum yield;  $\tau_{fl}$  — fluorescence life-times;  $k^r = Q_{fl}/\tau_{fl}$  — radiative decay rate constant;  $k^{nr} = (1 - Q_{fl})/\tau_{fl}$  — nonradiative decay rate constant;  $\Delta\nu^{St}$  — Stokes shift between the maxima of the absorption and fluorescence bands; DMSO — dimethylsulfoxide.

\*\* Inaccuracy of defining  $Q_{fl}$  for solutions amounts to  $\pm 5$  %; superscripts near values of  $Q_{fl}$  added in the Table define statistical straggling of the values measured for different samples of matrices.

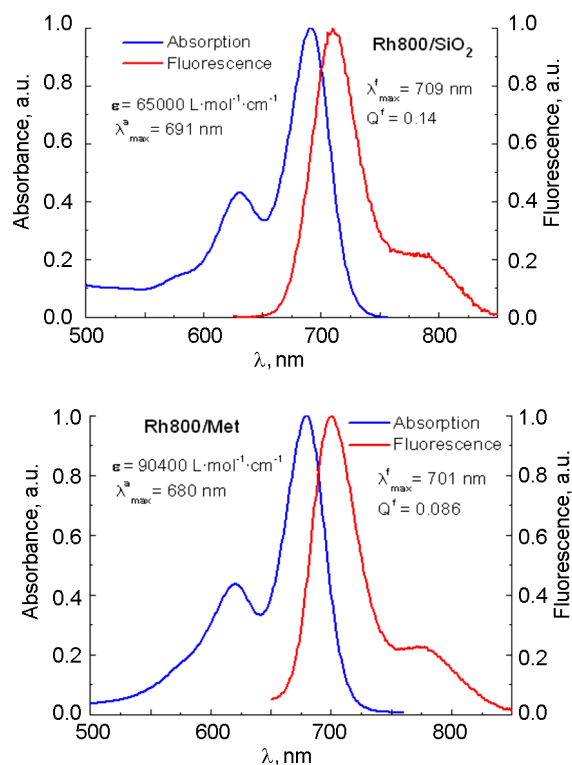


Fig. 2. Absorption and fluorescence spectra of Rh800 dye in  $\text{SiO}_2$  matrix and methanol.

diminished (see the Table) and the quantum yield of fluorescence of DCM is appreciably grown and become more than its value in strong polar dimethylsulfoxide (DMSO). The spectra shift is probably caused the smaller polarity of DCM surroundings in  $\text{SiO}_2$  matrix than in methanol and subsiding of its effect upon DCM molecule in  $S_1$  excited state. It was earlier shown [19] that fluorescence quenching of DCM occurs by means of twisted molecule form of this dye. Thus we may presume that molecular surroundings of the dye in the matrix hinders generation of this form and as a result non-radiating vibrating losses in the excited  $S_1$  state. This assumption is confirmed with measured values of fluorescence decay time  $\tau_{fl}$  and calculated from them rate constants of nonradiative transition of DCM in methanol, DMSO, and the matrix. When methanol was changed with DMSO value of  $k^{nr}$  was diminished by factor of about 1.9, and with  $\text{SiO}_2$  matrix — about 2.3.

In the case of Rh800 the change of alcohol solution by matrix results in the bathochromic shift of absorption as well as fluorescence maxima by  $\sim 10$  nm, here the Stokes losses are slightly diminished but the quantum yield of fluorescence is essentially

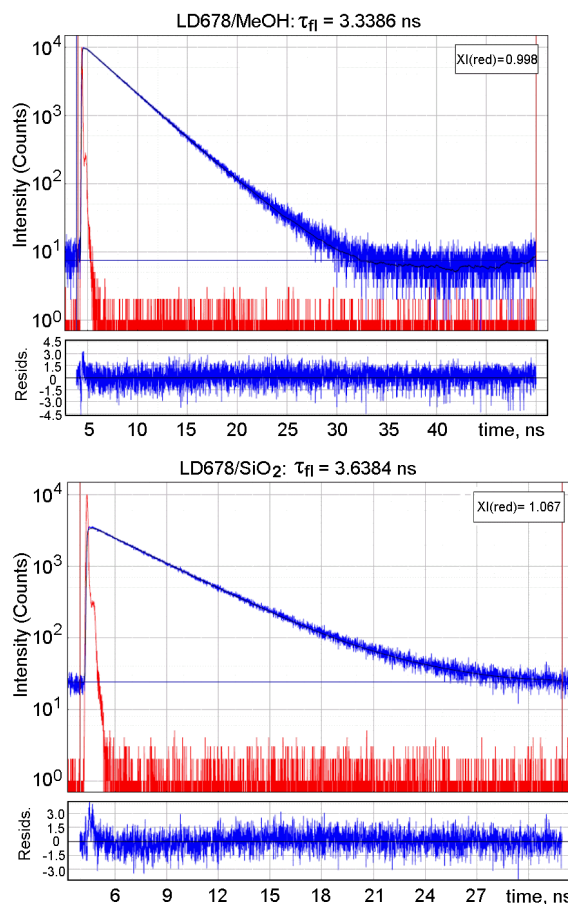


Fig. 3. Decay of fluorescence ( $\lambda_{ex} = 531$  nm,  $\lambda_{em} = 620$  nm) for LD678 dye in methanol and  $\text{SiO}_2$  matrix.

increased (by factor  $\sim 1.6$ ). Laser dye Rh800 was synthesized by Karl Drexhage. This dye had a wide tuning range of lasing spectrum [20] in NIR region ( $730 \div 835$  nm) with the maximum output emission near 800 nm. K.Drexhage had shown considerable impact of CN-group in the dye structure on the process of fluorescence quenching when weakly polar dichloroethane [21] was changed by alcohols.

The increase of  $Q_{fl}$  for Rh800 in the matrix that we have obtained was corroborated by rise of radiative transition rate constant by the factor of  $\sim 1.6$  (see Tabl.). At the same time unlike DCM rate constant of the non-radiative transactions did not practically change (within the measure of  $Q_{fl}$  and  $\tau_{fl}$  inaccuracy). Thus we may assume that  $\text{SiO}_2$  matrix exerts favorable influence upon spatial structure of the fluorescent molecule of Rh800 in the excited  $S_1$  state.

As regards the Rh6G and LD678 dyes their transfer from the solvents to matrix does not produce noticeable changes of the

spectrum position and therefore in interactions of dipole moments of these molecules with their surroundings. The Stokes shift  $\Delta\nu^{St}$  between maxima of the fluorescence and the absorption bands for LD678 both in methanol and in matrix is smaller than for DCM by the factor more than ten. At the same time if for LD678 in the matrix the shift is some smaller than in alcohol then for Rh6G the Stokes shift slightly increases in the matrix and exceeds its value for strongly polar DMSO. The small changes of measured  $Q_{fl}$  and  $\tau_{fl}$  values and calculated rate constants  $k^r$ ,  $k^{nr}$  are observed for these dyes too under the transfer them from alcohols to the matrix. Fig. 3 show decay curves of fluorescence for LD678 dye in methanol and SiO<sub>2</sub> matrix. The single-exponential character of the fluorescence decay (with confidence interval  $\leq 0.021$ ) is well apparent in this figure.

#### 4. Conclusion

The measures of values of the fluorescence quantum yields and times of its decay for the studied laser dyes have been fulfilled and changes of nonradiative losses for them in the first excited state  $S_1$  have been analyzed. It was shown for Rh6G and LD678 dyes, on which solvent surroundings exert weak influence, transfer to the matrix does not cause the noticeable changes of  $Q_{fl}$  and  $\tau_{fl}$  values. At the same time for the dyes, which fluorescence is strongly dependent on the solvent, that are DCM and Rh800 — the matrix has the stabilizing influence upon molecules of these dyes in  $S_1$  state, and as the results their nonradiative losses are diminished and the quantum yield of fluorescence increases.

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