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Spectral and fluorescent characteristics of laser dyes for 650–800 nm range

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Spectral, fluorescence and lasing characteristics of several laser dyes for far red and near IR wavelength range have been measured and considered. The laser performances of the dyes have been obtained under monochromatic excitation near maxima of their absorption spectra. The stimulated emission of the dyes has been tuned continuously within 635–805 nm region. The characteristics obtained make it possible to use the dyes purposefully both as active laser media and as fluorescent labels and probes.

Измерены и проанализированы спектрально-флуоресцентные и генерационные характеристики серии лазерных красителей для дальнего красного и ближнего ИК диапазона длин волн. Лазерные параметры красителей получены при монохроматическом возбуждении вблизи максимумов их спектров поглощения. Осуществлена непрерывная перестройка вынужденного излучения красителей в области 635–805 нм. Полученные характеристики позволяют целенаправленно использовать эти красители как в качестве активных лазерных сред, так и флуоресцентных меток и зондов.

Tunable lasers of far red and near IR spectral range (650 to 800 nm) and fluorophors for the same wavelength region are used in spectral studies of biological and medical objects and of novel material for photonics. For example, a due fluorescensing in this spectral region provides the diagnostics of amyloid deposition in brain blood vessels that is a precursor of the Alzheimer disease [1]. The use of such dyes is especially important in detailed elucidation of biological activity at the molecular level because those dyes can be excited by semiconductor lasers [2].

Before [3], a series of laser dyes for the above-mentioned generation region has been reported. The dyes have been synthesized at the Chair for fine organic synthesis and dye chemistry, D.Mendeleyev Moscow Institute for Chemical Technology (now Russian University for Chemical Technology) [4]. To design the tunable lasers based on those dyes and to use them as fluorescent labels or probes, it is necessary to know their absorption and fluorescence characteristics that have been not reported in [4]. In this work, presented are the main spectral characteristics of those dyes, including those of lasing under monochromatic excitation, in solvents recommended in [4].

The absorption and fluorescence spectra of the dye solutions in methanol (MeOH) and acetonitrile (AcN) were recorded using standard procedures by Hitachi U-3210 and Hitachi F-4010 instruments. When measuring the fluorescence spectra and the fluorescence quantum yields q^f, diluted dye solutions were used having the absorption coefficient at the excitation wavelength $k(\lambda_{ex})$ did not exceed 0.02 cm^{-1}. To improve the q^f measurement accuracy using the equal absorption method, the $k(\lambda_{ex})$ values were measured in a 5 cm optical length cell using a VSU2-P spectrophotometer. When measuring q^f, the LD-2 dye alcoholic solution was used as a reference [5]. Its fluorescence quantum yield $q^f = 1$ and absorption and fluorescence spectra do not differ significantly from those of compounds under study.

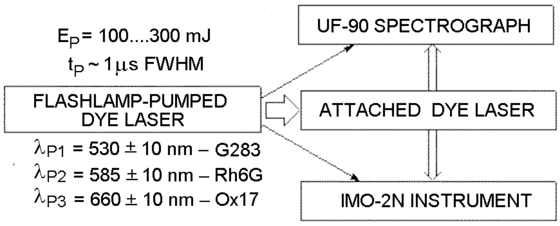

Fig. 1. Schematic diagram of the setup for measuring the generation characteristics of dyes under laser pumping.

The generation characteristics of the dyes under laser excitation were measured using a setup shown schematically in Fig. 1. The dye solutions were poured into a cylindrical quartz cell (11 mm in dia. and 15 mm long) of the extending laser, its resonator being formed by a wide-band mirror with the reflection coefficient in the generation region $R \geq 95$ % and a plane-parallel plate made of K8 glass. The dye solutions were excited near the maximum of their absorption band according to transversal scheme using an additional dye laser with lamp pumping [6]. The pumping laser generated light pulses of about 1 μs duration (at 0.5 level) at up to 300 J energy at the following wavelengths: 510±10 nm on iminocoumarin G283 [6], 585±10 nm on Rhodamin 6G (Rh6G) and 660±10 nm on Oxazin 17 (Ox17). The pumping laser emission was focused by a quartz cylindrical lens (F = 110 mm) into a horizontal band of about 1 mm height on the cell with the solution being studied. The generation and pumping energy values were monitored using an IMO-2N device and the laser emission spectra were photographed using Isopanchrom plates in an UF-90 camera with diffraction grating (1200 lines per mm). The measurements were done at room temperature. The known laser dye RhG6 was used as the reference. The absorption coefficients of all the due solutions under laser pumping amounted 7±0.3 cm^{-1}. The main measurement results are presented in the Table, while the absorption and fluorescence spectra of the dyes, in Fig. 2. The dyes are enumerated as in [4] and the solvents are chosen as in that work, namely, alcohol for LD678 dye and acetonitrile for all others.

As is seen from the Table, the long-wavelength absorption band maximum λ^a_m in the solutions of studied dyes varies over a range exceeding 100 nm, from 609 to 710 nm. The extinction in the maximum varies by a factor exceeding 3. According to the extinction value, the studied dyes can be subdivided into two groups. The first one consists of LD678, LD703 and LD747 where $\varepsilon_m > 10^5$ L/(mole·cm). The second group includes LD790, LD800, and LD840 having $\varepsilon_m \leq 6.5 \cdot 10^4$ L/(mole·cm).

The fluorescence band maximum λ^f_m of the studied dye solutions varies by more than 130 nm, from 626 to 759 nm. The Stokes shift value $\Delta\upsilon^{St}$ between the absorption and fluorescence maxima varies from 450 to 910 cm^{-1}. This quantity is 1.5 to 2 times higher in the second group of the dyes (620 to 910 cm^{-1}) than in the first one

Table. Main spectral characteristics of the dyes

Dye	Solvent	λ^a_m, nm	$\Delta\tilde{\nu}^a$, cm^{-1}	$\varepsilon_m \cdot 10^{-3}$, $L \cdot mole^{-1} \cdot cm^{-1}$	λ^f_m, nm	$\Delta\tilde{\nu}^f$, cm^{-1}	$\Delta\tilde{\nu}^{St}$, cm^{-1}	q^f	$\lambda^{las} \pm \Delta\lambda^{las}/2$, nm	E^{las}, r.u.
LD678	MeOH	609	930	109	626	1090	450	0.67	650±10	1.3
LD703	AcN	620	1040	130	648	1040	700	0.61	674±+7	1.4
LD747	AcN	638	880	150	658	800	480	0.42	675±5	0.9
LD790	AcN	685	970	43	730	1200	900	0.14	755±2	1.1
LD800	AcN	692	850	65	723	830	620	0.10	743±7	0.8
LD840	AcN	710	900	37	759	730	910	0.16	779±8	0.4
Rh6G	MeOH	530	1100	102	554	1250	820	0.94	583±10	1.0

λ^a_m is the long-wavelength absorption band maximum, $\Delta\tilde{\nu}^a$ is its width at 0.5 level, ε_m is molar extinction coefficient at λ^a_m, λ^f_m is wavelength of fluorescence spectrum maximum, $\Delta\tilde{\nu}^f$ is its width at 0.5 level, $\Delta\tilde{\nu}^{St}$ is Stokes shift, q^f is fluorescence quantum yield, λ^{las} is mean generation wavelength, $\Delta\lambda^{las}/2$ is its half-width at 0.1 level, E^{las} generation energy of dyes under identical laser pumping conditions near λ^a_m. Characteristics of Rhodamin 6G (Rh6G) are presented for comparison.

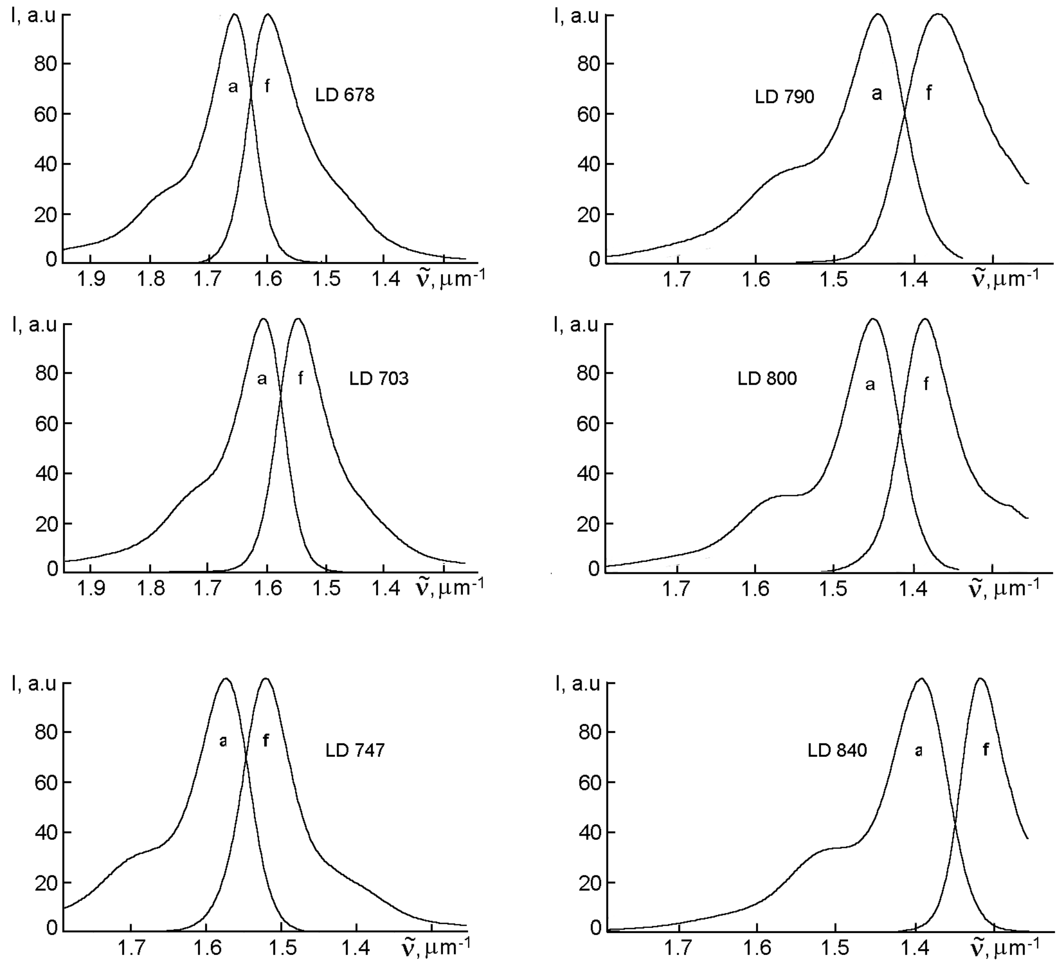

Fig. 2. Absorption (a) and fluorescence (f) spectra of the dyes studied.

(450 to 700 cm^{-1}). The quantum yield varies from 42 to 67 % for the 1st group of dyes and from 9 to 16 % in the second one. The Stokes shift increase and the quantum yield drop when passing from the 1st to 2nd group of dyes evidence that for those of the 2nd group, the non-radiative losses at the $S_1 \rightarrow S_0$ transition are much more intense.

Note that five of the dyes studied show a good laser efficiency under excitation near $\lambda^a{}_m$ that is comparable to or exceeds that of Rhodamin 6G. Under that excitation, those dyes in the grating resonator [7] have generated a tunable emission within a range exceeding 75 nm each. The emission spectrum width $\Delta\lambda^{las}$ did not exceed 0.3 nm and the total spectral interval of tuning included the 635 to 805 nm region.

Thus, the spectral, luminescence, and energy characteristics of the dyes demonstrate a rather high efficiency thereof in the far red and near IR spectral regions and made it possible to use the dyes purposefully both as active laser media and as fluorescent labels and probes.

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Спектральні та флуоресцентні характеристики лазерних барвників для діапазону 650–800 нм

В.В.Маслов

Вимірювано та проаналізовано спектрально-флуоресцентні і генераційні характеристики серії лазерних барвників для дальнього червоного і ІЧ діапазону довжин хвиль. Лазерні параметри барвників отримано при монохроматичному збудженні біля максимумів їх спектрів поглинання. Здійснено безперервне перенастроювання змушеного випромінювання барвників в області 635–805 нм. Одержані характеристики дозволяють цілеспрямовано використовувати ці барвники як в якості активних лазерних середовищ, так і флуоресцентних міток і зондів.