

Two-photon absorption and up-converted fluorescence of novel triphenylamine-based oligomers

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Abstract

Three new conjugated oligomers (referred to as **P1**, **P2** and **P3**), of “D– π –A” structure with the same donor group of 4-methyl triphenylamine but different acceptor groups such as naphthalene for **P1**, dibenzothiophene for **P2**, and dibenzofuran for **P3**, were synthesized and characterized. The linear optical properties, including absorption and one-photon induced fluorescence, fluorescence quantum yield (Φ) and lifetimes of the oligomers are reported. Two-photon absorption (TPA) properties were measured by open-aperture Z-scan techniques, while two-photon induced fluorescence (TPF) behaviour was recorded using a CCD spectrosensitometer, employing a Ti:sapphire femtosecond laser pulse. It was found that **P1** displayed the greatest two-photon absorption coefficient (β) due to its larger intermolecular charge transfer and stronger interactions between donor and acceptor groups. In contrast, **P3** exhibited strongest one- and two-photon fluorescence due to its dibenzofuran acceptor group possessing more preponderant radiation dynamics, in comparison with its dibenzothiophene- and naphthalene-based counterparts.

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Keywords: Two-photon absorption; Two-photon induced fluorescence; Dibenzothiophene; Dibenzofuran

1. Introduction

Conjugated oligomers are important materials for application in two-photon induced fluorescence (TPF) microscopy that has gained widespread popularity in the biology community owing to its ability to image at high penetration depth in tissue with reduced photodamage. The key ingredients for efficient molecular TPF applications such as high resolution 3D microscopy, deep tissue-penetrating photodynamic therapy (PDT), 3D microfabrication, high-density optical data storage and optical power limiting [1–5], depend critically on the availability of materials that possess large TPA cross-section and high two-photon excited fluorescence (TPF). Numerous

organic compounds have been investigated both experimentally and theoretically in order to understand the structure–property relationship of materials with strong TPA. For example, some one-dimensional dipolar systems, heteroaromatic ring systems, octupolar molecules, multibranched and dendrimer systems can effectively enhance TPA absorptivity [6–16]. Recently, we reported the TPA and up-converted fluorescence properties of some chromophores based on triphenylamine and heterofluorene units, whose two-photon fluorescence intensity and TPA cross-section are correlated to electron coupling between the individual branch and obvious excited charge redistribution [17–21]. In this paper, we report three, newly synthesized conjugated oligomers with 4-methyl triphenylamine as donor group and naphthalene, dibenzothiophene or dibenzofuran as acceptor group. To understand the influence of the different electron-acceptors upon photoluminescence properties, linear absorption/emission spectra including fluorescence quantum yield (Φ_f) and

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emission dynamics as well as two-photon absorption and two-photon induced fluorescence behaviour were investigated. On the basis of correlated quantum-chemical calculation and experimental measurement results, we further demonstrate that **P1**, which contains a naphthalene unit displays large $\Delta\mu_{ge}$ and intramolecular charge transfer as well as strong electronic interaction between donor and acceptor, which contribute so as to enhance two-photon absorption cross-section. Moreover, we found that the dibenzofuran unit is a good fluorophore in both one- and two-photon fluorescence due to its more preponderant radiation dynamics, in comparison with dibenzothiophene and naphthalene.

2. Experimental

2.1. Instrumental measurement

IR spectra were measured on a Nicolet FT-IR 5DX instrument using solid samples dispersed in KBr disks. Hydrogen nuclear magnetic resonance spectra were determined on a GCT-TOF NMR spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the oligomer powder was performed under a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ using a Diamond TG/DTA and Diamond DSC instruments. Oligomer number average molecular weight (M_n) was determined by gel permeation chromatography (GPC), using polystyrene standards and THF as eluent.

Linear absorption measurement of dilute solutions were obtained using an Hitachi U-3500 recording spectrophotometer equipped with 1 cm path length quartz cuvettes. Steady-state fluorescence (OPF) and time-resolved decay curves were measured on an Edinburgh FLS 920 fluorophotometer equipped with a time-correlated single-photon counting (TCSPC) card. Lifetime values were measured by reconvolution fit analysis of the time-resolved decay profiles with the aid of nF 920 software. In all fluorescence decay profiles, the dual-exponential-fits of three oligomers gave acceptable statistical parameters ($\chi^2 < 1.2$, residuals = ± 3.5). Fluorescence quantum yield (Φ_f) of all chromophores were determined using the same concentration of fluorescein in 0.1 mol dm^{-3} aqueous NaOH as standard [15]. Two-photon fluorescence (TPF) spectra and two-photon absorption (TPA) coefficient (β) were measured using a Ti:sapphire femtosecond laser system (140 fs and at a repetition rate of 1 kHz) as the pump source.

2.2. Materials

THF was distilled over sodium/benzophenone. Both dibenzothiophene and dibenzofuran were purchased from Acro and all chemicals are used without further purification. The synthetic procedure is displayed in Scheme 1.

2.2.1. Synthesis of compound 2

A mixture of 1,4-bis(chloromethyl)-naphthalene (1.67 g, 7.14 mmol) and distilled phosphorous acid triethyl ester (5 ml) were added to a 50 ml-flask. The reaction mixture was heated under reflux for 2 h and then excess phosphorous

acid triethyl ester was distilled off and the residual viscous liquid **2** was then used in the subsequent reaction without further purification.

2.2.2. Synthesis of **P1**

Under anhydrous and oxygen-free conditions, 0.45 g (0.018 mol) NaH was placed in a flask in the presence of 4-methyl-4',4''-diformyl triphenylamine [17] (1 g, 0.003 mol) and 2.4 g (0.003 mol) of compound **2** in dry DMF (100 ml). The mixture was refluxed for 80 h at $130\text{ }^{\circ}\text{C}$ and the ensuing mixture was cooled to room temperature, poured into warm methanol, and the yellow precipitate was washed with hot water and then filtered and dried. The crude products were dissolved in THF and poured into methanol to provide orange powders (**P1**), 44%. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 2.378 (s, CH_3 -, 3H), 6–8 (m, Ph-, 21H), 9.825 (s, -CHO, 0.5H). IR (KBr, cm^{-1}): 3384.6, 2923.6, 2853.6, 1504.4, 1437.0, 1190.1, 1190.8, 721.5. GPC analysis revealed that the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer were 891 and 1300, respectively, with a polydispersity index of 1.46.

2.2.3. Synthesis of compound 5

A solution of bromine (2.9 ml, 0.04 mol) dissolved in acetic acid was added dropwise to a solution of dibenzothiophene (5 g, 0.02 mol) in 100 ml acetic acid at room temperature under stirring over 2 h and the mixture was then heated at $120\text{ }^{\circ}\text{C}$ for 5 h. The mixture was filtered to give a white powder which was recrystallized from chloroform to yield 8 g of white 2,8-dibromic dibenzothiophene.

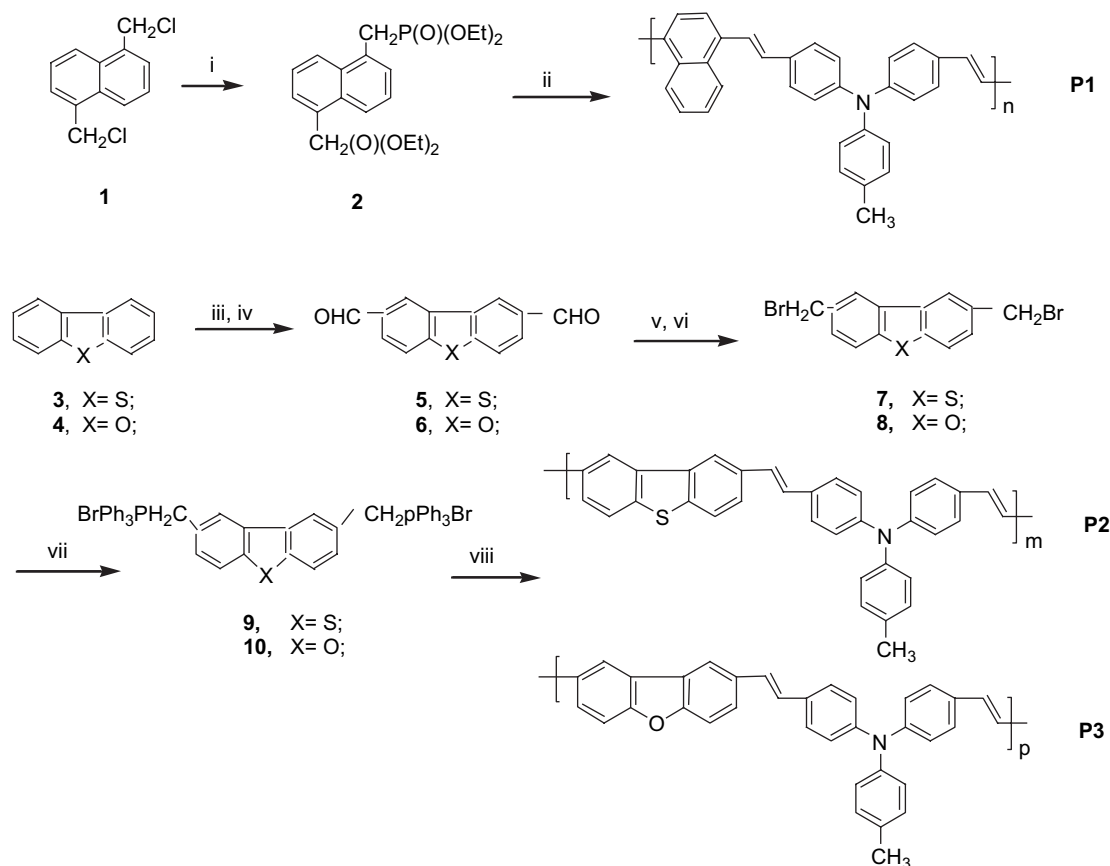
To a flask fitted with a magnetic stirrer under N_2 atmosphere, a mixture of dry ether (100 ml) and $n\text{-C}_4\text{H}_9\text{Li}$ (30 ml) was injected at room temperature and stirred for 1 h; 7 ml of DMF was then added and the mixture stirred at room temperature for 8 h. Finally, 30 ml of HCl (10%) was added to neutralize the reaction solution. The yellow product was filtered and recrystallized from chloroform to yield 4 g of 2,8-diformyl dibenzothiophene (**5**). MS (TOF EI): m/z 240. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 8.039–8.059 (d, J 8.0 Hz, 4H, Ar-H), 8.762 (s, 2H, Ar-H), 10.21 (s, 2H).

2.2.4. Synthesis of compound 7

A mixture of compound **5** and KBH_4 was stirred in ethyl alcohol for 24 h at room temperature and the mixture was then refluxed for 2 h after the addition of 200 ml HBr (32%) and HAC (50 ml); the ensuing mixture was stirred for 11 h at room temperature. The crude product was filter and crystallized in chloroform to give a white solid (2,8-bis(bromomethyl) dibenzothiophene; **7**), yield 58% and m.p. $217\text{--}219\text{ }^{\circ}\text{C}$. MS (EI): m/z (%): 369.88 (100) [M^+].

2.2.5. Synthesis of compound 9

A flask fitted with a magnetic stirrer and condenser was charged with 7.4 g (0.02 mol) of 2,8-bis(bromomethyl) dibenzothiophene (**7**) and then 5.24 g (0.02 mol) of triphenylphosphine in the presence of fresh toluene was added. The mixture was refluxed for 2 h and then cooled to room temperature and



Scheme 1. The synthetic route for **P1–P3**. Reagents and conditions: (i) $\text{P}(\text{OC}_2\text{H}_5)_3$, absolute ethanol, reflux; (ii) 4-methyl-4',4''-diformyl triphenylamine, dry THF, potassium *tert*-butoxide, reflux; (iii) Br_2/AcOH , reflux, 8 h (iv) *n*-BuLi, dry DMF and ethyl ether; (v) KBH_4 , ethanol, rt, overnight; (vi) HBr, AcOH; (vii) triphenylphosphine (PPh_3), methylbenzene, reflux; (viii) 4-methyl-4',4''-diformyl triphenylamine, dry THF, potassium *tert*-butoxide, reflux.

filtered; the resulting white powder was recrystallized from ethanol in high yield to give a pale yellow solid (**9**) [4]. ^1H NMR (DMSO- d_6 , ppm): δ 5.495, 5.531 (d, 2H, J 14.4 Hz, Ar- CH_2Br), 4.744–4.775 (d, 2H, J 12.4 Hz, *trans*- $\text{CH}=\text{CH}$), 7.618–7.821 (m, 15, Ph-H), 7.076, 7.056 (d, 1H, J 8.0 Hz, aromatic H), 7.484, 7.466 (d, 1H, J 7.2 Hz, aromatic-H), 7.908 (s, 1H, aromatic-H).

2.2.6. Synthesis of **P2**

Under anhydrous and oxygen-free conditions, 0.45 g (0.018 mol) NaH was added to a flask in the presence of 4-methyl-4',4''-diformyl triphenylamine (1 g, 0.003 mol) and 2.4 g (0.003 mol) of compound (**9**) in dry DMF (100 ml). After the addition, the mixture was refluxed for 80 h at 130 °C and the reaction mixture was then cooled to room temperature, poured into warm methanol and the yellow precipitate obtained was then dried to get yellow product (**P2**, 54%). ^1H NMR (CDCl_3 , ppm): δ 2.378 (s, CH_3 -, 3H), 6–8 (m, Ph-, 21H), 9.825 (s, -CHO, 0.5H). IR (KBr, cm^{-1}): 3444.1, 3024.4, 2921.8, 1597.3, 1504.3, 1320.0, 1279.3, 817.0. GPC analysis revealed that the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer were 1688 and 2657, respectively, with a polydispersity index of 1.57.

Following the procedures mentioned above, compounds **6**, **8**, **10** and **P3** were obtained. Compound **6**. ^1H NMR (DMSO- d_6 , ppm): δ 9.87 (d, -CHO, 2H), 7.6–8.1 (m, Ph-, 6H). MS (EI): m/z (%): 224.1(100) [M^+]. Compound **8**. ^1H NMR (DMSO- d_6 , ppm): δ 4.6 (d, CH-, 2H), 7.0–7.3 (m, Ph-, 6H). MS (EI): m/z (%): 353.9 (100) [M^+]. Compound

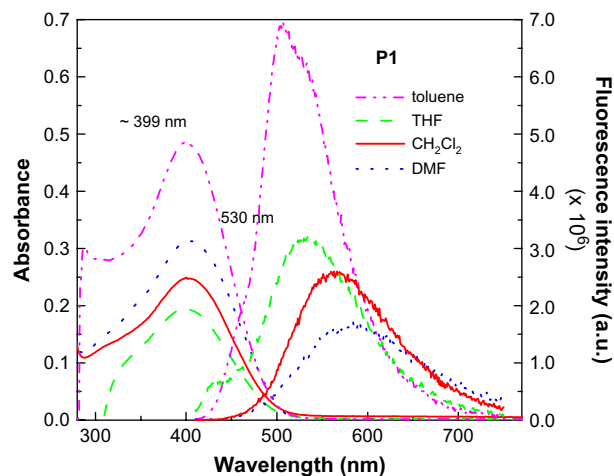


Fig. 1. Linear absorption (left) and fluorescence (right) of **P1** in different solvents (0.02 mg ml^{-1}).

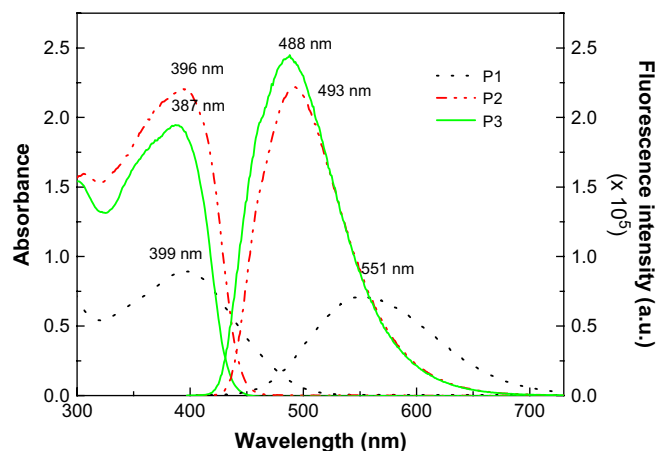


Fig. 2. Linear absorption (left) and fluorescence (right) of **P1**–**P3** in DMF (0.02 mg ml^{-1}).

10. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ 2.6 (s, CH_2 –, 4H), 7.2–7.6 (m, Ph–, 36H). MS (EI): m/z (%): 906.8 (100) [M^+].

Oligomer **P3**, in the form of a pale yellow powder, is of yield 76%. ^1H NMR (CDCl_3 , ppm): δ 2.378 (s, CH_3 –, 3H), 6–8 (m, Ph–, 21H), 9.825 (s, $-\text{CHO}$, 0.25H). IR (KBr , cm^{-1}): 3431.8, 3024.8, 2920.4, 1594.8, 1541.9, 1320.6, 1194.0, 817.0. GPC analysis revealed that the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer were 1393 and 1797, respectively, with a polydispersity index of 1.29.

3. Results and discussion

The absorption and fluorescence spectra of **P1** in different solvents are shown in Fig. 1 from which it is evident that the λ_{max} was $\sim 399 \text{ nm}$ for **P1** was independent of the solvent's polarity. The fluorescence spectra, however, showed that luminescence intensity decreased with increasing solvent polarity,

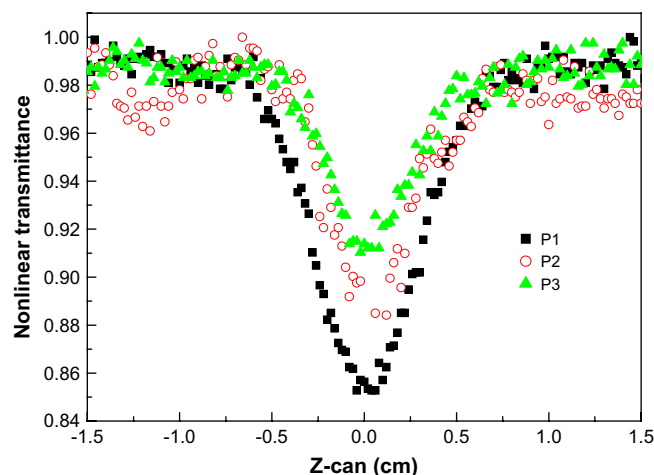


Fig. 3. Open-aperture Z-scan curve for **P1**–**P3** in THF at $c = 10 \text{ mg ml}^{-1}$.

along with a red shift from toluene to THF, to CH_2Cl_2 and to DMF, which strongly suggests that **P1** has “D– π –A” characteristics [22,23]. Thus, as shown in Scheme 1, 4-methyl triphenylamine and naphthalene in **P1** act as the electron-donor and the electron-acceptor, respectively. Upon replacing the naphthalene group with dibenzothiophene and dibenzofuran, respectively, one observed a blue shift of the short-wave absorption band to 396 nm for **P2** and 386 nm for **P3** (Fig. 2, left). This implies that the electronic interactions between the donor and acceptor groups induce a spectral shift to lower energy in the order: naphthalene > dibenzothiophene > dibenzofuran. The one-photon fluorescence spectra of the oligomers in DMF, shown in Fig. 2 (right), revealed that the fluorescence peak was blue shifted from **P1** (551 nm) to **P2** (493 nm) and to **P3** (488 nm) with the fluorescence intensity increasing in the order: **P3** > **P2** \gg **P1**. These results suggest that heterofluorene groups such as dibenzothiophene and dibenzofuran exhibit good luminescence when incorporated with the electron-donating group of triphenylamine.

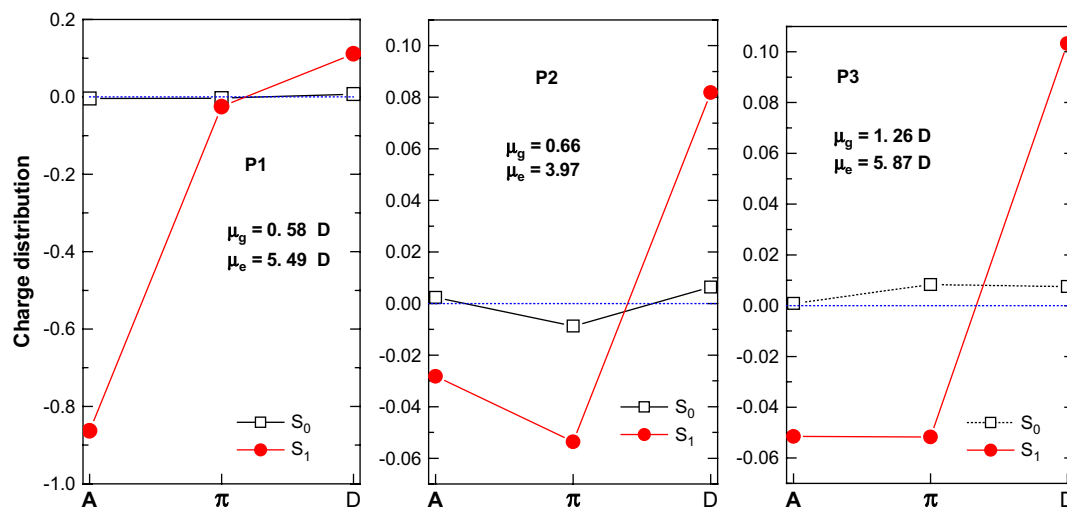


Fig. 4. Intramolecular charge density distributions for **P1**, **P2** and **P3** in S_0 and S_1 states.

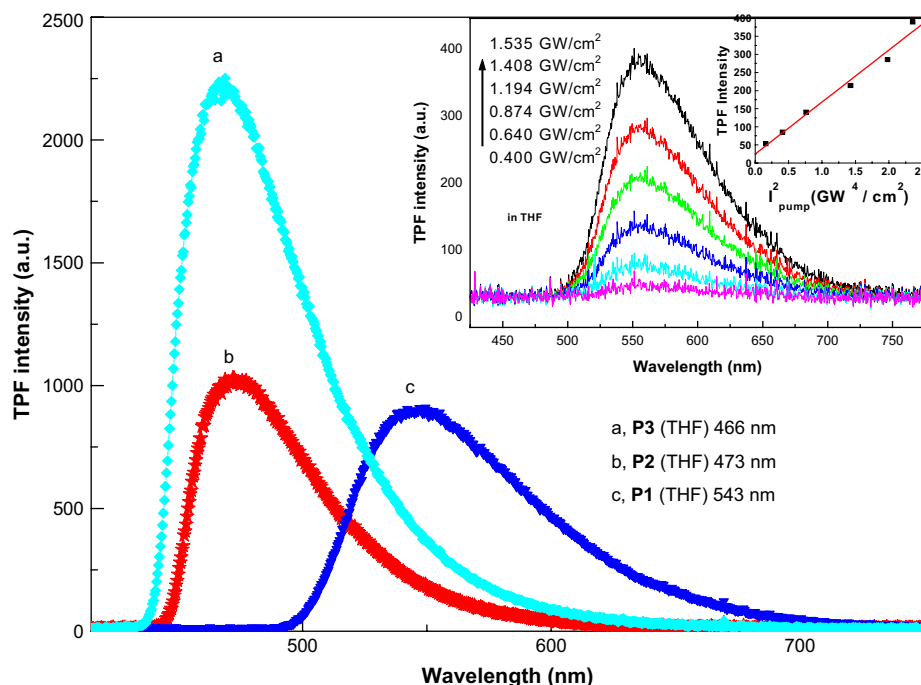


Fig. 5. Two-photon fluorescence of oligomers **P1–P3** in THF ($c = 10 \text{ mg ml}^{-1}$), pumped by femtosecond laser at 800 nm; inset shows the linear dependence of fluorescence intensity for **P1** on the square of the excitation intensity.

The open-aperture Z-scan curves of **P1–P3** in THF ($c = 10 \text{ mg ml}^{-1}$), according to the system reported previously [24], are presented in Fig. 3. The TPA coefficients (β) for the oligomers were obtained according to equation:

$$Ti = [\ln(1 + \beta LI_0)] / \beta LI_0,$$

which gives β values as in the order of **P1** ($2.5 \times 10^{-11} \text{ cm/W}$) > **P2** ($1.2 \times 10^{-11} \text{ cm/W}$) > **P3** ($1.0 \times 10^{-11} \text{ cm/W}$). The structures of the oligomers **P1–P3** lie on their different electron-acceptors, which may strongly influence the intramolecular excited charge redistribution and the electronic interaction of the donor–acceptor groups. As shown in Fig. 4, the intramolecular charge transfer of each repeat unit within the oligomers, calculated by the HF *ab initio* method contained within the Gaussian 98 program, showed the positive charge on the donor of 4-methyl triphenylamine and the negative charge on the acceptor such as naphthalene (**P1**), dibenzothiophene (**P2**) and dibenzofuran (**P3**) in the excited state. One can see that the charge density change for **P1** is about one order of magnitude larger than those of **P2** and **P3**. Taking **P1** and **P2** as examples, the excited charge densities on naphthalene and dibenzothiophene were -0.86 e , and -0.03 e , respectively; while those on 4-methyl triphenylamine were $+0.11 \text{ e}$ for **P1** and $+0.08 \text{ e}$ for **P2**, which is an evidence for the large charge redistribution on the two-terminals in the case of **P1**. Therefore, the TPA coefficient of **P1** is more than twice as large as that of **P2**. In contrast, while the excited intramolecular charge transfer and $\Delta\mu_{ge}$ of **P2** were smaller than those of **P3**, the electronic interaction between donor and acceptor in **P2** was larger than that in **P3**, according to the spectroanalysis

shown in Fig. 2. As a result, both oligomers present almost the same TPA coefficients.

The two-photon fluorescence of oligomers **P1–P3** in THF pumped by Ti:sapphire femtosecond laser pulses, show intense frequency up-converted fluorescence located at 543 nm for **P1**, 473 nm for **P2** and 466 nm for **P3** (Fig. 5). The inset shows, in the case of **P2**, a linear dependence of the fluorescence intensity on the square of the excitation intensity, which suggests that the frequency up-converted fluorescence can be attributed to a TPA mechanism namely, two-photon induced fluorescence (TPF). The comparison of the TPF fluorescence intensity of the three oligomers reveals that **P3** exhibited the

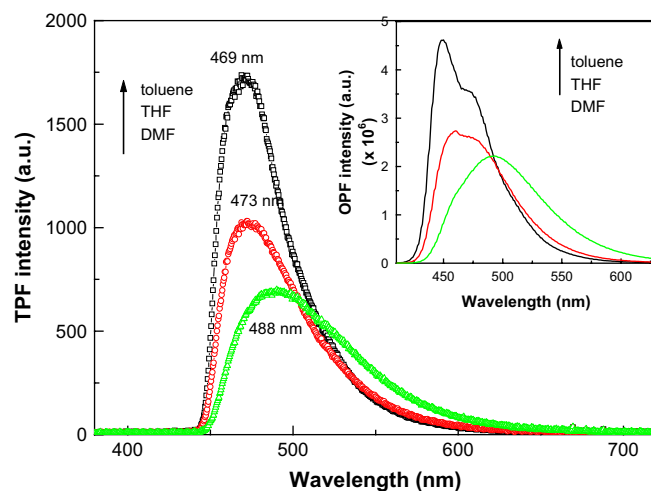


Fig. 6. Two-photon fluorescence of **P2** in different solvents ($c = 10 \text{ mg ml}^{-1}$); inset is the one-photon fluorescence ($c = 0.02 \text{ mg ml}^{-1}$).

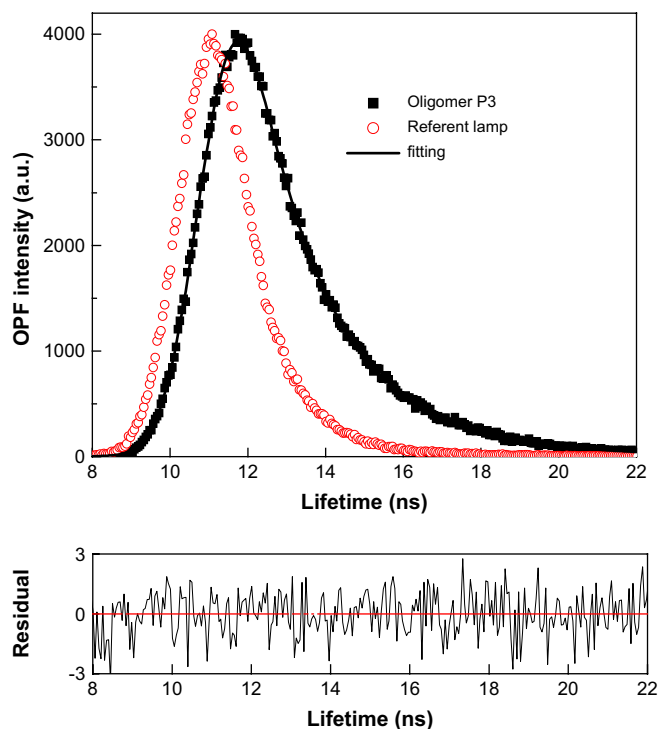


Fig. 7. Fluorescence decay curves of **P3** in THF at 0.02 mg ml^{-1} , in which the solid lines are the fitting result and the residual of corresponding lifetime, respectively.

strongest TPF luminescence, although its TPA coefficient was relatively small. It is reasonable to propose that the two-photon fluorescence quantum yield (Φ_{TPF}) is correlative to the two-photon absorption cross-section (δ_{TPA}) and one-photon fluorescence quantum yield (Φ_{OPF}), since the luminescence behaviour on OPE and TPE are very much alike, *i.e.*, in the emission from the first excited state (S_1) to the ground state (S_0), the only difference of the one-photon fluorescence and the two-photon fluorescence is mainly from their excitation process. Thus, we try to explain the TPF behaviour using one-photon emission dynamics. Fluorescence decay curves associated with the lamp profile and the residual for **P3** in THF, presented in Fig. 7, show that it possessed double lifetimes (τ) with a long lifetime at 2.19 ns and a short lifetime at 0.48 ns. The other two oligomers also showed double lifetimes (Table 1). The fluorescence lifetime measurements of **P1**–**P3** in different solvents confirmed that the long lifetimes derive from the planar intramolecular charge transfer excited state (abbreviated “ICT” state), whilst the short lifetime results from the twisted intramolecular charge transfer (TICT) state [23,25].

Table 1
Summary of one-photon and two-photon properties for the oligomers in THF

Compd.	λ_{OPA} (nm)	λ_{OPF} (nm)	Φ_f	τ (ns)	k_f $\times 10^7 \text{ s}^{-1}$	k_{nr} $\times 10^7 \text{ s}^{-1}$
P1	399	410	0.19	2.02, 0.65	9.41	40.11
P2	394	439	0.12	2.05, 0.46	5.85	42.90
P3	366	485	0.79	2.19, 0.48	36.07	9.59

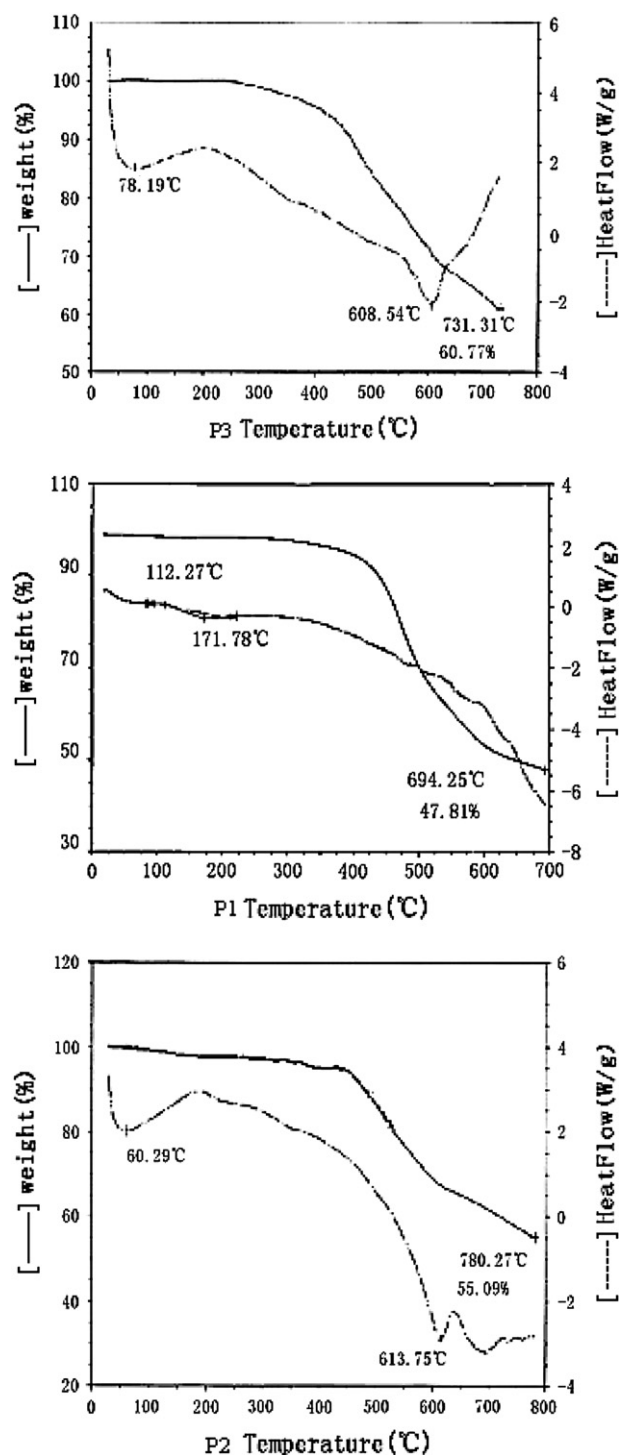


Fig. 8. The TG curves and DSC curves for **P1**–**P3**.

The fluorescence quantum yield (Φ_f) and the radiative ($k_f = \Phi_f/\tau$) as well as nonradiative ($k_{\text{nr}} = k_f(1 - \Phi_f)/\Phi_f$) decay constants are reported in Table 1. As can be seen, the fluorescence quantum yields follow the order: **P3** (0.79) > **P1** (0.19) > **P2** (0.19). This can be explained in terms of the k_f and k_{nr} values for the three oligomers. The radiative decay constant (k_f) is 6 times larger for **P3** and 1.6 times larger for **P1**, in comparison with **P2**; in contrast, the nonradiative decay constants (k_{nr}) of **P3** are 6 times lower than those of **P1** and **P2**.

This explains why the fluorescence quantum yields of **P1** and **P2** are smaller than that of **P3**. The heavy atom effect of the sulfur atom on the dibenzothiophene within **P2** and the naphthalene group within **P1** may increase the intersystem crossing of singlet to triplet, which results in a loss of PL efficiency. Thus, it is deduced that **P3**, which contains the dibenzofuran group, displays the best emission behaviour including single- and two-photon induce fluorescence, which is an important prerequisite for TPA-based applications such as fluorescence microscopy and diagnostics applications. Fig. 6 shows the two-photon fluorescence (TPF) of **P2** in different solvents. It can be seen that TPF intensity increases with decreasing solvent polarity; this means that the heavy atom effect is prohibited in a polar solvent such as toluene, which contributes to both one-photon and two-photon fluorescence as shown in Fig. 6 and the inset.

The inherent thermal stability of **P1–P3**, is represented by the DSC and TG curves presented in Fig. 8. For example, the oligomers start to decompose at $\sim 423^\circ\text{C}$ for **P1**, $\sim 483^\circ\text{C}$ for **P2** and $\sim 412^\circ\text{C}$ for **P3**, which is another important prerequisite for TPA-based applications such as power limiting.

4. Conclusions

We have synthesized three new conjugated triphenylamine-based oligomers that display TPA absorption and two-photon fluorescence as well as excellent thermal stability; such characteristics offer potential for a wide range of photonic applications such as optical power limiting and three-dimensional fluorescence microscopy.

Due to the contribution of a large dipole moment difference ($\Delta\mu_{\text{ge}}$) and excited charge redistribution as well as strong electronic interaction between donor and acceptor, **P1** exhibits greatest TPA cross-section. **P3** shows better luminescence including OPF and TPF, indicating that the rigid conjugated ring of the dibenzofuran group may enhance radiation disintegration.

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