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7-Dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins: two-photon absorption in solution and in polymer film

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Experimental part

7-Dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins **1a-c** and **2** have been prepared as reported [S1].

A solution of polymethylmethacrylate (PMMA) in a toluene-ethyl acetate mixture (1:1, v/v) containing pyrazoline **1a-c** or **2**, lactone form of Rhodamine B and hexachloroethane (1:1:30, w/w/w, respectively), was poured into a horizontally placed Petri dish. Concentrations of the compounds **1a-c** and **2** in PMMA films were calculated with use of mass ratios and density of polymer film. The solvent was then evaporated. The film (thickness around 80-100 μm) was then removed from the dish before subjecting to irradiation.

Electronic absorption spectra were recorded on an APELPD_303UV spectrometer and fluorescent spectra – on Cary Eclipse (Varian) spectrofluorimeter.

Pulsed Yb^3–doped fiber laser which generated pulses with duration of 300 fs and repetition rate of 1 kHz on wavelength of 1060 nm was used in experimental Z-scan setup [S2] to measure the optical nonlinear characteristics of our samples. The Z-scan technique was carried out with open aperture scheme for recording only nonlinear absorption [S3]. The sample with solute in 2-mm-thick cell or photosensitive polymer film was able to move along the laser beam (Z-coordinate) near the focusing region. The focal length of the lens was 12 cm. The radius of the waist r_0 at the e^{-2} level in the focusing point was 26 μm. The peak intensity of the incident radiation in the waist point can be calculated from the expression:

$$I_0 \approx \frac{E}{\pi r_0^2 \times \tau} \quad (1)$$

where E is the energy of the incident pulse; τ is the duration of the laser pulse (full width at half maximum of the profile). When the sample moved along the Z-coordinate, the incident intensity on the sample gradually changed according to:

$$I(z) = \frac{I_0}{1 + \left(z / z_0 \right)^2} \quad (2)$$

where the Rayleigh length $z_0=\pi r_0^2/\lambda$ and λ is the laser wavelength. The experiments were performed with incident pulse energy of 800 nJ, while the peak intensity in the waist of the probe beam reached 120 GW cm^{-2}. The sample transmittance was measured as the ratio of average power passing through the sample and incident on it. In the waist zone, where the maximum peak intensity of the incident radiation is reached, a decrease in the sample transmittance was observed, which is associated with nonlinear two-photon absorption. The experimental Z-scan curves for normalized transmittance of the compounds **1b**, **1c** and **2** in acetone are shown in Figure S1 from which the modulation depths ΔT for each sample were found. The Z-scan curves for the PMMA films with compounds **1a-c**, **2** are shown in Figure S2.

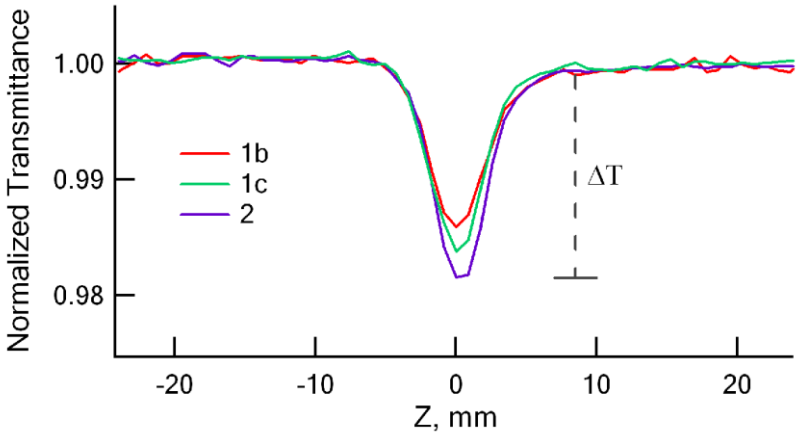

Figure S1 The normalized transmittance Z-scan curves of the compounds **1b, 1c**, **2** in acetone for incident pulse energy of 800 nJ. $\Delta T\approx0.018$ is the modulation depth for compound **2**.

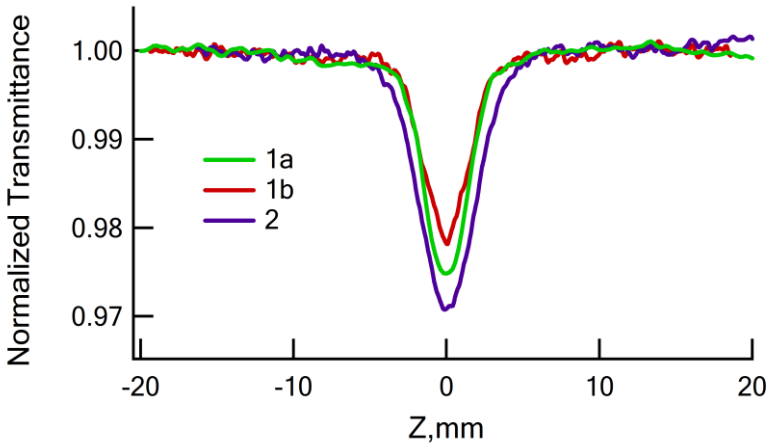

Figure S2 The normalized transmittance Z-scan curves for the PMMA films with compounds **1a, 1b**, **2** for incident pulse energy of 800 nJ.

Then, the TPA coefficient β was calculated using the equation:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L} \quad (3)$$

where L is the thickness of the cell. The TPA cross section for each sample in units of $cm^4 \cdot s$ per photon was found from:

$$\delta_{TPA} = \frac{\beta \times h\nu}{N_a \times 10^{-3} C} \quad (4)$$

where N_a is the Avogadro constant, C is the sample concentration (mol dm^{-3}), h is the Planck constant and ν is the laser frequency [S4].

Spectra

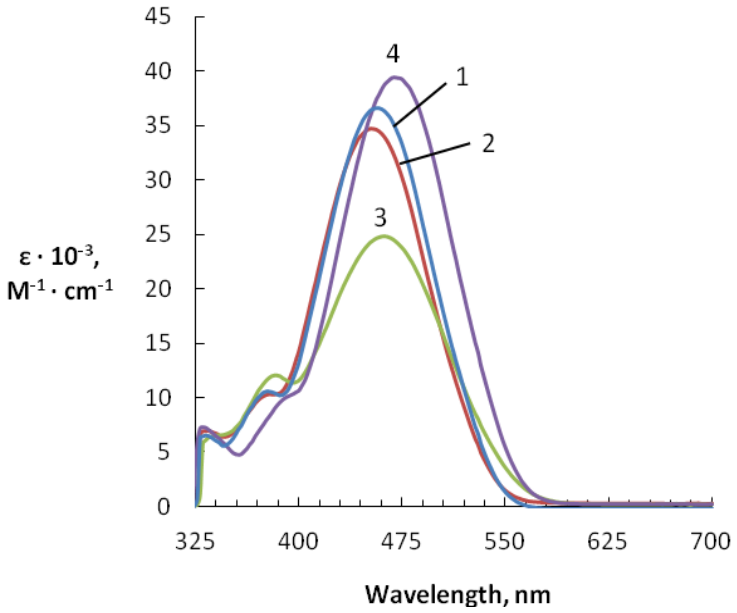

Figure S3 Electronic absorption spectra of compounds **1a** (*1*), **1b** (*2*), **1c** (*3*) and **2** (*4*) in acetone.

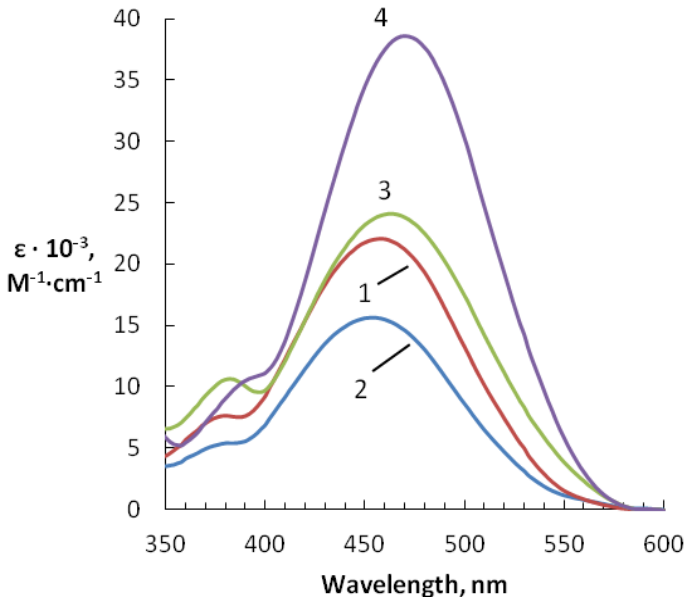

Figure S4 Electronic absorption spectra of compounds **1a** (*1*), **1b** (*2*), **1c** (*3*) and **2** (*4*) in PMMA film.

References

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[S3] D. V. Khudyakov, A. A. Borodkin, A. S. Lobach, A. V. Ryzhkov and S. K. Vartapetov, *Appl. Opt.*, 2013, **52**, 150.

[S4] M. Shigeiwa, S. Maeda, H. Gorohmaru, S. Imamura and M. Irie, *Mol. Cryst. Liq. Cryst.*, 2005, **430**, 173.