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Synthesis, tunable two and three-photon absorption properties of triazine derivatives by branches

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ABSTRACT

Three novel triazine derivatives, (*E*)-4-(2-(4,6-dimethyl-1,3,5-triazin-2- *yl*)vinyl)- *N*,*N*-di-*p*-tolylaniline (**a**), 4,4'-((1*E*,1'*E*)-(6-methyl-1,3,5-triazine-2,4-*diyl*) bis(ethene-2,1-*diyl*))bis(*N*,*N*-di-*p*-tolylaniline) (**b**), and 4,4',4''-((1*E*,1'*E*,1''*E*)-(1,3,5- triazine-2,4,6-triyl)tris(ethene-2,1-*diyl*))tris(*N*,*N*-di-*p*-tolylaniline) (**c**), were designed and synthesized. Their photophysical and photochemical properties were investigated systematically including single-photon absorption, nonlinear optical absorption (NOA) and up-converted fluorescence. Interestingly, the compound **a** with single branch showed pure three-photon absorption phenomenon, while the corresponding **b** and **c** indicated two-photon induced excited-state absorption properties, showing structure-dependence relationship. The results offer a method to design and synthesize organic molecules for multiphoton materials. It was noted that the three-photon cross-section value (δ_3) of **a** was up to 1.35 × 10⁻⁷⁶ cm⁶ s². Correspondingly, the two-photon (δ_2) and excited-state cross-section (δ_e) values of **b** and **c** also were obtained, and value of them were 485 GM and 1.03 × 10⁻¹⁷ cm² for **b**, and 1100 GM and 1.27 × 10⁻¹⁸ cm² for **c**, respectively.

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1. Introduction

Organic nonlinear optical materials have attracted intensive research interest due to their possible applications in a number of fields, including two-photon fluorescence imaging [1], threedimensional optical data storage [2], optical power limiting [3], and photodynamic therapy [4]. Especially, the flexible synthesis and tunable structures of electronic-states have made organic molecules promising candidates for applications based on nonlinear absorptions. In the past decade, much effort has been paid to the development highly efficient two-photon absorption (2PA) [5] and twophoton excited fluorescence (2PEF) materials [6]. Some effective strategies for molecular design to enhance two-photon absorption and emission have been found such as donor-bridge-acceptor $(D-\pi-A)$ structures, donor-bridge-donor $(D-\pi-D)$ quadruples structures, multi-branched molecules, and so on. However, the study for their higher-order nonlinear absorption including threephoton absorption (3PA), two-photon induced excited-state absorption (2PEA) and four-photon absorption (4PA), is still rather

* Corresponding authors. E-mail address: ouyangxh@nimte.ac.cn (X. Ouyang). limited [7,8]. Commonly, the higher-order nonlinear absorption strongly depends on molecular structures of electronic-states and so on parameters (wavelength, pulse duration and peak irradiance) of the incident laser beam. Up to now, the laser sources with ultrafast pulse durations offer the feasibility to observe different kinds of higher-order nonlinear absorption phenomena. However, to this day, organic molecules, showed 3PA or higher-order nonlinear optical properties, are still very a few. Therefore, organic materials with the higher-order nonlinear absorption or emission will be attracting extensively interests.

As an intriguing type of organic functional materials, triazine and its derivatives have recently received attention due to their special and significant properties [9–11]. Actually, triazine and its derivatives were extensively used as emitters in organic lightemitting materials, or as frequency converted fluorescent and nonlinear absorption in octupolar molecules [9]. Moreover, triazine can also be functionalized with a variety of substitutions and obtain excellently chemical and physical performance for the nonlinear optical application.

Triphenylamine and their derivatives, known as important chemical intermediates, are some of the typical aromatic amines and possess superior electron-donating properties [12,13]. However, to the best of our knowledge, triazine derivatives





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containing triphenylamine unit, showing tunable 3PA and 2PEA with structure dependence in femotosecond timescales, have still been reported very a few during the past decade.

Here, we designed and synthesized several molecules with different branches containing triphenylamine and triazine units. (Scheme 1)Their nonlinear absorptive, and up-converted fluorescent properties were studied systematically using open Z-scan, frequency up-converted, and pump-probe methods by femtosecond laser pulses using 780 nm-wavelength as excitation.

2. Experimental

2.1. Materials and characterization

4-(di-p-tolylamino)benzaldehyde were purchased from Tokyo Chemical Industry Co., LTD. All other reagents were used as received from commercial sources, unless otherwise stated. Melting points were determined using an X-4 apparatus and the thermometer was uncorrected. ¹H NMR spectra were determined in CDCl₃ with a Bruker DRX 400 MHz spectrometer. Chemical shifts (d) were given relative to tetramethylsilane (TMS). Elemental analyses were recorded with a Perkin-Elmer 2400 analyzer. MALDI-TOF-MS were acquired using a Voyager-DE STR MALDI-TOF mass spectrometer (PerSeptive Biosystems) in the linear positive mode with delayed extraction. Samples were analyzed using a dichloromethane solution of the sample (1 L) mixed with 10 L of dithranol matrix (10 mg mL⁻¹ in 70:30 CH₂Cl₂/EtOH) before loading onto a metal sample plate. Fluorescent and UV-vis spectra of the derivatives were measured with a FLSP920 and HITACHI U3010 spectrophotometers.

2.2. Synthesis of compounds **a**, **b** and **c**

Compounds **a**, **b** and **c** were synthesized by the condensation reaction between 4-(*di-p*-tolylamino)benzaldehyde and 2,4,6- trimethyl-1,3,5-s-triazine by potassium hydroxide (KOH) as catalysis. 4-(*di-p*-tolylamino)benzaldehyde reacts particularly slowly because of its low nucleophilicity.

Compound **a**: A solution of 2,4,6-trimethyl-1,3,5-s-triazine (0.26 g, 2.12 mmol), 4-(*di-p*-tolylamino)benzaldehyde (0.647 g, 2.12 mmol), and KOH (0.107 g) in 30 mL methanol were added into a 100 mL flask under refluxing temperature, The reaction mixture was refluxed for a further 12 h and then solvent was removed. The residue was purified by column chromatography on silica gel using toluene/ethanol (10/1) as eluent and white powder was obtained. Yield, 0.355 g, 41.3%, m.p.97~99 °C; ¹HNMR (CDCl₃, 400 MHz) δ : 2.63 (s, 6H), 3.91 (s, 6H), 7.11–7.44 (m, 10H), 8.11 (d, *J* = 15.8 Hz, 1H), 8.12 (d, *J* = 16.2 Hz, 1H), 8.18 (d, 2H, Ar–H); ¹C NMR (CDCl₃, 400 MHz) δ : 24.9, 26.9, 112.7, 122.1, 127.6, 129.3, 133.3, 133.7, 137.7, 140.3, 173.7, 177.7; MS (MALDI-TOF) m/z: 406.1(M⁺); Anal. Calcd for C₂₇H₂₆N₄: C 79.77; H 6.45; N 13.78; found C 79.54; H 6.47; N 13.82.

Compound **b**: A solution of 2,4,6-trimethyl-1,3,5-s-triazine (0.26 g, 2.12 mmol), 4-(*di*-*p*-tolylamino)benzaldehyde (1.294 g, 4.24 mmol), and KOH (0.214 g) in 60 mL methanol were added into a 150 mL flask under refluxing temperature, The reaction mixture was refluxed for a further 10 h and then solvent was removed. The residue was purified by column chromatography on silica gel using toluene/ethanol (10/1) as eluent and light yellow powder was obtained. Yield, 0.548 g, 38.6%, m.p.156~158 °C; ¹HNMR (CDCl₃, 400 MHz) δ : 2.35 (s, 12H), 3.92 (s, 3H), 7.13–7.46 (m, 20H), 7.47 (d, J = 15.8 Hz, 2H), 8.40(d, J = 16 Hz 2H), 8.51 (d, 4H, Ar–H); ¹CNMR



Scheme 1. The synthetic route of compounds a, b and c.

 $({\rm CDCl}_3,400~{\rm MHz})$ δ : 24.3, 26.1, 112.8, 122.3, 127.6, 129.3, 133.3, 133.7, 137.7, 140.7, 173.3, 177.7; MS (MALDI-TOF) m/z: 690.3 (M + H)+; Anal. Calcd for $C_{48}H_{43}N_5$: C 83.57; H 6.28; N 10.15; found C 83.35; H 6.30; N 10.18.

Compound **c**: was synthesized by the following procedure. Under refluxing temperature, a solution of 2,4,6-trimethyl-1,3,5-s-triazine (0.13 g, 1.06 mmol) in 20 mL methanol were added dropwise into a 100 mL flask containing methanol (10 mL), 4-(*di-p*-tolvlamino) benzaldehyde (0.97 g, 3.2 mmol) and KOH (0.168 g) in 2 h. The reaction mixture was refluxed for a further 24 h and then solvent was removed. The residue was purified by column chromatography on silica gel using toluene/ethanol (10/1) as eluent. The light yellow powder was obtained. Yield, 0.451 g, 43.7%; m.p.94–95 °C; UV-vis (THF) λ_{max} : 424 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 2.39 (s, 18H), 7.12-7.19 (m, 18H), 7.47-7.51 (m, 12H), 7.55 (d, J=15.80 Hz, 3H), 8.04 (*d*, *J*=16.03 Hz, 3H), 8.60–8.61 (*m*, 6H); ¹³C NMR (CDCl₃) δ: 175.8, 142.8, 142.4, 141.9, 129.7, 127.4, 126.3, 126.0, 123.5, 123.3, 123.0, 121.0, 120.3, 120.3, 115.1, 110.2, 110.0, 25.9; MS (MALDI-TOF) m/z: 973.5 (M + H)⁺; Anal. calcd for C₆₉H₆₀N₆: C 85.15, H 6.21, N 8.63; found C 84.93, H 6.23, N 8.66.

2.3. Z-scan and pump-probe measurements

The laser pulses were produced by a mode-locked Ti:Sapphire laser (Quantronix, IMRA), which seeded a Ti:Sapphire regenerative amplifier, and focused onto a 1-mm-thick quartz cuvette containing the solutions of the derivatives. The incident and transmitted laser pulse energy were monitored by moving the cuvette along the propagation direction of the laser pulses. The Z-scan experimental system was calibrated using a piece of cadmium sulfide (CdS) bulk crystal as a reference because it possesses large 2PA at the wavelength of 780 nm and has been well investigated in our laboratory. The 2PA coefficient of CdS was determined to be 6.4 ± 0.6 cm GW⁻¹, which was in good agreement with theoretical values within the experiment uncertainty [14].

The standard degenerate pump-probe experiment was carried out using 450-fs laser pulses at 1 kHz repetition rate with lower average power to minimize accumulative thermal effects. The laser pulses were produced by the same laser used in the Z-scans described above. To eliminate any coherent effects, the polarizations of the pump and the probe pulses were perpendicular to each other. The pump and probe beams were focused onto the solutions of these samples with a minimum beam waist of $30 \pm 5 \ \mu m$. The probe pulse energy was a small fraction (<a few percentage) of the pump pulse energy.

2.4. The up-converted fluorescent measurements

The up-converted fluorescence was tested using an experimental setup given in Fig. 1. The intensity of the laser pulse incident on the sample is controlled by a half-wave plate/Glan—Thompson polarizer system. The excitation radiation (linearly polarized) with a desired intensity is split into two beams: one beam (less than 1%) to a power meter (Newport 1835C) to monitor the incident intensity, and the other beam is focused with a lens (focal length 150 mm) on the sample, which is placed in a glass tube with an ID of 10 mm. The fluorescence light emitted from the sample collected at 90° from the propagation direction of the excitation beam is detected by a photomultiplier (PM) tube (Hamamatsu R1767).

3. Results and discussions

3.1. Synthesis

2,4,6-trimethyl-1,3,5-triazine was synthesized based on Jung's method [13]. In order to improve the yield of this reaction, we also



Fig. 1. The setup of up-converted fluorescent measurement.

investigated the inletting velocity and concentration of hydrogen chloride (HCl) gas. One can be concluded the HCl gas should be fast inlet at the beginning of the reaction by analyzing the results of many experiments. About 24 h later, the velocity should be reduced to a half of the beginnings. When the ratio of HCl and acetonitrile reaches about 1.2: 1, we can found the yield was also improved significantly. For the synthesis of compound **c**, the concentration of potassium hydroxide (KOH) was considered as a crucial factor to obtain high yield of **c**. When the concentration is very low, the reaction will not start or be very slow. If the concentration is very high, a side product will be found in the system by itself condensation of 4-(di-p-tolylamino)benzaldehyde. The optimization concentration is 0.1 M by analyzing the results of many experiments.

3.2. UV-vis and fluorescent spectra

The UV-vis spectra of the derivatives were measured in THF with concentration 2×10^{-5} M as shown in Fig. 2(a). Obviously, all of them show only one absorptive band within a wavelength range from 450 to 850 nm. They are highly transparent in the near infrared range (\sim 780 nm). As increasing numbers of branches, the position of the maximal peak is bathochromically shifted from 318 nm (\mathbf{a}), to 378 nm (\mathbf{b}) and, to 392 nm (\mathbf{c}) nm, respectively, and their absorptive coefficients also increase significantly owing to the increased π -conjugated length. Their optical band gaps (E_g) are calculated according to the onset of the absorption spectrum. The value lies in ca. 3.46 ev for a, 2.95 for b, and 2.89 eV for c. The nonlinear absorption is attributed to 3PA for a because the excitation wavelength (λ_{exc}) used for the measurements fulfills the requirement (2 λ abs < λ exc < 3 λ abs) for 3PA studies at 780 nm as shown in Fig. 1. On the other hand, the corresponding **b** and **c** will exhibit 2PA or 2PEA processes owing to their energy gaps at the range of λ_{exc} to $2\lambda_{exc}$. Their fluorescent spectra are shown in Fig. 2 (b) with the concentration of 2×10^{-5} M in THF. In Fig. 2(b), one notices that three derivatives have similar fluorescence profiles, and none of them have multiple peaks. All of the derivatives exhibit strong one-photon fluorescence with the maximal peaks at 460 nm, 483 nm and 490 nm, respectively. One can be found in the figure **a**, **b** and **c** show a gradual red-shift to about 490 nm, which are attributed to the gradually increase of π -conjugated length in the derivatives.

3.3. The nonlinear absorption properties of \boldsymbol{a} , \boldsymbol{b} and \boldsymbol{c}

Fig. 3(a-c) summarizes the nonlinear absorption (NLA) results of **a**, **b** and **c** with the concentration of 0.001 M by the Z-scan measurement technique. As in shown Fig. 3(a-c), all Z-scans display a symmetric valley with respect to the focus, typical of an



Fig. 2. (a) The UV absorption spectra of a, b and c; (b) The fluorescent spectra of a, b and c.

induced positive NLA effect. By fitting the trances of Z-scan theories by two-photon and three-photon theory [14], we obtain the nonlinear absorption coefficient β (2PA) and γ (3PA) at different levels of I_0 . And their nonlinear absorption cross-sections (σ_2 and σ_3) are calculated from the equations of $\sigma_2 = \beta \hbar \omega / N$ and $\sigma_3 = \gamma (\hbar \omega / N)$ $(\omega)^2/N$, respectively, where $\hbar \omega$ is the photon energy and N is the molecular concentration. Interestingly, the calculated σ_3 value of **a** remain nearly constant in a straight line within the experimental errors at different levels of I_0 , confirming the independence of the laser intensity, which indicates the presence of pure 3PA nonlinearities. However, the measured σ_2 values of **b** and **c** are independence of intensity in the intensity range of ~ 58 GW/cm² for **b** and ~ 63 GW/cm² for **c** or less, which indicates the presence of pure 2PA nonlinearities. The calculated σ_3 value of **a** is $1.35 \times 10^{-76} \text{ cm}^6 \text{ s}^2$, which is the same order of magnitude as the measurement by Jang et al. [13]. Notably, the presence 3PA

phenomenon was firstly observed in femotosecond timescale using 780 nm-wavelength as excitation. The critical intensity I_c is estimated to 58 GW/cm² for **b** and ~ 63 GW/cm² for **c**; As the intensity exceeds I_c , however, the value of σ_2 increases with increasing intensity, suggesting the simultaneous occurrence of 2PA and higher-order nonlinearities. In order to deeply confirm the 3PA phenomenon in **a**, we plotted the absorbance $(1 - T_{OA})$ (where T_{OA} is the open-aperture transmittance) as a function of the maximum laser intensity on the *Z*-axis as shown in insert figures of Fig. 3. The slope of **a** was about two, which also indicates the presence of pure 3PA nonlinearities.

On the base of the above-discussed results of UV absorption, the appeared higher-order nonlinear absorption is impossible from 3PA in **b** and **c** due to their energy gaps in the regime of λ_{exc} to $2\lambda_{exc}$, we make sure that the arisen higher-order nonlinear absorption is from the 2PA induced exited-state absorption. To extracted 2PA and



Fig. 3. (a) The Z-scan trance and fitting curve of a; (b) The Z-scan trance and fitting curve of b; (c) The Z-scan trance and fitting curve of c; (d) The relationships of incident intensity and cross-section of a, b and c.



Fig. 4. The transit transmittance of compounds a, b and c.

exited-state absorption, we use 2PA theory [14] to fit experiment data at the lowest incident intensities, then, use 2PA + ESA theory data at the lowest incident intensities, then, use 2PA + ESA theory with the formula of $T_{OA} = (\ln(1 + q_0)\ln[(1 + p_0^2)^{1/2} + p_0]/(q_0p_0))f_0$ to fit high incident intensities (I_0 gt; I_c) and obtain values of γ_{eff} , qand p are given by $q = q_0/(1 + z^2/z_0^2)$ and $p = p_0/(1 + z^2/z_0^2)$ respectively, where $q_0 = \beta I_{00}L_{eff}$ and $p_0 = (2\gamma_{eff}I_{00}^2L'_{eff})^{1/2}$ are the on-axis peak phase shifts caused by the third- and fifth-order nonlinear absorption processes, respectively. Here, I_{00} is the onaxial peak intensity at the waist, $z_0 = \pi \omega_0^2 / \lambda$ the Rayleigh length, $L_{eff} = [1 - \exp(-\alpha L)] / \alpha$, $L'_{eff} = [1 - \exp(-2\alpha L)] / 2\alpha$. The 2PA and excited absorption coefficients of $\beta = 1.14 \times 10^{-2}$ cm/GW, $\gamma_{eff} = 2.1 \times 10^{-4}$ cm³/GW² for **b**, and $\beta = 2.59 \times 10^{-2}$ cm/GW, $\gamma_{eff} = 0.63 \times 10^{-4}$ cm³/GW² for **c**, respectively. Notability, the obtained β and γ_{eff} values are independent of I_0 . The calculated σ_2 values of **b** and **c** are 485 GM and 1100 GM, respectively. Clearly, with the increase of branches from 2 to 3, the σ_2 value increases about 2.3-fold, which may be attributed to the stronger internal charge transfer in the **c** than that of **a**. Furthermore, it is to be noted that the numbers of branches increase from 1 to 2 and, to 3, their nonlinearities change suddenly from 3PA to 2PEA and, to 2PEA, respectively. The results give us a new approach to obtain higherorder nonlinear absorption materials by manipulating the organic molecular structures. The exited-state absorption cross-sections (σ_e) of **b** and **c** are calculated by the formula of $\sigma_e = 2 \omega \gamma_{eff}/(\beta \tau)$, where the τ is the lifetime from exited-state to ground-state, it can be determined by pump-probe measurements, which will be discussed in the next segment. The decay time of **b** and **c**

are 0.92 ps and 0.98 ps by fitting pump-probe data with a twoexponential-component model, respectively. The σ_e values are 1.03×10^{-17} cm² for **b** and 1.27×10^{-18} cm² for **c** respectively.

The decay process of excited state was demonstrated by pumpprobe experiment as shown in Fig. 4. The relaxation process may be described quantitatively by using a double-exponential fitting with the formula of $\Delta T/T = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where the fastest component, τ_1 , about 0.45 ps. is found to be independent of the pump intensity and is interpreted as the autocorrelation between the pump and probe pulses. The slowest component, τ_2 , on the picoseconds or femotosecond scale is attributed to radiative, band-to-band recombination. The maximum transmittance change $(\Delta T/T)$ in these solutions were found to be negative, showing the absorption is reverse saturation absorption, it is good agreement with the results of Z-scans. In the figure, compounds **b** and **c** both display a measure of excited-state absorption, and the compound a shows only instantaneous 3PA. This is somewhat surprising as the electronic levels in **b** and **c** are expected to be closely governed by the transition dipoles and geometry. For example, the lowest lying energy state in the centrosymmetric **c** is expected to be two-photon forbidden, while having a higher-energy state that is one-photon forbidden but two-photon allowed. The response time of these samples were evaluated to be 0.46, 0.92 ps and 0.98 ps for **a**, **b**, and **c**, respectively. The values of **b**, and **c** are near the reported values of decay time about excite state in organic materials. In addition, comparing the 2PA cross-section values of **b** and **c**, it can be found **c** is more than two times than that of **b**, which is agreement with the branches strategies about enhancement of 2PA cross-section. One can be concluded the increases of donor strength and the conjugation length play the important roles in enhancing in these derivatives, and the other factors, such as dipole moment and starshaped molecules which possess different central rings and the same peripheral groups with electron-accepting capability, also affect significantly their absorption cross-section. Noticeably, the derivatives were firstly observed with two kinds of different nonlinear absorption phenomena (3PA for **a**, 2PEA for **b** and **c**) by changing the number of branches. The findings open a new avenue for designing highly-efficient 3PA or 2PEA materials for nonlinear optical applications.

3.4. The up-converted fluorescent properties of **b** and **c**

When the samples was excited by a laser pulse with 780 nm wavelength, their up-converted fluorescent spectra with the concentration of 0.001 M are shown in Fig. 5. It can be seen that **b** and **c** emit blue-green up-converted fluorescence with the maximal peaks at 490 nm and 495 nm, respectively. By comparing



Fig. 5. The two-photon excited fluorescence spectra of b and c; The relationships of Log (I₀) and Log(PL) of b and c in insert figures.

the profiles of one-photon fluorescent with two-photon fluorescent spectra, two-photon fluorescent spectra of them are similar with that of one-photon, except that their maximal peaks in 2PF have shifted to red about 5–7 nm. This red-shifts should be due to the reabsorption of the higher concentration solution (0.001 M) used in up-converted fluorescence compared to concentration of 10^{-5} M for one-photon fluorescent measurements. Furthermore, the relationships between up-converted fluorescence excitation intensities and incident intensities of **b** and **c** were also plotted shown in the insert Fig. 5. We fitted the data using linear formula: y = kx + b, and their slopes of **b** and **c** were obtained with the values of 1.82 for **b** and 1.71 for **c**, suggesting the up-converted fluorescence of **b** and **c** are induced by two-photon at low incident intensities, which is also good agreement with the above-said results of nonlinear absorption in **b** and **c**.

4. Conclusions

In this paper, we have investigated systematically the nonlinear optical properties of three triazine derivatives with different numbers of branches using femtosecond Ti:Sapphire laser pulse. Their nonlinear optical studies are undertaken by performing open Z-scan, frequency up-converted and pump-probe measurements. Importantly, strong three-photon absorption was observed in this work with a value of 1.35×10^{-76} cm⁶ s², which was firstly observed in femotosecond timescale using 780 nm-wavelength as excitation. Furthermore, as increasing the numbers of branches from 1 to 2 and, to 3, their nonlinear absorption changed from 3PA to twophoton induced excited absorption, showing strong structure dependence. The values of two-photon and exited-state absorption cross-sections were measured with 1230 GM and $1.03 \times 10^{-17} \text{ cm}^2$ for **b**, and 485 GM and 1.27 \times 10⁻¹⁸ cm² for **c**, respectively. The findings offer a new avenue to obtain two and multi-photon absorption organic materials for optical applications by controlling molecular structures.

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