

# The effects of donor acceptor end groups of heterocyclic molecules on two-photon absorption properties

Z.C. Wei<sup>a</sup>, H.H. Fan<sup>a</sup>, N. Li<sup>a</sup>, H.Z. Wang<sup>a,\*</sup>, Z.P. Zhong<sup>b</sup>

<sup>a</sup>State Key Laboratory of Optoelectronic Materials and Technologies, Zhongshan (Sun Yat-Sen) University, Guangzhou 510275, People's Republic of China

<sup>b</sup>Chemical Department, Zhongshan University, Guangzhou 510275, People's Republic of China

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## Abstract

A series of new heterocyclic molecules with different donor acceptor end groups, which possess different strength of charge transfer dipole moment, are studied by ultrafast laser spectroscopy in this work. The experimental results show that  $\pi$ -conjugated plane of these molecules mainly determine their fluorescent quantum efficiencies and spectra, while their strength of charge transfer dipole moment, which mainly dependent on the donor acceptor end groups, play the key role on the two-photon absorption cross-section. This results implies that design of the donor acceptor end group is important for developing molecule with large two-photon absorption cross-section in short wavelength.

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## 1. Introduction

Development of molecules with a large two-photon absorption (TPA) cross-section has been a subject of great interest in recent years due to a variety of applications, including two-photon-excited fluorescent microscopy, three-dimensional optical data storage, infrared detector, optical limiting, short wavelength tunable laser, and fabrication of photonic band gap crystals [1–20]. Quantum chemical calculations indicate that substantial symmetric charge redistribution occurs upon excitation and provides large TPA cross-section [1]. Some basis of the concept for synthesis of molecules with large TPA cross-sections has been provided by theoretical studies [1,21]. One of the current important works is to synthesize stable molecules with large TPA cross-sections; and another current important work is to further explore the mechanism of large TPA cross-sections, which is of great importance to

their synthesis and application, and becomes an urgent and attractive area of research.

In this work, a series of new heterocyclic molecules with different donor acceptor end groups are studied. It shows that charge transfer dipoles of donor acceptor end groups, are important for TPA cross-sections.

## 2. Experimental

In this work, the organic molecules are heterocyclic molecules with different donor acceptor end groups dissolved in dimethyl sulphoxide (DMSO). These molecules consist of a typical D- $\pi$ -A charge transfer structure, in which, carbazole group is employed as donor, and pyridinium group or thiazole group is employed as acceptor. The molecular structures of these new molecules are shown in Fig. 1. The names of these new molecules are:

- (A) 4-[2-(9-Butyl-9H-carbazol-3-yl)-vinyl]-1-methyl-pyridinium; iodide,
- (B) 4-[2-(9-Butyl-9H-carbazol-3-yl)-vinyl]-1-methyl-quinolinium; iodide,
- (C) 1-Methyl-4-[2-(9-methyl-9H-carbazol-3-yl)-vinyl]-pyridinium; iodide,

\* Corresponding author. Tel.: +86 208 411 3679; fax: +86 208 403 7423.

E-mail address: [stswzhz@zsu.edu.cn](mailto:stswzhz@zsu.edu.cn) (H.Z. Wang).

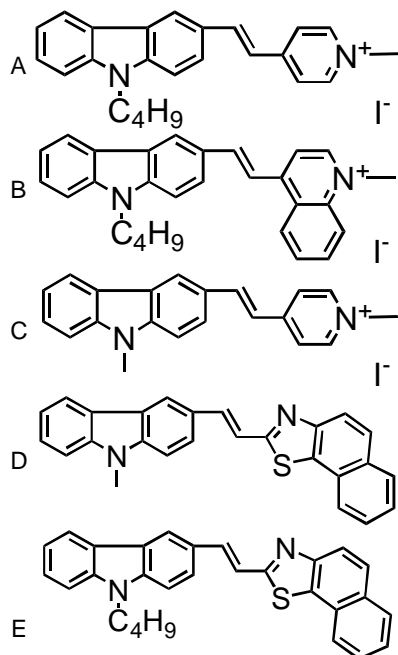


Fig. 1. The structures of the molecules.

- (D) 2-[2-(9-Methyl-9H-carbazol-3-yl)-vinyl]-naphtho[2,1-d]thiazole,  
 (E) 2-[2-(9-Butyl-9H-carbazol-3-yl)-vinyl]-naphtho[2,1-d]thiazole.

The linear absorption spectra were recorded by a Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer. The single-photon fluorescent spectra and quantum-yield were measured by a Hitachi model F-4500 fluorescence spectrophotometer. The quantum-yield  $\eta$  was measured by the standard comparison method [22] using Coumarin 120 or Rhodamine 6G as the reference standard.

The two-photon induced up-converted fluorescent experiment was measured with a optical multi-channels analyzer as a recorder; and the excitation source was a pulse train laser, which was obtained from an optical parametric generator (Spectra Physics, Model:OPA-800C) pumped by a mode-locked Ti:sapphire laser oscillator-amplifier system (Spectra Physics, Model: Hurricane). The pulse duration of the laser was 120 fs, and its repetition rate was 1 kHz.

The TPA cross-sections were measured by two-photon induced fluorescence method [23]. Femtosecond laser firstly passed through a couple of Nicol's prisms, which were used as an attenuator to obtain a tunable excitation intensity, then the laser was split into two beams. The weaker one was used as a reference beam, which entered directly into the detector of a power meter (Coherent, Field Master NO.33-0506) in order to monitor the intensity of the excitation beam. The intense beam was focused into the sample by a lens. The fluorescence was collected at the direction perpendicular to the pump beam. To minimize re-absorption effect, the excitation beam was focused as close to the front wall of

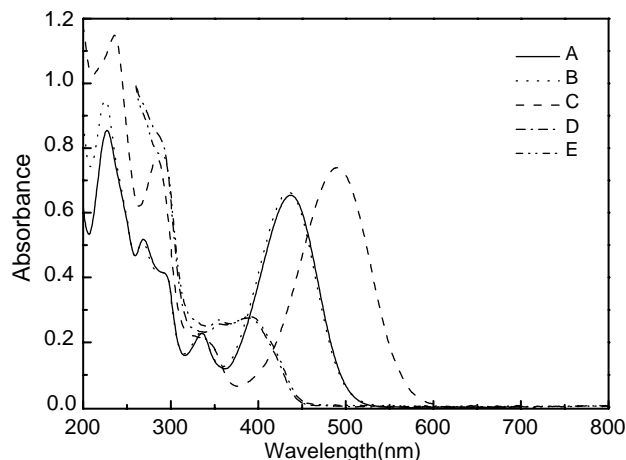


Fig. 2. The absorption spectra of the new molecules.

the quartz cell as possible. The two-photon induced fluorescence was recorded by an optical multi-channels analyzer. The TPA cross-sections  $\sigma_2$  was determined by comparing its TPF to that of Rhodamine 6G (both at the concentration of  $5 \times 10^{-4}$  mol/l) according to [23,24]

$$\sigma_2 \eta = \sigma_{2\text{cal}} \eta_{\text{cal}} \frac{C_{\text{cal}}}{C} \frac{n_{\text{cal}} F}{n F_{\text{cal}}}$$

where  $C$  is the concentration,  $n$  is the refractive index and  $F$  is the time-averaged fluorescence. The cal subscript refers to the standard reference solution.

### 3. Results and discussion

The linear absorption spectra of these new molecules are shown in Fig. 2. The peaks of linear absorption are listed in Table 1. The molecules in solution have no linear absorption in the range of 550–1.1  $\mu\text{m}$ .

The fluorescent spectra of these new molecules are shown in Fig. 3. The peaks of the fluorescent spectra and their fluorescent quantum efficiency are listed in Table 1. The TPA cross-section of these new molecules have also been measured and listed in Table 1.

As shown in Table 1, molecule A has the largest TPA cross-section (617.3 GM), because it has the largest strength of electron transfer dipole moment. In molecule A, the electron transfer acceptor is methyl-pyridinium, which have very high electron-accepting ability; while the electron

Table 1  
Spectral properties, fluorescent quantum yields and TPA cross-sections of the new molecules

Molecule	$\lambda_{\text{Amax}}(\text{nm})$	$\lambda_{\text{Emax}}(\text{nm})$	$\Phi_f(\%)$	$\sigma_2$ (GM)
A	436	579	2.5	617.3
B	489	633	5.36	21.6
C	433	578	3.34	107.8
D	390	470	1	10.7
E	392	473	0.88	116.9

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