

Experimental

Two-photon absorption (TPA) spectra of the compounds studied were measured using TPA photoluminescence (TPA PL) spectroscopy [1]. Fluorescence was excited in samples via TPA by directing tightly collimated ($\sim 120 \mu$) high-intensity laser beam on a sample (See Fig. 1). The emission from the sample was collected at 90° angle by a high numerical aperture lens and directed to a spectrometer's entrance slit. The radiation dispersed by the spectrometer was detected by a thermoelectrically cooled charge coupled device (CCD) camera (Roper Scientific Spec10:100B/TE). Excitation pulses with typical duration 90 fs and energy ~ 6 nanoJoules (nJ) within the spectral range 690 - 1000 nm were produced by the modelocked laser (Spectraphysics Tsunami) with repetition rate of 82MHz. For the spectral range 600-700 nm, femtosecond optical parametric amplifier (OPA) has been used. Signal output of the OPA (Spectraphysics OPA-800C) was upconverted into the visible range of spectrum using the second harmonic generation (SHG) process in β -barium borate crystal. SHG process yielded ~ 120 fs pulses with energy $\leq 30 \mu$ J and repetition rate 1 kHz. Neutral density filter wheel has been used to attenuate the energy of the laser pulses down to desirable level.

According to [1], the spectrally integrated intensity of the fluorescence excited via TPA process this configuration can be determined by the following expression:

$$I = A\eta \int_{-\infty}^{\infty} \frac{I_0^2(t)\delta cl}{1 + I_0(t)\delta cl} dt. \quad (1)$$

Here, δ is the TPA cross-section, c – concentration of the TPA-active molecules, l – interaction length, and η is the fluorescence efficiency. Factor A includes all constant parameters specific for a given experimental setup (Geometric factors, spectrometer and detector efficiencies, *etc.*). Function $I_0(t)$ describes temporal profile of the excitation pulse. In case of the weak excitation regime, one can assume that $I_0(t)\delta nl \ll 1$. Then expression (1) takes form:

$$I = A\eta\delta cl \int_{-\infty}^{\infty} I_0^2(t)dt = B\eta\delta clP^2, \quad (2)$$

P and B are excitation light power and a constant, respectively. Since B is difficult to determine, we employed relative measurements technique using reference sample with known TPA spectrum. In this case, the ratio of the integrated PL intensities for the reference and studied samples can be expressed as:

$$\frac{I}{I_{ref}} = \frac{\eta\delta c}{\eta_{ref}\delta_{ref}c_{ref}} \frac{P^2}{P_{ref}^2} K^{-1}. \quad (3)$$

Here, the index *ref* denotes values related to the reference measurements. Also, we assume that *all* experimental parameters were identical during the whole series of measurements, except the power of the pump radiation P and sample specific parameters η , δ , and c . K is a correction factor taking into account the difference in refractive indices of the studied and the reference material (solvent). It depends on the excitation beam geometry. In our case of nearly-collimated beams $K = n^2 / n_{ref}^2$. From (3), one can easily find the TPA cross-section of the compound studied:

$$\delta = \frac{\eta_{ref}\delta_{ref}c_{ref}}{\eta c} \frac{P_{ref}^2}{P^2} \frac{I}{I_{ref}} K. \quad (4)$$

As one can see from (4), both studied and reference samples must be characterized precisely in order to determine δ with descent accuracy. In our studies, molar concentrations of both compounds were determined from optical absorption spectra, using molar absorptivity values supplied by compound

manufacturer or obtained from volumetric measurements. In all measurements, concentration of material did not exceed 10^{-4} M, in order to avoid selfquenching of emission. Fluorescence quantum yields have been verified using referenceless technique described in [2] and adopted for the liquid phase measurements. It is worth to mention, that both absorption and emission spectra of samples had been monitored during the whole series of measurements. Being properly degassed, our samples did not exhibit any sign of degradation within the scope of the experiment.

As reference materials, we used three laser dyes: Coumarin 503 (aka Coumarin 307, purchased from Exciton Inc.), Fluorescein (purchased from Acros Inc.), and Rhodamine 610 (aka Rhodamine B, purchased from Exciton Inc.). Coumarin 503 and Rhodamine 610 were dispersed in methanol, and fluorescein was dissolved in water with addition of NaOH (pH=11). 10^{-4} M solution of *p*-bis(*o*-methylstyryl)benzene in cyclohexane was used as a reference for measurements in the spectral range 600-700 nm .TPA spectra in the spectral interval of interest were taken from the literature [1, 4]. Interestingly, previously reported values of the fluorescence quantum yield for these compounds (especially for Coumarin 503) vary significantly (see, e.g. [5-7]). Being strongly dependent on the solution parameters (dye concentration, solvent properties, purity, etc), uncertainty of emission efficiency value for reference dyes and studied materials could be the main source of error in the TPA cross-section measurements. This prompted us to measure the emission yield for all materials used in our experiments, using solutions in which TPA PL measurements were actually done.

In order to use equation (3), TPA PL studies were performed in low excitation regime. This was verified by measuring fluorescence intensity pump dependence. In all cases, it was very close to pure quadratic function. In its turn, this indicates that fluorescence has not been excited via regular single-photon absorption and what we have measured is a pure non-linear process. Using setup shown in Fig .1, we collected TPA PL spectra at different excitation wavelengths. In all cases, they match single-photon fluorescence spectra. This proves that both linear and non-linear emissions originate from the same excited energy state and quantum yield is identical for multi- and single-photon excited fluorescence. The recorded spectra were integrated numerically and resulting values were substituted in formula (3) along with the excitation power. The latter values were measured using thermopile optical power meter (Newport-815C).

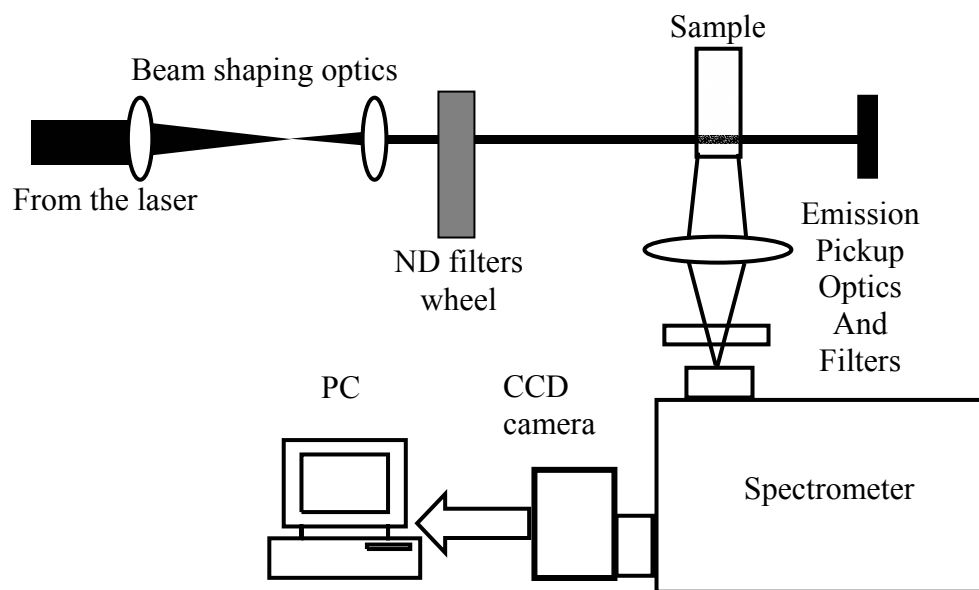


Figure 1. Experimental setup for the TPA cross-section measurements.

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