

Large three-photon absorption cross-section in a novel class of bis-(*N*-carbazolyl) fluorene derivatives

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Abstract

Two novel symmetrical charge transfer fluorene derivatives (abbreviated as *BCZF* and *BVCZF*) with carbazole end-group as the donor moieties have been synthesized. Three-photon absorption cross-sections of these two compounds have been determined by using a Q-switched Nd:YAG laser pumped with 38 ps pulses at 1064 nm in DMF. The measured 3PA cross-sections are 140×10^{-78} and $400 \times 10^{-78} \text{ cm}^6 \text{ s}^2$ for *BCZF* and *BVCZF*, respectively. The geometries, electronic structures and electronic spectra of these two compounds are systematically studied by AM1 and ZINDO/S methods. On the basis of correct UV-vis spectra, the influence of different molecular structure on three-photon absorption cross-sections is discussed micromechanically.

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1. Introduction

In the early 1930s multiphoton absorption of an atom was introduced into the literature as a new concept by Göppert-Mayer [1]. Multiphoton absorption can be defined as simultaneous absorption of two or more photons through virtual states in a medium. Two-photon technology has been at central focus for the molecular photonics community in the last several years. Two-photon absorption (TPA) process could, because of a quadratic dependence of excitation on intensity, produce a spatially confined excitation useful for numerous technological applications [2–4]. These successes have created interest in exploring applications based on three-photon excitations [5]. For a three-photon absorption (3PA) process, the greater penetration depth and less damage in some materials (especially in biomaterial) can be obtained because of the use of a longer excitation wavelength, which possibly make the 3PA

process even more appropriate than TPA in the emerging fields of bioimaging and light-activated therapy. Also, the cubic dependence of the three-photon process on the input light intensity provides a stronger spatial confinement, so that a higher contrast in imaging can be obtained.

The success of the two-photon technology owes much to the discovery of certain classes of organic molecules that possess very large two-photon absorption cross-sections [6,7]. Analogously to that, it can be expected that the development in the molecular design of three-photon absorption active materials holds the key to three-photon technologies. Much effort has been undertaken recently to develop organic molecules with large three-photon absorption cross-sections, for example, the measured 3PA cross-sections σ'_3 for some stilbazolium-like dyes have been reported to be as high as $10^{-76} \text{ cm}^6 \text{ s}^2$ at 1064 nm for ps pulses by Wang and Zhan et al. [8,9]. Hernández [10] investigated the 3PA cross-sections of two fluorene derivatives with donor–bridge–donor (D– π –D) and donor–bridge–acceptor (D– π –A) structural motifs, it was shown that symmetric intramolecular

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charge transfer in the D- π -D molecule enhances 3PA in these fluorene derivatives.

In this Letter, we investigate a new family of fluorene derivatives with the same symmetric, D- π -D, conjugated structure but with carbazole end-group as the donor moieties, which are named as 9,9-diethylhexyl-2,7-bis-(*N,N*-carbazole) fluorene (*BCZF*) and 9,9-diethylhexyl-2,7-bis-(*N,N*-vinylcarbazole) fluorene (*BVCZF*). Carbazole substitution is studied as a route to increased stability and nonlinearity. We use intensity dependent transmission measurement to obtain the three-photon absorption cross-sections of these two compounds at 1064 nm pumped with ps laser, and combined with the quantum chemistry calculations, we discuss the influence of different molecular structure on three-photon absorption cross-sections.

2. Experiment

2.1. Materials

Two fluorene derivatives, *BCZF* and *BVCZF*, were synthesized by Cu-mediated Ullmann condensations reactions [11] and Pd-catalyzed Heck coupling reactions [12], respectively. The synthetic routes were shown in Fig. 1. The chemical structure of these two compounds has been identified by elemental analysis, MS, IR spectrum, and UV-vis spectrum. The linear absorption spectra of two compounds in DMF were measured by using Lambda 9 UV/VIS/NIR recording spectrophotometer with a concentration of 1.4×10^{-5} mol/l.

2.2. Measurement of nonlinear transmission

In the measurement of nonlinear transmission, the incident 1064 nm lasing was provided by a Q-switched Nd:YAG laser (Continuum, PY61C-10) with pulse duration of 38 ps, repetition rate of 10 Hz. The pump

energy was controlled by rotating a half-wave plate between two polarizers. The energies of the incident and transmitted beams were measured using two large-area silicon photodiodes connected to a two-channel energy meter (Molelectron EPM 2000). The input energy was adjusted from low to high and corresponding output energy can be obtained simultaneously.

2.3. Computational methods

Ab initio calculations were performed on an AMD XP 2500+ (1.84 GHz) personal computer with 256MB of RAM using GAUSSIAN 98W program, version 5.1 [13]. The geometries of two molecules are optimized by AM1 method. The excited states are characterized, and the electronic transitions are computed by ZINDO/S method [14,15] on the optimized geometries.

3. Results and discussion

3.1. Linear absorption spectra

Fig. 2 shows the linear absorption spectra of the two fluorene derivatives in DMF. The influence of the cuvette and the solvent has been excluded. The both two compounds show strong UV absorption in the spectral range of 300–360 nm. In Fig. 2, the absorption peaks located at 330 and 338 nm for *BCZF* and *BVCZF*, respectively, are all correspond to transitions $S_1 \leftarrow S_0$ [16]. Because of the larger conjugated system in *BVCZF*, the absorption peak of *BVCZF* is red-shifted around 8 nm compared with that of *BCZF*. There is no one-photon absorption for these two compounds in the entire near IR and most (>360 nm) of the visible spectral range. The three-photon energy of 1064 nm radiation just falls into the strong UV absorption region, and therefore

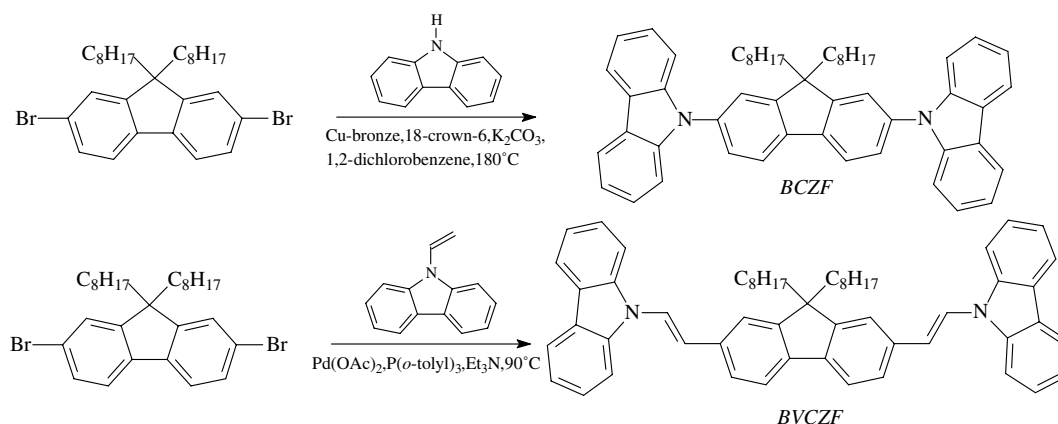


Fig. 1. The synthetic routes of *BCZF* and *BVCZF*.

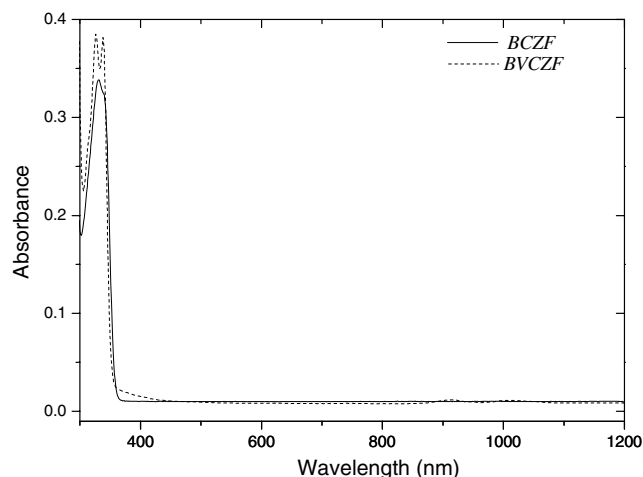


Fig. 2. One-photon absorption spectra of *BCZF* and *BVCZF* in DMF at concentration of 1.4×10^{-5} mol/l.

three-photon absorption in these two compounds may be expected.

3.2. Three-photon absorption cross-sections

In an optical event if simultaneous absorption of three-photon is the only process involved, the intensity change of an excitation beam along the optical propagation path z is given by

$$dI(z)/dz = -\gamma I^3(z), \quad (1)$$

where γ is the three-photon absorption coefficient of the given sample medium. The solution of Eq. (1) can be simply obtained as [17]

$$I(z) = I_0 / \sqrt{1 + 2\gamma z I_0^2}, \quad (2)$$

where I_0 is the incident intensity of the excitation beam and z is the propagation distance within the sample medium. From the relationship between $I(z)$ and I_0 , the three-photon absorption coefficient γ can be easily deduced.

Fig. 3 shows the transmitted intensity as a function of the incident intensity of *BCZF* and *BVCZF* in DMF at 0.028 mol/l. The data in Fig. 3 are fitted by Eq. (2) with the γ as the adjustable fitting parameter. The γ values corresponding to the best fit (represented by the solid line) are 6.78×10^{-20} and 1.93×10^{-19} cm³/W² for *BCZF* and *BVCZF* in DMF, respectively. One can see that the theoretical curve agreed with the measured data. Based on the known γ value of the measured solution sample, the molecular absorption cross-section σ'_3 (in the units of cm⁶ s²) for given sample in solution is obtained by [10]

$$\sigma'_3 = \frac{\gamma}{N_A \cdot d_0 \times 10^{-3}} \left(\frac{hc}{\lambda} \right)^2. \quad (3)$$

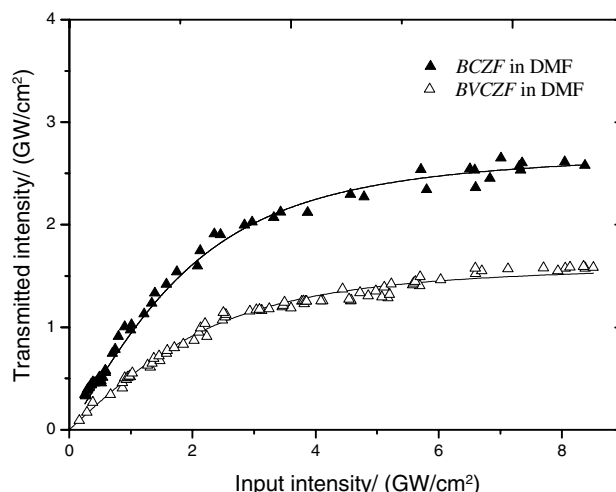


Fig. 3. Transmitted intensity versus input intensity of *BCZF* and *BVCZF* in DMF at 0.028 mol/l, pumped by ps laser (38 ps, 1064 nm). The solid lines are the theoretical best-fit curve with the parameter of $\gamma = 6.78 \times 10^{-20}$ cm³/W² (▲) and 1.93×10^{-19} cm³/W² (△).

Here, N_A is Avogadro constant, d_0 is the concentration of the sample in solution (in the units of mol/l), and $h(c/\lambda)$ is the energy of an incident photon at 1064 nm. So the intrinsic sample molecular σ'_3 values can be easily estimated as 140×10^{-78} and 400×10^{-78} cm⁶ s² for *BCZF* and *BVCZF*, respectively. Due to the influence of the quartz and the uncertainty of the incident intensity, the final results of γ and σ'_3 of these two compounds have an experimental uncertainty of 10%.

It can be easily found that these two compounds possess large 3PA cross-sections in DMF, especially for *BVCZF*, the σ'_3 value is as high as 400×10^{-78} cm⁶ s², which is 4.9 times greater than that for analog, 9,9-didecyl-2,7-bis-(*N,N*-diphenylamino) fluorene [10], in hexane, and significantly larger than that previously reported for stilbazolium and stilbazolium-like derivatives [8,9] under the similar experiment conditions. In addition, it should be pointed out that bis-(*N*-carbazolyl) fluorene derivatives not only possess the large 3PA cross-sections, but may have high stability. For example, the new compound 9,9-diethylhexyl-2,7-bis-(*N,N*-carbazole) fluorene (*BCZF*) with carbazole end-group is more stable than analog, 9,9-didecyl-2,7-bis-(*N,N*-diphenylamino) fluorene with diphenylamine end-group (the melting point of *BCZF* is raised to 150, 67 °C higher than that of 9,9-didecyl-2,7-bis-(*N,N*-diphenylamino) fluorene [11]), which due to the carbazole end-group is a rigid plane and it possesses more planarity than diphenylamine end-group. The large 3PA cross-sections, along with their high stability make bis-(*N*-carbazolyl) fluorene derivatives particularly promising in nonlinear optical applications.

By comparison of the σ'_3 value of *BCZF* and *BVCZF* measured in picoseconds at 1064 nm, it is

observed that the σ'_3 values are strongly related to chemical structures of these two compounds. The only difference of *BCZF* and *BVCZF* in molecular structure is the increasing conjugation length in *BVCZF* (Fig. 1), but the σ'_3 value of *BVCZF* is almost three times greater than that of *BCZF*. We systematically studied the geometries, electronic structures and electronic spectra of these two compounds using AM1 and ZINDO/S methods. On the basis of correct UV–vis spectra, the influence of different molecular structure on three-photon absorption cross-sections is discussed in the following section.

3.3. Ground-state geometries and electronic excitations

Optimized ground-state geometries of two fluorene derivatives have been obtained by AM1 method. The ethylhexyl groups at the 9 position have been replaced by ethyl groups to reduce the time of calculation [18]. The optimized dihedral angle between fluorene-ring and carbazole-ring is ca. 49° and 26° for *BCZF* and *BVCZF*, respectively. One can see that these two molecules show nonplanar structures. Also, it is clearly indicated that the increase of the conjugation length observed for *BVCZF* significantly affect the conformation of the molecule.

The energy of the frontier orbital has also been compiled using AM1 calculations (Table 1). From Table 1, we can find that the increase of the conjugation length in *BVCZF* slightly destabilizes the HOMO orbitals and stabilizes the LUMO orbitals. Indeed, the increase in the dihedral angle of *BCZF* should enhance the antibonding character between fluorene-ring and carbazole-

ring and thus stabilize the HOMO. On the other hand, the decrease of the planarity between the subunits should reduce the electronic conjugation over the whole molecule and thus destabilize the LUMO. This causes a decrease in the LUMO–HOMO energy gap of *BVCZF* compared to that of *BCZF*, which is in favor of transition of electron from HOMO to LUMO.

Recently, theoretical investigation revealed that there are more possible transition paths from ground to final states, S_f , involved in a three-photon absorption process, such as (I) $S_0 \rightarrow S_i \rightarrow S_j \rightarrow S_f$, (II) $S_0 \rightarrow S_f \rightarrow S_0 \rightarrow S_f$, (III) $S_0 \rightarrow S_i \rightarrow S_i \rightarrow S_f$, (IV) $S_0 \rightarrow S_i \rightarrow S_f \rightarrow S_f$, (V) $S_0 \rightarrow S_f \rightarrow S_f \rightarrow S_f$. Among them, path (II) is present in both symmetrical and asymmetrical systems and is also an important contributor. In other words, a strong one-photon absorption state can be a strong 3PA state as well [19]. The ZINDO/S semi-empirical method has been used to obtain the nature and the energy of the first 10 singlet-singlet electronic transitions of the two compounds and we find that the first excited state, S_1 , is the strongest one-photon absorption state for these two fluorene derivatives. Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO, which are both delocalized over the whole molecule. The excitation energies, oscillator strength (f) and transition dipole moments from the ground state to the first excited state are reported in Table 2. Their absorption maxima of the two fluorene derivatives in DMF are also reported in Table 2 for comparison with theoretical results. From Table 2, one can find that the excitation energy of *BVCZF* is 3.62 eV, smaller than that of *BCZF* because of the lower energy gap in *BVCZF*. Also, the transition dipole moment (atomic units a.u.) (X axis) of *BVCZF* is 4.87 a.u., significantly larger than that of *BCZF*, which shown that more efficient charge transfer may occur in *BVCZF*. Thus it can be seen that lower excitation energy and larger transition dipole moment of the $S_0 \rightarrow S_1$ electronic transition enhance the 3PA cross-section of *BVCZF*.

Table 1

Energies (eV), the gaps (eV) between the HOMO and LUMO for the studied molecules

Molecules	HOMO (eV)	LUMO (eV)	LUMO–HOMO (eV)
<i>BCZF</i>	−8.045	−0.713	7.332
<i>BVCZF</i>	−7.896	−0.750	7.146

Table 2

Electronic transition data obtained by the ZINDO/S semi-empirical method for *BCZF* and *BVCZF* at the AM1 optimized geometry

Electronic transitions	Excitation energies (ev)	λ_A^a (nm)	f	MO/character	Coefficient	Transition dipole moment (a.u. ^c)			λ_A^d (nm)
						X^b	Y	Z	
<i>BCZF</i>									
S ₁ ← S ₀	3.86	321.1	1.225	LUMO ← HOMO	0.605	3.60	0.016	−0.0004	330
<i>BVCZF</i>									
S ₁ ← S ₀	3.62	341.9	2.11	LUMO ← HOMO	0.63	4.87	−0.059	0.0689	338

^a Results are from ZINDO/S computations.

^b X is the long molecular axis.

^c a.u. is atomic units.

^d Absorption maxima of the two fluorene derivatives in DMF.

4. Conclusions

In summary, the 3PA cross-sections of two novel bis-(*N*-carbazolyl) fluorene derivatives, *BCZF* and *BVCZF*, were determined using a ps pulse at 1064 nm. The large 3PA cross-sections and high stability are found in these two compounds. The measured 3PA cross-sections are 140×10^{-78} and $400 \times 10^{-78} \text{ cm}^6 \text{ s}^2$ for *BCZF* and *BVCZF*, respectively. It is found that the 3PA cross-section is related to molecular structure, and the increasing conjugation length make *BVCZF* have larger 3PA cross-section than *BCZF*. The theoretical analysis results revealed that to lower excitation energy and to increase transition dipole moment of the $S_0 \rightarrow S_1$ electronic transition are a way of enhancing the 3PA cross-section in these fluorene derivatives.

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