

Influence of surroundings on radiative characteristics of benzopyran derivatives

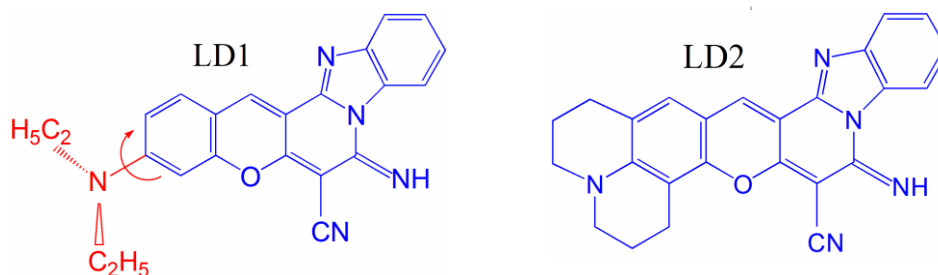
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Fluorescent contrast agents and nanoparticles are widely employed in biomedical research. They can also be coated in silica, which enables them to resist shape change, maintain their optical properties, and improves uptake by cells as a result of lowered resistance to water [1]. Furthermore they can comprise the core contained far red fluoresce dyes to enhance brightness, detection sensitivity, and depth penetration in biological tissue. Whispering-gallery mode (WGM) resonance-based sensors have currently found applications for detection and quantification of proteins and cancer biomarkers [2]. For creating new solid-state fluorescent probes, markers and new laser elements activated with the dyes it is necessary to know their spectral-fluorescence parameters in the matrix medium.

The purpose of the present paper is to summarize and analyze influence of molecular structure of laser dye and its closest surroundings on spectroscopic and fluorescent properties, and lasing characteristics of the dye both in solution and in silica gel. For that we have selected two efficient and photostable red laser dyes [3] – benzopyran derivatives with condensed benzimidazole bi-cycle: LD1 and LD2 that were synthesized at V.N. Karazin Kharkiv National University. The structure formulas of these dyes are presented below.



We have fulfilled additional measurements of spectroscopic, fluorescence, and lasing characteristics of these derivatives in preliminarily annealed silica xerogel matrices and some solvents. Methods and instrumentation for measuring spectral, fluorescence and laser characteristics of the dyes in solutions and matrices were described in our previous articles [4, 5]. The results of these measures are presented in the Table. Some characteristics of the dyes that we have earlier obtained [6] are presented in it too for comparison and summarizing. While analyzing the measured spectroscopic and laser characteris-

tics of the dyes we note the next. The bands of their absorption, fluorescence, and laser emission were shifted to the red long-wave side when solvent polarity or its proton-donating activity increased. In this connection the medium of the SiO₂-matrices exerts influence upon these dye characteristics (namely on the spectral shifts) approaching to acidulous alcohols.

Table

Characteristics* of the red laser dyes

Medium	λ_a , nm	λ_f , nm	Q	τ_f , ns	$k^r \cdot 10$, ns ⁻¹	$k^{nr} \cdot 10$, ns ⁻¹	Δv^{St} , cm ⁻¹	λ_{las} , nm	Δv^{las} , cm ⁻¹
LD1									
Benzene	544	562	0.93	3.72	2.50	1.88	590	609	1370
Methanol	550	571	0.96	3.98	2.41	0.100	670	593	650
Ethanol	549	572	1.00	4.15	2.41	≤0.24	730	595	730
Ethanol +HCl	571	594	0.48	3.67	1.3	1.42	680	628	910
SiO ₂ – 60 °C	566	582	0.42				490	–	–
SiO ₂ – 700 °C	556	563	0.98	4.44	2.21	0.045	220	616	1500
LD2									
Methanol	565	586	1.00	4.20	2.38	≤0.24	660	605	
Methanol +HNO ₃	567	586	0.94	4.15	2.26	0.144	570	618	880
Ethanol	567	586	1.00	4.30	2.33	≤0.23	570	608	
Ethanol +HCl	576	602	0.81	3.88	2.09	0.49	360	626	640
SiO ₂ – 60 °C	575	587					420	–	–
SiO ₂ – 700 °C	572	586	0.95	4.60	2.06	0.109	420	622	990

* λ_a – maximum of long-wavelength absorption band, λ_f – wavelength of fluorescence maximum, Q – fluorescence quantum yield, τ_f – fluorescence lifetime, k^r and k^{nr} – radiative and nonradiative decay rate constants respectively, Δv^{St} – Stokes shift between the maxima of the absorption and fluorescence bands, λ_{las} – central lasing wavelength, Δv^{las} – shift between the fluorescence maximum and midpoint of the laser spectrum, +HCl – presence of 1.5 mmol/L HCl in solution, +HNO₃ – presence of 0.37 mmol/L HNO₃ in solution, SiO₂ – 60 °C – silica gel matrices synthesized at $T_{sol-gel} \leq 60$ °C, SiO₂ – 700 °C – silica gel matrices preliminarily annealed at 700 °C.

Note that the structure distinctions of the dyes have resulted in different values of nonradiative losses in excited S₁ state. The LD1 dye has a terminal diethylamino group of the electron-donor type that may go out of the molecule flat in S₁ state (see arrow in structure formula). In the issue “twisted” TICT conformations was produced and nonradiative losses in this state are increased. The structure of LD2 involves amino group that fixed to benzopyran moiety by two saturated six-membered rings and therefore these losses are absent. Though the dyes have high quantum yields of fluorescence those approach to unit in alcohols but when proton-donating activity of the medium increases the radiative decay rate constant k^r decreases and nonradiative one k^{nr} rises. At that this response is essentially larger for LD1 than for LD2.

Furthermore when these two derivatives were incorporated in silica gel matrices by sol-gel process with low temperature treatment $T_{sol-gel} \leq 60$ °C, the

essential decolorization of those was occurred during the polycondensation process and no lasing was achieved [6] in the issue. Therefore for making laser matrices on the basis of LD1 and LD2 dyes we have applied the method [4] of preliminarily annealing non-activated with the dyes matrices at temperature of 700 °C and the next impregnating them with methanol solutions of these dyes. The matrices made in this manner were pumped ($\lambda_p = 551$ nm) in nonselective cavity with subsidiary flashlamp-pumped dye laser on iminocoumarin G283 [3] and their lasing have been obtained with specific output energy (i.e. normalized to the active element length) that was equal about one of their alcoholic solutions.

Calculated rate constants of radiative k^r and nonradiative k^{nr} transitions have showed that distinctions of molecular structures of the dyes 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 methanol to the pre-annealed xerogel SiO₂ matrices (Table). At the same time Stokes losses were reduced for the first dye to about three times and for the second – by a factor of 1.4. Thus stabilizing impact of the matrix on the dye molecules was accomplished in exited S₁ state.

Stokes shift among fluorescence and absorption maxima for LD1 and LD2 dyes essentially smaller than that for widely used red laser dye DCM, namely about by order [7]. Therefore laser spectra of these dyes were disposed at the long-wavelength edge of their fluorescence bands with a substantial red shift from the maximum more than 22 nm or $\Delta\nu^{las} \geq 650$ cm⁻¹. Especially large displacement of laser spectrum that exceeded the magnitude of 50 nm ($\Delta\nu^{las} = 1500$ cm⁻¹) has been observed for pre-annealed matrix activated with LD1 dye. This laser spectrum shift was produced by reabsorption of laser radiation in the active medium because of considerable overlapping of absorption and fluorescence spectra. However this effect will be useful for the WGM biosensor on the basis of these matrices since it shifts the emission spectrum to the range of deeper penetration into biological tissues.

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