

## LETTER TO THE EDITOR

## Excitation density and photoluminescence studies of polyfluorene excited by two-photon absorption

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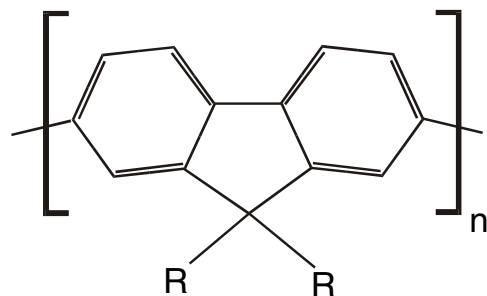
### Abstract

Highly efficient photoluminescent organic materials are excellent alternatives to inorganic crystals for non-linear optics applications. One candidate, polyfluorene with an absorption onset of about 3 eV, was studied in this paper by means of transmission and photoluminescence measurements with an ultra-fast laser source at 1.54 eV with 250 fs pulses. We studied the two-photon absorption and emission properties of polyfluorene as a function of the concentration in toluene solvent at 300 K. It is demonstrated that both the two-photon absorption and the associated emission exhibit the same saturation intensity, which does not depend on the concentration. It is shown that although we achieve excitation rates of 1% to 10% of all repetition units, the excited units do not interfere before luminescent recombination occurs.

Organic materials have become very attractive for applications in light emitting devices for several years [1–3]. Not all of the materials' properties are fully understood yet, especially excited species dissociation and transport dynamics. However, recent research efforts have enhanced the theoretical understanding and have thus improved processing techniques [4–7].

In order to maximize the efficiencies of the aforementioned devices, in recent years, materials were synthesized with the focus high photoluminescence quantum yields, most notably polyfluorene (PFO) [8–10]. Due to its specific structure of having a repetition unit of two benzene rings that are planarized by a ladder type bond, but rotationally free with respect to adjacent units, its electronic character can be varied in the bulk as has been noted that symmetries can be broken or established by simple film forming techniques [11, 12] or similarly by using microcavities [13]. With this important property, PFO is also a very interesting candidate for any non-linear optics (NLO) application, since broken symmetries are a prerequisite for all even order effects to be relevant. The centrosymmetry in PFO is broken due to the 'bridged' structure, as seen in figure 1. Additionally, side groups influence the electronic clouds on the backbone as has been shown theoretically in [14]. Thus, the lack

of symmetry can be fine tuned by exchange of the sidegroups. Polymers can be tuned to also exhibit a higher third order NLO coefficient [15].



**Figure 1.** Structure of the polyfluorene used for this paper. The exact name is (Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl), the abbreviation is PF2/6.

Thus, there is a strong necessity to determine the two-photon absorption (TPA) and the associated luminescence (TPPL) from electron–hole pairs created by TPA, in order to characterize the NLO and determine the applicability. One possible application for this transparent (onset of optical absorption at 3 eV) deep blue emitting material would be a translucent screen that could be written via TPA with a red/NIR laser.

Additionally, recombination times in polymers are found to be in the range of tens—for high intensity experiments—to a thousand picoseconds [16, 17], making them eligible for some NLO anti-Stokes applications [18].

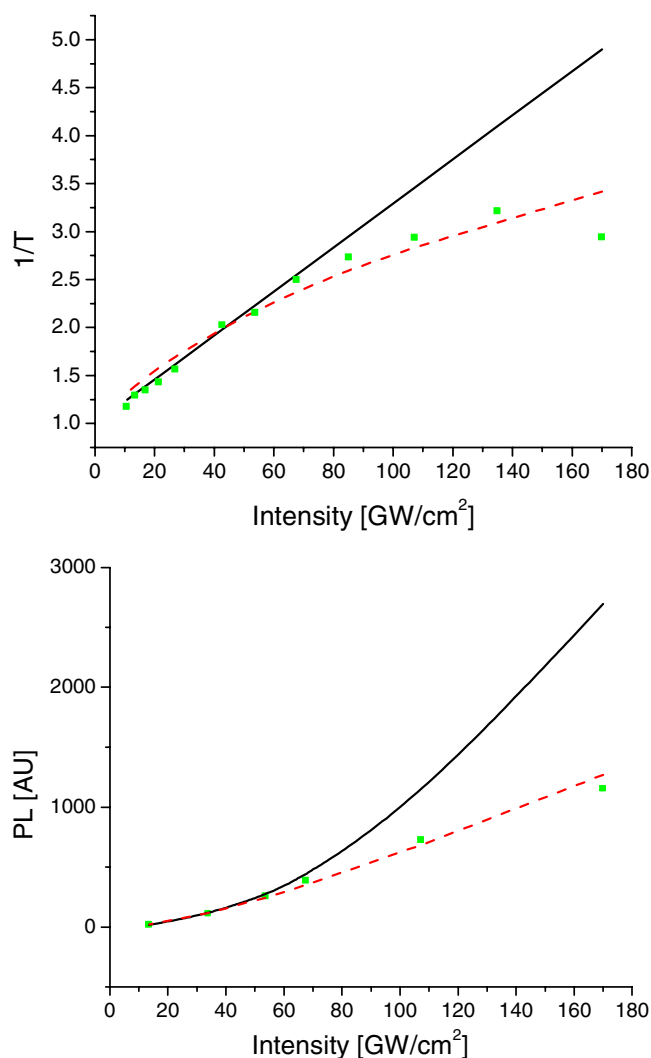
In order to determine the suitability for any application that requires the recombination of electron–hole pairs created by TPA, the TPPL has to be characterized—especially in the region where the TPPL is purely a quadratic function of the incident intensity. The threshold intensity of the excitation above which the dependence is sub-quadratic is called saturation intensity. It is important to know how the saturation intensity  $I_{\text{sat}}$  depends on the concentration of the material in solution as well.

With the availability of ultrashort, high power laser systems, two-photon absorption in particular, or anti-Stokes transitions in general, have been studied in more detail than with previously available longer pulses of lower peak intensities. During the interaction of the sample with ultrashort pulses the system cannot relax into thermal equilibrium during the excitation process—thus it is possible to study the dynamics of the system far from equilibrium. When the repetition rate of the laser pulses is sufficiently low, at least smaller than one GHz, the system can return to the optical ground state for the recombination values cited above before the next laser pulse hits the sample. Finally, an excitation density of several hundred  $\text{GW cm}^{-2}$  in a 250 fs pulse and a repetition rate of 249 kHz correspond to a cw power of about one Watt. Combined with the weak absorption for two photon processes, the heating of the sample during the experiment is small.

In this letter we discuss the TPA and the TPPL of Poly (9,9-bis (2-ethylhexyl) fluorene-2,7-diyl) [PF2/6] in a toluene solvent. The two-photon absorption coefficient ( $\alpha_2^0$ ) has been measured as a function of the incident light intensity and the concentration of PF2/6 in solution. Also, the TPPL emission spectra have been recorded to observe possible changes in the spectral shape.

In order to study the possible systematic influences of the detectors in such a high excitation density measurement, the transmission was recorded first using an Ocean Optics (OOI) UV-VIS fiber optics spectrometer—slit width of 20  $\mu\text{m}$ , fiber with a diameter of 200  $\mu\text{m}$ , resolution on the order of one nanometer—and with a spectrally calibrated Oriel silicon photodiode—attached to a Keithley picoammeter. The TPPL emission spectra were recorded with the Ocean Optics Spectrometer. The excitation source was a Coherent argon-ion 30 W laser system

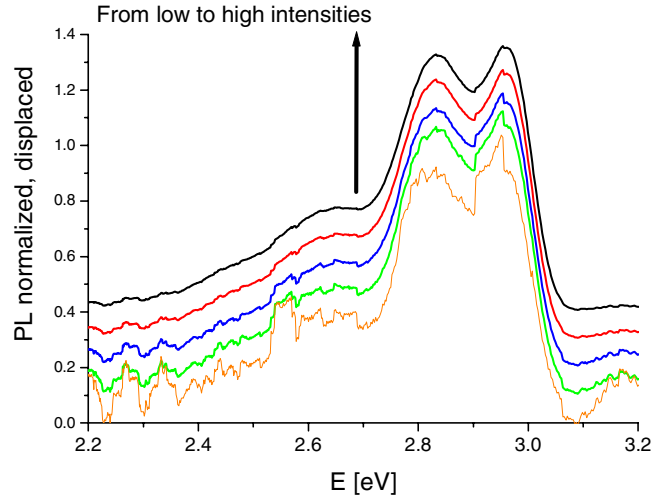
that pumped a ‘Mira’ femto-second titanium-sapphire oscillator and a ‘Rega’ amplifier. The resulting laser pulses were measured to have a pulse width of 250 fs, a repetition rate of 249 kHz, and a cw output power between 0.7 and 1.2 W. The photon energy was 1.54 eV, just exceeding half of the ‘optical gap’ energy of PF2/6, which is 3 eV. The beam had a diameter of about 100 microns near the focal point. Thus, the maximum laser power on the focal point per pulse was 180–240  $\text{GW cm}^{-2}$ . The laser beam was focused into the solution, and the detectors were set up in transmission for the TPA measurements, and off-axis,  $90^\circ$  to the side, for the TPPL measurements. Due to specific geometry used, the TPA and TPPL could be recorded



**Figure 2.** (a) Two-photon absorption of PF2/6 solution of  $0.4 \text{ mmol l}^{-1}$ . The squares represent the experiment, the solid line and the dashed line are fitted with equations (3) and (5) respectively. (b) The squares represent the experimental data of the photoluminescence emission due to the two-photon excitation. The solid curve depicts a general square dependence. The dashed curve represents the saturated square dependence, where the saturation intensity is chosen identically to the value for the dashed curve in 1(a).

at the same time, if the transmission was recorded by the silicon diode. For the transmission measurement the contribution of any other light source (stray light, TPPL) was negligible with respect to the transmitted laser line. All experiments were carried out at 300 K.

The TPA as a function of the incident light intensity measured with the OOI is shown in figure 2(a), the TPPL peak emission value in figure 2(b). The normalized TPPL emission spectra are shown in figure 3.



**Figure 3.** The two-photon excitation photo-luminescence: Comparison of the emission spectra for 5 different excitation intensities. From bottom to top: 19.5 GW cm<sup>-2</sup>, 50.0 GW cm<sup>-2</sup>, 77.6 GW cm<sup>-2</sup>, 97.7 GW cm<sup>-2</sup>, 155 GW cm<sup>-2</sup>, 245 GW cm<sup>-2</sup>. For clarity, the curves are displaced relatively to each other by 0.1. The spikes between 2.2 and 2.6 eV result from some laser light pollution.

In principle, the change in number of photons per length element for a two-photon process is described by the following equation:

$$\frac{dI}{dx} = -\alpha_2^0 I^2 \quad (1)$$

which leads to equation (2) assuming  $\alpha_2^0$  is not a function of the intensity:

$$\frac{1}{I_t} - \frac{1}{I_0} = \alpha_2^0 t \quad (2)$$

or:

$$\frac{1}{T} = \alpha_2^0 t I_0 + 1 \quad (3)$$

where  $T$  is the transmission,  $I_t$  is the transmitted intensity,  $I_0$  is the incident intensity, and  $t$  is the thickness of the glass cuvette.

This fit is depicted as a solid line in figure 2(a). It is seen that this fit represents the data very well up to a saturation intensity  $I_{\text{sat}}$ . At that point, the incident number of photons is high enough to remove a significant number of the ground state electrons in the highest occupied molecular orbital (HOMO) to induce a change in  $\alpha_2$ . Thus, the TPA coefficient cannot be assumed to remain constant throughout the measurement. A common approach is to assume the TPA coefficient depends hyperbolically on the incident intensity [19]:

$$\alpha_2 = \frac{\alpha_2^0}{1 + \frac{I}{I_{\text{sat}}}} \quad (4)$$

Substitution for the TPA coefficient from equation (4) in equation (1) and integration leads to:

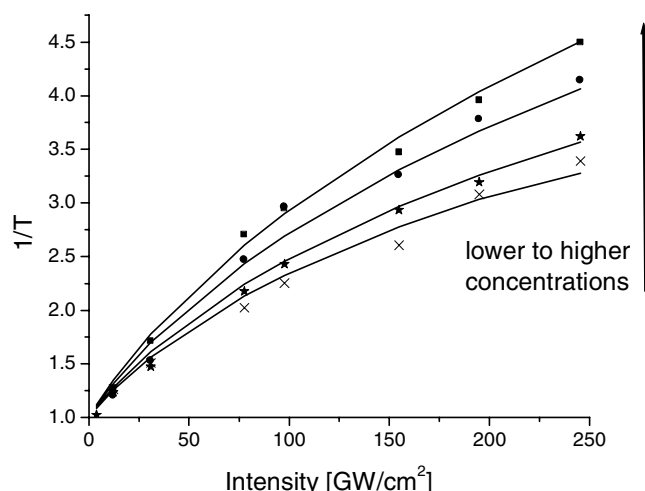
$$T = \frac{I_{sat}}{\ln(T)I_0 + \alpha_2^0 I_{sat} I_0 + I_{sat}} \quad (5)$$

a transcendental equation that converges very quickly using a self-consistent approach. This fit is represented as the dashed line in figure 2(a). The solid line in figure 2(b) represents a two-photon process (emission in this case) assuming that there is no saturation. Equation (6) with a constant  $\alpha_2^0$  governs this case. The dashed line in figure 2(b) represents a two-photon process with saturation, according equation (6) where  $\alpha_2$  is taken from equation (4).

$$I_{PL} \propto \alpha_2 I_{exc}^2 \quad (6)$$

In figures 2(a) and 2(b) the saturation occurs at the same point, further reinstating the assumption of beginning ground state depletion. From the comparison of the TPPL emission spectra in figure 3, no difference in shape or line width is observed. Therefore we conclude that equation (6) is valid within the whole intensity range of the experiment.

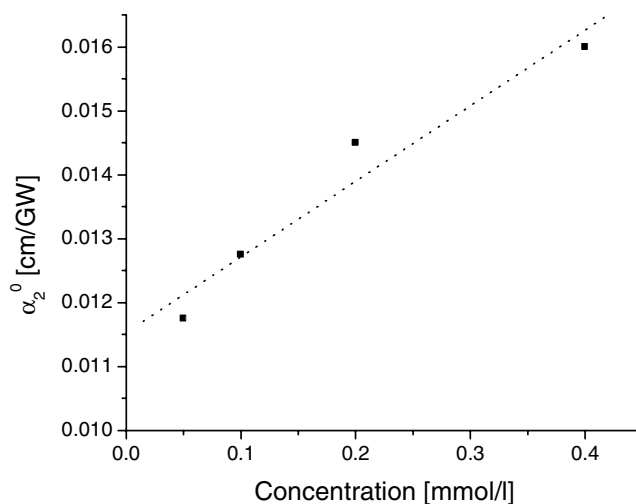
In order to see how the interaction between absorbers influences the NLO behavior we want to address the question of how the parameters in equation (5), namely  $I_{sat}$  and  $\alpha_2^0$ , depend on the concentration. In solution, the interaction between two adjacent, but distant by means of electronic interaction, chains should be negligible. The absorption cross-section for one chain should thus remain the same, and we expect the saturation intensity to not depend on the concentration of PF2/6 in the solvent. However, the TPA coefficient will depend on the concentration.



**Figure 4.** Two-photon absorption coefficient measured as a function of the incident laser intensity under variation of the concentration. From bottom to top: cross 0.05 mmol l<sup>-1</sup>, star 0.1 mmol l<sup>-1</sup>, circle 0.2 mmol l<sup>-1</sup>, square 0.4 mmol l<sup>-1</sup>. The curves depict the hyperbolic fits using equation (5).

In figure 4 the results of the TPA are shown as a function of intensity and concentration. These values have been measured with a silicon diode. The top curve with the highest concentration corresponds to figure 2(a), measured with the OOI spectrometer. The optical density (defined as  $OD = -\log(I/I_0)$  for the single photon absorption) has been measured to be  $OD = 16$  at the peak absorption wavelength of 384 nm, which corresponds to a concentration of 0.4 mmol l<sup>-1</sup>. Since no transmission spectrometer can measure  $OD = 16$ , the value was obtained using two different methods. First,  $OD = 2$  for the 0.05 mmol l<sup>-1</sup> solution was

multiplied with eight. Also, the onsets of the two absorption spectra were matched and this factor again was used to obtain the OD for the concentrated solution. The values agreed very well. The other graphs from top to bottom are always half the concentration of the previous,  $0.2 \text{ mmol l}^{-1}$ ,  $0.1 \text{ mmol l}^{-1}$ ,  $0.05 \text{ mmol l}^{-1}$ , respectively. The concentrations were calculated from the measured optical density. The extinction coefficient for PF2/6 was determined to be  $38\,000 \text{ l (mol cm)}^{-1}$ . The dimension of the cuvette was 2 cm in the direction of the laser beam. Our initial assumption of a constant saturation intensity holds, and the slopes of the linear sections—corresponding to  $\alpha_2^0$ —increase with the concentration. Comparing the saturation intensities of the TPA using the two detectors—fiber spectrometer and silicon diode—it is found that the results lay within the margin of error. The TPA coefficients for the highest concentration solution are identical for the two methods, being a strong indication that there are no saturation effects at the respective detectors.



**Figure 5.** Two-photon absorption coefficient as a function of the PF2/6 concentration in toluene. The dashed line is a guide for the eyes.

In figure 5,  $\alpha_2^0$  is plotted against the concentration. The results for the TPA coefficients are summarized in table 1. The values for the two-photon absorption coefficient are of course lower than those of solids, which are typically on the order of  $10^0$ – $10^1 \text{ cm GW}^{-1}$  [20]. The dependence cannot be clearly categorized, but is close to a linear behavior. Assuming that the dependence is indeed linear, the plot clearly does not go through the origin. One explanation is that there are other non-linear processes that we do not take into account, namely intensity dependent scattering and mainly white light generation by the toluene. In this experiment, toluene did not show any TPA in a measurable amount. However, white light continuum generation was visible. Thus, what appears to be an offset of the  $\alpha_2^0$  is the contribution of the experimental setup. Therefore, the  $\alpha_2^0$  values given in figure 5 need to be corrected for the offset of  $0.0115 \text{ cm GW}^{-1}$ .

Finally, it is interesting to estimate how many of the PF2/6 repetition units are excited at the saturation intensity. The *generation rate per pulse* is:

$$G_{\text{pulse}} = \frac{E_{\text{pulse}}(1 - T)}{2E_{\text{photon}}V} = 1 \cdot 10^{16} [\text{cm}^{-3} \text{ pulse}^{-1}] \quad (7)$$

with  $E_{\text{pulse}} = 1.63 \text{ } \mu\text{J}$  (the pulse energy at the saturation intensity),  $E_{\text{photon}} = 1.54 \text{ eV} = 2.5 \times 10^{-19} \text{ J}$ ,  $V = 1.6 \times 10^{-10} \text{ m}^3$ ,  $T \approx 50\%$  (for a PF2/6 concentration of  $0.4 \text{ mmol l}^{-1}$

at the saturation intensity). The volume is obtained for a beam diameter of 0.1 mm and a 10 cm beam length in the cuvette. The reason why there is an additional factor of two in the denominator is that two photons contribute to the creation of one electron–hole pair. Alternatively we could assume that the ‘effective’ photon energy is 3.08 eV. As has been mentioned above, the excited electrons return to the ground state in a timescale three orders of magnitude lower than the time between two pulses. Therefore, a cw generation rate cannot be given.

The number of repetition units per  $\text{cm}^3$  can be given as follows (it is important to bear in mind that the concentration of  $\text{mmol l}^{-1}$  is a value for the repetition units, not the chains):

$$n_{\text{rep}} = \frac{0.4 \text{ mmol}}{l} = \frac{2.4 \cdot 10^{20}}{l} = 2.4 \cdot 10^{17} \text{ cm}^{-3} \quad (8)$$

Using the generation rate obtained above, roughly 1%–5% of the repetition units are excited at the saturation intensity. For the highest excitations of  $I = 250 \text{ GW cm}^{-2}$  this value further increases by a factor 3. However, in figure 3 there is no evidence for any exciton–exciton interaction that would influence the shape of the PL spectra, and in figure 2(b) no evidence for PL exciton–exciton quenching is seen. This result supports the notion that polyfluorene is a high luminescence yield polymer even at high excitations.

Also, the saturation intensity remains constant while varying the concentration, since both the number of repetition units per volume as well as the TPA coefficient scale linearly with the concentration.

In conclusion, we report the first concentration dependent measurement of TPA coefficients of dissolved PF2/6. It is demonstrated that the straightforward underlying model—general dependence on the squared intensity and the hyperbolic dependence of the TPA coefficient on the intensity—describes the experimental results very well. The most important results are the independency of the saturation intensity— $85 \text{ GW cm}^{-2}$ —against the concentration and the linear scaling of the two-photon absorption with concentration as shown in figures 4 and 5, respectively. The ratio of excited to unexcited repetition units is on the order of 1 : 20. It was also shown that the saturation of the TPPL peak emission intensity is purely a result from the TPA photobleaching and we do not observe exciton–exciton interactions in the emission process.

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