ISSN 1027-5495. Functional Materials, 29, No.4 (2022), p. 488-493.
doi:https://doi.org/10.15407/fm29.04.488

Environment effect on emitting characteristics of laser dye DCM

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Received September 15, 2022

The spectral, fluorescent, temporal, and lasing characteristics of the DCM laser dye in solutions and silica gel matrices were investigated to ascertain the influence of the dye surroundings on the processes of its energy relaxation in the excited state. Quantum yields of fluorescence Q_{fl} and rate constants of radiative k^r and nonradiative k^{nr} transitions both in solutions and silica gel matrices have been calculated. It was found that the microenvironment of the DCM molecule in a preliminarily annealed (PA) matrix most strongly affects the processes of nonradiative relaxation in the S_1 state, which leads to their significant weakening. As a result, the quantum yield of fluorescence increases by 85 % compared to the methanol solution; at the same time, the specific yield energy of laser radiation increases almost twice. The analysis of DCM dye characteristics measured in the four media shows that the PA matrix has a greater stabilizing effect on the spatial structure of the dye molecule than bipolar solvent dimethyl sulfoxide.
Keywords: DCM laser dye, environment, nonradiative relaxations, silica gel, preliminary annealing, stabilizing effect.

Вплив оточення на випромінювальні характеристики лазерного барвника DCM. *В.В.Маслов, О.М.Безкровна, І.М.Притула*

З метою зіясування впливу оточення молекули лазерного барвника DCM на процеси релаксації енергії її збудження в S_1 стані були досліджені спектральні, флуоресцентні, часові та лазерні характеристики цього барвника в розчинах та силікагельних матрицях. Були розраховані його квантові виходи флуоресценції Q_{fl}, а також сталі швидкостей випромінювальних k^r та безвипромінювальних k^{nr} переходів, як в розчинах, так і в матрицях. Виявлено, що найбільшу дію на процеси безвипромінювальної релаксацій в S_1 стані, яка приводить до суттєвого їх зменшення, оказує мікрооточення молекули DCM у попереднє відпаленій (ПВ) матриці. В результаті зростає квантовий вихід флуоресценції на 85 % в порівнянні з метанольним розчином, і при цьому питома вихідна енергія лазерного випромінювання підвищується майже вдвічі. Аналіз досліджених характеристик барвника DCM, виміряних у чотирьох середовищах показує, що ПВ матриця оказує більшу стабілізуючу дію на просторову структуру молекули барвника ніж біполярний розчинник діметілсульфоксид.

1. Introduction

The spectral properties of laser dyes and sources of tunable radiation on their basis make them topical objects of explorations for the development of new photonics and biophotonics elements. In addition, we can highlight the red region of the spectrum as very relevant for many practical applications [1, 2] including the biomedical diagnostics [3]. A.Hamja et al. [1, 4] developed a system based on a low-cost blue laser

diode as a pump source and a sealed cell with propanol or ethanol solutions of DCM laser dye without a flow circuit; the result is a device that combines the convenience and size of a solid-state device with the stability of a liquid organic laser. They obtained a very high photostability (up to $1.2 \cdot 10^9$ pulses, which corresponds to 12 days of operation at a pulse repetition rate of 1 kHz), which is five orders of magnitude higher than a solid-state dye laser operating under similar conditions. The compact dye laser on DCM with an unexpectedly high long-term stability [4] had an optical efficiency of 18 % and a high beam quality ($M^2 = 1$). The authors supposed that such a high stability obtained without circulation could presumably be due to the existence of strong thermal gradients in the medium and the convective diffusive transport of photobleached molecules outside the pump region, ensuring a complete replenishing of the gain medium between each pulse.

A low-threshold random laser enhanced by TiN nanoparticles (NPs) suspended randomly in gain solutions of DCM is reported in [2]. The localized surface plasmon resonance of individual TiN NPs increased the pump efficiency and strengthened the fluorescence amplification efficiency of DCM. T.Li et al. [3] investigated the rates of two-photon absorption fluorescence in DCM laser dye and in fluorescein biomarkers, induced by coherent CW excitation light and bright two-mode squeezed light. The method of biosensing and bioimaging proposed in [3] is promising for studying the deep tissues of biological specimens *in vivo* by means of the two-photon DCM absorption method.

Y.Wan and L.Deng [5] studied recyclable coherent random lasers assisted by plasmonic nanoparticles in polyvinyl alcohol (PVA) thin films doped with DCM dye. They showed that the emission spectrum of the DCM-PVA film with Au nanoparticles of 50 nm in diameter is optimal, and its threshold is about 6.53 μJ/pulse. The authors proposed a method of obtaining recyclable samples and showed that recyclable coherent random lasers with a low-threshold and a good performance after several cycles can be realized with this method. L.Chen and co-authors [6] proposed and fabricated in PDMS an optofluidic dye laser with a distributed Bragg reflector with a new combination of optofluidic waveguide and combination of optofluidic waveguide and ridge waveguide gratings. The generation wavelength can be tuned in the range of more than 450 nm by changing the tuning liquid in the gratings as well as the laser dye in the waveguide. The DCM laser dye was dissolved in dimethyl sulfoxide (DMSO) and used to cover the red wavelength range. The proposed configuration permits to realize an on-chip tunable single mode laser source.

A whispering gallery mode (WGM) resonance-based temperature sensor was proposed and realized in [7], where the microresonator was made of a DCM dye-doped oil droplet immersed in the water solution. The authors excited lasing in the oil droplet and measured the shifts of the resonance wavelength at different temperatures. The developed temperature sensor improved the thermal sensitivity and provided a possibility for sensing in liquid samples.

Choubey et al. [8] developed a statistical analysis of fluctuations in the intensity of random laser (RL) radiation in a thin film DCM doped polyvinyl alcohol waveguide as a spectroscopic tool for studying material properties. 0.08 wt. % DCM was added to the PVA matrix. DMSO has been used as a common solvent for dye and polymer dissolution. The ability to use the RL intensity fluctuations as a tool for material analysis is very important for material characterization. M.M.Prenting et al. [9] investigated the absorption and fluorescence spectra of five laser dyes, including DCM dissolved in some solvents as tracers in the two-colour laser-induced fluorescence thermometry. They showed that the temperature sensitivity strongly depends on the tracer and solvent.

In [10], two-photon fluorescence excited in thin films by a thermally activated delayed fluorescence of an electron donor-acceptor (DA) exciplex and exciplex doped with a fluorescent emitter was observed and studied. One of the fluorescent emitters used in this work was DCM dye. It was found that the upconversion fluorescence intensities of the exciplex samples increased dramatically after doping a tiny amount of the fluorescent emitter.

Authors [11] realized low-threshold, narrowband emission, and stable random lasing in a composite of carbon quantum dots and DCM nanowires doped with TiN nanoparticles. The DCM nanowires were prepared by a self-assembled process. The FRET process resulted in a high fluorescence efficiency for this composite, allowing for significant random lasing effects; since the TiN particles were doped, this greatly enhanced the

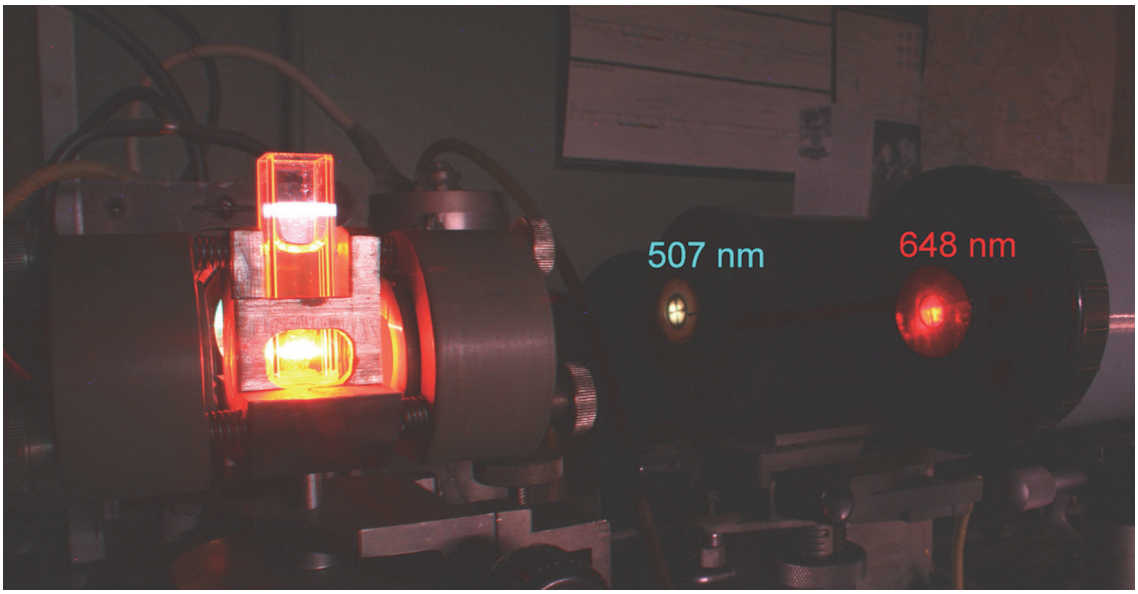


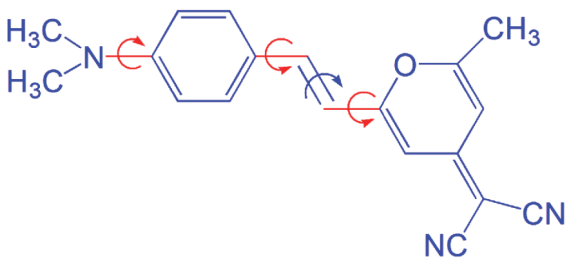
Fig. 1. Setup for measuring laser characteristics of the DCM dye in the matrices and solutions in the moment of lasing of PA matrix (λ_{las} = 648 nm) under pumping by the BDL with λ_{pump} = 507 nm.

emission efficiency through plasmon resonance and random scattering.

As is obvious from the above, the interest in the use of DCM laser dye, known since 1974 [12], is remains to this day. This is due to the remarkable emission properties of this dye [14]. Earlier, we carried out a series of studies of laser media on the basis of silica gel matrices doped with the dyes [14–16]. In this work, we study the influence of the spatial structure of the DCM laser dye molecule and its nearest environment on the relaxation processes in the excited S_1 state of this molecule.

2. Experimental

We have carried out additional measurements and calculations to analyze the effect of the DCM molecular structure and its environment both in solution and silica gel on the spectral, fluorescent, and laser characteristics. The structural formula of this laser dye is given below. Arrows in it show the directions of potential relaxation swings of molecular fragments in the exited S_1 state [17].



The characteristics of this dye in matrices synthesized by hydrolysis and subsequent polycondensation of tetramethoxysilane (TMOS, Aldrich) in aqueous-methanol solutions of DCM (Aldrich) were studied by us earlier [13]. At the same time, the temperature of ageing and drying of matrices did not exceed 60°C. Since, after such a synthesis of matrices by the low-temperature method (LTM) at $T_{sol\text{-}gel} \leq 60$°C, DCM dye worsened its lasing characteristics in comparison with the methanol solutions, therefore, we applied preliminary annealing (PA) of the matrices, which were not doped with the dye. The annealing temperature was 600°C. After the matrices were cooled, they were impregnated with a methanol solution of the dye [15].

The solutions of DCM in methanol and DMSO were also examined for estimating the influence of the neighboring environment of the dye molecule on its characteristics. The instrumentation and methods for measuring and calculating spectral, fluorescence, temporal and laser characteristics of the dye in the solutions and matrices were described in our previous articles [14–16]; the absorption spectra of the samples were measured on an Optizen 3220UV spectrophotometer (Mecasys Co. Ltd.), fluorescence spectra were measured on a FluoroMax-4 fluorimeter (Horiba Jobin Yuon), and DCM fluorescence decay curves were measured on a Fluo-Time 200 spectrofluorimeter (PicoQuant). To calculate

Table. Spectral, fluorescent, temporal, and lasing characteristics of DCM

Medium	λ_a, nm	λ_{fl}, nm	Q	τ, ns	$k^r \cdot 10$, ns^{-1}	$k^{nr} \cdot 10$, ns^{-1}	$\Delta\nu^{St}$, cm^{-1}	λ_{las}, nm	$\Delta\nu^{las}$, cm^{-1}
Methanol	467	630	0.43	1.31	3.28	4.35	5540	635	125
DMSO	480	643	0.50	2.16	2.31	2.31	5280	654	260
LTM matrix	469	616	0.61	2.38	2.56	1.64	5100	634	460
PA matrix	420	584	0.65	2.28	2.84	1.53	6690	648	1690

λ_a is the maximum of long-wavelength absorption band, λ_f is the wavelength of fluorescence maximum, τ is the fluorescence lifetime, $\Delta\nu^{St}$ is the Stokes shift between the maxima of the absorption and fluorescence bands, λ_{las} is the central lasing wavelength, $\Delta\nu^{las}$ is the shift between the fluorescence maxima λ_f and lasing spectra λ_{las}.

quantum yields Q in silica gel matrices, methanol solutions of DCM dye ($Q_0 = 0.43$) were used as references [16].

After measuring the laser characteristics, the matrices were put into a quartz cuvette with internal dimensions of 10×10×40 mm^3 filled with immersion liquid, ethylene glycol, to reduce optical distortions within the laser cavity by untreated end planes of the matrix. The characteristics of the DCM solutions were measured in the same cuvette. The studied dye in the matrices and methanol was excited by booster dye laser (BDL) based on an ethanol solution of coumarin 314 with a wavelength λ_{ex} = 507 nm, output energy up to 150 mJ, pulse duration ~1 μs, and a spectrum half-width of 3–5 nm (Fig. 1).

3. Results and discussion

The main results of measurements of the spectral, fluorescent, temporal, and lasing characteristics of the dye in solutions and matrices are given in the Table along with the calculated fluorescence quantum yields Q and the rate constants of the radiative $k^r = Q/\tau^f$ and nonradiative $k^{nr} = (1 - Q)/\tau^f$ transitions.

Normalized absorption and fluorescence spectra of DCM in methanol (Met) and in the preliminary annealed matrix (PAM) are shown in Fig. 2; fluorescence decay curves of DCM recorded with a Fluo-Time 200 are shown in Fig. 3.

The DCM dye has a long-wavelength absorption band that disposed in the blue-greenish region of the spectrum (Fig. 2), while it differs from other red laser dyes in the largest Stokes shift ($\Delta^{St} > 5000$ cm^{-1}). This value indicates a noticeable increase in the dipole moment of the DCM molecule in the excited S_1 state, and an increase in its interaction with the nearest molecular surroundings. It was shown [18], that the dipole moment of the DCM molecule in the S_1 state increases by more than 20 Debye compared to the ground state S_0. Such a large increase in the dipole moment in the first excited singlet state is explained by an important intramolecular charge transfer from the electron-donating diethylamino group to the electron-withdrawing dicyanomethylene group [19] at the $S_0 \rightarrow S_1$ transition.

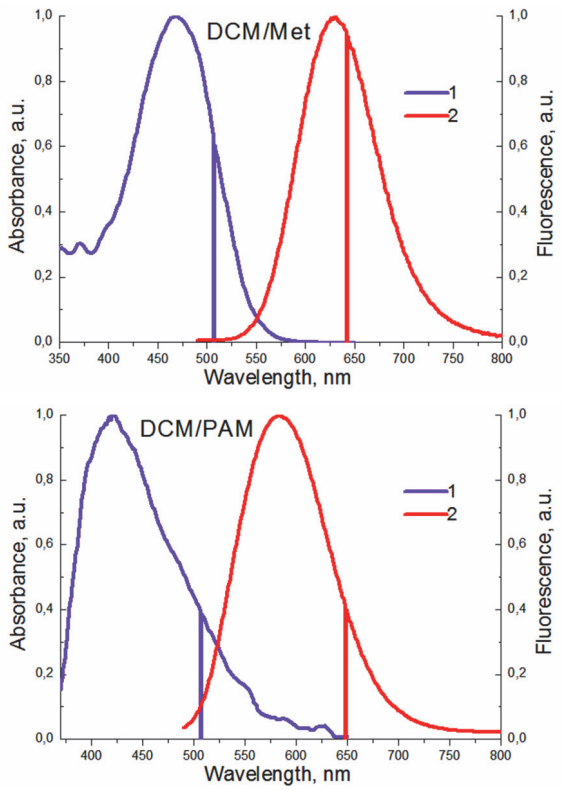


Fig. 2. Absorption (*1*) and fluorescence (*2*) spectra of DCM in methanol (Met) and the PAM. Vertical lines within them indicate the center positions of pumping (1 vertical) and lasing (2 vertical) spectra.

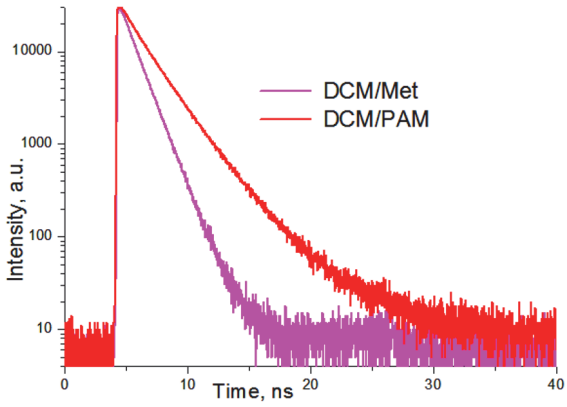


Fig. 3. Fluorescence decay of DCM in methanol (Met) and the PAM. Fluorescence was excited at λ_{ex} = 531 nm, and its registration was close to λ_{fl}.

Moreover, in the S_1 state, "twisted" configurations of the DCM molecule, TICT conformations, can occur. The possible torsions of the molecule fragments are shown in its structural formula with arrows. These torsions lead to a violation of the planarity of the molecule, which increases the probability of nonradiative transitions to the ground state S_0 and quenching of fluorescence. In addition, this molecule can undergo the trans-cis photoconversion as a result of the formation of a sterically hindered and less planar cis isomer, which reduces the fluorescence and laser characteristics [19]. However, the negative influence of the "twisted" forms and cis isomers of the DCM molecule decreases with increasing solvent polarity. Thus, in bipolar dimethyl sulfoxide, 92 % of these molecules are in the coplanar transform [20].

The results of our measurements of DCM dye characteristics (see Table) indicate that the impact of the nearest surroundings on its molecule, which results in a bathochromic shift of the absorption band, grows in the row: methanol, the LTM matrix, and DMSO. Here we note that DCM dye undergoes a short-wavelength shift of the maxima of the absorption and fluorescence spectra simultaneously when passing from the LTM matrix to the PA matrix. This is due to the residuals of non-evaporated organic liquid and acid in the LTM matrix [15], which are completely removed in the PA matrix. It is these residues that give the bathochromic shift of both spectra in the LTM matrix compared to PAM.

While the wavelength of fluorescence maximum is minimal in the PA matrix, it is maximal in bipolar DMSO. Moreover, the Stokes shift slightly decreases in the LTM matrix, but the fluorescence quantum yield noticeably increases and becomes greater than in bipolar DMSO. The blue shift of the fluorescence spectrum of DCM in the matrices relative to methanol is apparently due to a decrease in the energy losses of its molecule in the S_1 state in the environment of the matrix compared to proton-donor methanol.

Since DCM fluorescence is quenched due to the twisted forms of its molecule [16], it can be assumed that the formation of this form is hindered by the environment of the matrix and nonradiative losses of vibrations in the S_1 state. This assumption is confirmed by the measured fluorescence lifetimes τ and the calculated nonradiative decay rate constants k^{nr} of DCM in methanol, DMSO, and the matrices. The value of k^{nr} is reduced by 1.88 times when passing from methanol to DMSO, by 2.65 times — to the LTM matrix, and by 2.84 times — to the PA matrix. So microenvironment of the dye molecule in the matrices has a larger polar and stabilizing impact upon its spatial structure than bipolar solvent dimethyl sulfoxide. Moreover, the fluorescence quantum yield of DCM dye in the PA matrix has the maximal value. This is due to the absence of residual organic liquids and acid in it in contrast to the LTM matrix where these residues negatively affect the molecules of the laser dye [15].

The laser radiation spectrum of a methanol solution of DCM in a nonselective resonator (see Table) is located near its fluorescence maximum with a small shift red $\Delta\nu^{las}$ = 125 cm^{-1}. This is due to the large Stokes shift and the small overlap of the absorption and fluorescence bands of this dye and, as a consequence, the low reabsorption of laser radiation in solution. However, the shift between the maxima of fluorescence bands λ_f and lasing spectra λ_{las} increases in the following order: methanol, DMSO, silica gel matrix. At the same time, the PA matrix saturated in a ~ 1 mM methanol solution, has a bathochromic shift of the laser spectrum relative to the LTM by one 14 nm. And in the connection with the blue displacement of the DCM fluorescence maximum in the PA matrix by 46 nm relative to the methanol solution, the shift between the maxima of the fluorescence band λ_f and the lasing spectrum λ_{las} has the maximal value of $\Delta\nu^{las}$ = 1690 cm^{-1}. This shift $\Delta\nu^{las}$ is useful in constructing biomedical sensors on the basis of the PA matrices since their

emission spectra are shifted to a region of deeper penetration into biological tissues.

Moreover, if earlier [14] laser radiation of DCM in the LTM matrix was obtained under maximal possible pumping energy, then in the PA one the lasing threshold was two times lower than for an LTM matrix under equal conditions. The specific laser energy of DCM (i.e., the energy related to the length of the laser active element) was almost twice as high in the PA matrix as in methanol. The fluorescence quantum yield of DCM in the PA matrix increased by 85 %, k^{nr} decreased by 2.84 times, $\Delta\nu^{las}$ increased by 1390 cm^{-1} (5.6 times), and the Stokes shift increased by 1150 cm^{-1} compared with methanol solution.

4. Conclusion

Thus, the studies of the spectral, fluorescent, temporal, and laser characteristics of the DCM dye in four media revealed a noticeable effect of the nearest environment in these media on the processes of nonradiative relaxation of the DCM molecule in the S_1. excited state. The greatest decrease in this relaxation occurred in the PA matrix, in which nonradiative losses decreased by almost three times, but the fluorescence quantum yield and specific laser energy increased noticeably. Furthermore, in this matrix, the maximum value of the shift of the central lasing wavelength relative to the fluorescence maximum was obtained, $\Delta\nu^{las}$ = 1690 cm^{-1} , which increases the penetration of laser radiation deep into biological tissues.

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