Investigation of two-photon absorption of merocyanine dyes in Nd:YAG laser excitation

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The two-photon excited fluorescence of two merocyanine dyes excited by nanosecond radiation of an Nd:YAG laser (532 nm) is investigated. The two-photon absorption cross sections of merocyanines are measured and equal to 25 ± 5 and 115 ± 15 GM. Features of nonlinear absorption of the investigated molecules are discussed.

Introduction

Major advances have been achieved during last years in design of powerful short-pulse laser sources, applicable not only in scientific researches but in modern laser technologies. The radiation parameters of such lasers, first of all, pulse radiation intensity, allow quite easy two-photon excitation in different media. In view of this, two-photon absorption (TPA) technologies are intensively developing.

At present, the most developed is the multiphoton confocal fluorescence spectroscopy[1,2] and 3D microfabrication.[3,4] 3D optical memory[5,6] and photodynamic therapy with two-photon excitation[7] are very promising. Other ways of TPA use in laser technologies (optical radiation power limitation, two-photon sensory, two-photon excitation of induced radiation) continue to develop. Two-photon excitation of aerosols with fluorescent particles and TPA-rendering[8] are also among prospective problems.

In addition to corresponding excitation sources, matters with large two-photon absorption cross sections are required for successive development of TPA technologies. Last years, several classes of organic compounds with large TPA cross section have been found and studied (fluorene[9,10] and stilbene[11] derivatives, porphyrin, pyridine, etc.). Merocyanine dyes (merocyanines), e.g., DCM,[12,13] are prospective for use in two-photon laser technologies.

Merocyanines are first characterized by pronounced solvatochromism, capability to essentially change dipole moment in transferring into an excited state and sensitize different physico-chemical processes. Owing to such properties, they are used more and more in modern optical technologies, e.g., organic electronics and nonlinear optics.[14–17] In addition, applicability of merocyanines in photodynamic therapy is of interest.[18]

In this work, TPA of a number of merocyanines[14] in Nd:YAG laser excitation (1064 nm, 12 ns) is studied for the first time. Two-photon excited fluorescence is registered; TPA cross section of merocyanines is obtained by the fluorescent method. The TPA cross section of studied molecules is considered with those of DCM molecules. Prospects of their use in nonlinear optics are discussed.

1. Subjects and technique of the study, linear and spectral-luminescent properties of merocyanines

For the study, we have chosen a series of three merocyanine molecules, which differs only in length of polymethine chain. The structural formulas of dyes are shown in Fig. 1. These merocyanines have positive solvatochromism, their dipole moments increases in exciting.[14] Spectral-luminescent characteristics are given in the Table; absorption spectra of the molecules in ethanol are shown in Fig. 2.

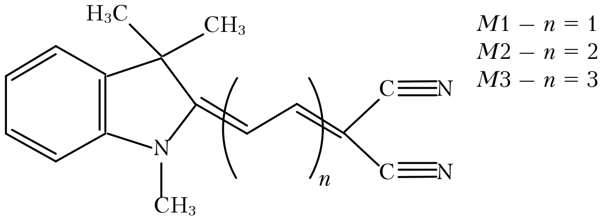

Fig. 1. Structural formulae of merocyanines.

Table. Spectral-luminescent characteristics and TPA cross sections of *M*1–*M*3 merocyanines

Dye	λ_{abs}, nm	ε, $M^{-1}\cdot cm^{-1}$	λ_{fl}, nm	η, rel. un.	$\delta^{(2)}$, GM	<*R*>, Å
Rhodamine G	532	100000	560	0.95	12.9 [Ref. 1]	1.70
*M*1	435	73700	466	0.0037	–	–
*M*2	525	88800	562	0.013	25±5	2.24
*M*3	611	86000	664	0.061	115±15	4.69

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The *M*1 compound absorbs in the blue spectral range and fluoresces a little (fluorescence quantum efficiency is less than 0.37%). It is evident from Fig. 2 that this molecule does not linearly absorb in the 532 nm region, corresponding to the total energy of two quanta of the first Nd:YAG laser harmonics.

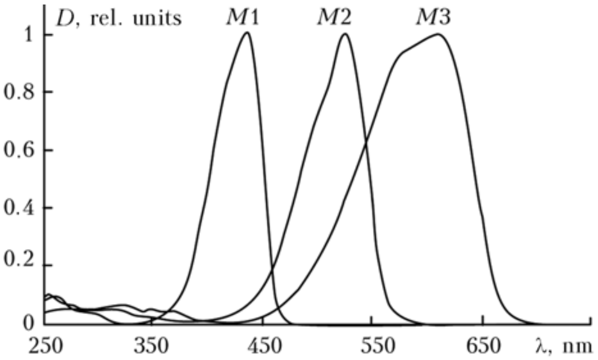


Fig. 2. Linear absorption spectra of merocyanines.

Thus, Nd:YAG radiation (1064 nm) excitation of *M*1 is possible only due to three-photon absorption.

Elongation of the polymethine chain results in bathochromic shift of absorption bands from 435 nm for *M*1 to 611 nm for *M*3 and the enhancement of fluorescence quantum efficiency from 0.37 to 6.1%. The *M*2 dye is two-photon excited by the 1064 nm radiation virtually to the maximum of long-wavelength absorption band while *M*3 – to the short-wave edge of long-wavelength absorption band.

To determine TPA cross section of merocyanine solutions, the fluorescent method of two-quantum standard, worked out in Refs. 19 and 20, has been used. An advantage of the method is in absence of severe requirements for spatial and temporal distribution of energy parameters of a laser beam, which allows the use of beams with non-Gaussian distribution without complicated mathematical apparatus. But the use of this method requires a thorough choice of a standard[21] and validation of the quadratic dependence of the intensity of two-photon excited fluorescence (TPEF) on the intensity of exciting radiation.

The block-diagram of the setup for TPEF study and TPA cross section determination by the method of standard at Nd:YAG laser nanosecond radiation excitation is shown in Fig. 3.

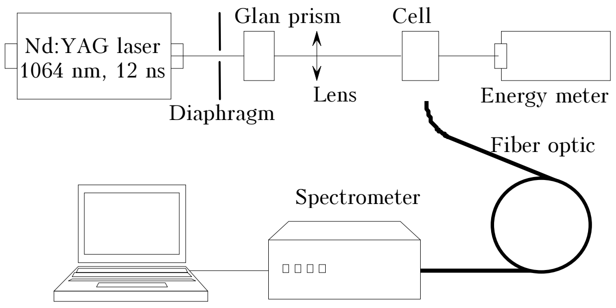


Fig. 3. Experimental setup.

Parameters of the setup were considered earlier[22,23] in detail. Here, a precision Glan prism (Thorlabs) is used to measure the intensity of exciting radiation instead of calibrated light filters, used in Ref. 23. This allows smooth intensity variation and improved measurement accuracy.

Similar calibrated cells with the standard and investigated solutions were placed at the setup in turn (so-called single-beam technique), which provides for a similar geometry of excitation and radiation accumulation. The TPA cross section of the investigated compound $\delta_x^{(2)}$ was calculated according to the equation

$$\delta_x^{(2)} = \frac{\delta_{\mathrm{st}}^{(2)} \eta_{\mathrm{st}} C_{\mathrm{st}} I_x^{\mathrm{TPEF}}}{\eta_x C_x I_{\mathrm{st}}^{\mathrm{TPEF}}}, \qquad (1)$$

where $\delta_{\mathrm{st}}^{(2)}$ is the TPA cross section of the standard; η_{st} and η_x are the fluorescence quantum efficiencies; C_{st} and C_x are the molar concentrations; $I_{\mathrm{st}}^{\mathrm{TPEF}}$ and I_x^{TPEF} are the fluorescence intensities of standard and investigated solutions, respectively.

Ethanol solution of Rhodamine 6G with the known TPA cross section and fluorescence quantum efficiency[24] was chosen as a standard.

2. Two-photon absorption investigation results

Figure 4 shows TPEF spectra of ethanol solutions of *M*2 and *M*3 ($C = 10^{-4}$ M). The shape and positions of the maxima of TPEF bands correspond to spectra of usual fluorescence at linear excitation (see the Table). For *M*1 dye, fluorescence in Nd:YAG laser excitation has not been recorded.

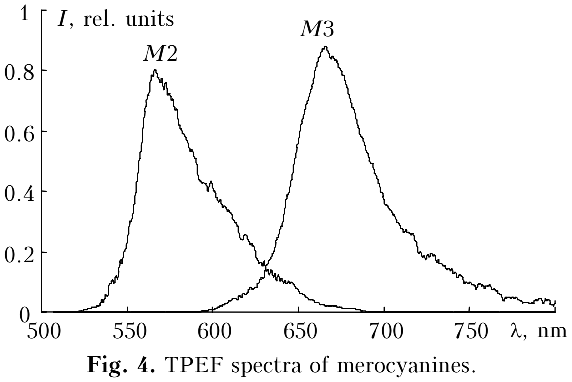
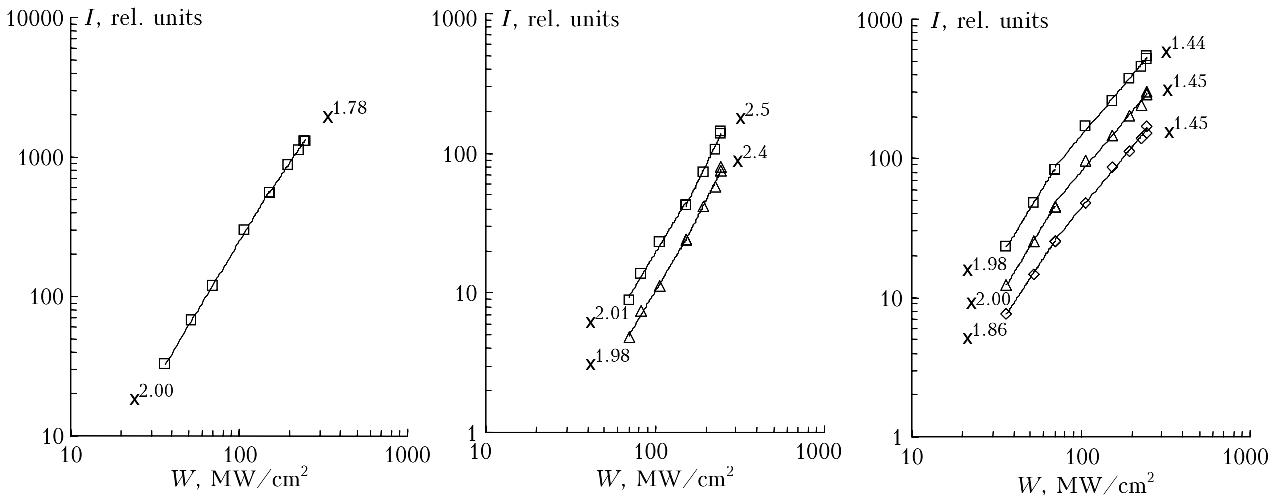


Fig. 4. TPEF spectra of merocyanines.

The dependence of TPEF intensity on exciting radiation power density is shown in Fig. 5. The quadratic dependence of fluorescence intensity of the standard Rhodamine 6G solution is observed up to about 100-MW/cm^2 radiation power density.

At larger radiation power densities, excitation is observed due to quenching in powerful light field.[25] Quadratic dependences for *M*2 and *M*3 dyes are observed up to power densities of 100 and 70 MW/cm^2, respectively.



a *b* *c*

Fig. 5. TPEF intensity I as a function of exciting radiation power density W for Rhodamine 6G (*a*) ($C = 10^{-4}$ M); *M*2 (*b*) ($C = 4$ (the upper curve) and 2 (the lower curve) $\cdot\ 10^{-4}$ M); and *M*3 ($C = 2.6$ (the upper curve), 1.3 (the middle curve), and 0.65 (the lower curve) $\cdot\ 10^{-4}$ M).

Thus, in the considered experimental conditions, the TPA cross sections of merocyanines can be determined by the method of double-quantum standard up to radiation power densities of about 70 MW/cm^2.

The measured TPA cross sections are given in the Table: it is equal to (25 ± 5) GM for *M*2 and to (115 ± 15) GM for *M*3 at a wavelength of 1064 nm, which is 2- and 9-time higher than the TPA cross section of Rhodamine 6G at this wavelength, respectively. Using the approximate geometric model,[26] connecting the sizes of delocalized π-electron clouds of a molecule with TPA cross section, their average radii can be calculated:

$$\langle R\rangle = \sqrt[3]{\frac{3\,\langle\delta^{(2)}\rangle\, c}{2\pi\,\langle\sigma_{\lambda/2}\rangle}}, \qquad (2)$$

where c is the speed of light in vacuum; $\sigma_{\lambda/2}$ is the cross section of single-photon absorption at half-length of excitation wave (in our case, 532 nm). The calculation results $\langle R\rangle$ are given in the Table. However, a significant increase of sizes of a π-electron cloud of *M*3 molecule in comparison with *M*2, as is follows from Eq. (2), does not agree with geometrical proportions of these molecules.

The standard dye Rhodamine 6G and *M*2 dye are excited into the maximum of long-wavelength absorption band, while *M*3 – to the long-wavelength edge of the band. The "blue" shift of the TPA maximum relative to the spectra of single-photon absorption is observed for many classes of organic dyes,[27–29] i.e., the TPA maximum within one transition corresponds to transition to one of higher vibrational sublevels of electronic excited state.

Though there are no corresponding data for merocyanine dyes, one can suppose that a significant increase of TPA cross sections of *M*3 relative to *M*2 is caused not only by an increase in size of π-electron cloud of the molecule, participating in TPA, but also the "blue" shift (is not taken into account in geometrical model of TPA) for the given class of molecules, which is related to different selection rules for single- and two-photon transitions.

When the radiation power density is higher than 70 MW/cm^2 for *M*3 dye and Rhodamine 6G, the TPEF intensity saturation is observed. The dependence for *M*2 is another. When the exciting radiation power density is higher than 100 MW/cm^2, the TPEF intensity dependence rises more sharp (the slope is 2.4÷2.5), which can well be due to the presence of nonlinear absorption of a higher order, e.g., three-photon, at a wavelength of 1064 nm.

Study of multiphoton absorption at simultaneous presence and competition of different nonlinear processes is of essential interest, but the use radiation with a pulse length longer than 10 ns for excitation does not allow the study in a wide intensity range of exciting radiation due to damage of optical elements. In future, it is reasonable to study the nonlinear absorption by *M*2 at excitation by pico- and femtosecond laser radiation.

Conclusion

The two-photon excited fluorescence of *M*2 and *M*3 dyes in Nd:YAG laser nanosecond excitation was studied for the first time. The TPA cross sections of the dyes were determined as equal to (25 ± 5) and (115 ± 15) GM, respectively. It was revealed, that three-photon absorption for *M2* dye appears along with two-photon one at exciting radiation power density higher than 100 MW/cm^2. It was suggested that "blue" shift of TPA spectra relative to single-photon ones appears for the molecules under study in long-wavelength absorption band excitation.

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