Two-photon absorption cross section of DCM derivatives in solutions and in PMMA

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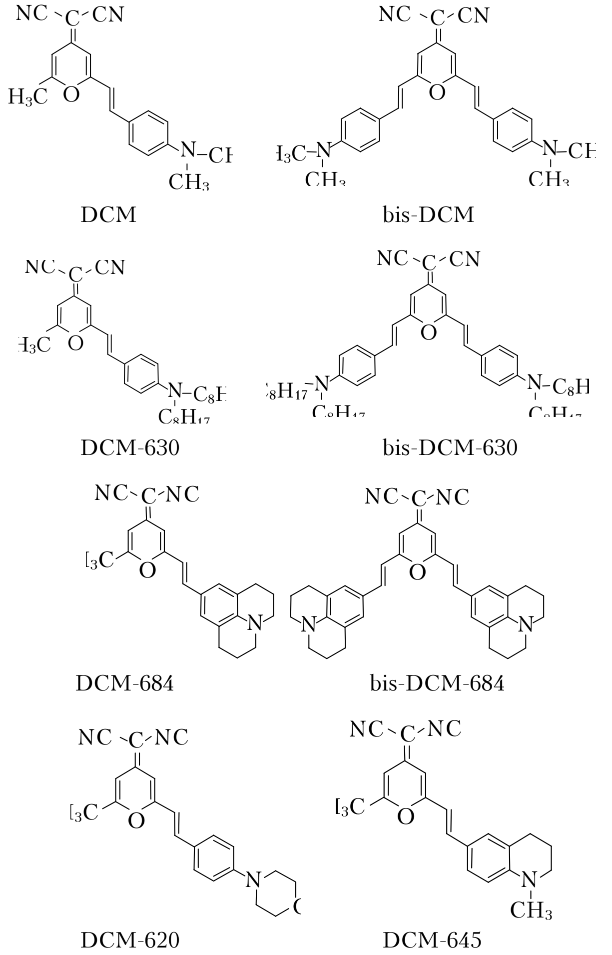
The two-quantum standard method is applied to determine the efficiency of two-photon pumped fluorescence (TPPF) and the two-photon absorption (TPA) cross sections of high-efficiency red laser dyes, *viz.,* dicyanomethylene-pyran derivatives in solutions and polymeric matrices. The highest TPA cross section for a Nd–YAG laser radiation (1064 nm) is observed in DCM-684 ethylacetate solution – 15.7 GM. The influence of the structure pyran derivatives and solvents on the change of TPA cross section and the TPPF efficiency is discussed.

Introduction

In recent years, the interest in the study of organic materials with high cross section of the two-photon absorption (TPA) has increased significantly in connection with the prospects of their practical use in limiters of optical radiation, laser spectroscopy, remote sensing of the atmosphere, 3D optical memory and 3D displays, stereolithography, fluorescent microscopy, and two-photon pumped lasers.[1] Therefore, it is an urgent task to search for new organic molecules possessing high TPA cross section and good emitting properties.

This paper considers, for the first time, the emitting characteristics of some efficient laser dyes: derivatives of dicyanomethylene-pyran (Fig. 1) in solutions and in polymethylmetacrilates (PMMA) in the case of two-photon pumping by the Nd–YAG laser radiation with the wavelength of 1064 nm and nanosecond pulse duration. The base of the dicyanomethylene-pyran (DCM) series – 4-(dicyanomethylene)-2-methyl-6-p-[(dimethyl-amino) styryl]-4H-pyran molecule – was synthesized in 1970s [Ref. 2] and initially it was intended for use as active media of tunable dye lasers. The DCM and other compounds of the dicyanomethylene-pyran series have some unique properties, which have found wide application in quantum electronics.

Laser active media based on the pyran derivatives efficiently generate in the red spectral region both in liquid solutions and in solid matrices.[3,4] In addition to high efficiency and photostability, these compounds are characterized by a wide band of laser tuning, because the width of fluorescence bands of these molecules achieves 100–120 nm. Since the pyran derivatives have a large Stokes shift (up to 6000 cm^{-1}), their absorption and fluorescence spectra almost do not overlap, which allows the efficient lasing in the longitudinal and transversal pumping schemes with minimum losses due to reabsorption even at high concentrations.



DCM bis-DCM
DCM-630 bis-DCM-630
DCM-684 bis-DCM-684
DCM-620 DCM-645

Fig. 1. Structure formulas of DCM derivatives.

In Ref. 5, it was shown that the DCM is an efficient fluorophore in electroluminescent devices, emitting in the spectral region from orange to red (570–620 nm). Since 1989, the Kodak Company has begun synthesizing the DCM class compounds for Organic Light Emitting Diodes (OLEDs).

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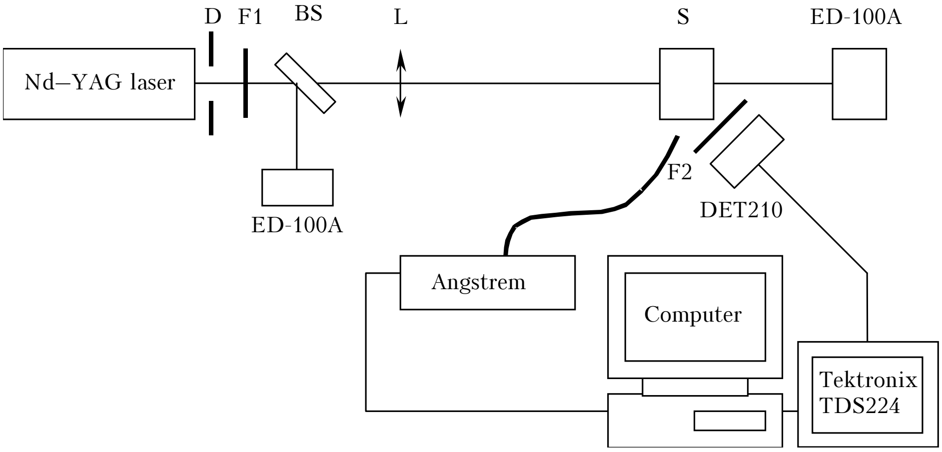

Fig. 2. Experimental setup for investigation of TPPF: diaphragm D; filters F1, F2; spherical lens L; beam splitter BS; sample under study S; ED-100A pyroelectric detectors; DET210 photodiode; Angstrem spectrometer; Tektronix TDS224 oscilloscope.

Pyran derivatives have unique nonlinear properties,[6,7] in particular, they have high two-photon absorption cross section.[8] In Ref. 9, the lasing in DCM was obtained in a polymeric optical fiber due to two-photon pumping.

Experiment

The TPA cross section was estimated from the secondary process – fluorescence – by the two-quantum standard method[10] as

$$\sigma_{2x} = \frac{\sigma_{2x\mathrm{st}}\eta_{\mathrm{st}}C_{\mathrm{st}}I_x^{\mathrm{TPPF}}}{\eta_x C_x I_{\mathrm{st}}^{\mathrm{TPPF}}}, \qquad (1)$$

where $\sigma_{2\mathrm{st}}$ is the cross section of the TPA standard; η_{st} and η_x are the quantum yields of fluorescence of the standard and the substance under study, respectively; C_{st}, C_x are the concentrations of the standard and the substance under study, respectively; $I_{\mathrm{st}}^{\mathrm{TPPF}}$, I_x^{TPPF} are the intensities of the two-photon pumped fluorescence in the standard and in the substance under study.

Another measure of the efficiency of two-photon pumping can be the TPPF efficiency equal to

$$\sigma_{2x}\eta_x = \frac{\sigma_{2\mathrm{st}}\eta_{\mathrm{st}}C_{\mathrm{st}}I_x^{\mathrm{TPPF}}}{C_x I_{\mathrm{st}}^{\mathrm{TPPF}}}. \qquad (2)$$

This characteristic is important in the case, when, in addition to the high TPA cross section, good emitting properties are needed, for example, in two-photon fluorescent microscopy, two-photon pumping of aerosols with fluorescent probes, or two-photon pumped lasers.

The experimental setup for TPPF recording is shown in Fig. 2. As a standard, we used the ethanol solution of Rhodamine 6G with the concentration of 10^{-4} M, having known TPA cross section: $\sigma_2 = 12$ GM (1 GM = 10^{-50} $\mathrm{cm}^4 \cdot \mathrm{s} \times \mathrm{photon}^{-1} \cdot \mathrm{mol}^{-1}$) [Ref. 11]. The pump laser pulse had the following characteristics: $\lambda_{\mathrm{las}} = 1064$ nm; $t_{1/2} = 6$ ns; $E_{\mathrm{pulse}} = 4$ mJ; $W_{\mathrm{pump}} = 100$–150 MW/cm^2.

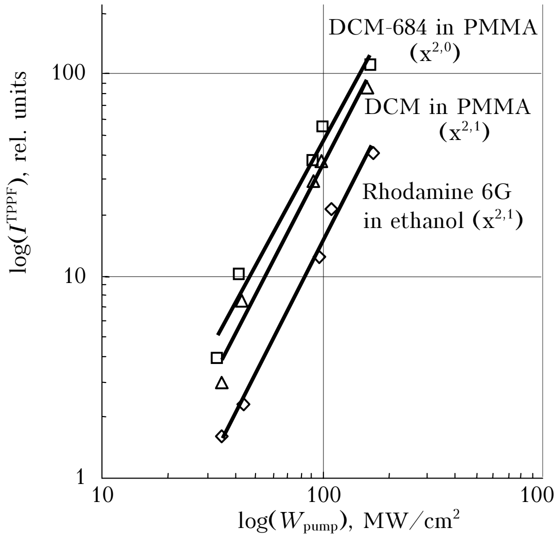

Fig. 3. TPPF intensity as a function of the pump radiation power density.

This technique can be used for measurement of the TPA cross section in the case of linear two-photon process, that is, when the dependence of the TPA intensity on the pump intensity $I^{\mathrm{TPPF}}(W_{\mathrm{pump}})$ is quadratic or close to it. At the high pump intensities (tens and hundreds of MW/cm^2), this dependence can be violated,[12] and therefore we continuously monitored the dependence $I^{\mathrm{TPPF}}(W_{\mathrm{pump}})$. For all the molecules studied, the dependence $I^{\mathrm{TPPF}}(W_{\mathrm{pump}})$ was close to the quadratic one. Figure 3 shows the dependence $I^{\mathrm{TPPF}}(W_{\mathrm{pump}})$ for the standard solution of Rhodamine 6G in ethanol, DCM and DCM-684 in PMMA.

Results

The spectral-luminescent characteristics and measurement results on the TPA cross section and the TPPF efficiency for dicyanomethylene-pyrans in comparison with the standard (Rhodamine 6G) upon the excitation by the fundamental harmonic of a Nd–YAG laser (1064 nm) are tabulated below.

Substituted DCMs absorb in the shorter-wave region as compared to Rhodamine 6G, and pumping by the Nd–YAG laser is not optimal for two-photon absorption by these molecules. The optimal wavelength for the two-photon pumping of these molecules should be shorter than 1000 nm. For the shortest-wave compound – DCM-620 in ethylacetate (absorption peak at 435 nm), no TPPF was observed upon the pumping with radiation at 1064 nm wavelength. The absorption spectrum of the same dye in dimethylsuloxide (DMSO) shifts to the long-wave region (455 nm), and we can observe, though weak, fluorescence upon the two-photon pumping. The same regularity can also be seen for DCM and DCM-630; namely, a small shift of the absorption spectrum to the long-wave region upon the alternation of a solvent causes the increase of the TPA cross section at excitation at the wavelength of 1064 nm.

The DCM-645 dye and, especially, DCM-684 one demonstrate quite a different behavior: in spite of the long-wave shift in polar DMSO, the TPA cross section does not increase, and for DCM-684 it is much lower than in ethylacetate. This can be related to the fact that these two molecules have a somewhat different structure of energy levels as compared to that of the DCM.[13] The calculations show that the scheme of energy levels for DCM-684 and DCM-645 dyes includes the second triplet $T_{4\pi\pi}$, lying near the $S_{1\pi\pi}$ level, which can lead to the increase in the rate constant of the intercombination conversion and to the drop of the quantum yield of fluorescence. With such a scheme of molecular energy levels, the solvation sphere of the molecule (solvent) can strongly affect the efficiency of its fluorescence.

The presence of such a triplet state cannot directly affect the TPA cross section of the molecule, but it can influence its fluorescence properties, the information about which is important in fluorescent methods of measurement of the TPA cross section. There is no doubt that the dependence of the TPA cross section on the solvent revealed in this study requires further investigation of the photoprocesses in pyran substitutes by quantum-chemistry methods.

The analysis of data on the two-photon absorption cross section and the TPPF efficiency for the pairs: DCM – bis-DCM, DCM-630 – bis-DCM-630, and DCM-684 – bis-DCM-684, has shown that the TPA cross section in vapor almost does not change, while the increase of the TPPF efficiency for the bis-DCM molecules as compared to DCM in PMMA can be explained by the possible increase of the quantum yield of dye fluorescence in this polymeric matrix.

The tabulated data indicate that for all the studied molecules the TPPF efficiency in the polymeric matrix is higher than in solutions. If for DCM-684 and bis-DCM this increase may be assumingly related to the increase of the quantum yield of molecular fluorescence, which was not measured in PMMA, because we had samples with high concentration, then for DCM and DCM-630 the significant increase in the TPPF efficiency cannot be explained by only the change in the quantum yield of fluorescence. The analysis of the literature data has shown that usually the TPA cross section in a solid matrix is lower than in solutions.[11,14] The inverse dependence was observed earlier only for Phenalemine 512 [Ref. 15]. Thus, dicyanomethylene-pyrans form a unique class of organic molecules, which can be used for two-photon applications in solid polymeric matrices.

It should be noted that, for substituted dicyanomethylene-pyrans, aggregative and concentration quenching of fluorescence practically are not observed, at least, up to 10^{-2} M. Because of the large Stokes shift in these molecules (up to 6000 cm^{-1}, as mentioned above), their absorption and fluorescence spectra do not overlap and reabsorption is not observed even at high concentrations. This allows the DCM derivatives to be used for two-photon pumping in aerosols and as active media of two-photon pumped lasers.

Spectral-luminescent characteristics, TPA cross section, and TPPF efficiency of dyes

Compound	Solution/matrix	λ_{abs}, nm	λ_{fl}, nm	Stokes shift $\Delta\lambda$, nm	η_{fl}	σ_2, GM	$\sigma_2\eta_{fl}$, GM
Rhodamine 6G	ethanol	532	560	28	0.95	13 [Ref. 11]	12.4
	PMMA	535	565	30	0.95	13.5	12.9
DCM	etylac.	455	585	80	0.5	4.0	2.0
	PMMA	455	585	80	–	–	6.8
	DMSO	476	647	171	0.5	9.2	4.6
bis-DCM	etylac.	476	625	49	0.22	10	2.2
	PMMA	475	625	50	–	–	17.6
	DMSO	488	650	162	0.01	–	–
DCM-630	etylac.	476	595	119	0.5	8.2	4.1
	PMMA	476	590	114	–	–	15.0
	DMSO	493	650	157	0.6	9.2	5.5
bis-DCM-630	PMMA	490	636	146	–	–	17.6
DCM-684	etylac.	490	615	125	0.75	15.7	11.8
	PMMA	500	625	125	–	–	28.2
	DMSO	515	650	145	0.7	4.1	2.9
bis-DCM-684	PMMA	500	630	130	–	–	36.0
DCM-620	etylac.	435	580	145	0.4	–	–
	PMMA	435	580	145	0.5	–	0.9
	DMSO	455	630	175	0.6	2.2	1.3
DCM-645	etylac.	500	605	105	0.5	11.2	5.6
	PMMA	495	580	85	0.5	–	14.0
	DMSO	510	650	140	0.5	8.2	4.1

Conclusions

The method of two-quantum standard has been used to determine the TPA cross section and the TPPF efficiency of eight dyes belonging to the dicyanomethylene-pyran series in different solvents and in polymeric matrices pumped by a pulsed Nd-YAG laser radiation (1064 nm) of nanosecond duration. The effect of molecular structure in the series and the solvent on the two-photon pumping efficiency has been investigated.

It has been shown that, in the series studied, the best dyes for the two-photon pumping are DCM-684 and its bis-analog. The high, as compared with the solutions, the TPPF efficiency of substituted dicyanomethyls in PMMA makes them promising media for creation of solid-state two-photon materials for quantum electronics.

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