



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

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ARTICLE INFO

Article history:

Received 17 February 2008

Revised 18 July 2008

Accepted 22 July 2008

Available online 25 July 2008

Keywords:

Four-branched chromophore

Starburst linker

Two-photon

Vibronic coupling

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.

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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-limiting⁵ 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 octipolar⁸ systems. More recently, focus has turned towards multibranch structures including dendrimers.⁹ Investigations have revealed that multibranch 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 triazine¹¹ and imidazole¹² 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 coupling¹⁵ within the multibranch 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 multibranch 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 Clasién's alkali¹⁸ 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*-tolylphosphine, oxidative addition would take place between Pd-catalyst and C–Br bond to form reactive arylpalladium intermediate. Trace amount of H₂O 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.

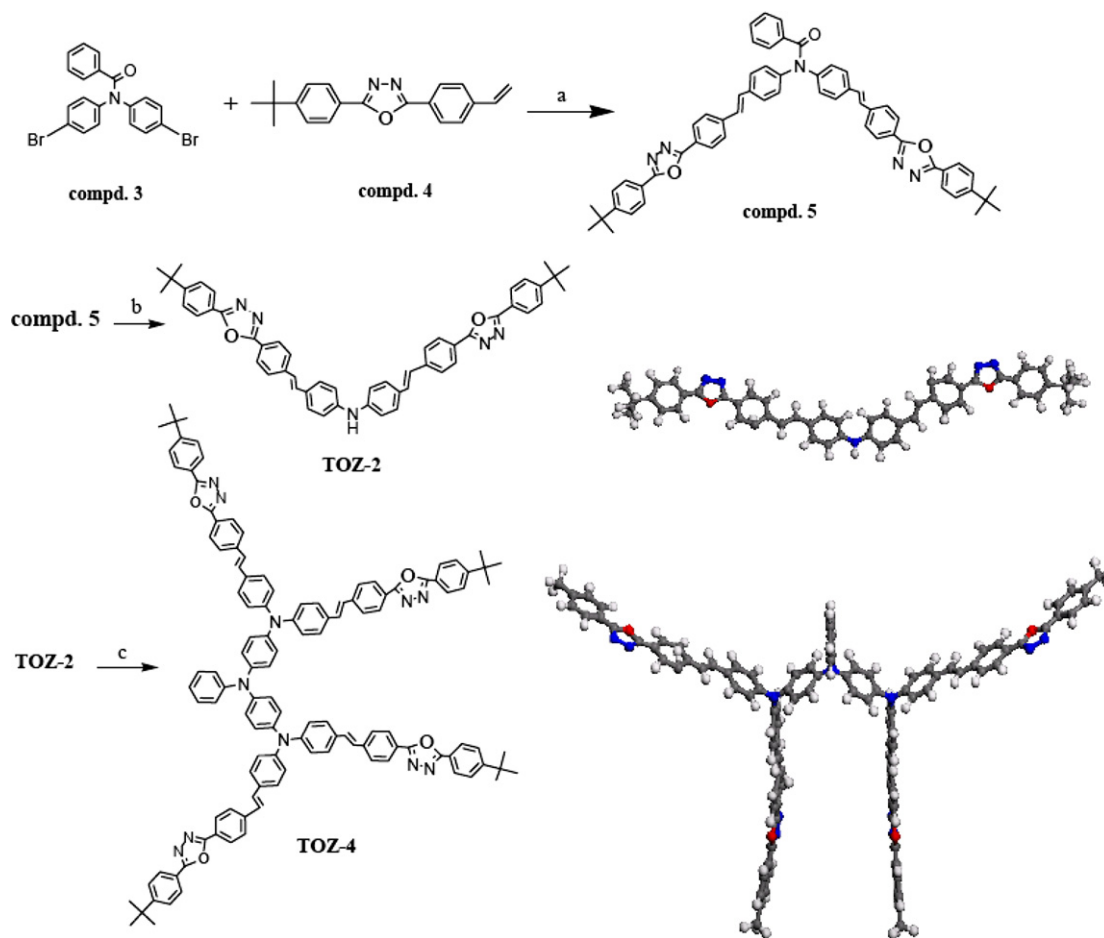
N,N-Bis-(4-bromo-phenyl)-benzamide (compound **3**):¹⁹ Benzoyl chloride (1.68 mL, 14.4 mmol) was added slowly into a 50 mL round-bottomed flask in the presence of diphenylamine (compound **1**) (2.0304 g, 12 mmol) and pyridine (6 mL) with stirring at 0 °C. The reaction mixture was warmed to room temperature 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, CH₂Cl₂/ petroleum ether = 5:1, 2.32 g, yield 70.9%). ¹H NMR (CDCl₃, 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 (CDCl₃, 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), Et₃N (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/Et₃N and DMF, reflux; (b) Clasién's alkali/THF; (c) tris(4-bromophenyl)amine, Pd(OAc)₂, P(*t*-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.

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