# Dramatic Enhancement of Intrinsic Two-Photon Absorption in a Conjugated Porphyrin Dimer

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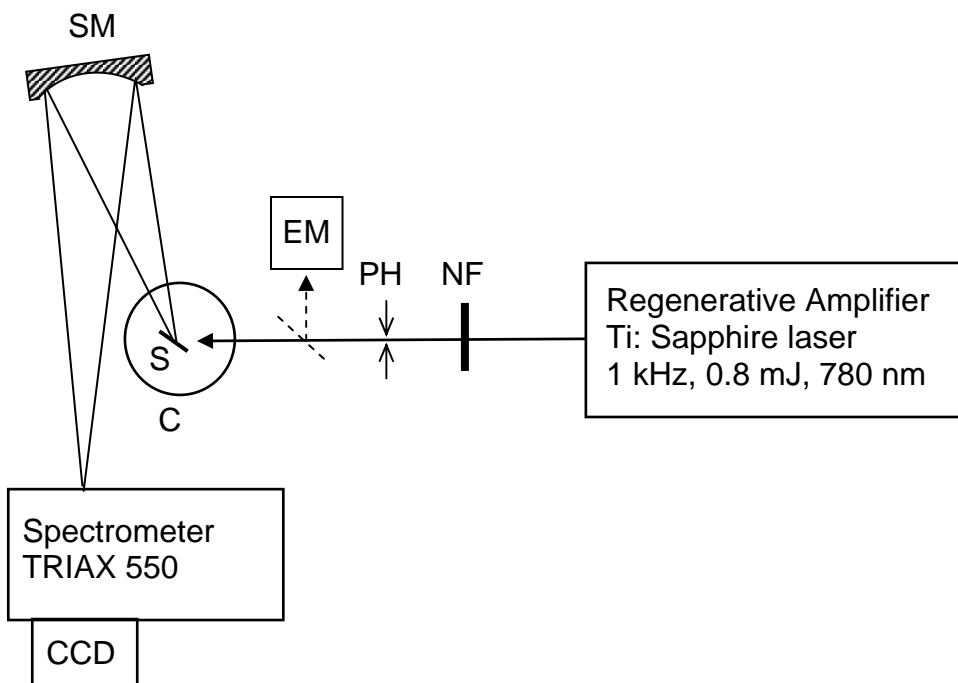
**Experimental Setup:**



**Fig. 1** Experimental setup. NF – variable neutral filter attenuator, PH – pinhole, EM – laser pulse energy meter, C – regulated temperature cryostat, S – sample, SM – spherical mirror.

Fig. 1 presents our experimental setup. The laser system comprised a Ti:sapphire regenerative amplifier (CPA-1000, Clark, MXR), which was operated at 1 kHz repetition rate and produced 150-fs duration pulses (FWHM) of 0.8 mJ energy per pulse at wavelength $\lambda = 780$ nm. First ($\lambda = 780$ nm) and second ($\lambda = 390$ nm) harmonic of the amplifier were used for two- and one-photon excitation in two-photon cross section measurements (see below for details). Neutral filter with variable optical density was used to adjust the power of the excitation light. The fluorescence was collected by the

spherical mirror ($f$ = 50 cm) and focused on the entrance slit of the Jobin Yvon/Spex TRIAX spectrometer. The resulting signal was measured by a liquid nitrogen cooled CCD (CCD-3000, Jobin Yvon). The pinhole in front of the sample assured that the radius of the laser beam on the sample was always the same, which is particularly important for the TPA experiments because the absorption efficiency depends on the square of the laser light power density. Absorption spectra were measured by Lambda 900 Perkin-Elmer spectrophotometer. Low temperature measurements were carried out on the polyvinylbutyral PVB film doped with the porphyrin molecules in an optical helium cryostat (Kiev, Ukraine). The cryostat control unit allowed to change and to stabilize the temperature with accuracy $\pm$ 1 K.
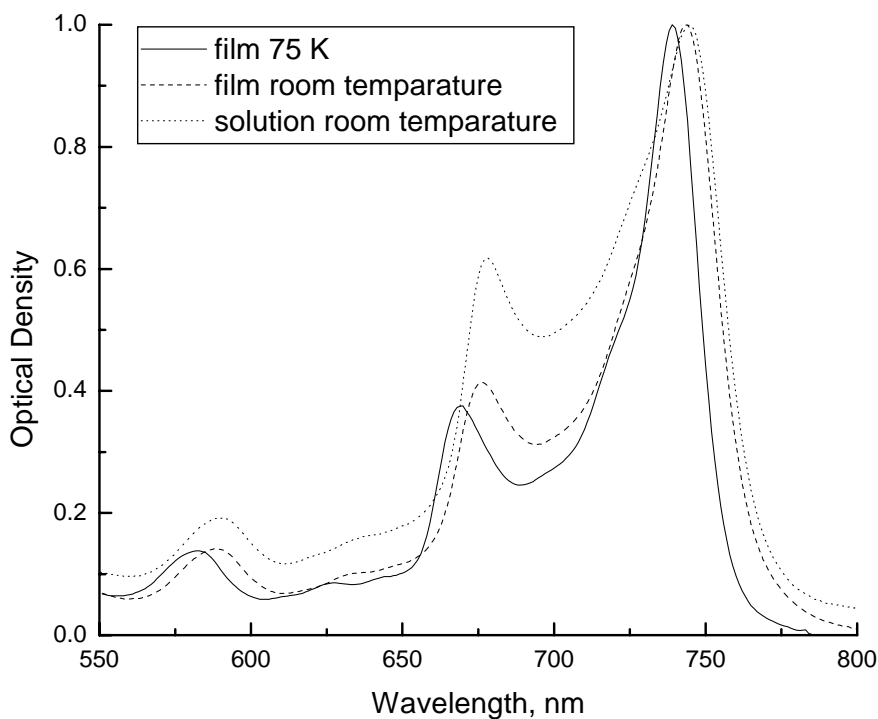
**Sample Preparation**



**Fig. 2** Linear absorption spectra of the dimer: (solid) in PVB film at 75 K; (dash) in PVB film at room temperature; (dot) in dichloromethane-pyridine (95:5) solution at room temperature.

The synthesis and characterization of monomer and dimer were described in [1,2]. Two-photon cross section measurements were performed on monomer and dimer molecules doped into PVB films. The samples were prepared by mixing a dichloromethane-pyridine (95:5) solution of dye with dichloromethane solution of PVB powder (Aldrich) and casting the mixture on a glass substrate overnight. The resulting films were removed from the glass substrate after evaporation of the dichloromethane and pyridine. The concentration of porphyrin molecules in the film is ~ $5 \cdot 10^{-4}$ M. Linear absorption spectra of monomer and dimer (Fig. 2) show only minor changes upon transition from the solvent to the film. The consecutive lowering of the temperature of the PVB film doped with dimer also results only in some minor changes.

**Two-Photon Cross Section Measurement:**

For the two-photon cross section measurements we use a method consisting in comparison of the efficiency of one- and two-photon excitation of fluorescence. The important advantage of this method is that it is absolute by its nature, i.e. we do not need to use a reference compound. The method was first proposed by M. D. Galanin and Z. A. Chizhikova [3] and latter used with some modifications in a number of studies [4,5,6,7]. Below we presents the theoretical description and experimental implementation of the method that we use. We checked the validity of this method by measuring two-photon cross section of Rhodamine B in methanol at excitation wavelength $\lambda_{ex}$ = 782 nm. The resulting value $\sigma_2$ = 105 GM is in good agreement with literature data [8].

*Theoretical description*

Consider a homogeneous two-photon absorbing medium of length $L$ and molecular density $n$ irradiated by a laser pulse of intensity $I_0(r,t)$, were $r$ is the distance from the geometrical center of the pulse to the observation point, and $t$ is the time. The intensity just after the sample will be

$$I(r,t) = \frac{I_0(r,t)}{1 + \sigma_2 nLI_0(r,t)}. \tag{1}$$

If the TPA is weak, i.e. if $\sigma_2 nLI_0(r,t) \ll 1$, which is the case in our experiments, then

$$I(r,t) \simeq I_0(r,t)(1 - \sigma_2 nLI_0(r,t)). \tag{2}$$

The total energy absorbed by the medium from the pulse can be found by integrating over the pulse duration and its cross section:

$$\Delta E_{TPA} = \sigma_2 nL \int_0^\infty 2\pi r dr \int_{-\infty}^\infty I_0^2(r,t)dt . \tag{3}$$

In our experiment we used a pinhole of radius, $r_0 < r_L$, in front of the sample ($r_L$ is the radius of the laser beam), and in a good approximation we can neglect variation of the intensity within $r$. In the time domain, the pulse intensity has nearly Gaussian shape:

$$I_0(r,t) = I_{0i} Exp[-\frac{4t^2 ln2}{\tau^2}] , \tag{4}$$

where $I_{0i}$ is the pulse intensity at its maximum, $\tau$ is a time duration of the pulse (FWHM). Then,

$$\Delta E_{TPA} = \frac{\sigma_2 nL \pi^{3/2} r_0^2 I_{oi}^2 \tau}{\sqrt{8ln2}} . \tag{5}$$

Experimentally, one measures an average intensity of the excitation light, but not the peak intensity. To make the transition to the average intensity, we initially derive expression for the total energy of the laser pulse used for two-photon excitation in terms of the peak intensity.

$$E_{TPA} = \int_0^{r_0} 2\pi r dr \int_{-\infty}^\infty dt I_{0i} Exp[-\frac{4t^2 ln2}{\tau^2}] = \frac{\pi^{3/2} \tau r_0^2 I_{oi}}{2\sqrt{ln2}} . \tag{6}$$

Then the following expression for the absorbed energy can be obtained:

$$\Delta E_{TPA} = \frac{\sqrt{2ln2} \sigma_2 nL E_{iTPA}^2}{\pi^{3/2} \tau r_0^2} . \tag{7}$$

Since the total energy of one pulse is equal to the average intensity of the excitation light divided by the repetition rate of the laser the expression (7) can be rewritten in the following form:

$$\Delta E_{TPA} = \frac{\sqrt{2ln2} \sigma_2 nL \langle I_{TPA} \rangle^2}{\pi^{3/2} \tau^3 r_0^2 g^2} , \tag{8}$$

where $\langle I_{TPA} \rangle$ is the average intensity of the laser light used for two-photon excitation and $g$ is the repetition rate of the laser. The number of molecules in a sample excited during one second is:

$$N_{TPA} = \frac{\Delta E_{TPA} g}{2h\nu_{TPA}} = \frac{\sqrt{2Ln2}\sigma_2 nL\langle I_{TPA} \rangle^2}{2h\nu_{TPA}\pi^{3/2}\tau r_0^2 g}, \tag{9}$$

where $h$ is the Plank constant, $\nu_{TPA}$ is the frequency of the two-photon excitation light. Note, that two photons are required to excite one molecule. In the case of one-photon excitation, the energy absorbed by the same sample from one pulse is:

$$\Delta E_{OPA} = E_{OPA}(1 - exp[-\sigma_1 nL]) \simeq E_{OPA}\sigma_1 nL, \tag{10}$$

where $E_{OPA}$ is the energy of laser pulse and $\sigma_1$ is the one-photon (linear) absorption cross-section. The number of excited molecules excited during one second is:

$$N_{OPA} = \frac{\Delta E_{OPA} g}{h\nu_{OPA}} = \frac{\sigma_1 nL E_{OPA} g}{h\nu_{OPA}} = \frac{\sigma_1 nL \langle I_{OPA} \rangle}{h\nu_{OPA}}, \tag{11}$$

where $\nu_{OPA}$ and $\langle I_{OPA} \rangle$ are the frequency and average intensity of the laser light used for one-photon excitation. If the geometry of one- and two-photon excitation is the same, then the corresponding fluorescence intensity, $F_{TPA}$ and $F_{OPA}$, should be proportional to the number of excited molecules in each case. We also suppose that the quantum yield of fluorescence does not depend on the mode of excitation. The ratio of fluorescence intensities obtained upon two- and one-photon excitation is:

$$\frac{F_{TPA}}{F_{OPA}} = \frac{\sqrt{2\ln 2}\sigma_2 \langle I_{TPA} \rangle^2 \nu_{OPA}}{2\nu_{OPA}\pi^{3/2}g\tau r_0^2 \sigma_1 \langle I_{OPA} \rangle}, \tag{12}$$

which leads to the final expression for TPA cross section:

$$\sigma_2 = \sqrt{\frac{2\pi^3}{\ln(2)}} \frac{F_{TPA}\nu_{TPA}g\tau r_0^2 \langle I_{OPA} \rangle}{F_{OPA}\nu_{OPA} \langle I_{TPA} \rangle^2} \sigma_1. \tag{13}$$

It was supposed everywhere that the same sample was used for both one- and two-photon excitation. If the two-photon excited fluorescence is too weak, then one can improve signal to noise ratio by increasing the concentration. In this case expression A1.13 turns into the following:

$$\sigma_2(cm^4 s/W) = \sqrt{\frac{2\pi^3}{\ln(2)}} \frac{F_{TPA} \nu_{TPA} g \tau r_0^2 \langle I_{OPA} \rangle}{p F_{OPA} \nu_{OPA} \langle I_{TPA} \rangle^2} \sigma_1, \tag{14}$$

where $p$ is the coefficient equal to the ratio of the optical density of the sample used for two-photon excitation at some wavelength to the optical density of the sample used for one-photon sample at the same wavelength. The two-photon cross section is typically quoted with intensities measured in $cm^4 s / photon$. To obtain TPA cross section in this units, expression (14) should be multiplied by an energy of one excitation photon $h\nu_{TPA}$:

$$\sigma_2(cm^4 s / photon) = \sqrt{\frac{2\pi^3}{\ln(2)}} \frac{F_{TPA} h\nu_{TPA}^2 g \tau r_0^2 \langle I_{OPA} \rangle}{p F_{OPA} \nu_{OPA} \langle I_{TPA} \rangle^2} \sigma_1. \tag{15}$$

*Experimental Implementation*

The following experimental procedure is followed. Initially a sample is excited by means of two-photon excitation with Ti:sapphire regenerative amplifier. The diameter of the laser beam is about 1 cm. A 1.6-mm pinhole is used just in front of the sample. The pinhole cuts out only the central part of the beam, which gives nearly constant intensity distribution over the whole beam cross section. In this case the only parameters of the laser excitation light that have to be determined are excitation wavelength, pulse duration (FWHM) (we suppose that temporal profile of the laser pulses are Gaussian), average intensity of the excitation light, repetition rate of the laser pulses, and intensity of the excited fluorescence.

The next step consists in one-photon excitation of the sample in the same geometry. The optical density of the samples used for one-photon excitation is less than 0.1 at the one-photon excitation wavelength and provides for constant excitation along the whole length of the sample. Second harmonic of Ti:sapphire regenerative amplifier is used ($\lambda_{ex} \sim 390$ nm) for one-photon excitation. The fundamental wavelength of the amplifier is cut off from the excitation beam by UV-filter. Note, that the one-photon excitation of the sample is possible by any laser source because quantum yield of fluorescence of organic molecules does not depend on excitation wavelength. We do not have to reach exactly the same electronic transition that was populated in two-photon excitation. The only parameters that one has to know in case of one-photon excitation are excitation laser

wavelength, average intensity of excitation light, one-photon extinction coefficient at the one-photon excitation wavelength, and fluorescence intensity.

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