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A novel multibranched chromophore doped polymer as two-photon optical limiter

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A novel multibranched nonlinear chromophore , 4, 4´, 4´´-tris(9-carbazyl-*trans*-styryl) triphenylamine (TCSTPA) , has been synthesized and doped in polymethylmethacryate (PMMA) as a passive optical limiter. One-photon and two-photon absorption (TPA) optical properties were demonstrated in solution and doped polymer, respectively. When pumped with a femtosecond laser, remarkable two-photon induced optical limiting behavior was observed and a large TPA cross section of 2.35×10^{-47} cm^4 s photon^{-1} molecule^{-1} was obtained at 800 nm.

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1. Introduction

Two-photon absorption (TPA) is characterized by the simultaneous absorption of two separated photons *via* virtual states in nonlinear materials irradiated with a tightly focused laser. TPA process shows quadratic dependence of incident light intensity so that the subsequent chemical and physical changes are confined to a highly localized area of volume λ^3 (λ is the wavelength of the incident laser beam) in the vicinity of focal point. The intrinsic advantages of two-photon absorption make materials with large TPA cross sections potential candidates in a variety of third-order based applications, including two-photon fluorescence microscopy, frequency up-conversion lasing, three-dimensional optical data storage and optical limiting [1-5].

As an important third-order nonlinear optical phenomenon, TPA induced optical limiting depends mainly on TPA cross sections of the involved nonlinear optical materials. Extensive studies have been conducted in an attempt to get the optimized structural motifs of organic nonlinear chromophores for the realization of above TPA applications. A variety of nonlinear chromophores, including dipolar molecular structure of D-π-A (D represents electron donor, π is conjugated bridge and A is electron acceptor) and quadrupolar molecular structure of D-π-D, have received considerable attention in earlier reports [6-9]. Recently many works have focused on octupolar and multibranched structures with higher molecular symmetry and multidimensionality, whose TPA cross sections have been greatly enhanced as a result of a cooperative enhancement of two-photon absorption between the branches. Theoretical calculations have further elucidated the newly developed structure-property relationship based on the symmetric and multibranched π-electron conjugation framework [10, 11].

In this paper we report on a newly synthesized multibranched nonlinear chromophore , 4, 4´, 4´´-tris(9-carbazyl-*trans*-styryl) triphenylamine (abbreviated as TCSTPA) by using this design strategy. The molecular structure of TCSTPA is shown in Fig. 1. The multibranched chromophore contains triphenylamime as core and carbayl group as peripheral electron donor and has C_{3h} molecular symmetry and extended conjugated length. Practical nonlinear optical devices need solid nonlinear materials for a certain purpose. Thus we choosed to dope the solid matrix of polymethylmethacryate (PMMA) by the TCSTPA chromophore and to study the nonlinear optical properties of the resulting blend. As an excellent polymer matrix, PMMA attracts particular interests for its transparency in the entire visible and near IR range, simple synthesis, low cost and good compatibility with organic dyes. One- and two-photon absorption photophysical properties of the chromophore were studied in solution and doped solid polymer, respectively. Large TPA cross section of TCSTPA was obtained by the best-fitting of two-photon induced optical limiting curve in doped PMMA at the wavelength of 800 nm pumped by a femtosecond laser.

2. Experimental

When preparing TCSTPA doped PMMA, the chromophore was first dissolved in methylmethacryate (MMA) which was used as both monomer and solvent in a glass cuvette with the concentration of 1×10^{-2} mol/L. Then radical polymerization was initiated by dibenzoyl peroxide (1% weight content of MMA) at 80℃. After the polymer solidified completely, a 1-cm long doped PMMA rod, which was used in the experiments of two-photon induced fluorescence and optical limiting, was obtained by cutting off the unwanted part and the two surfaces in the optical path were kept parallel and smooth by polishing with sand paper.

The one-photon absorption and excited fluorescence spectra were measured on Shimadzu UV-2401 UV-Vis recording spectrophotometer and Shimadzu RF5301pc spectrofluoriphotometer, respectively. The concentration of TCSTPA solution in chloroform was 1×10^{-5} mol/L. A mode-locked femtosecond laser with Gaussian transverse intensity distribution was used for two-photon induced fluorescence and optical limiting. The laser system is composed of Nd:YLF laser (Verdi-5) and a resonant cavity of Ti:Sapphire to create femtosecond laser pulses. Parameters of the femtosecond pump source include the pulse width of 80 femtosecond, the central wavelength of 800 nm and the repetition frequency of 80 MHz.

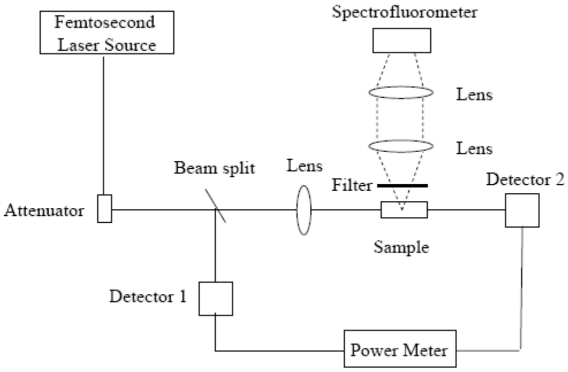

Fig. 1. Experimental set-up for the measurement of two-photon two-photon induced fluorescence and optical limiting.

The femtosecond laser beam was focused by a 15-cm convex lens into the doped PMMA rod. The strong two-photon induced fluorescence was collected transversely by a spectrofluorometer (USB2000-FLG) after two collimating lens. A 700 nm short pass filter was used to rule out the effect of incident light. The light beam from the laser firstly was divided into two beams by an optical splitter. The weaker one was acted as a signal beam connected to a detector of a laser energy meter (Molectron, EPM2000) to monitor the intensity of the pump beam. The other beam was focused into the sample and the transmitted intensity was measured by another detector of the energy meter. The diameter of the laser beam in the sample was 0.6 mm measured by knife-edge method. The schematic diagram of experimental set-up for the measurement of two-photon induced fluorescence and optical limiting is illustrated in Fig. 1.

3. Results and discussion

Fig. 2 also shows the one-photon absorption spectrum of a 1-mm path TCSTPA solution in chloroform with a concentration of 1×10^{-5} mol/L. The contribution of the solvent had been subtracted. One can see the strongest absorption wavelength located at 405 nm, attributed to the solute molecules. There is no linear absorption for the solution in the spectral range from 500 to 900 nm with the prediction that strong two-photon induced fluorescence should occur around 800 nm.

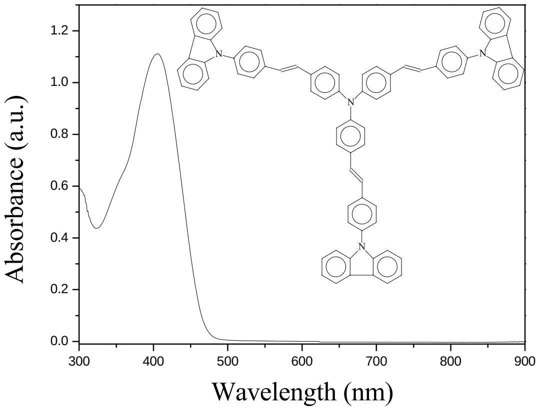

Fig. 2. One-photon absorption spectrum of TCSTPA solution in chloroform and the chemical molecular motif of TCSTPA.

The fluorescence peak of one-photon excitation in TCSTPA chloroform solution at 1×10^{-5} mol/L is located at 490 nm as shown in Fig. 3 and indicated by a dotted line. The spectral shape and peak location of one-photon induced fluorescence are very similar to those of two-photon induced fluorescence as shown in Fig. 3 indicated by a solid line. This suggests that the one-photon and two-photon induced fluorescence are emitted from the same excited singlet state (S_1), although the mechanism and selection rules of the two-photon process may differ from that of one-photon process. However, the peak of two-photon fluorescence is somewhat red-shifted by 5 nm in contrast with that of one-photon fluorescence. This can be explained by a reabsorption effect of the sample containing a higher concentration of 1×10^{-2} mol/L in the measurement of two-photon fluorescence and the reabsorption also caused the left part of spectral shape in two-photon fluorescence

In order to confirm if the observed fluorescence is a real two-photon excitation process, the power-law dependence is examined at 800 nm. The quadratic dependence of the fluorescence signal intensity on incident intensity is shown in Fig. 2 with the plots on log-log scales. We find that two-photon induced fluorescence obeys the quadratic-law dependence with the slope of 1.97.

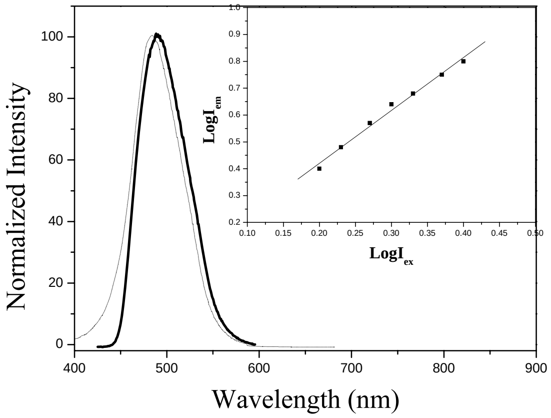

Fig. 3. Normalized one-photon (dot line) and two-photon (solid line) induced fluorescence spectra of TCSTPA solution in chloroform and TCSTPA doped PMMA rod. The inset is a typical log-log plot of quadratic dependence of the fluorescence signals on incident intensity.

The optical limiting experiment of 1-cm long TCSTPA doped PMMA is demonstrated in Fig. 4, which shows the transmitted intensity as a nonlinear function of the incident intensity. Each data was an average of 50 laser shots measured by a boxcar averager. According to basic theoretical considerations [2], if the nonlinear transmission change is only due to a TPA process and the incident beam has a uniform Gaussian intensity distribution in the sample, the transmitted intensity I_0 can be expressed as

$$I' = \ln(1 + I_0 L\beta) / L\beta \qquad (1)$$

where I_0 is the incident intensity, L is the thickness of the given sample, and β is the TPA coefficient of the given chromophore, which is independent of the input intensity I_0.

The TPA coefficient β can be experimentally measured and the molecular two-photon cross section σ_2 is further determined using the following expression

$$\beta = \sigma_2 N_A d \times 10^{-3} / h\nu \qquad (2)$$

Here β is in units of cm/GW, d is the concentration of the chromophore in units of mol/L, N_A is the Avogadro constant, $h\nu$ is the energy of the incident photon and σ_2 is in units of cm^4 s photon^{-1} molecule^{-1}.

In the measurement of optical limiting behavior, the incident intensity was kept below a power threshold level to avoid cavity lasing and other nonlinear absorption. At the same time quadratic relationship between two-photon fluorescence signal intensity and the incident intensity was monitored to ensure a real TPA process. In Fig. 4 the solid line is the theoretical curve of transmitted intensity versus input intensity fitted by Eq. (1) with best-fit parameter of β = 0.56 cm/GW. The straight dotted line corresponds to linear transmission assuming β = 0. From Fig. 4 one can see the optical limiter is transparent to the incident laser beam at relative low power and a clear optical limiting behavior appears in a broad power range with the lowest optical transmittivity less than 40%. Based on the known β value and Eq. (2), the value of the molecular TPA cross section of TCSTPA was estimated as 2.35×10^{-47} cm^4 s photon^{-1} molecule^{-1}, which is a large value for two-photon absorption pumped with femtosecond laser beam at 800 nm.

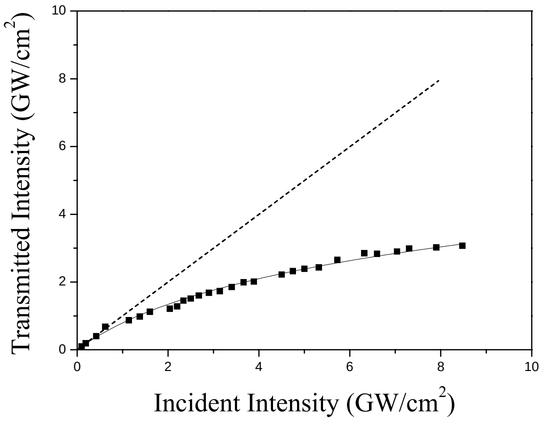

Fig. 4. Measured transmitted intensity as a nonlinear function of incident intensity demonstrating optical power limiting behavior in the 1-cm long TCSTPA doped PMMA rod. The solid line is the theoretical curve with best-fit parameter of β = 0.56 cm/GW. The straight dotted line corresponds to linear transmission assuming β = 0.

4. Conclusion

The TCSTPA doped polymer rod as passive optical limiter induces a remarkable two-photon optical limiting with a large TPA value of 2.35×10^{-47} cm^4 s photon^{-1} molecule^{-1} at 800 nm, which proves TCSTPA doped polymer a promising material for two-photon absorption. Multibranched nonlinear chromophores with high molecular symmetry and extended conjugated length could be further explored for more third-order nonlinear practical applications, such as frequency up-conversion lasing and three-dimensional optical data storage.

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