

# Large irradiance limiting induced by three-photon absorption of a symmetrical fluorene-based molecule

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**Abstract:** Herein, three-photon absorption (3PA) effect of a symmetrical fluorene-based molecule, pumped with 38 ps Q-switched 1064 nm laser pulses, is reported. An accurate Gaussian fitting method is used to obtain the three-photon absorption cross-section. The obtained three-photon absorption cross-section,  $8.54 \times 10^{-76} \text{ cm}^6 \text{ s}^2$ , is very high. The irradiance limiting nonlinear transmittance is as low as 2% when the incident irradiance is 120 GW/cm<sup>2</sup>. The geometry and electronic transition of the molecule are systematically studied by AM1 and TD SCF/DFT methods.

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## 1. Introduction

In recent years, three-photon absorption (3PA) has received considerable attention from the scientific community because of its potential applications in photonics and biomedical fields. 3PA refers to simultaneous absorption of three photons in a single event through virtual states [1]. In organic molecules, 3PA typically occurs at longer wavelengths in the near infrared region (NIR). This introduces some advantages, which include minimization of the scattered light losses as wavelength increases and reduction of undesirable linear absorption [2], so that greater radiation penetration depth and less damage in these materials can be obtained. Consequently, molecules with large 3PA cross-sections can be easily applied in multiphoton fluorescence imaging [3-5], up-converted stimulated emission [6], optical limiting [7,8,9] and so on. A dynamical theory has been developed to explain recent experimental results on multiphoton excited amplified stimulated emission [10].

Much effort on studying 3PA in organic molecules has been made to enhance cross-section  $\sigma_3$  since relatively small 3PA cross-section values of present nonlinear organic molecules have deferred their practical applications. In this article, we investigate 3PA-induced upconversion fluorescence emission and 3PA cross-section of a novel fluorene-based molecule with the symmetric conjugated structure D- $\pi$ - $\pi$ - $\pi$ -D, which is named as 9,9-diethylhexyl-2,7-bis-(N,N-vinylcarbazole)fluorene (Fig. 1). D and  $\pi$  represent an electron-donor and a conjugated  $\pi$ -electron bridge, respectively. It is found that its  $\sigma_3$  value is very high, so this molecule has promise for irradiance limiting applications. Intensity dependent transmission measurement and an accurate Gaussian fitting method are used to obtain the three-photon absorption cross-section of the compound pumped by ps pulses at 1064 nm. Furthermore, in an effort to investigate the process of 3PA transition, quantum chemistry calculations are performed.

## 2. Experiment

The compound was synthesized by Cu-mediated Ullmann condensations reactions [11]. The linear absorption and steady fluorescence spectra of the compound in DMF at  $2 \times 10^{-5}$  mol/L were measured using a UV-VIS-NIR Cary5000 spectrophotometer and a Spex fluorescence spectrometer, respectively.

In measurements of upconversion fluorescence and optical limiting of the compound in DMF, the incident 1064-nm laser excitation were provided by a Q-switched Nd:YAG laser (Continuum, PY61-10) with a pulse width of 38 ps and a repetition rate of 10 Hz. The solution concentration is 0.028 mol/L. The pump energy was controlled by a rotational Glan-Taylor prism. The incident and transmitted beam energy was measured using two J3-05 probes (made by Molelectron Co. in American).

Quantum chemistry calculations were performed on an intel personal computer using GAUSSIAN program. The compound geometry was firstly optimized by AM1 method. The transition process was computed by TD SCF/DFT method on the optimized geometry.

## 3. Results and discussions

### 3.1 Linear absorption and steady fluorescence emission

Figure 1 shows linear absorption and steady fluorescence spectra of the compound in DMF. Influences from the quartz liquid cell and the solvent have been subtracted. The molecule shows strong UV absorption in the spectral range of 300-400 nm, but no linear absorption in longer wavelength range. This indicates that excitation in longer wavelength range can only occur through multiphoton absorption processes. The three-photon energy of 1064 nm irradiation just falls into a strong UV absorption region, and therefore three-photon absorption in the compound may be expected.

### 3.2 Three-photon induced fluorescence

A blue fluorescence emission could be readily observed by human eyes when incident

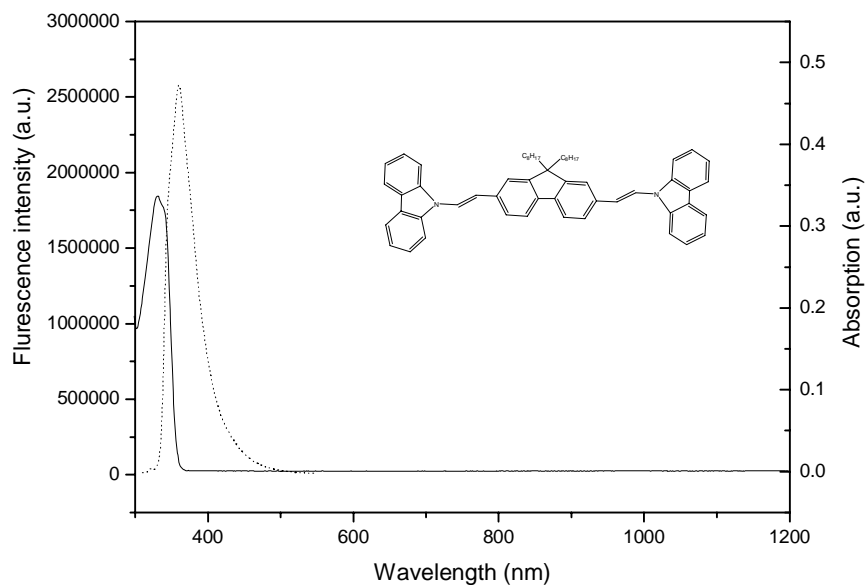


Fig. 1. Linear absorption (solid line) and steady fluorescence spectra (dot) of the molecule in DMF at  $2 \times 10^{-5}$  mol/L. The molecular structure of the solute is given in the top-right corner.

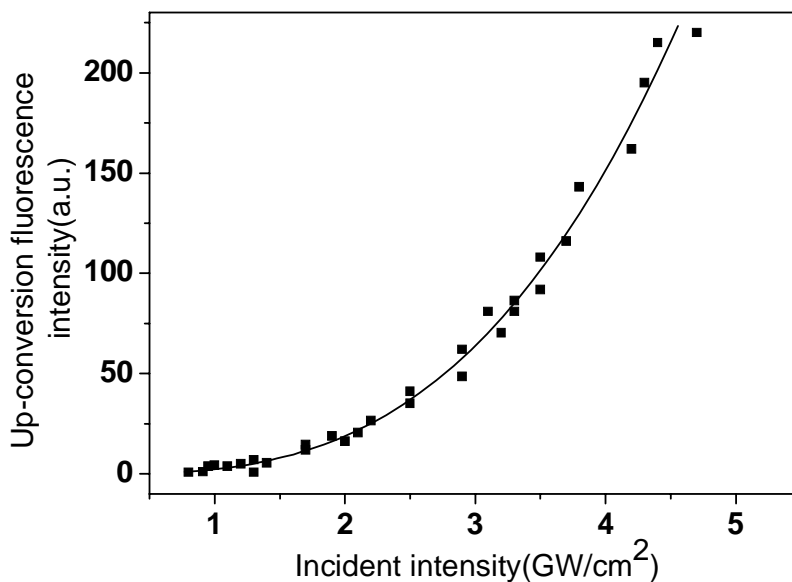


Fig. 2. Cubic dependence of the 3PA induced fluorescence intensity vs incident intensity at 1064 nm for this compound in DMF. The solid line is the best-fitted curve based on the function  $y = ax^n$  with the best-fitted exponent  $n = 2.98$ .

intensity reached several hundred megawatts per square centimeter. A characteristic feature of 3PA-induced fluorescence is the cubic dependence of the fluorescence intensity on incident

laser intensity. The emission intensity vs incident intensity (as shown in Fig. 2) was measured. The upconversion fluorescence intensity, measured at the maximum emission wavelength of 445 nm, exhibits a cubic dependence on incident intensity. The best-fitted exponent is  $n=2.98$  (within a permissible error) through the relation  $y=ax^n$ , as is characteristic of three-photon processes. The possibility of excited state absorption can be discarded at this pulse width. On one hand, the lifetime of the excited state on the molecule is in nanosecond range, so that there is no time for excited state absorption during the pulse [12]. On the other hand, 1PA (1064 nm) and 2PA (532 nm) at the working wavelength of 1064 nm (as shown in Fig. 1) are absent. Although picosecond pulses are employed, there is no intermediate state between the ground state and the excited state [2]. Consequently, one can be confident that the excitation processes are induced by simultaneous absorption of three photons.

### 3.3 Three-photon absorption cross-section

The measurement of 3PA coefficient of the compound in DMF solution at 0.028 mol/L was performed in a 10-mm-long quartz cell pumped with the same laser described above. High 3PA coefficient  $\gamma$  of the compound was obtained with the intensity dependent transmittance measurement (Fig. 3), fitting with the following Gaussian method.

Assuming a light beam traveling within a nonlinear sample in the +z direction. Neglecting linear absorption and two-photon absorption at the pump wavelength, the light beam propagating through the sample is governed by the following equation,

$$dI(z', r, t) / dz' = -\mathcal{A}(z', r, t)^3 \quad (1)$$

where  $z'$  is the propagation length inside the sample and  $I(z', r, t)$  is the irradiance that depends on the propagation distance. The solution of Eq. (1) is

$$I(L, r, t) = \frac{I(z=0, r, t)}{\sqrt{1 + 2\mathcal{A}I^2(z=0, r, t)}} \quad (2)$$

The above method can not be directly used in Gaussian beam, or a considerable error can not be avoided, particularly in a thick sample, because the Gaussian beam propagates in the collective or dispersing direction, i.e.,  $r$  in Eq. (1) is not a constant. In addition, the irradiance varies along the  $r$  direction.

However, if sample length is small enough that the change of beam diameter within the sample can be neglected, the medium is regarded as "thin", in which case Eq. (2) can be used to fit experimental curves.

Now we divide the sample passed by laser into  $m$  cylinders along  $z$  direction, and then divide every cylinder into  $n$  annuluses along  $r$  direction; hence, there will be  $m \times n$  annuluses in the sample.  $(i, j)$  ( $0 \leq i \leq n, 0 \leq j \leq m$ ) can be regard as the coordinates of every annulus. The light intensity in a given annulus is approximately assumed to be homogeneous along the  $r$  direction and parallel along the  $z$  direction, so that Eq. (2) can be used for all the annuluses.

$$I''(i, j, t) = \frac{I'(i, j, t)}{\sqrt{1 + 2\mathcal{A}'I'^2(i, j, t)}} \quad (3)$$

$$I'(i, j+1, t) = \frac{S''(i, j)}{S'(i, j+1)} I''(i, j, t) \quad (4)$$

$$T = \frac{\sum_{i=1}^{i=n} I''(i, m, t) S''(i, m) t_p}{\sum_{i=1}^{i=n} I'(i, 1, t) S'(i, 1) t_p} \quad (5)$$

Where  $L' = L/m$  is the thickness of every annulus,  $L$  is the distance traveled by the beam through the sample, and  $t_p$  is the pulse width.  $I(i, j, t)$  is the incident irradiance at the front side of the  $(i, j)$  annulus;  $I'(i, j, t)$  is the transmitted irradiance of the same annulus; and  $S''(i, j)$  and  $S'(i, j+1)$  are the area of the exit plane of the  $(i, j)$  annulus and the area of the incident plane of the  $(i, j+1)$  annulus, respectively. Eq. (3) shows the transmission process in every annulus. Eq. (4) simulates gradual change of the light beam. The numerator and denominator of Eq. (5) are the summations of the exit plane ( $j=m$ ) and the incident plane ( $j=1$ ), respectively, so  $T$  is the transmittance of every pulse energy. When larger values for  $m$  and  $n$  are used, the  $\gamma$  value obtained is more accurate. The 3PA coefficient  $\gamma$  can be obtained with the given  $m$  and  $n$  value. The error is as low as 0.05% at  $m=n=10^4$ . More importantly, one can obtain the irradiance  $I$  at any position in the sample with this method. In addition, we fit the experimental data of another fluorene derivative using the above method, and the material is the same with that reported in Ref. 9, in which the 3PA cross section is  $1.14 \times 10^{-76} \text{ cm}^6 \text{ s}^2$ . The best fit value is  $1.65 \times 10^{-76} \text{ cm}^6 \text{ s}^2$ . The discrepancy between the two methods is produced by the fact that the theoretical fitting method in Ref. 9 assumes an equivalent rectangular pulse shape to give a rough estimate of intensity  $I_0$  or  $I_z$  instead of a Gaussian distribution.

Figure 3 shows the transmitted on-axis intensity vs. incident on-axis intensity curves of this compound. The value of this parameter was determined by trial and error. The solid line represents a theoretical fitting with the best-fit parameter  $\gamma$ . The obtained 3PA coefficient is  $\gamma = 41.2 \times 10^{-20} \text{ cm}^3/\text{W}^2$ . After relating this coefficient to the solute concentration  $d_0$  and the photon energy  $hc/\lambda$  using the following equation:

$$\sigma_3' = \frac{\gamma}{N_A \cdot d_0 \times 10^{-3}} \left( \frac{h \cdot c}{\lambda} \right) \quad (6)$$

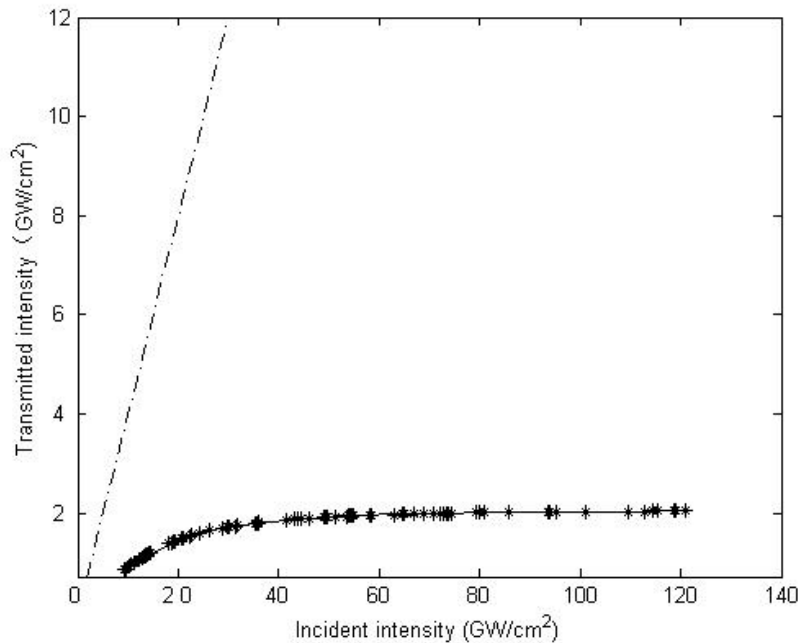


Fig. 3. Transmitted on-axis intensity vs. incident on-axis intensity curves of the compound at 0.028 mol/L, fittings using the above method. The dash dot line are the best-fit curve with  $\gamma = 0$ . The solid line represent the theoretical fitting. The best-fit parameters was  $\gamma = 41.2 \times 10^{-20} \text{ cm}^3/\text{W}^2$

the 3PA cross-section for the compound,  $\sigma_3=8.54\times 10^{-76} \text{ cm}^6 \text{ s}^2$ , was obtained. The intrinsic molecular three-photon absorption cross-section is quite high. The lower the polarity the larger the 3PA cross-section [13]. As we know, the polarity of DMF used in our experiments is high, which indicates that the value of the 3PA cross section,  $8.54\times 10^{-76} \text{ cm}^6 \text{ s}^2$ , is intrinsically high, rather than being enhanced by solvent.

The measured  $\sigma_3$  value is larger than that of stilbazolium-like derivatives (less than  $2\times 10^{-76} \text{ cm}^6 \text{ s}^2$ ) [8] under similar experimental conditions, and comparable to that of BBTDOT ( $8.8\times 10^{-76} \text{ cm}^6 \text{ s}^2$ ) [7] excited by nanosecond pulses. The large  $\sigma_3$  value is the result of the electron delocalization along the molecular system, large  $\pi$ -electron conjugation, and strong electron donors.

As the compound exhibits large 3PA cross-section, the irradiance limiting performance based on the 3PA effect may be expected. Figure 4 shows the on-axis irradiance nonlinear transmittance response. The transmittance nonlinearly decreases with the incident irradiance ranging from 10 to 112  $\text{GW}/\text{cm}^2$ . The transmittance is about 23% at the initial irradiance 10  $\text{GW}/\text{cm}^2$ , and the nonlinear transmittance can reach 2% when the incident irradiance is 120  $\text{GW}/\text{cm}^2$ . This result is much better than that reported formerly for BMOSF [9]. It means that this compound has promise for irradiance limiting applications induced by 3PA.

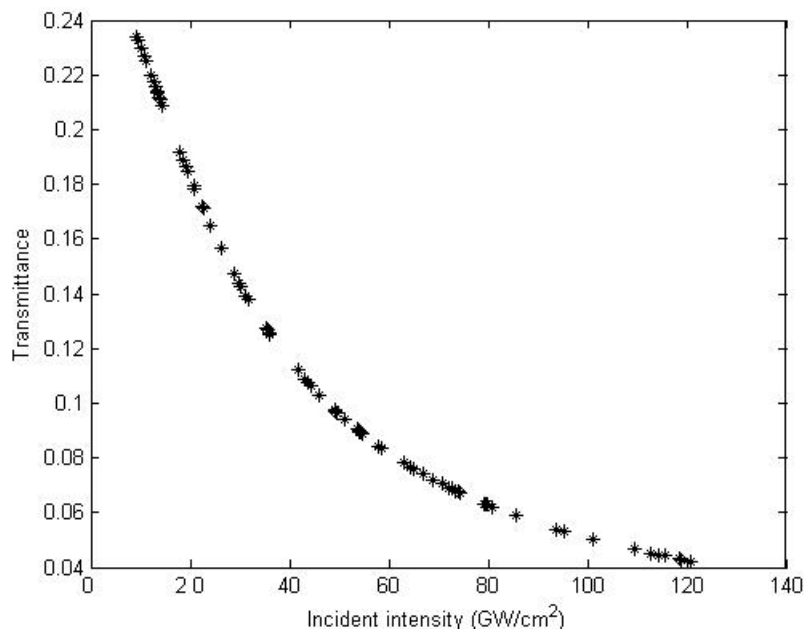


Fig. 4. Nonlinear transmittance versus incident intensity at 1064 nm for the compound in DMF at 0.028 mol/L.

### 3.4 Quantum chemistry computation

The AM1 semi-empirical method has been used to optimize the ground-state geometry of the compound and the TD SCF/DFT first-principle method has been used to obtain the first 6 singlet-singlet electronic transition data of the compound at the optimized geometry. The value of the broadening is 44 nm. The computations were performed within the Franck-Condon approximation. The electronic transition data are shown in Table 1. The theoretical calculation results show that there are no states close to the one-photon energy and two-photon energy. The lowest excited state is 2.9968 eV (413.72 nm) above the ground state, which is larger than the energy of the 2PA at the working wavelength of 1064 nm. This

confirms that the excitation process is induced by the simultaneous absorption of three photons.

One can see that the oscillator strength ( $f$ ), the transition velocity dipole moments, and the transition dipole moment along the long axis of the molecule (X) of the  $S_0 \rightarrow S_1$  electronic transition is the largest, which indicates that the excitation scheme for the compound is dominated by the transition to the first excited state. In addition, the energy of the transition  $S_0 \rightarrow S_4$  just equals three times the energy of one single excitation photon. A one-photon absorption state can be a three-photon absorption state as well [14]. Consequently, the 3PA process in this compound can be deemed: a molecule simultaneously absorbs three photons and is transmitted to  $S_4$  state, and then relaxes to  $S_1$  state. Finally, it returns to  $S_0$  through fluorescence emission. Phosphorescence emission hasn't been detected, so the transition between singlet states and triplet states is not supposed to exist.

Table 1. Electronic transition data obtained by the TD SCF/DFT semi-empirical method for the two molecules at the AM1 optimized geometry.

Ground to excited state	X <sup>a</sup>	Y	Z	Excitation energies (eV)	Oscillator strengths
Transition electric dipole moments (a.u. <sup>b</sup> )					
$S_0 \rightarrow S_1$	-3.8982	-0.0690	-0.0680	2.9968 (413.72 nm)	1.1164
$S_0 \rightarrow S_2$	0.3370	-0.2611	-0.0218	3.1642 (391.84 nm)	0.0141
$S_0 \rightarrow S_3$	-0.3648	-0.3192	-0.0087	3.4710 (357.20 nm)	0.0200
$S_0 \rightarrow S_4$	-0.5290	0.2502	0.0596	3.4875 (355.51 nm)	0.0296
$S_0 \rightarrow S_5$	-0.0203	0.0862	0.0129	3.7624 (329.54 nm)	0.0007
$S_0 \rightarrow S_6$	-0.1409	-0.0883	-0.0105	3.7810 (327.92 nm)	0.0026
Transition velocity dipole moments (a.u.)					
$S_0 \rightarrow S_1$	0.2886	0.0052	0.0046		
$S_0 \rightarrow S_2$	-0.0264	0.0200	0.0018		
$S_0 \rightarrow S_3$	0.0296	0.0273	0.0005		
$S_0 \rightarrow S_4$	0.0436	-0.0214	-0.0055		
$S_0 \rightarrow S_5$	0.0027	-0.0101	0.0006		
$S_0 \rightarrow S_6$	0.0145	0.0100	0.0032		

<sup>a</sup> X is the long molecular axis. <sup>b</sup> Electric dipole moments are given in atomic units (a.u.)

#### 4. Conclusions

In summary, pure 3PA in this compound has been proven through the measurements of the transmittance and the up-conversion fluorescence emission dependence with the excitation intensity. The 3PA cross-section was determined using an accurate Gaussian fitting method. The measured 3PA cross-section,  $8.54 \times 10^{-76} \text{ cm}^6 \text{ s}^2$ , is very high. It is also indicated that this compound is a good kind of optical limiting material induced by three-photon absorption. The 3PA transition process of the compound has been obtained by AM1 and TD SCF/DFT semi-empirical methods.

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