Three-photon up-conversion lasing of a novel multibranched nonlinear chromophore in doped poly(methyl methacrylate)

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A novel nonlinear chromophore, 4, 4´, 4´´-tris((3,6-di-*tert*-butyl)-9-carbazyl-(9,9-dioctyl)-2,7-fluorenylidene-vinylidene) triphenylamine (TCFVTPA), which possesses multibranched molecular structure and extended coplanar conjugation length, has been designed, synthesized and characterized. One-photon induced photophysical properties were studied in 1×10^{-5} mol/L chloroform solution. Three-photon induced fluorescence was obtained in poly(methylmethacryate) (PMMA) with the doped concentration of 1×10^{-2} mol/L pumped by a femtosecond laser system at 1300nm and the correspoding cross-section of TCFVTPA was measured as 8.3×10^{-75} cm^6 s^2 by nonlinear transmission method. When the energy of input irradiation excceds a certain value of 0.3 μJ, three-photon induced up-conversion lasing occurs with the spectral width of ~7 nm and the net up-conversion efficiency of 1.54%.

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1. Introduction

Multiphoton processes play an important role in modern nonlinear optics and opto-electronics for its widely potential applications in frequency up-converted laser, three-dimensional (3D) microfabrication, optical power limiting, biologic fluorescence imaging and photodynamic therapy [1-7]. Multiphoton processes originate from the simultaneous absorption of two, three and even more separated photons *via* virtual states in nonlinear materials irradiated with a tightly focused laser. Two-photon absorption (TPA) has been widely investigated from molecular design, nonlinear optical properties to applications in related fields [8-12]. However, as a fifth-order nonlinear effect, three-photon absorption (3PA) has limited exploration and applications at present due to the small 3PA cross-sections of common materials. Nowsdays three-photon absorption is becoming an intriguing possibility in the biological and medical fields due to the cubic dependence on the incident light intensity and the utilization of longer excitation wavelength in the near infrared region with greater penetration ability, which can minimize scattered light loss and reduce unwanted linear absorption in the low absorption window in living organisms, so that a higher contrast in imaging can be obtained.

However, it is essential to explore the relationship between chemical structures and nonlinear optical properties for this higher order nonlinear process which is fundamental to provide the basis for molecular engineering to maximize the strength of 3PA cross-sections and is also the key to the practical applications of 3PA technology. From the point of view of structure-property relationship of nonlinear organic materials, the delocalization of π-electrons occurring in the conjugated molecules can lead to significant enhancement of the high order optical nonlinearities. Recently many works have focused on octupolar and multibranched structures with higher molecular symmetry and multidimensionality, whose 3PA cross-sections have been greatly enhanced as a result of a cooperative enhancement between the branches. Theoretical investigations have revealed that major contribution to the static value of high order polarizability originates from the transition dipole term that involves the difference between the dipole moments in the ground state and in the lowest excited state.

In this paper, we synthesized a multibranched nonlinear chromophore with extended coplanar conjugated length, 4, 4´, 4´´-tris((3,6-di-tert-butyl)-9-carbazyl-(9,9-dioctyl)-2,7-fluorenylidene-vinylidene) triphenylamine (TCFVTPA), according to the above molecular design strategy. The core of the chromophore was chosen as triphenylamine, which combines 9,9-dioctyl-fluorenyl by a vinylidene π-bridge. Fluorene derivatives show unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution of octyl group at the remote C9 position of fluorene can improve the solubility and processibility of the nonlinear chromophore without significant increase in steric interactions in the nonlinear chromophore backbone. The carbazyl group is incorporated into the chromophore as a peripheral electron donor and the molecular motif has

C3h molecular symmetry and extended conjugated length. When irradiation with a tightly focused laser, π-electrons can be delocalized in the whole multibranched nonlinear chromophore and can be excited with high optical activity.

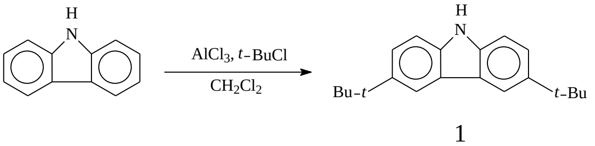
The 3PA application in optical device needs solid material as matrix and thus we doped the chromophore into the optical transparent PMMA matrix when carrying out the studies of the 3PA photophysical properties. The three-photon induced fluorescence occured with lower excitation light intensity. However, as the pump beam energy was higher than a certain threshold value, a strong highly directional up-converted visible lasing could be easily observed, which was generated by the reflection feedback of the two parallel surfaces of the sample.

2. Experimental

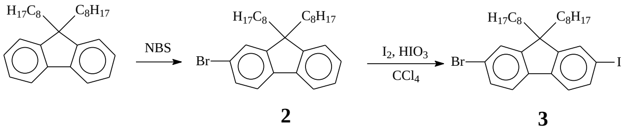
2.1 Chemicals and synthesis

All reagents were purchased commercially in analytical reagent (A.R.) grade and used without further purification. The solvents for synthesis and measurements were purified according to conventional methods. The chemical characterizations were described in detail elsewhere.

3,6-di-*tert*-butylcarbazole (**1**) was synthesized from the starting reagent carbazole in dichloromethane with anhydrous aluminium chloride, and then adding *tert*-butylchloride dropwise at room temperature. Two *tert*-butyls were grafted to 3,6 positions of carbazole by C-alkylation reaction.

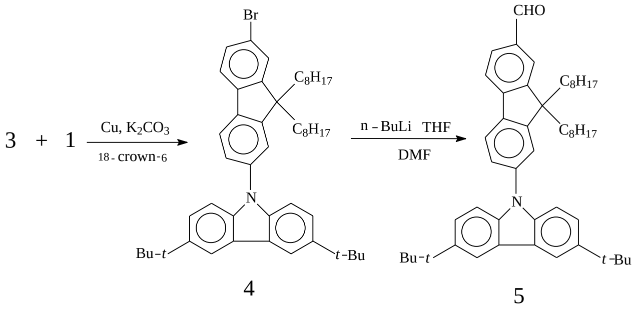


9,9-dioctylfluorene reacted with N-bromosuccinimide (NBS) in propylene carbonate, and then the mixture was diluted, extracted and distilled. Compound **2**, which is the momobromo substituted fluorene, i.e., 2-bromo-9,9-dioctylfluorene, was obtained by collecting the fraction at 155-165 °C under the reduced pressure. A mixture of compound **2**, iodine and iodic acid in carbon tetrachloride was maintained at 80-85 °C with mechanical stirring. The product slurry was cooled to room temperature, filtered, washed and recrystallized to get compound **3**.

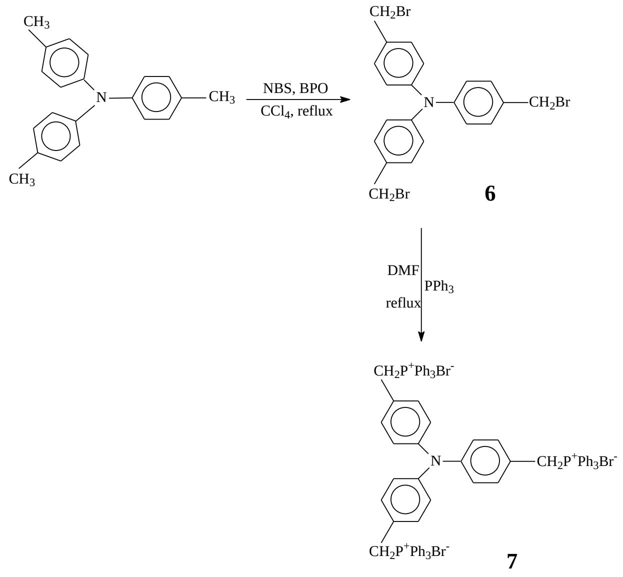


9-(7-bromo-9,9-dioctyfluoren-2-yl)-3,6-di-*tert*-butylcarbazole (**4**) was a product from copper-catalyzed amination of amine derivative (**1**) and halogen derivative (**3**). A selective reaction was carried out between compound **3** and compound **1,** in which iodine atom with higher activity reacted with secondary amine preferentially. A mixture of 2-bromo-7-iodo-9,9-dioctylfluorene, 3,6-di-*tert*-butylcarbazole, potassium carbonate, copper bronze and 18-crown-6 in 1,2-dichlorobenzene solution was kept refluxing for 6 h, cooled, and filtered. The residue after concentration of the filtrate was transferred to a column of silica gel and eluted with hexane to remove the dichlorobenzene and unreacted bromofluorene.

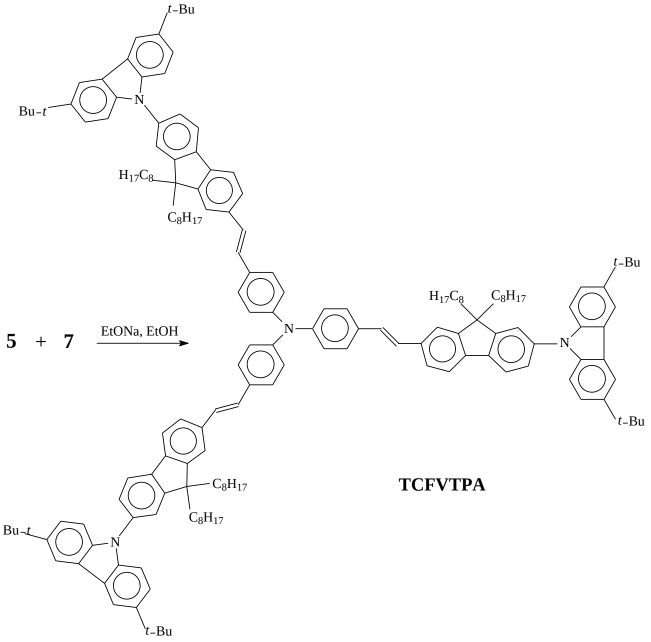
The halogen-metal exchange reaction of bromine atom in compound **4** with *n*-butyllithium in DMF and THF mixing solution was carried out at -50 °C, followed by chromatograph with silica gel, producing 7-(3,6-di-*tert*-butyl-9-carbazyl)-9,9-dioctylfluorene-2-carboxaldehyde (**5**) in high yield.



Bromomethylation is a good reaction for molecules containing symmetric methyl groups. The slow start to the reaction is necessary, as it can go out of control if heated too rapidly. 4, 4´, 4´´-trimethylphenylamine, as the starting agent, stirred with N-bromosuccinimide and benzoyl peroxide in carbon tetrachloride for 2 h and then heated slowly to keep refluxing for 12 h. The succinimide formed was removed by filtration and the solvent was evaporated to give a yellow colored solid, i.e., 4, 4´, 4´´-tribromomethylphenylamine (**6**).



In DMF and exccessive amount of triphenylphosphine, compound **6** can be converted quantitatively to tris-phosphonium salt **7**, which has strong electron-donating ability and good solubility in most organic solvents. The subsequent Wittig reaction of compound **5** and **7** produced alkenes by the reaction of aldehydes with the ylide generated from the phosphonium salt in EtONa/EtOH under a moderate condition for 6 h. The base was removed by filtration and the product was treated with silica-gel chromatograph to obtain the target compound (TCFVTPA). Stabilized ylides give (E)-alkenes due to the existence of benzene rings.



TCFVTPA

2.2 Instruments and measurements

The linear absorption and one-photon excited fluorescence spectra were measured on a Shimadzu UV-3600 UV-Vis-NIR recording spectrophotometer with wavelength resolution of 1 nm and Shimadzu RF5301pc spectrofluoriphotometer, respectively. The concentration of TCFVTPA solution in chloroform was 1×10^{-5} mol/L.

In the three-photon photophysical measurements, the excitation source came from an optical parameter amplifier (OPA) system pumped with a Legend Elite-F ultrafast Ti:Sapphire amplifier (Coherent Inc.), which was operated at TEM00 mode with a pulse width of 80 fs and a repetition rate of 1 kHz. The central wavelength was set at 1300 nm in the near infrared region to ensure the energy of three photons falling into the strong one-photon absorption band of the chromophore.

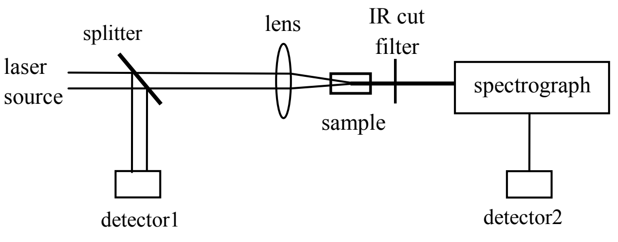


Fig. 1. The optical setup for three-photon photophysical measurements

Fig. 1 shows the diagram of optical setup for three-photon photophysical measurements. The excitation source 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 one detector of a two-channel power-meter in order to monitor the intensity of the excitation beam. The intense beam was focused into the sample by a convex lens (f = 15 cm).

After cutting the excitation wavelength by a 700 nm short pass filter, the emitted signal was collected into the slit of the imaging spectrograph by two convex lenses with short focal length after attenuation. The 3PA fluorescence was collected at the direction perpendicular to the pump beam and was recorded by an optical multi-channel analyzer. The output energy of up-conversion 3PA lasing was recorded by another detector of the two-channel powermeter.

To get the sample for three-photon lasing measurement, the chromophore TCFVTPA was first dissolved in methylmethacryate (MMA) in a glass cuvette with the concentration of 1×10^{-2} mol/L, then carried out radical polymerization initiated by dibenzoyl peroxide (1% weight content of MMA) at 80℃, and finally solidified MMA completely to form PMMA matrix containing the chromophore TCFVTPA. A 1-cm thick doped PMMA rod with two parallel and smooth surfaces was obtained after taking off the cuvette, cutting and polishing the sample. As an excellent polymer matrix, PMMA has many advantages such as its transparency in the entire visible and near infrared range, simple synthesis, low cost and good compatibility with organic chromophores.

3. Results and discussion

3.1 One-photon induced photophysical properties

Fig. 2 shows the normalized one-photon induced photophysical properties with 1-cm optical path in chloroform at the concentration of 1×10^{-5} mol/L. The contribution of the solvent had been subtracted using a blank solvent reference when measured. The strongest absorption wavelength (solid line in Fig. 2) appeared at 430 nm, which has a red-shift of about 30 nm compared to its analog [13]. Much larger conjugated length makes the chromophore of TCFVTPA easier in transition from ground state to excited state. The solution is optical transparent in the region from 500 to 1400 nm, and thus up-convention fluorescence, even lasing, could be expected in the near infrared region without linear absorption.

One-photon induced fluorescence spectrum (dot line in Fig. 2) shows peak wavelength of 522 nm with a Stokes shift of 92 nm. There is a partial overlap between absorption spectrum and fluorescence spectrum. The overlap becomes larger as the concentration increases, which will lead to self-absorption of fluorescence at high concentrations.

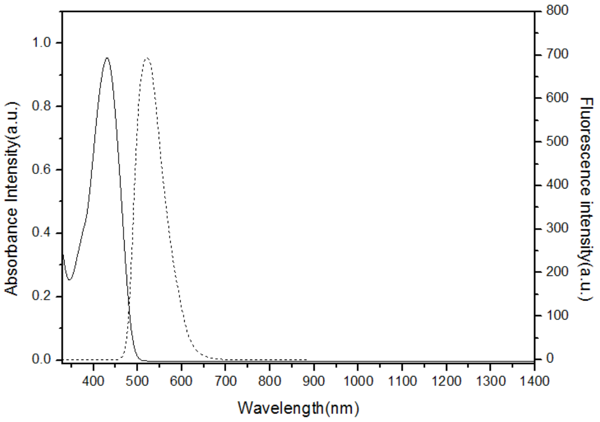


Fig. 2. Normalized one-photon absorption spectrum(solid line) and fluorescence spectrum(dot line) of TCFVTPA in chloroform at 1×10^{-5} mol/L

3.2 3PA fluorescence and lasing

The peak wavelength of 3PA induced fluorescence spectrum in Fig. 3(a) lies in 525 nm, which has a red shift of 3 nm in contrast to that of one-photon induced fluorescence. This phenomenon arises from the reabsorption effect of the sample containing a higher concentration of 1×10^{-2} mol/L in the measurement of 3PA fluorescence. Using the same pump source, 3PA cross-section of TCFVTPA was measured by nonlinear transmission method[13,14], which was determined as 8.3×10^{-75} cm^6 s^2 with 15% uncertainty.

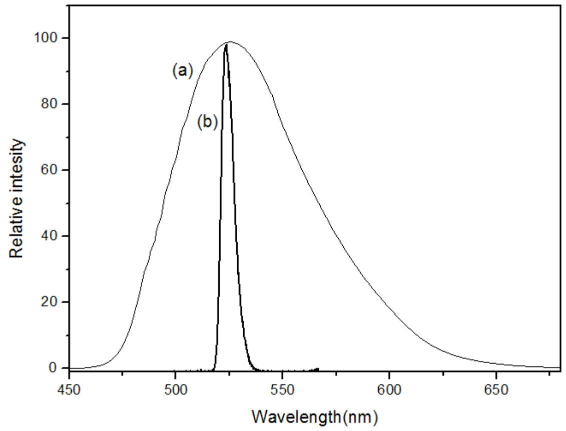


Fig. 3. Normalized 3PA induced up-convertion fluorescence (a) and lasing (b) spectra in PMMA with doped concentration of 1×10^{-2} mol/L

The three-photon absorption induced fluorescence occured with lower excitation light energy. However, as the pump beam energy was higher than a certain threshold value of 0.3 μJ, a strong highly directional frequency up-convertion visible lasing could be easily observed. Fig. 3(b) shows the 3PA lasing spectral distribution with a spectral width of ~7 nm (full-width at half maximum) which is about 10 times narrower than that of the 3PA fluorescence spectrum. One can also see from Fig. 3(b) that the central wavelength of lasing spectral distribution has a slight blue shift with that of 3PA fluorescence spectrum. This is induced by the difference for the method of fluorescence collection. The fluorescence was collected from the side of the sample, where more chromophores lie in ground state in the optical path and thus the re-absorption coefficient is larger. The lasing was collected from the front of the sample, where the chromophores in excited state prevailed and the re-absorption coefficient is smaller.

This lasing could contribute to the high 3PA cross-section of the chromophore. The strong three-photon absorption make effective population inversion and thus the reflected light of the two parallel surfaces of the sample can be magnified. Such a type of lasing based on organic materials has no restriction of phase matching and minimization of local thermal damage by usage of near infrared wavelength.

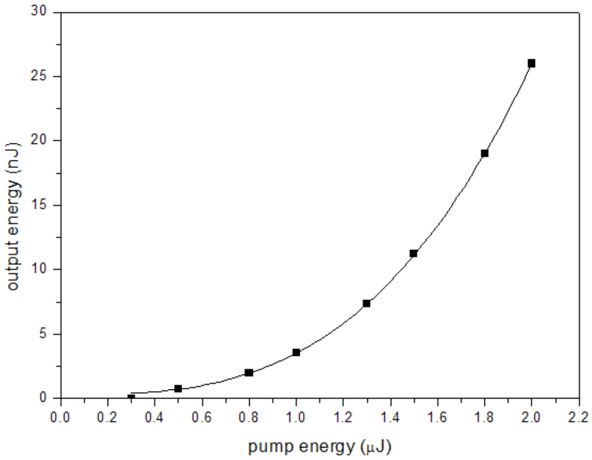


Fig. 4. The relationship of output energy versus pump energy curve of 3PA lasing

The characteristic curve of 3PA lasing between output energy and pump energy is shown in Fig. 4. At the highest pump energy of 2.0 μJ, the output lasing energy is 26 nJ and the correspoding up-conversion efficiency is 0.77%. Considering that the measured nonlinear transmission was 0.5 at this pump level, the net up-conversion efficiency from the absorbed pump energy to the output up-conversion lasing energy is 1.54%. The up-conversion efficiency has the space to be further enhanced considering the uncoated two surfaces of the sample, which will be studied in our next researches.

4. Conclusions

In conclusion, the chromophore of TCFVTPA with multibranched structural motif and extended coplanar conjugation has been designed and synthesized. The large 3PA cross-section of 8.3×10^{-75} cm^6 s^2 was obtained in the near infrared region which exhibits sensitive three-photon response at femtosecond pulse levels. The spectral properties of three-photon induced fluorescence and lasing with 1.54% up-conversion efficiency at higher pump energy were studied. Efficient three-photon absorption at 1300 nm has the potential application in short-pulse optical fibre communications and biophotonics because the near infrared radiation provides a greater penetration into biological tissues and less damage to the cells than the visible wavelength radiation.

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