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Enhanced two-photon absorption of novel four-branched chromophore via vibronic coupling

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ABSTRACT

A novel four-branched chromophore **TOZ-4** with starburst linker was synthesized and showed two-photon absorption cross-section (δ) as large as 5254 GM, which was principally resulted from vibronic coupling enhancement.

Two-photon absorption (TPA) has become one of the most remarkable and sought after nonlinear optical (NLO) effects owing to its wide-range of applications such as two-photon fluorescence microscopy,[1] three-dimensional microfabrication,[2] high-density optical data storage,[3] up-converted lasing,[4] optical-limiting[5] and photodynamic therapy.[6] These applications call for the design of specifically engineered compounds with large TPA cross-section. In the exploration of strong TPA molecules, attention has been firstly paid to asymmetrically and symmetrically substituted π-conjugation chromophores,[7] then to octpolar[8] systems. More recently, focus has turned towards multibranched structures including dendrimers.[9] Investigations have revealed that multibranched architectures can substantially enhance TPA cross-section due to the increase of chromophore density.[10] So, many efforts have been made to develop novel dendrimers wherein triphenylamine,[8] triazine[11] and imidazole[12] acting as the connection units. Meanwhile, some four-branched structures based on coupled thiophene and benzene, etc. have also been reported.[13] It is reported that the cooperative enhancement of molecular TPA cross-section is associated with electronic coupling (i.e., π-electron delocalization)[14] or vibronic coupling[15] within the multibranched system. Theoretically, when dendrimer generation is increased, the linear absorption spectrum gradually shifts to lower frequency due to electronic coupling (i.e., π-electron delocalization), which inevitably brings the nonlinearity-transparency trade-off.[16] For nonlinear optical applications, it is important to make chromophores with large nonlinearity (such as large TPA cross-section) without shifting spectra peak away from the given optical windows. Therefore, development of the new chromophores that display the increasing TPA without shifting their TPA spectra peak is of major interest from viewpoint of theoretics and applications. Herein, we report on the synthesis of a new four-branched chromophore (named as **TOZ-4)** based on new starburst linker, N^1-(4-(diphenylamino)phenyl)-N^1,N^4,N^4-triphenylbenzene-1,4-diamine, and measured its two-photon absorption by femtosecond two-photon fluorescence technique.[17] To understand the TPA enhancement by either electronic coupling or vibronic coupling, a new two-branched chromophore (named as **TOZ-2)** was synthesized by comparison.

To achieve synthesis of the multibranched chromophores, Heck-type, Wittig-type condensations and Ullmann reactions have been explored. Diphenylamine (compound **1**) was firstly protected by benzoyl chloride in pyridine at room temperature to obtain *N*,*N*-diphenylbenzamide (compound **2**); then followed by addition of bromine to get *N*,*N*-bis(4-bromophenyl)benzamide (compound **3**). Compound **5** was produced by Heck coupling reaction of compound **3** with compound **4** under oxygen-free condition; then

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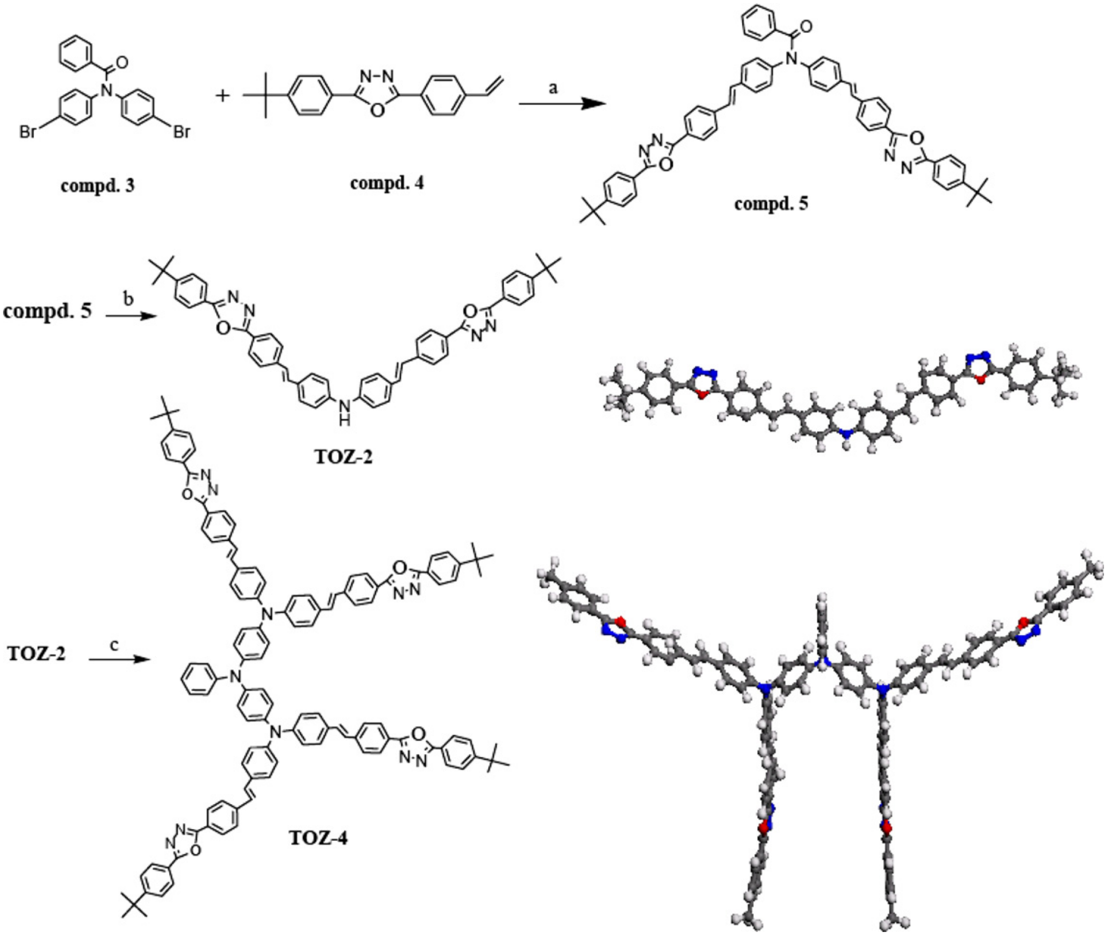
treated in Clasien's alkali[18] solution to obtain the object product **TOZ-2**. Four-branched **TOZ-4** was prepared by means of Ullmann reaction of tris(4-bromophenyl)amine with **TOZ-2** in Schlenk tube and heated at 140 °C for 2 days. Further measurements revealed that bromine located at 4′-position of triphenylamine in **TOZ-4** was gone. One possible mechanism is that under the catalysis of $Pd(OAc)_2$/tris-o-tolyphophine, oxidative addition would take place between Pd-catalyst and C–Br bond to form reactive arylpalladium intermediate. Trace amount of H_2O in the reaction system would quench the intermediate to afford protonized triphenylamine. Synthesis and characterization: IR spectra were measured by the Nicolet FT-IR 5DX instrument. MALDI (Mode laser) mass spectra were obtained on 4700 Proteome Analyzer produced by ABI Company. And EI mass spectra were obtained on HP 5989 mass spectra instruments. Nuclear magnetic resonance spectra were determined on Bruker NMR spectrometer. Palladium (II) acetate, tri-*tert*-butylphosphine, NaO-*t*-Bu and tri(*o*-tolyl)phosphine were purchased from Aldrich and are used as received without further purification. Other reagents and solvents were purified before use. The synthetic routes of multibranched chromophores **TOZ-2** and **TOZ-4** are shown in Scheme 1.

N,N-Bis-(4-bromo-phenyl)-benzamide (compound **3***):*[19] Benzoyl chloride (1.68 ml, 14.4 mmol) was added slowly into a 50 ml-round-bottomed flask in the presence of diphenylamine (compound **1**) (2.0304 g, 12 mmol) and pyridine (6 mL) with stirring at 0 °C. The reaction mixture was warmed to room temperature for overnight, then poured into the solution of dilute HCl (10%) and ice-water and extracted by chloroform. The chloroform solution was washed with 100 mL of water, 5% HCl solution and 5% NaOH solution, successively. The solvent was evaporated to give compound **2** and then was purified by column chromatography (silica gel, CH_2Cl_2/ petroleum ether = 5:1, 2.32 g, yield 70.9%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.84–7.50 (m, 15H). MS (EI): 273, 180, 167, 105, 77.

A chloroform solution (20 mL) of compound **2** (0.87 g, 3.2 mmol) was treated with bromine (0.36 g, 7.0 mmol). The mixture was stirred at 40 °C for 8 h and monitored by TLC until compound **2** was consumed. Compound **3** was obtained after crystallization from ethanol to give the pure product (1.310 g, yield 95%). MS (EI): 431, 166, 105, 77.

2-(4-tert-Butylphenyl)-5-(4-vinylphenyl)-1, 3,4-oxadiazole (compound **4***)*: This compound was synthesized according to the procedures reported paper.[20] ^1H NMR ($CDCl_3$, 300 MHz): δ 8.12, 8.105 (d, 4H, J = 6.0 Hz), δ 7.57, 7.55 (d, 4H, J = 6.0 Hz), δ 6.83, 6.79 (m, 1H), δ 5.92, 5.88 (d, 1H, J = 12.0 Hz), δ 5.42, 5.38 (d, 1H, J = 12.0 Hz), δ 1.38 (s, 9H); MS (EI): 304, 289, 161, 131, 103.

N,N-Bis-[4-(2-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}- vinyl)-phenyl]-benzamide (compound **5***)*: To a Schlenk tube equipped with a Teflon valve was added compound **3** (0.237 g, 0.548 mmol), compound **4** (0.4 g, 1.316 mmol) and $Pd(OAc)_2$ (8.2 mg, 0.037 mmol) in the presence of tri(o-tolyl)phosphine (22.1 mg), Et_3N (1.1 mL) and DMF (3.3 mL). The reaction mixture was degassed, refilled with nitrogen three times and heated at 140 °C for 3 days. Then, the mixture solution was



Scheme 1. Reagents and conditions: (a) $Pd(OAc)_2$, tri-*o*-tolylphosphine/Et_3N and DMF, reflux; (b) Clasien's alkali/THF; (c) tris(4-bromophenyl)amine, $Pd(OAc)_2$, $P(t\text{-}Bu)_3$, NaO-*t*-Bu/DMF, 140 °C. The synthesis routes and the optimized geometry of two-branch (**TOZ-2**) and four-branch (**TOZ-4**). The *tert*-butylphenyl groups on terminal ends in optimized geometry of **TOZ-4** were replaced by methyl group.

poured into water and extracted with dichloromethane. Compound **5** was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 10:1, 0.178 g, yield 37%). MS (MALDI) M^+ = 877.2.

*Bis-[4-(2-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-vinyl)-phenyl]-amine (***TOZ-2***)*: Ten millilitres of Clasien's alkali were added to the flask in presence of 0.15 g (0.17 mmol) of compound 5 and 10 mL of THF. The resulting solution was refluxed for 24 h. The mixture was poured into water and extracted with dichloromethane. The crude product was recrystallized from ethyl acetate to give yellow powder (**TOZ-2**) in 96% yield. MS (MALDI) M+ = 773.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48–7.50 (m, 8H), δ 7.35–7.40 (m, 8H), δ 7.17–7.19 (d, 4H, J = 6.0 Hz), δ 6.99, 6.95 (d, 4H, J = 12.0 Hz), δ 6.46–6.48 (d, 4H, J = 6.0 Hz), δ 1.38(s, 18H). Element Anal. Calcd for $C_{52}H_{47}N_5O_2$: C, 80.70; H, 6.12; N, 9.05. Found C, 81.20; H, 6.51; N, 8.85.

*N^1-(4-(bis(4-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)styryl)phenyl)amino)phenyl)-N4,N^4-bis(4-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)styryl)phenyl)-N^1-phenylbenzene-1,4-diamine (***TOZ-4***)*: To a Schlenk tube equipped with a Teflon valve was added two-branch **TOZ-2** (120 mg, 0.155 mmol), tris-(4-bromophenyl)amine (21.9 mg, 0.0456 mmol), $Pd(OAc)_2$ (5 mg), $P(t\text{-}Bu)_3$ (2 μL) NaO-*t*-Bu (0.025 g) and DMF (4 mL). The reaction mixture was degassed and refilled with nitrogen three times. The tube was sealed and heated at 140 °C for 2 days. The reaction mixture was then poured into water and extracted with dichloromethane. The crude product was recrystallized from ethyl acetate to give bright yellow powder (66.8 mg, yield 78%). MS (MALDI) M^+ = 1788.7. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48–7.50 (m, 16H), δ 7.35–7.40 (m, 16H), δ 7.17–7.19 (d, 8H, J = 6.0 Hz), δ 6.99–7.01 (m, 10H), δ 6.62–6.65 (m, 1H), δ 6.46–6.48 (m, 10H), δ 6.21–6.24 (m, 8H), δ 1.38 (s, 36H). Element Anal. Calcd for $C_{122}H_{105}N_{11}O_4$: C, 81.90; H, 5.92; N, 8.61. Found C, 82.29; H, 5.953; N, 7.895.

Linear photophysical properties of **TOZ-2** and **TOZ-4** are shown in Tables 1,2 and Figure 1a–c. Interestingly, the absorption peaks in the same solvent show very close from two-branched **TOZ-2** to four-branched **TOZ-4**. For example, the CT bands in long wavelength region for both chromophores (Fig. 1a) give the identical position at 419 nm in THF and at 409 nm in CH_2Cl_2, except for the significant enhancement in molar extinction coefficient for **TOZ-4**. And emission peaks of **TOZ-2** and **TOZ-4** (Fig. 1b) are located about 507 nm in THF and 502 nm in CH_2Cl_2. Similar results were obtained in other solvent. Generally, the bathochromic shift in absorption/emission is a sign of π-electron delocalization that results from the electronic coupling for chromophore.[14] However, we failed to observe red-shifts of the maximum absorption/emission from **TOZ-2** to **TOZ-4**; moreover, the Stokes shift ($\Delta\nu = \nu_{ab} - \nu_{em}$) calculated by the difference between maximum absorption and emission shows very close for both chromophores (see

Table 1

Linear spectral properties for **TOZ-2** and **TOZ-4** in different solvents

	Solvent	Ethyl acetate (EA)	THF	CH_2Cl_2	DMF
TOZ-2	λ_{abs} (nm)	415	419	409	428
	λ_{em} (nm)	499	507	502	547
	$\Delta\nu_{abs} - \nu_{em}$ (cm^{-1})	4055	4142	4529	5082
TOZ-4	λ_{abs} (nm)	414	419	409	428
	λ_{em} (nm)	498	506	500	548
	$\nu_{abs} - \nu_{em}$ (cm^{-1})	4074	4130	4450	5115

Table 2

One-photon and two-photon property[a] as well as molecular energy level data[b]

	Φ_f	τ (ns)	λ_{max}^{TPF} (nm)	λ_{max}^{TPA} (nm)	δ_{TPA} (GM)	HOMO (eV)	LUMO (eV)	E_g (eV)
TOZ-2	0.29	1.39	504	730	1914	−5.585	−2.901	2.684
				760	1804			
				780	1200			
TOZ-4	0.20	1.44	504	730	5178	−5.588	−2.875	2.713
				760	5254			
				780	4107			

[a] In THF.

[b] In CH_2Cl_2.

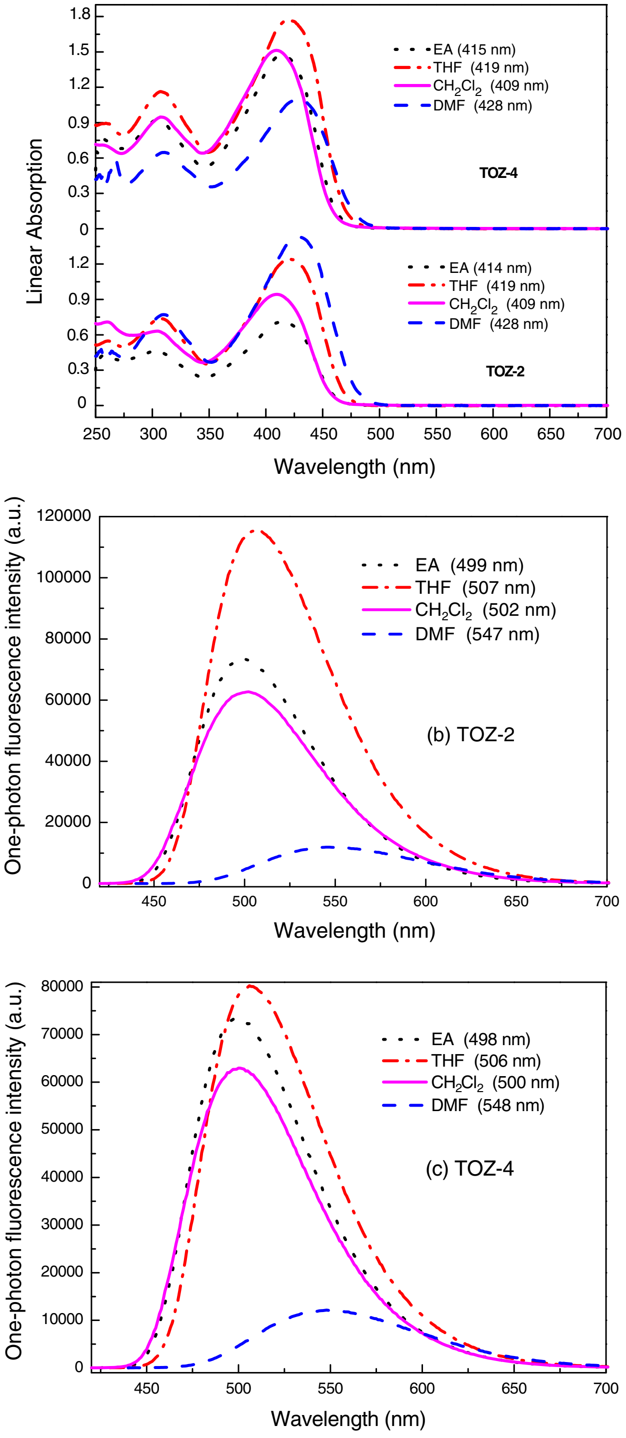


Figure 1. One-photon absorption (a) and fluorescence spectra (b and c) of **TOZ-2** and **TOZ-4** in different solvents at the concentration of 1×10^{-5} mol dm^{-3}.

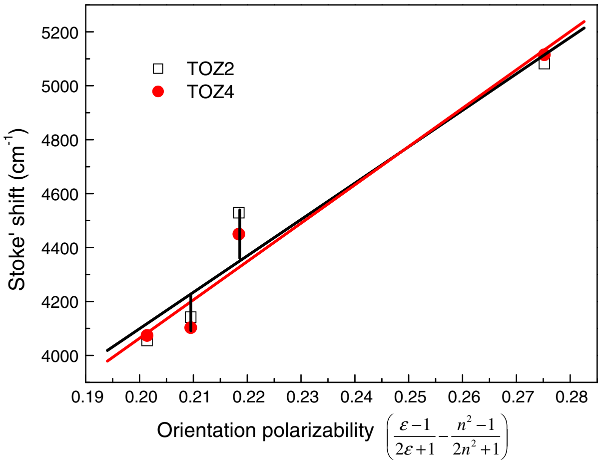


Figure 2. The relationship between Stoke's shift ($\Delta\nu$) and solvent orientation polarizability.

Fig. 2), strongly suggesting that delocalization of π-electron is not strong for our chromophores.

Pumped by Ti: sapphire femtosecond laser pulse under the same pumped power at 800 nm, both **TOZ-2** and **TOZ-4** in THF emit strong two-photon fluorescence (TPF), shown in Figure 3a. Figure 3b and c shows that TPF intensities of **TOZ-2** and **TOZ-4** are increased with the pumped power increasing from 30.1 to 106.9 mW. Insets show the value 1.8 of the logarithmic plots of the fluorescence integral versus pumped powers when the input laser power is below 60 mW, suggesting the two-photon excitation mechanism occurring below this threshold. Above 60 mW, however, two-photon fluorescence intensities of **TOZ-2** and **TOZ-4** increase slowly, implying some kind of saturation existence. So, the excitation powers in our TPA cross-section measurements are limited below 45 mW, and the experimental uncertainty for the calculation of the TPA cross-section is estimated to be about 10%, by the comparison of the TPA cross-section of fluorescein between our measurement and reported data. Thus, the TPA cross-sections (δ) of **TOZ-2** and **TOZ-4** were calculated[17] and presented in Figure 4 and Table 4. One can see that the shape and TPA maximum of **TOZ-2** and **TOZ-4** are similar but both the cross-sections are different. The δ values of **TOZ-4** were 5178 GM at 730 nm, 5254 GM at 760 nm and 4107 GM at 780 nm, which were about 3-fold increase relative to **TOZ-2** (1914 GM at 730 nm, 1804 GM at 760 nm and 1200 GM at 780 nm). These suggest that there is indeed cooperative enhancement in four-branched structure. If each branch in four-branched **TOZ-4** is not interactional, the δ value of **TOZ-4** should be 2-fold increase relative to **TOZ-2**. Lippert–Mataga relationship (see Fig. 2) has confirmed that the electronic coupling (i.e., the delocalization of π-electron) within four-branched structure is small. And the weak electronic coupling (i.e., the delocalization of π-electron) within four-branched structure cannot explain this cooperative enhancement of TPA, since the TPA spectra in the range of 700 nm $\sim$840 nm show no bathochromic shift from **TOZ-2** to **TOZ-4**. Also, one can notice that the TPF peaks for **TOZ-2** and **TOZ-4** are all at 504 nm, and the intensity of **TOZ-4** with broader FWHM (full width at half maximum) shows more than two times as strong as that of **TOZ-2**, strongly implying coupling enhancement in existence and the structured forms of TPF spectra in the long wavelength region distinctly express that TPF emissions are from the different vibrational states at the first excited electron state (S_1). We considered that vibrational electronic coupling found in **TOZ-4** is probably due to the use of the amino group as the connecting unit, which breaks the conjugation of the whole network.[15a] Further, optimization conformations of **TOZ-2** and

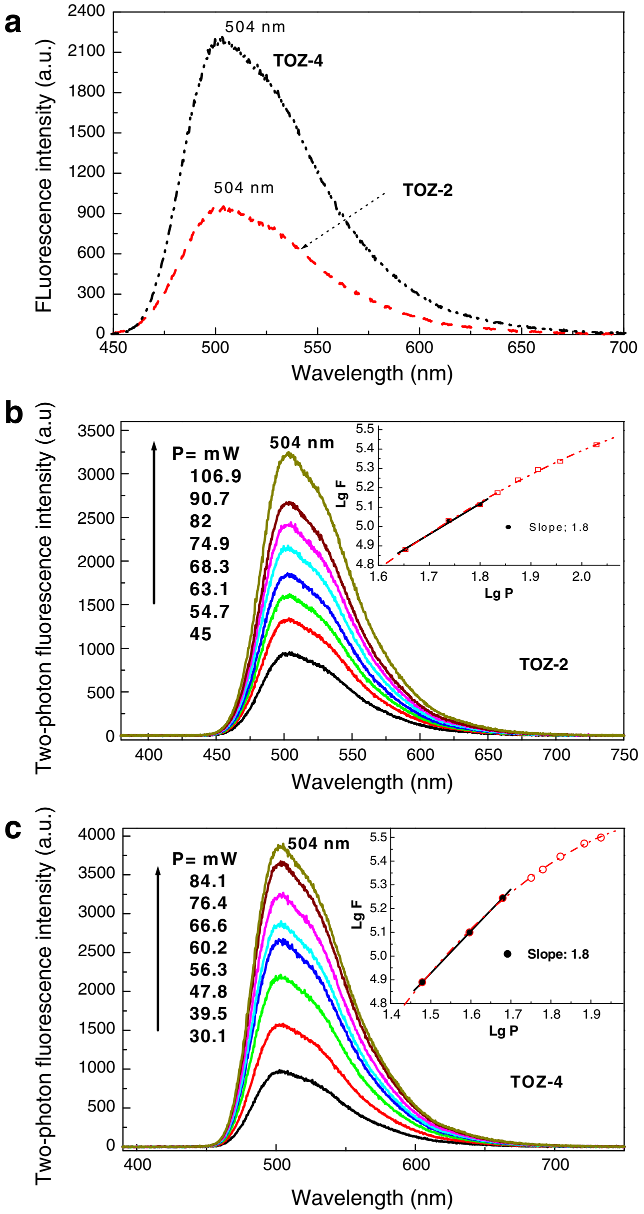


Figure 3. (a) Two-photon fluorescence (TPF) spectra at the same pumped power at 800 nm of **TOZ-2** and **TOZ-4**; (b and c) TPF spectra of **TOZ-2** and **TOZ-4** under different pumped powers at 800 nm; The concentrations (THF) are 1×10^{-4} mol dm^{-3} for TPF and 1×10^{-5} mol dm^{-3} for OPF measurements.

TOZ-4 (Scheme 1), obtained by Hyperchem program, show that two-branched **TOZ-2** possesses almost planar configuration with quasi-quadrupolar structure; while the four-branched **TOZ-4** with the linker of *N*^{1}-(4-(diphenylamino)phenyl)-*N*^{1},*N*^{4},*N*^{4}-triphenylbenzene-1,4-diamine presents the rigid propeller-shaped structure. We suggest that the linker with rigid and twisted feature blocks π-electron delocalization and resulting weaken electronic couple. So, the effective conjugation length of the four-branched structure is thus more or less the same as that of the two-branched structure and holds more excited electronic states energetically close, from which the vibronic intensity can be borrowed.[15a] Similar results have been theoretically confirmed in other multi-branched chromophores.[15a]It is also noticed that (see Fig. 4) the TPA maximum wavelength occurred at slightly less than the twice wavelength of the one-photon absorption maximum wavelength, indicating that one- and two-photon excitations are at the same excited state. For the symmetry selection rules, one-photon allowed transitions should not lead to two-photon activity; however, if a vibronic coupling mechanism works, such electronically forbidden transition becomes allowed.[21] Thus, it can be seen that the vibronic contributions to the TPA cross-section can play an important role in the cooperative enhancement within **TOZ-4**.

Cyclic voltammograms of **TOZ-2** and **TOZ-4**, shown in Figure 5, exhibit oxidative peaks for **TOZ-2** and **TOZ-4**, which are almost located at ~0.846 V. The calculated molecular HOMO/LUMO levels and the energy level difference (E_g), based on the linear absorption spectra and the cyclic voltammogram curves,[22] are presented in Table 2. One can notice that both multibranched chromophores (**TOZ-2** and **TOZ-4**) keep molecular HOMO (about −5.9 eV) and E_g (about 2.7 eV) unchanged with the branch number increasing. Theoretically, when branch within conjugated chromophore is increased, the linear absorption spectrum gradually shifts to lower frequency, which will inevitably bring nonlinearity-transparency trade-off.[16] It is found that four-branched **TOZ-4** with TPA enhancement can keep molecular HOMO/LUMO level unchanged, in comparison with two-branched **TOZ-2**.

In conclusion, novel four-branched **TOZ-4** with the new starburst linker has been designed and synthesized. The cooperative enhancement TPA within four-branched **TOZ-4** was shown to originate from vibronic coupling that is propitious with respect to the trade-off between optical transparency and NLO performance (two-photon absorption). The starburst linker with rigid propeller-shaped structure strengthens the vibronic coupling effect in the four-branched structure.

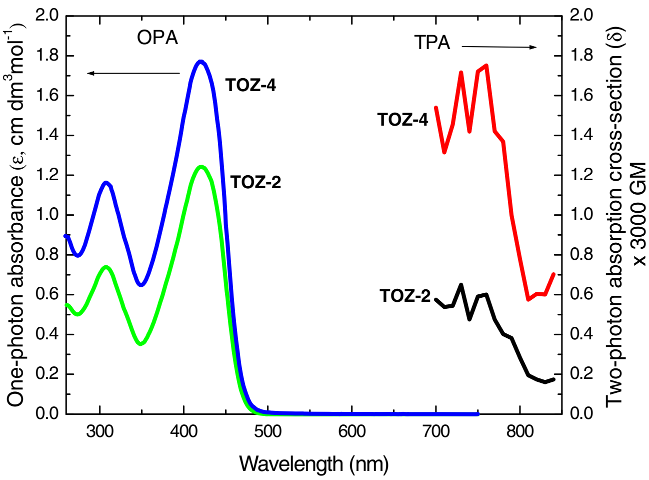


Figure 4. Two-photon excited spectra of **TOZ-2** and **TOZ-4** (THF, 1×10^{-4} mol dm^{-3}), one-photon absorption spectra of **TOZ-2** and **TOZ-4** (THF, 1×10^{-5} mol dm^{-3}) are presented for comparison.

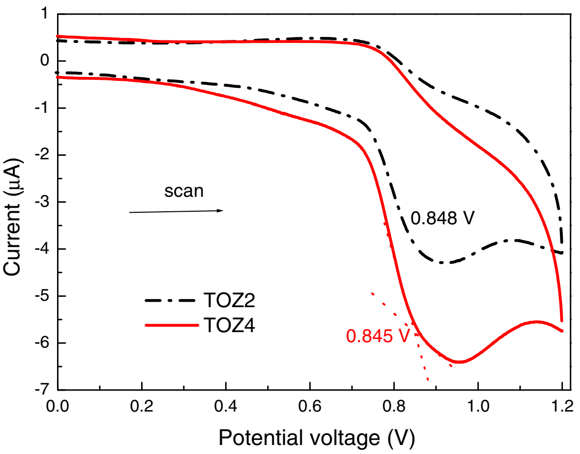


Figure 5. Cyclic voltammogram of chromophores in deoxygenated CH_2Cl_2, purged with nitrogen, containing 0.1 M of tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6), scan rate of 50 mV s^{-1}.

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