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The photophysical properties and two-photon absorption of novel triphenylamine-based dendrimers

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ABSTRACT

Novel triphenylamine-based dendrimers were synthesized and characterized by FT-IR, elemental analysis, ^{1}H NMR spectroscopy, and MALDI-TOF mass spectrometry. The linear photophysical properties including absorption, one-photon induced fluorescence and the fluorescence lifetimes in different solvents were investigated. The two-photon induced fluorescence behavior was recorded in toluene solution, employing a Ti:sapphire femtosecond laser pulse. The dendrimers both emit strong blue–green fluorescence under irradiation. Two-photon excited state fluorescence cross-sections were also obtained. The two dendrimers displayed a large two-photon absorption. The polytriphenylamine dendrimer shows larger two-photon excited state fluorescence cross-sections in toluene relative to the tristriphenylamine analog, indicating that there is cooperative enhancement originating from inter-branch coupling and an increase of light-harvesting ability with increasing dendrimer size.

1. Introduction

Over the past few years, a great interest has been shown in the field of two-photon absorption materials for their promising applications, such as in optical limiting [1,2], microfabrication [3], bioimaging [4], and two-photon pumped (TPP) up-converted lasing [5–10]. The two-photon absorption (TPA) process is a third-order nonlinear optical process, in which two photons are absorbed simultaneously via a virtual state. Recent applications of TPA have required molecules with an immense two-photon absorption cross-section [11–14]. During the exploration of strong TPA compounds, theoretical work has been applied to understand the nonlinear-optical response and fundamental limits of the dispersion of the two-photon absorption (TPA) cross-section [15–17], and a great number of symmetrically and asymmetrically substituted conjugated organic molecules with large TPA cross-sections have been described. Among these reported TPA compounds, dendrimers are beginning to attract significant interest. The use of organic dentritic structures in two-photon absorption applications has motivated the synthesis and characterization of many novel and intriguing structures. The way in which organic dendrimers combine novel semiconducting optoelectronic properties results in much simpler processing than their inorganic counterparts. Semiconducting dendrimers possess a modular architecture and consist of a core and dendrons, each of which contains conjugated units, and solubility-conferring surface groups. The modular architecture of a dendrimer allows for the independent tuning of its electrical, optical and processing properties. Importantly, cooperative enhancement was reported in dendrimers (including organometallic systems) [18,19]. Molecules with a large two-photon absorption cross-section can be obtained through the structural design of dendritic architecture and the formation of delocalized excited states [20–24]. Moreover, a higher density of effective chromophores as well as strong interchromophore coupling can be achieved, which is important for many nonlinear optical and light-harvesting applications [25–28].

The triphenylamine group is highly electron rich and possesses a propeller-shaped structure [29]. In this paper, we investigate the one- and two-photon excited fluorescence properties of conjugated three-branched dendrimers based on triphenylamine. The TPA cross-section was measured in the range from 700 nm to 850 nm. The effect of increasing the generation on the photophysics and nonlinear-optical properties were also examined. These systems were further investigated by a time-resolved spectroscopy method (time-corrected single photon counting) which probes physical events after the excitation has taken place. These methods are

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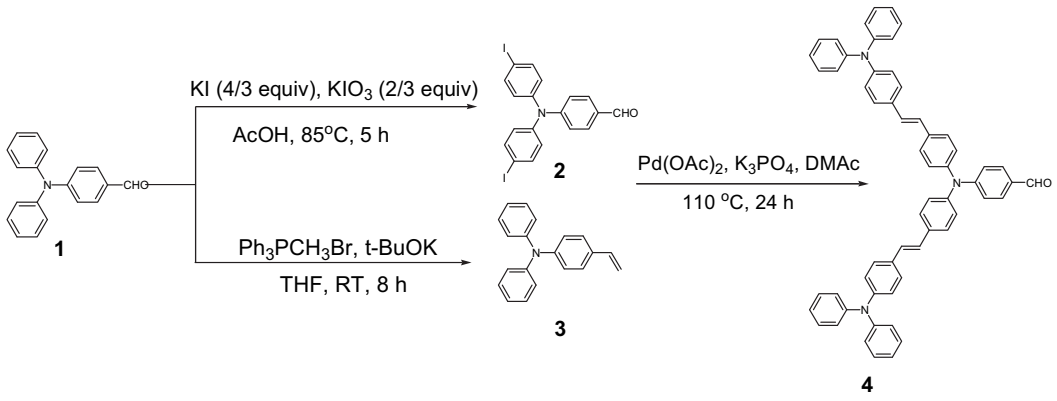


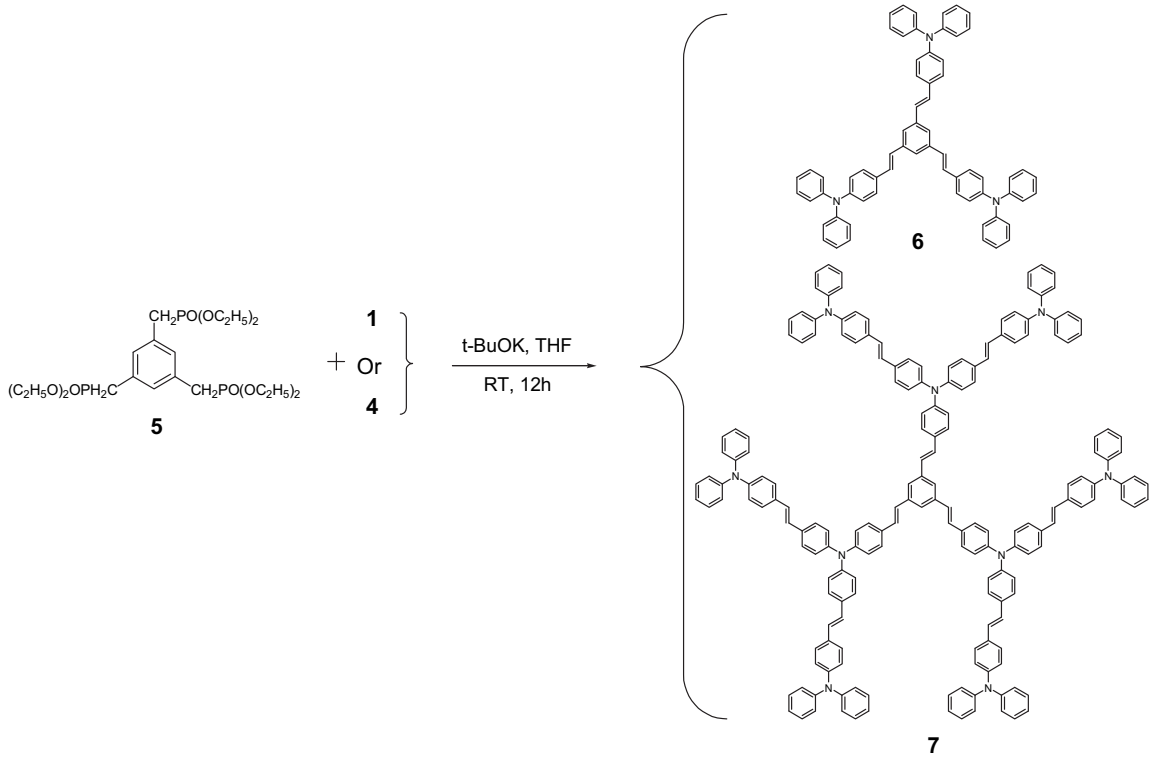
Scheme 1. Synthetic route to compounds **2**–**4**.

probably the only possible means to fully characterize the states that are important to instantaneous TPA and thus derive the relationship between the structure and property of dendrimers.

2. Experimental

2.1. General procedure

All reagents were purchased from Aldrich Chemical Co. and used as received without further purification except for the following. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. N,N-Dimethylacetamide (DMAc) was dried with CaH_2. The ^1H NMR spectra were recorded on either a Bruker Avance 500 or Varian Mercury-300 NMR spectrometer at 298 K using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry experiments were performed on a Kratos MALDI-TOF mass system, and the spectrum was recorded in the linear or reflect mode with anthracene-1,8,9-triol as the matrix. Linear absorption spectra of the compounds with a concentration of 1.0×10^{-4} mol/L in various solvents were recorded on a Shimadzu UV-2550 spectrophotometer using a cuvette with a 10 mm path length. Steady-state fluorescence spectra with a concentration of 1.0×10^{-4} mol/L were measured on a RF-5310PC fluorescence spectrophotometer. The melting points (mp) for compounds **6** and **7** were measured on the digital melting-point apparatus (OptiMelt, TG030702016). All the solvents used for absorption and fluorescence measurements were HPLC grade. The lifetime was measured by the time-correlated single photon counting (TCSPC).



Scheme 2. Synthetic route to compound **6** and compound **7**.

Two-photon excited fluorescence (TPEF) spectra were measured using an AvaSpec-2048 fluorescence spectrophotometer with a mode-locked Ti:sapphire laser (Spectra-Physics Inc., Tsunami) with a pulse duration of <120 fs and a repetition rate of 82 MHz as the pump source. The samples were dissolved in THF at a concentration of 1.0×10^{-4} mol/L. The TPA spectra were determined by using pulsed laser light (82 MHz, 120 fs) from 700 nm to 850 nm generated by a mode-locked Ti:sapphire laser. A spectrum analyzer (AvaSpec-2048) was used to monitor the excitation wavelengths.

2.2. General reaction procedure for compounds **6** and **7**

Compounds **1**–**4** were readily obtained according to the literature [24]. With stirring, the corresponding formyl substituted dendron either **1** or **4** and triphosphonate **5** were dissolved in dry THF (20 mL). The resulting solution was added dropwise slowly to t-BuOK (84 mg, 0.75 mmol) in dry THF (20 mL) at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 overnight. The mixture was poured into water (100 mL) and extracted with dichloromethane (4 × 20 mL). The organic phase was washed with water, brine and dried over $MgSO_4$. After removing the solvent, the product was purified by column chromatography using dichloromethane/petroleum ether (1:2) to give compound **6** (from **1**) and compound **7** (from **4**).

2.2.1. Compound **6**

The resulting dendrimer **6** was obtained as a yellow green powder with a yield of 73% with a mp of 190 °C [30].

2.2.2. Compound **7**

The resulting dendrimer **7** was obtained as a yellow powder with a yield of 65% with a mp of 240 °C ^{1}H NMR (500 MHz, CDCl3, TMS): δ(ppm) 7.52 (br, 3H, −vinyl), 7.52 (d, J = 8.5 Hz, 6H, −Ph), 7.363–7.409 (m, 24H, −Ph and vinyl), 7.23–7.27 (m, 18H, −Ph), 7.08–7.12 (m, 50H, −Ph), 7.01–7.06 (m, 31H, −Ph and vinyl), 6.97 (br, 9H, −vinyl). MALDI-TOF MS: Calcd for $C_{186}H_{141}N_9$: 2502.2; found: 2503.1. Elemental analysis calculated (%) for $C_{186}H_{141}N_9$: C89.28%, H5.68%, N5.04%, found: C89.25%, H 5.72%, N5.03%.

3. Results and discussion

3.1. Synthesis and characterization of dendrimers

The iterative strategy developed by our group used for the aldehyde-focused dendron synthesis is shown in Scheme 1. As illustrated, the two iterative steps for dendron formation involve a simple Wittig reaction followed by a Heck coupling to give dendron **4** with an aldehyde at its center. The first step in the iterative procedure was the formation of N,N-diphenyl-4-vinylbenzenamine 3 which was prepared in 76% yield from the reaction of 4-(diphenylamino)benzaldehyde 1 with methyltriphenylphosphonium bromide. The second step in the first cycle of the iterative procedure was the coupling of compound **3** with 4-(bis(4-iodophenyl) amino)-benzaldehyde 2 to give the first generation aldehyde-focused dendron **4** in 55% yield. The targeted dendrimers **6** and **7** were synthesized via the typical Wittig–Horner reaction between the core hexaethyl benzene-1,3,5-triyltris(methylene)triphosphonate **5** and aldehydes **1** and **4** in dry tetrahydrofuran in 73% and 65% yields, respectively, using potassium tert-butoxide as base (Scheme 2). As anticipated, the targeted dendrimers are soluble in most common organic solvents such as toluene, chloroform and THF. New dendrimer **7** was fully characterized by FT-IR, elemental analysis, ^{1}H NMR spectroscopy, and MALDI-TOF mass spectrometry.

3.2. Optical absorption, steady-state fluorescence and thermal properties

The linear absorption spectra and the single-photon excited fluorescence (SPEF) spectra of **6** and **7** are shown in Fig. 1 and Fig. 2. Possible solvent influence on the linear absorption behavior was investigated. The absorption maxima and shapes of the two materials exhibited weak solvent polarity dependencies for both **6** and **7**. The emission spectra used the same excitation wavelength of 350 nm for **6** and **7** in different solvents: $CHCl_3$, THF and Toluene. Regarding the small shoulder observed at longer wavelength in toluene solution, the emission spectra show that as the solvent polarity increases the shoulder undergoes a red shift. The position of the main peak in both absorption and emission shows a red shift with increasing dendrimer generation. A small red shift in the linear absorption can be observed from **6** to **7**, which is due to the incremental extension of the conjugation length with increasing dendrimer generation. The thermal properties are also characterized. The measured melting points (mp) for compounds **6** and **7** are 190 and 240 °C, respectively. The mp for the **7** is higher than the **6**. This may because the multibranched molecules with higher generation tend to hinder translational, rotational, and vibrational motions of the molecule and result in mp enhancement.

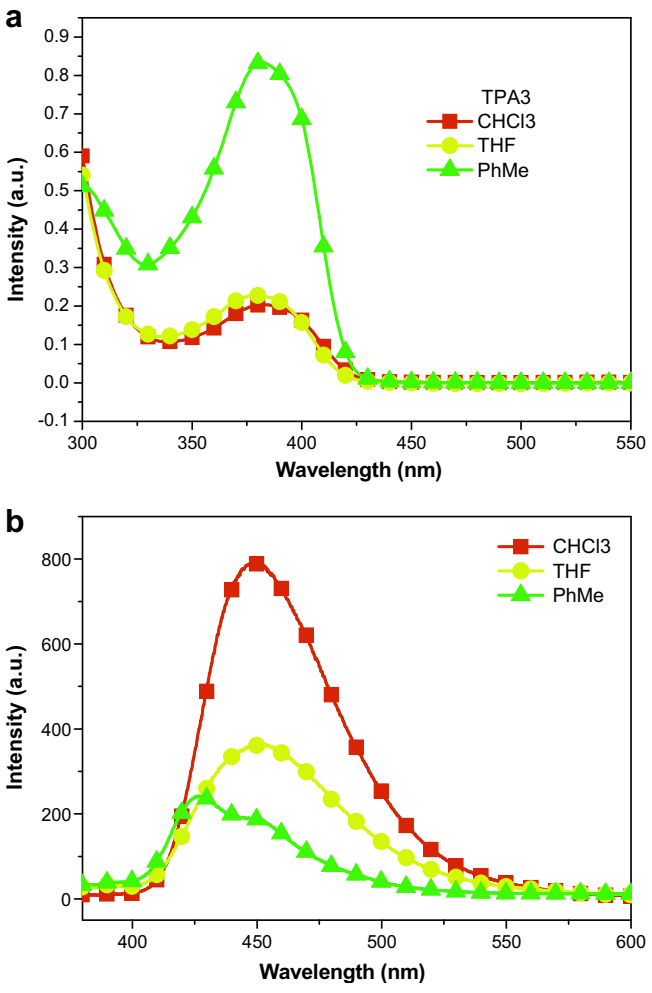


Fig. 1. The linear absorption spectra and the single-photon excited fluorescence (SPEF) spectra of **6**.

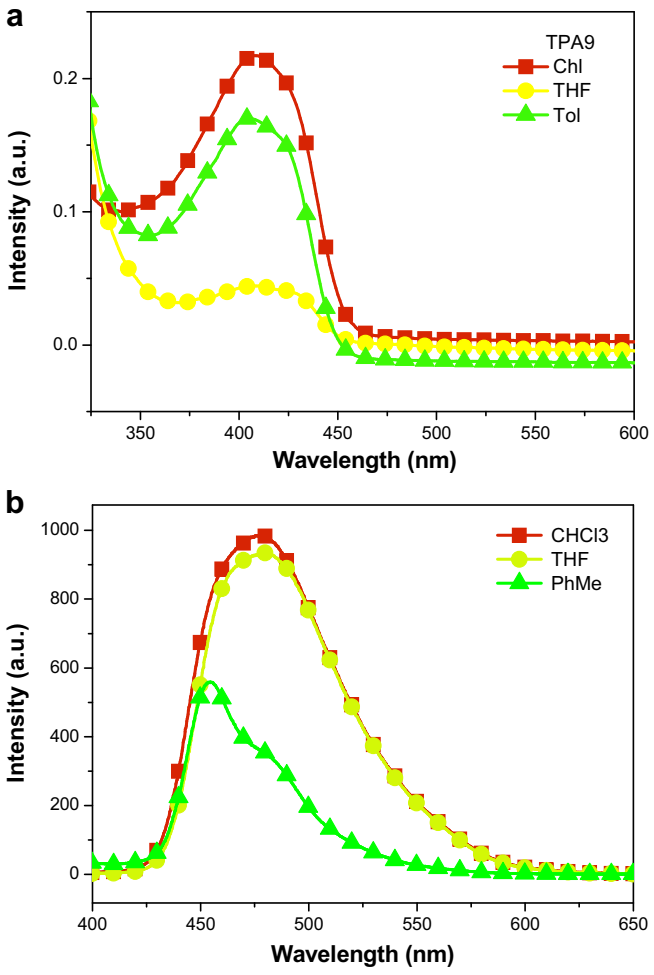


Fig. 2. The linear absorption spectra and the single-photon excited fluorescence (SPEF) spectra of **7**.

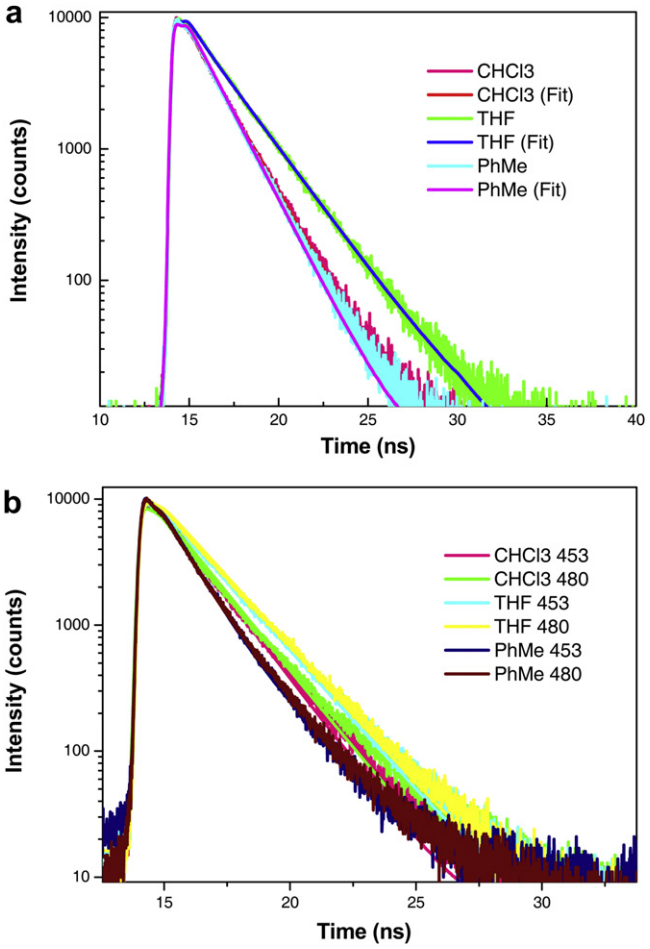


Fig. 3. The fluorescence decay lines for the Compound **6** and **7** in different solution.

3.3. Fluorescence lifetime measurements

The lifetime in different solvent solutions were measured. The fluorescence transients were fitted to multiexponential functions and were convoluted with the system response function obtained from TCSPC measurement. The fluorescence decay profiles for **6** and **7** in different solutions are shown in Fig. 3 and Fig. 4, respectively. For **6**, TCSPC gives two lifetimes: 0.38 ns (33.2%) and 1.81 ns (66.8%) in chloroform, and 2.36 ns (81.1%), 0.662 ns (18.9%) in THF and 1.62–1.65 ns in toluene. The lifetime shows weak dependency on the solvent polarity, indicating that the lifetime in the high polarity solvent (THF) is slightly longer. For **7** the lifetime is less solvent-dependent. Table 1 lists the measured lifetime for **6** and **7** in the different solutions.

3.4. Two-photon excited fluorescence and two-photon absorption cross-section

Two-photon excited fluorescence spectra of **6** and **7** with an excitation wavelength of 700 nm–850 nm were obtained using a femtosecond pulsed laser as the excitation source. An equation using a reference chromophore as a standard for the two-photon absorption cross-section value δ_{2s} for the sample is given below [31]:

$$\delta_{2s} = \frac{F_s \eta_r N_r}{F_r \eta_s N_s} \delta_r$$

where F is the observed two-photon induced fluorescence signal, η is the fluorescence quantum yield, and N is the concentration of the chromophore. Detailed experiments reveal that when the excitation wavelengths change from 700 to 850 nm, the peak positions and spectra shapes in the TPEF spectra of these compounds are independent of the excitation wavelengths, but the emission intensities of TPEF are dependent over that range. The TPEF cross-sections of **6** and **7** were obtained by referencing the TPEF cross-section of Rodamine B (in ethanol) and fluorescein (in water, pH 11), and which are shown in Fig. 4. From Fig. 4, it can be seen that the optimal excitation wavelengths of **7** are 720–760 nm, which are higher than that of **6**. This result indicates that in higher generations of this dendrimer family, larger δ_{2s} values were obtained. The TPEF spectra of the compounds shown in Fig. 5 were taken when they were excited at several different wavelengths in toluene. Both **6** and **7** exhibit much stronger frequency up-converted fluorescence than that of fluorescein. Compared with **6**, compound **7** exhibits a stronger TPEF and the TPEF intensity is about 20 times that of fluorescein. For applications that require strong TPA such as optical limiting and 3D microfabrication or strong TPEF such as upconversion lasing, molecules with large TPA cross-section per molecular weight (δ_{max}/MW) are needed. The calculated δ_{max}/MW

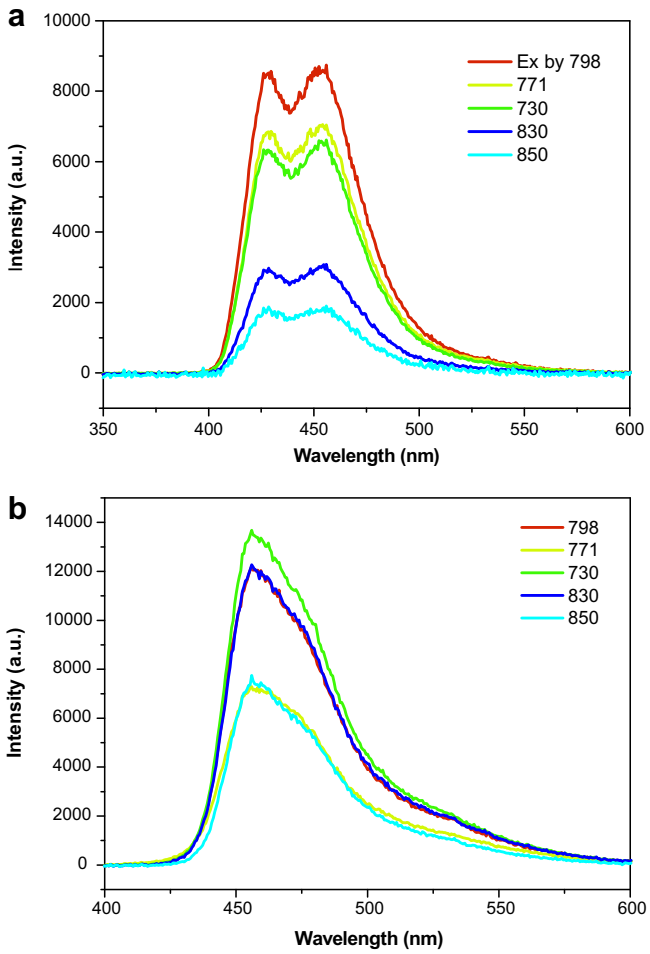


Fig. 4. The fluorescence decay lines for the Compound **6** and **7** in different solution.

for **7** increased significantly compared to that of **6**, which is about 2 times of the value of **6**. The results suggest that there is a strong cooperative enhancement in this system. Compared with SPEF spectra, the peak positions of TPEF and spectra shapes are highly similar. TPEF and SPEF spectra of all the compounds exhibit well-defined vibronic structure. In SPEF spectra, peaks with shorter wavelengths exhibit stronger fluorescence compared with other fluorescent peaks, but in the TPEF spectra, the corresponding peak intensity is much weaker than that of peaks with longer wavelengths. One reason might be the re-absorption of the fluorescence within the concentrated solution.

Table 1
The measured lifetime for Compound **6** and Compound **7** in different solutions.

Compound	Solvent	Detected wavelength (nm)	τ_1 (ns)	τ_2 (ns)
6	$CHCl_3$	450	1.81 (0.668)	0.38 (0.332)
	THF	450	2.36 (0.811)	0.662 (0.189)
	PhMe	426	1.62 (1.0)	
		450	1.65 (1.0)	
7	$CHCl_3$	453	0.74 (0.394)	1.91 (0.606)
		480	0.65 (0.467)	2.09 (0.533)
	THF	453	0.96 (0.332)	2.16 (0.668)
		480	1.18 (0.299)	2.16 (0.701)
	PhMe	453	0.93 (0.721)	2.02 (0.279)
		480	1.03 (0.788)	2.21 (0.212)

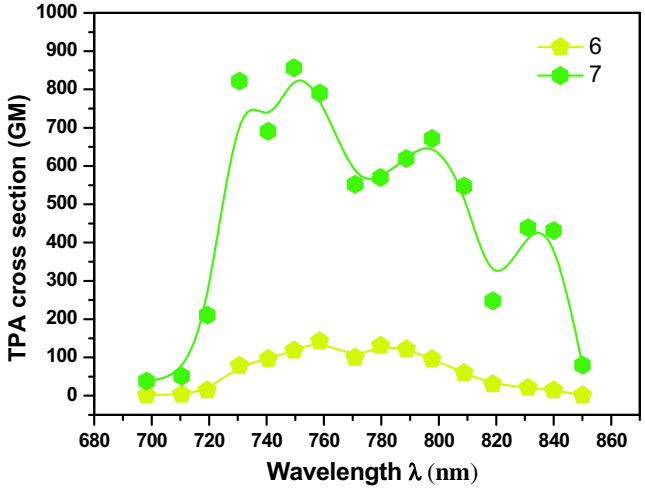


Fig. 5. The TPEF spectra of all these compounds.

4. Conclusions

A novel triphenylamine-based dendrimer has been synthesized. The linear photophysical properties in different solvents and two-photon absorption properties in toluene solution have been examined. Intense blue–green fluorescence emissions were detected in both **6** and **7**. The TPEF cross-sections of **6** and **7** were also measured. Comparing the two compounds, Compound **7** exhibits larger TPEF cross-sections in toluene relative to **6**, which gives clear evidence that inter-branch coupling may result in cooperative enhancement.

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