Spectral and generation properties of new bichromophores

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Generation properties of new bichromophore coumarin dyes and the influence on them of the structure changes of a coumarin molecule fragment have been studied. New bichromophores allow generation at lamp and laser pumping in a 585–640 nm spectral range, have high generative efficiency (up to 36%) and a high protochemical stability as compared to the best studied and usable coumarins. The influence of pumping frequency content on generation efficiency of new bichromophores has been investigated.

Introduction

It is known that the invention of the tunable organic dye lasers has stimulated the synthesis of new dyes having high fluorescence quantum yield and generation efficiency. The photostability of new-synthesized matters was of special importance. One of the most interesting and promising directions in investigation is the study and development of new active media on the base of bichromophore molecules. Bichromophores are compounds with two structure groups (chromophores); each of them, providing the presence of a long π-system in it, is responsible for both fluorescence and generation properties.

Bichromophore molecules are promising transformers of pumping radiation owing to more efficient its use due to effective intramolecular transfer of electron excitation energy from a donor to an acceptor. Such compounds are of great interest for the use as active media in lamp-pumping lasers, since the donor and the acceptor in bichromophore compounds can be chosen so that the triplet state will be effectively desactivated due to intramolecular energy transfer.

In this work, spectral-fluorescence and generation parameters of two new bichromophore coumarin dyes are studied.

1. Instrumentation

The experimental setup is based on a universal dye-solution laser system.[1] In this work, an emitter based on an improved Dzyubenko coaxial lamp[2] was used. A cavity of the lamp-pumping dye laser is formed from a dielectric flat mirror with reflectivity $R = 100\%$ and a pile of two plane-parallel plates made of K-8 glass, which is an optimal outcoupling mirror in this case. A discharge circuit consists of 10 parallel-connected low-inductive capacitors K75-48 of 2.2 μF total capacity and an the IRT-6 ignitron protector. The supply voltage is 17 kV. The lamp discharge gap is filled with Xe under a 20–30 torr pressure. A 0.5-level light pumping pulse length is 2 μs at the leading edge front of 0.8 μs. The pump pulse electric energy is 300 J. The generation energy was measured with an IMO-2N meter. Time parameters of pump pulses and generation were recorded with a FK-22 photocell, a signal from which arrived to a double-beam general storage oscilloscope C8-14. Dye-solution absorption spectra were measured with a “Spekord M-40” or SF-26 spectrophotometer.

To study generation parameters of coumarin compounds in coherent pumping, a two-stage dye laser converter was used. Its schematic view is shown in Fig. 1.

In case of coherent microsecond pumping, the above described dye laser with lamp pumping was the base of the first stage A, while in case of nanosecond pumping, an electric-discharge excimer XeCl laser was used. The cavity of the laser converter second stage B was formed from a flat totally reflected mirror, and the pile was used as an outcoupling one. Generation was excited by the quasicompressional scheme at an angle of 5–7° with respect to the cavity axis.

Ethanol solutions of standard effective laser dyes with a concentration of $1.2 \cdot 10^{-4}$ mol/l were used as an active medium at the stage A (see Fig. 1). Concentrations of the studied dyes at the stage B were chosen so that they can provide for the absorption coefficient $K \sim 15–25$ cm^{-1} at the pumping wavelength. Such absorption corresponds to a dye concentration of $5 \cdot 10^{16}$ cm^{-3} (10^{-4} mol/l). Solutions of the studied dyes were put into the plane-parallel cell with an active layer of 5 mm in thickness. Pumping radiation was focused to the cell in a spot of about 4 mm; the required excitation intensity was set with the use of neutral light filters. The recording system of generation parameters was similar to those at lamp pumping.

Spectral-fluorescence parameters of the dye solutions were studied with a nanosecond pulse spectrofluorimeter,[3] which is schematically shown in Fig. 2.

A Xe lamp was used as a source of exciting light. The length of excitation pulses was about 1 ns. The device was supplied with monochromators to emit both exciting and emitting light.

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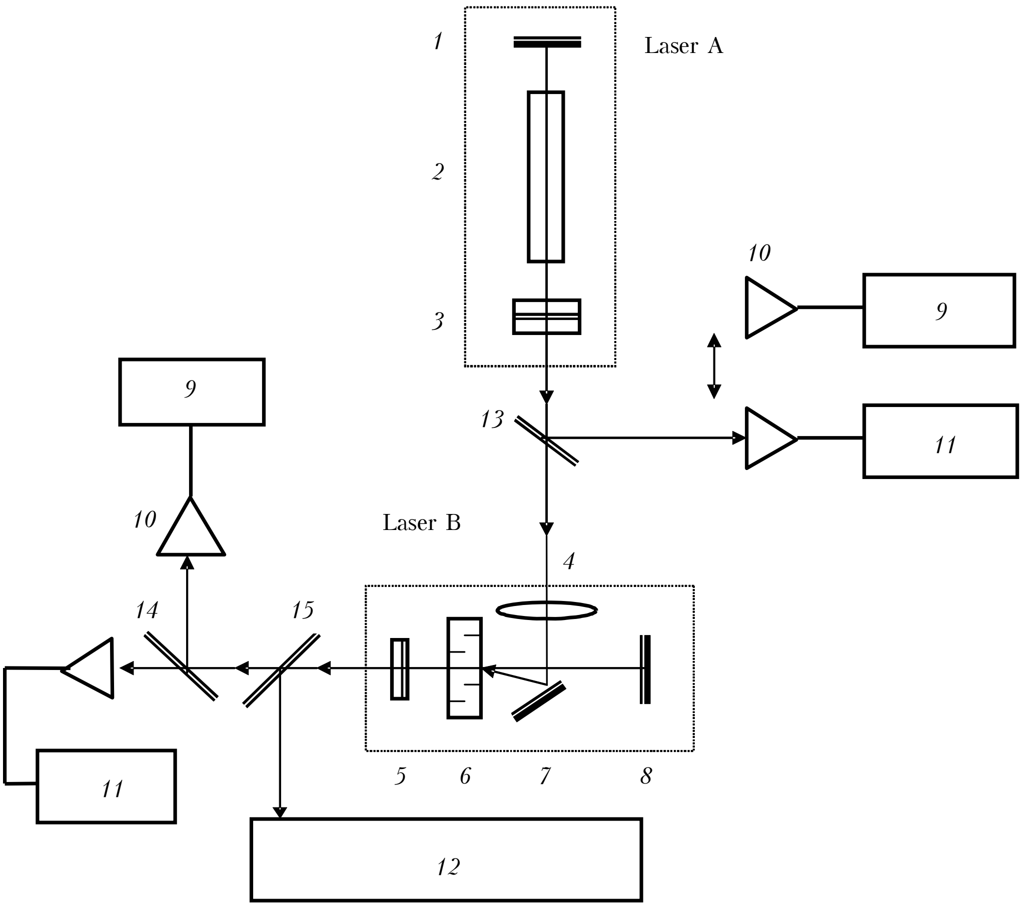
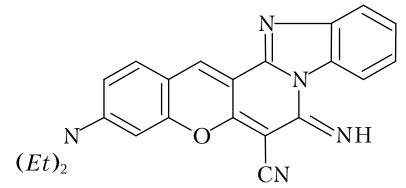


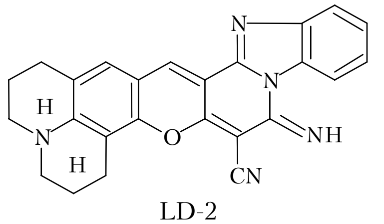
Fig. 1. Schematic view of the setup based on a two-stage dye laser: dye laser A on the base of a coaxial cell-lamp; dye laser B with coherent microsecond pumping (laser converter); cavity end mirror of the lamp-pumping dye laser (*1*); coaxial cell-lamp (*2*); pile – output mirror of the lamp-pumping dye laser (*3*); focusing lens (*4*); exit mirror of the laser converter (*5*); cell with ethanol solution of an investigated dye (*6*); rotating mirror (*7*); totally reflecting mirror of the laser converter (*8*); double-beam storage oscilloscope C8-14 (*9*); FK-22 meter (*10*); IMO-2N meter (*11*); diffraction spectroscope DFS-8 (*12*); rotating glass plates (*13*, *14*, and *15*).

2. Experimental results and discussion

Two bichromophore coumarins on the base of benzopyrans compounds were studied, differing in a substituent in the 7th position of the coumarin ring:



LD-1



LD-2

LD-1 has the dimethylamine group in the 7th position while LD-2 has a condensed saturated heterocycle.

Such change of the molecule structure essentially affected spectral fluorescent parameters. Absorption and fluorescence bands of LD-2 are bathochromically shifted almost by 20 nm as compared to LD-1. The saturated condensed heterocycle in the 7th position of LD-2 provided for a more rigid coplanar structure of the molecule, which resulted in an essential increase in the excited state lifetime and quantum yield of the fluorescence.

Comparison of spectral fluorescence parameters of the above LD-2 compounds has shown that extension of conjugated chain of coumarin dyes allows an essential shift of absorption and fluorescence spectra up to the red region.

It is established that LD-1 has two emitting centers while LD-2 has only one. One can suppose that condensing with the saturated heterocycle in the 7th position of coumarin ring enhances donor capabilities of the chromophore in comparison with the dimethylamine group. As a result, mobility of π-electrons enhances and intramolecular energy transfer in LD-2 occurs more freely and effectively in comparison with LD-1 due to the more rigid structure of the former molecule. Therefore, LD-2 has only one radiation center.

Generation parameters of the considered compounds were studied in conditions of intense incoherent lamp pumping, as well as laser pumping. The Table below presents the name, structure formula, generation efficiency η_{gen}, spectral range of generation $\Delta\lambda_{gen}$ for ethanol solution of the two compounds at optimal concentration and three different types of pumping, i.e., lamp and two laser: microsecond and nanosecond.

Analysis of the Table data shows that the generation by two new compounds at three considered excitation types has been obtained for the first time. New bichromophores allow lasing in a 585–640 nm spectral range. The most effective generation has been obtained for LD-1 at high-power incoherent pumping and for LD-2 – at laser excitation in both microsecond and nanonsecond pumping.

As is evident from the Table, a conversion factor higher than 36% has been attained for LD-1 in coherent microsecond excitation, as well as the double-band generation is observed. Higher conversion efficiency of LD-1 in the above types of coherent pumping can be explained by the presence of two effectively emitting centers in the molecule. Lower generation efficiency of LD-1 in comparison with LD-2 in lamp pumping is explained by a lower photostability of the former. It is known that julolidine coumarins, including LD-2, are essentially more photostable in comparison with 7-diethylamine and 7-hydroxycoumarins.

Experimental study of generation spectral efficiency of the considered bichromophore ethanol solutions in coherent microsecond pumping has shown (Fig. 3) that there is an anomalous dependence of the generation efficiency and spectral parameters on the pumping wavelength, namely, the generation efficiency first increases following the exciting radiation wavelength change and then drops near the absorption band maximum with further increase at the long-wave slope.

The obtained dependences of conversion efficiency on pumping spectral composition are of the same character that those for ethanol solutions of other different dye classes.[3,4] As for the behavior of generation spectra when changing pumping wavelength, the generated band widens to the short-wavelength range as the pumping wavelength increases, and, as it has been mentioned above, two-frequency generation is observed for LD-1 in the gap region when exciting by radiation with wavelength $\lambda_{pump}^{max} = 550$ nm.

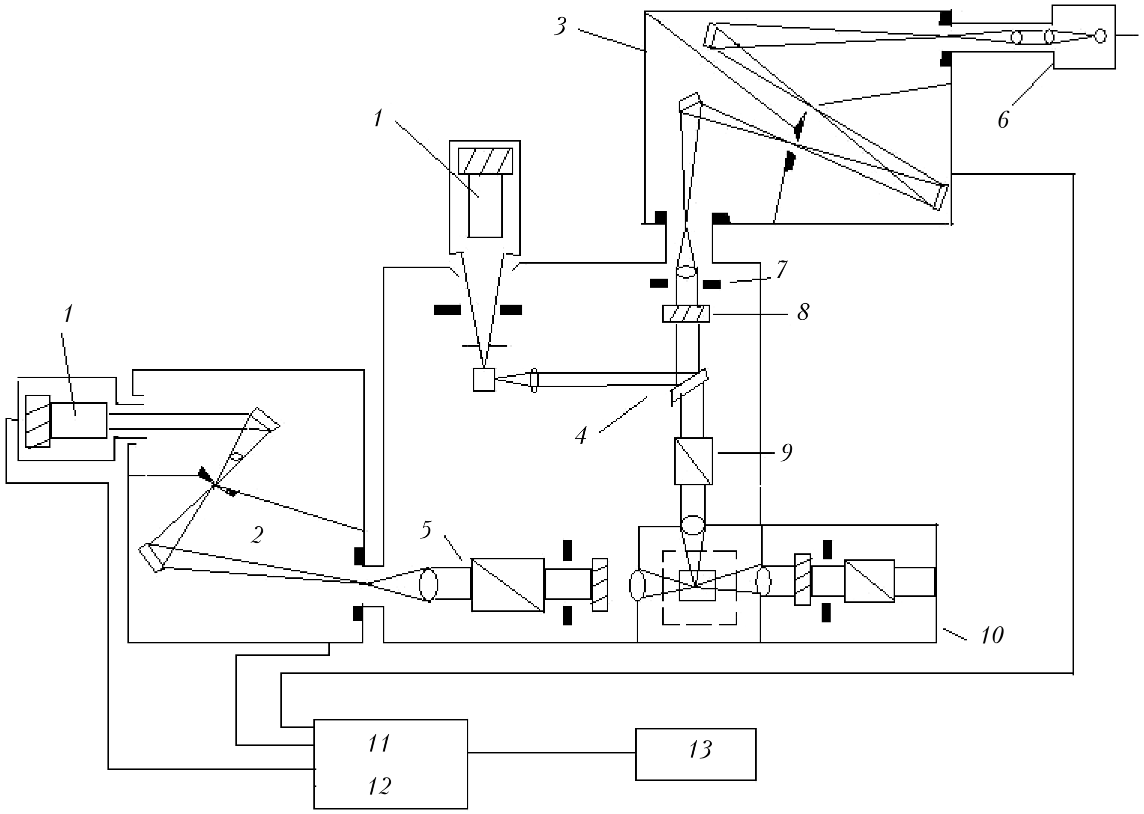
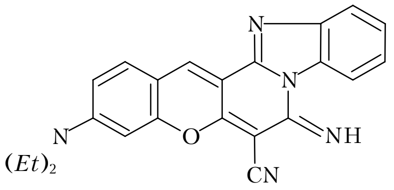
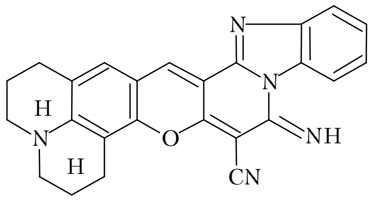


Fig. 2. Schematic view of the spectrofluorimeter: photorecording device (*1*); emitting monochromator (*2*); double-grating exciting monochromator (*3*); comparison cell (*4*); optical module (*5*); light source (Xe arc lamp) (*6*); gate (*7*); filter holder (*8*); polarizer (*9*); cell section (*10*); monochromator controller (*11*); data input and analysis (*12*); data output (IBM PC-compatible hardware and software complex) (*13*).

Table. Generation parameters of new bichromophores

No.	Structure formula	Generation parameters					
		Lamp microsecond pumping		Coherent microsecond pumping		Coherent nanosecond pumping	
		η_{gen}, %	$\Delta\lambda_{gen}$, nm	η_{gen}, % (λ_{pump})	$\Delta\lambda_{gen}$, nm	η_{gen}, %	$\Delta\lambda_{gen}$, nm
1	LD-1  	0.03	620–625	36.4 (550)	585–600 605–620	2	590–605 610–625
2	LD-2  	0.2	635–640	16.6 (550)	605–616	Threshold	610

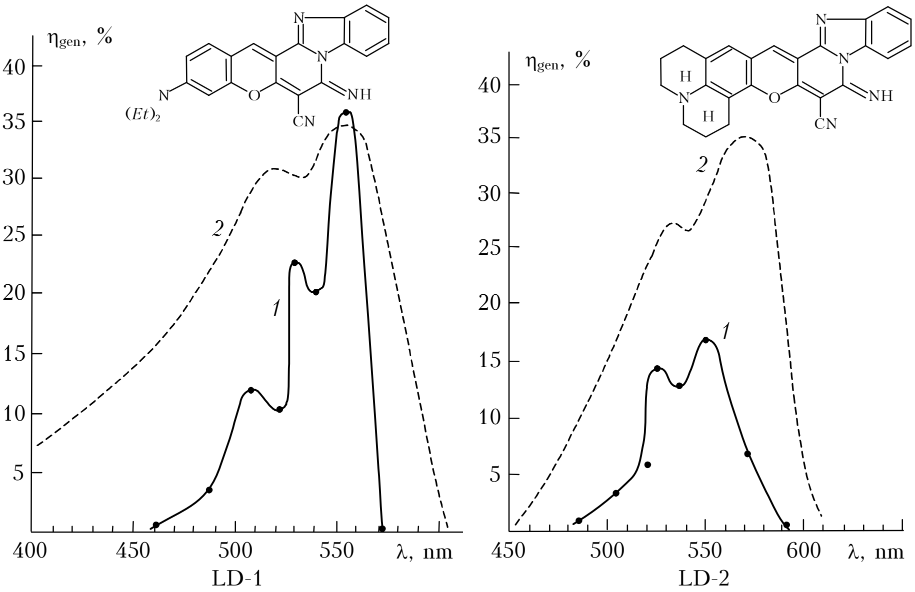


Fig. 3. Generation efficiency of ethanol solutions of LD-1 and LD-2 as functions of the pumping wavelength (*1*); the profile of absorption baseband (*2*).

As the LD-1 molecule has two emitting centers, there are two characteristic gaps in the exciting wavelength dependence of the conversion efficiency (Fig. 3).

To explain fully the observed effects, detailed investigations are required. However, even available literature data on spectral parameters of absorption in the channel of excited singlet levels for ethanol solutions of certain coumarin, rhodamine, and oxazine dyes allow a quite satisfactory explanation.[5,6] In Figs. 4*a–c*, curves *3* present spectra of Einstein coefficients for absorption in the channel of excited singlet levels $Bs_1 \to s_k(\nu)$ for solutions of Rhodamine 6G, Rhodamine C, and oxazine 9, respectively, obtained from Ref. 5.

The comparison of spectral behavior of losses in the channel of excited singlet levels with the excitation wavelength dependence of generation efficiency for the above compounds allows an assumption that reversible photoproducts are formed as a result of radiation absorption in the channel of excited singlet levels at microsecond coherent pumping of dye solutions (as in the case of nanosecond pumping); the photoproducts have strong absorption in a certain spectral amplification region, which results in a decrease of the generation efficiency.

The results of laser flash-photolysis of Rhodamine 6G ethanol solution at different levels of excitation intensity are given in Ref. 7. The integral absorption spectra of photoexcitation products in a 550–670 nm range were obtained when sensing synchronously with pumping and at a time delay of about 25 ns. Strong structuring of the spectrum at $P \geq 1.5\ \text{J/cm}^2$ and observed differences between the both variants indicate the formation of short- and long-living photoexcitation products, absorbing in a wide spectral range including the generation region. Estimates show that the phototransformation probability for the Rhodamine 6G molecule reaches a quite large value of about 0.005–0.007 at three-stage excitation by the radiation with $\lambda = 532$ nm.

Another confirmation of reversible photoproducts formation as a result of singlet-singlet absorption of the pumping radiation is the carried out experiment on measuring some spectral-fluorescent parameters of ethanol solution of DCM dye (see Fig. 4*d*) (this dye was chosen as an object of study to make the experiment easier).

Kinetics and quantum yield of fluorescence were measured at two exciting radiation wavelengths of 408 and 500 nm using a semiconductor picosecond laser as an excitation source. According to Fig. 4*d*, these wavelengths correspond to maximal and minimal generation efficiency. The fluorescence was recorded at a wavelength of 620 nm. The experiments have shown that the excited state lifetime decreases from 1.96 (at $\lambda = 408$ nm) to 1.76 ns in the gap region at 500 nm, as well as some decrease in quantum yield of fluorescence from 57 to 54% is observed. These experimental data show that the formed photoproducts quench the fluorescence and result in a fall of the generation efficiency.

Conclusion

The performed investigations allow us to propose new bichromophore coumarin dyes, generating at lamp and laser pumping in a 585–640 nm spectral range, with high generation efficiency (≈ 36%) and high photochemical stability, which is sometimes higher than those for the best known and commonly used coumarins.

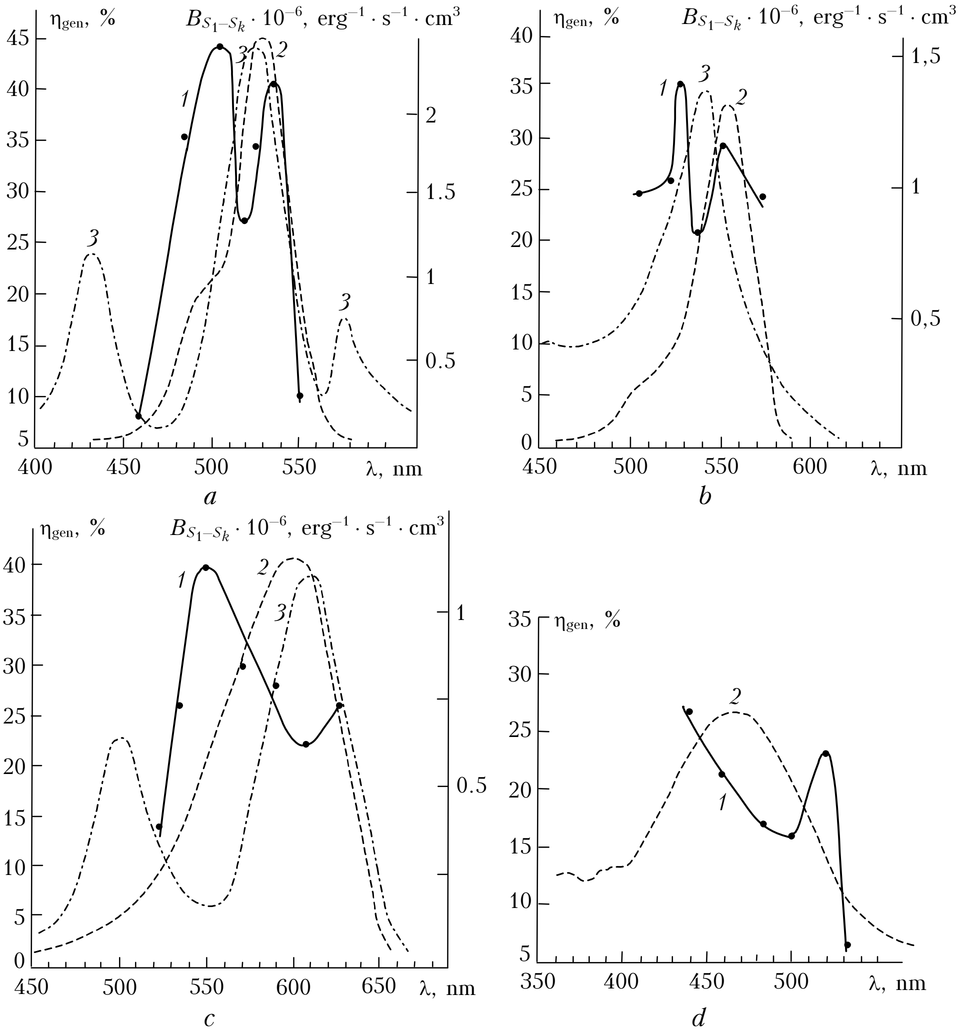


Fig. 4. Generation efficiency of ethanol solutions of certain laser dyes as a function of the excitation wavelength (*1*); profiles of the absorption basebands (rel. units) (*2*); spectra of Einstein coefficients for absorption in the channel of excited singlet levels (*3*) for Rhodamine 6G (*a*), Rhodamine C (*b*), and oxazine 9 (*c*).

It is shown that condensing with the saturated heterocycle in the 7th position of coumarin ring provides for a more rigid coplanar structure, which results in an essential increase in the excited state lifetime and the quantum yield of the fluorescence. This enhances donor capabilities of the heterocycle group in comparison with dimethylamine one. As a result, the oscillation mobility of π-electrons enhances, and intra-molecular energy transfer essentially increases due to the more rigid molecular structure.

An anomalous dependence of generation efficiency and spectral parameters on pumping wavelength is revealed for bichromophore coumarins, i.e., the generation efficiency first enhances when changing the exciting radiation wavelength, then drops near the absorption band maximum, and again enhances at the long-wave slope.

The observed anomalous dependences of energy and spectral generation parameters of the bichromophore dyes on exciting radiation wavelength can be explained by the presence of reabsorbing pumping radiation in the system of excited singlet levels, which results in origination of reversible photoproducts having a strong absorption in a certain amplification spectral region.

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