Synthesis and Three-photon Induced Nonlinear Properties of a Novel Organic Chromophore

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Abstract: A novel organic chromophore 4, 4′-bis(9-carbazyl-*trans*-styryl)-biphenyl (BCSBP) has been synthesized and characterized by ^{1}HNMR and elemental analysis. Three-photon absorption (3PA) induced upconvention fluorescence was observed and large 3PA cross section as high as 10^{-74} cm^6 s^2 was obtained for nanosecond laser pulses at 1064 nm from optical limiting measurements.

Keywords: Carbazole, three-photon absorption, upconvention fluorescence, optical limiting.

Multiphoton absorption plays an important role in modern nonlinear optics and opto-electronics for its widely potential application in frequency upconvertion laser[1,2], optical limiting[3,4], biologic fluorescence imaging[5]. In a three-photon process, the cubic dependence of the simultaneous absorption of three photons on the input light intensity provides stronger spatial confinement and deeper penetration length compared with the two-photon process. Three-photon absorption as an important mechanism for optical limiting has recently attracted considerable attention with the rapid development of laser technology. Organic nonlinear optical materials are promising candidates in the application of optical limiting devices for their very short response time and easily tailored molecular structure for certain range of laser wavelengths. In this letter, a novel nonlinear chromophore (BCSBP) was synthesized. The chromophore has extended conjugated structural motif of donor-π-donor. Carbazole was adoped at the ends of the molecule which extended the molecular conjugated length effectively and also enhanced the molecular photostability.

Experimental

As shown in **Scheme 1**, **2** was prepared by the copper catalyzed Ullmann arylation procedure to obtain the same product of the reaction of *p*-chlorobenzaldehyde with carbazole catalyzed by Pd/P(t-Bu$_3$)[6]. 4, 4′-Dichloromethylene-biphenyl reacted with triphenylphosphine quantitatively to give bisphosphonium salt **1** which was converted to

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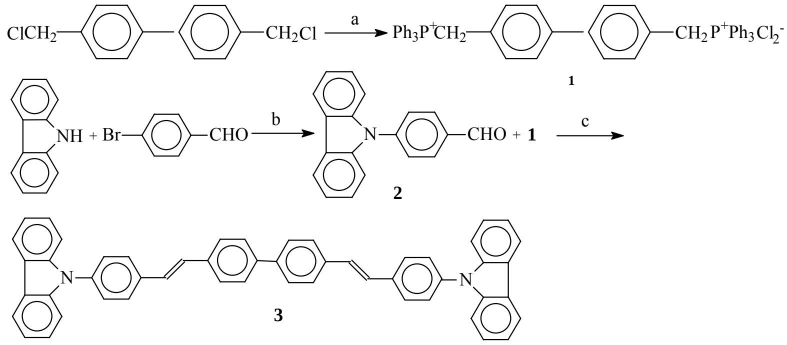
Scheme 1



(a) PPh_3, DMF; (b) K_2CO_3, Cu-bronze, nitrobenzene; (c) EtOH, EtONa

bisphosphonium "ylide" in ethanol solution of sodium ethoxide and then reacted with **2** by Wittig condensation with high yield.

4, 4′-Bis(9-carbazyl-*trans*-styryl)-biphenyl (BCSBP, **3**): 0.34 g (5 mmol) of sodium ethoxide was dissolved in 20 mL of ethanol and dropped into the solution of 0.50 g (1.85 mmol) of **1** and 0.62 g (0.80 mmol) of **2** in 40 mL of ethanol. Yellow precipitate soon appeared. After 5 hrs the yellow precipitate was collected and washed by 60% ethanol aqueous solution to get rid of triphenylphosphine oxide, purified with chromolographaic column on silica gel, yield 70%. m.p. 280°C. ^{1}HNMR (300MHz, $CDCl_3$), δ (ppm): 8.12 (q, 4H, J=8.4Hz), 7.75 (q, 4H, J=8.1Hz), 7.69 and 7.55 (dd, 8H, J=7.9Hz), 7.36 (m, 8H), 7.23 and 6.80 (dd, 8H, J=8.5Hz), 6.90 and 7.08 (d, 4H, J=16.4Hz). Elemental analysis: Calculated: C, 90.70; H, 5.23; N, 4.07. Found: C, 90.36; H, 5.35; N, 4.29.

Results and Discussion

Figure 1 shows the linear UV-Vis-NIR absorption and single-photon fluorescence spectra of BCSBP in chloroform at the concentration of 1×10^{-5} mol/L measured on

Figure 1 Linear absorption (a) and single-photon fluorescence spectra (b) of BCSBP

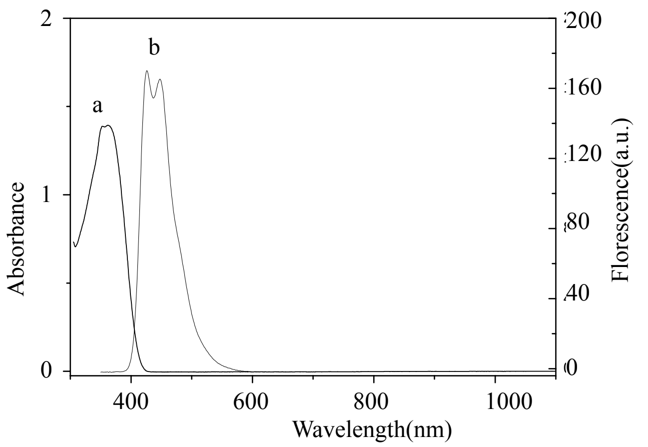


Figure 2 Upconversion fluorescence intensity as a function of input intensity

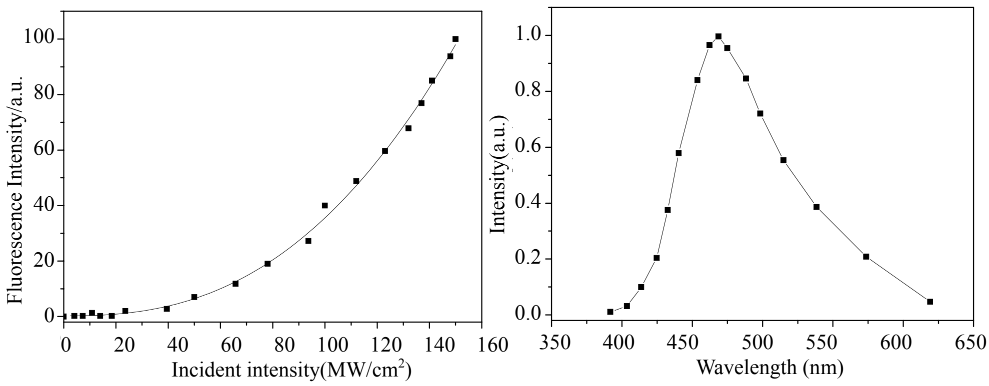
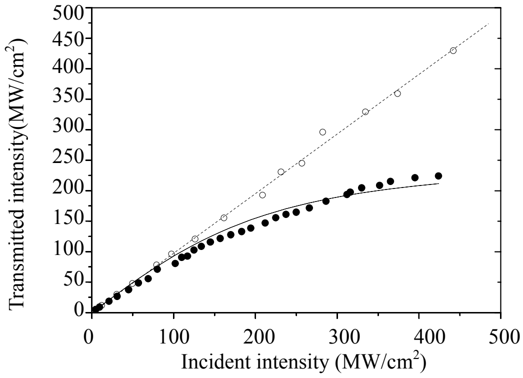


Figure 3 Transmitted intensity as a nonlinear function of input intensity



Shimadzu UV-365 UV-Vis-NIR recording spectrophotometer and Shimadzu RF5301pc spectrofluoriphotometer, respectively. The maximum absorption locates at 362 nm (ε_{max}=55800) and peak position of blue fluorescence emission at 448 nm. There is no linear absorption above the wavelength of 500 nm, *i.e.* the solution is completely transparent to the pump light at 1064 nm used in the optical limiting measurements.

Three-photon induced fluorescence signal was recorded in 0.01 mol/L chloroform solution pumped by a Q-switched (10 ns) Nd:YAG laser. As shown in **Figure 2**, the solid curve is the best fit to the cubic law that characterizes the three-photon absorption, absence of two-photon absorption at 532 nm. So two-photon absorption excited by one-photon absorption could be ruled out. The inset is the normalized spectrum of upconversion fluorescence emission induced by three-photon absorption. The peak of upconversion fluorescence appears at 468 nm with a red shift of 20 nm comparing to that of single-photon fluorescence.

For a laser pulse with Gaussian spatial and temporal profile, equation (1) can be used to calculate transmitted intensity *I (z)*[7]:

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

where I_0 is the incident intensity of the excitation beam, z is the optical propagation distance in the sample and γ is the 3PA coefficient (in the units of cm^3/W^2).

The 3PA cross section for the chromophore can be determined from the 3PA coefficient by equation (2):

$$\sigma_3 = N_A d_0 \times 10^{-3} / \gamma\ (h\nu)^2 \qquad (2)$$

where N_A is the Avogadro number, $h\nu$ is the photon energy of the incident laser beam, d_0 is the concentration of the sample in the units of mol/L and σ_3 represents the 3PA cross section.

Figure 3 demonstrates 3PA induced optical limiting behavior from intensity-dependent transmission measurements in 0.01 mol/L chloroform pumped by a Q-switched (10 ns) Nd:YAG laser. The opening circles represent the linear transmission curve of pure chloroform. The solid line is the theoretically best fitted curve given by equation (1) with the parameter γ , 8.80×10^{-18} cm^3/W^2. The value of σ_3 is found as high as 5.10×10^{-74} cm^6 s^2 about two orders larger than that obtained for the moleculer with limited conjugated length reported in previous work[8]. Intramolecular symmetric charge transfer in the extended conjugated molecular structure of donor-π-donor should account for the large σ_3 value[1,9]. The distinct optical limiting behavior shows BCSBP is a promising optical limiting material.

Acknowledgments

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References

1. M. Albota, D. Beljonne, J. L. Bredas, *et al.*, *Science*, **1998,** *281*, 1653.
2. Y. Ren, Q. Fang, W. T. Yu, *et al.*, *J. Mater. Chem.*, **2000**, *10* (9), 2025.
3. G. S. He, G.C. Xu, P. N. Prasad, *et al.*, *Opt. Lett.*, **1995**, *20* (5), 435.
4. D.Y. Wang , C. L. Zhan, Y. Chen, *et al.*, *Chem. Phys. Lett.*, **2003**, *369*, 621.
5. J. Balaji, R. Desai, S. Maiti, *Microsc. Res. Tech.*, **2004,** *63*, 67.
6. M. Watanabe, M. Nishiyama, T. Yamamoto, Y. Koie, *Tetrahedron Lett*., **2000**, *41*(4), 481.
7. J. D. Bhawalkar, G. S. He, P. N. Prasad, *Rep. Prog. Phys.*, **1996,** *59,* 1041.
8. G. S. He, J. D. Bhawalkar, P. N. Prasad, *Opt. Lett.*, **1995**, *20* (14), 1524.
9. F. E. Hernandez, K. D. Belfield, I. Cohanoschi, *Chem. Phys. Lett.,* **2004**, *391*, 22.

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