Journal of Molecular Structure 934 (2009) 86–90

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Third-order nonlinear optical property of non-identical three-branched molecules based on triphenylamine

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ARTICLE INFO

Article history:
Received 1 April 2009
Received in revised form 16 June 2009
Accepted 16 June 2009
Available online 23 June 2009

Keywords:
Multi-branched molecules
Third-order nonlinear optics
Nonlinear absorption
Nonlinear refraction

ABSTRACT

A series of non-identical three-branched molecules with two D–π–D′ and one D–π–A branchs were synthesized based on triphenylamine as a core. Both the λ_{max}^{ab} and λ_{max}^{fl} are red-shifted slightly with the strength of the peripherical acceptor reducing in these molecules. Their third-order nonlinear optical properties were measured by Z-scan technique with a Ti: Sapphire laser (2.5 ps, 76 MHz, 38 mW) at 800 nm in chloroform. All the six molecules display nonlinear refraction and nonlinear absorption response at this condition. The results indicate that both the nonlinear absorption and nonlinear refraction response increase with the strength of acceptor weakening in these molecules, and the $\mathrm{Re}(\chi^{(3)})$ of these molecules are three orders of magnitude larger than their $\mathrm{Im}(\chi^{(3)})$.

1. Introduction

Materials with large third-order nonlinear susceptibility and ultrafast response have attracted extensive attention due to their potential applications in ultrafast optical information processing [1–3]. Various types of nonlinear optical materials have been designed and fabricated [4–12]. Among all kinds of materials, organic materials are of major interest because of their high efficiency, fast nonlinear optical response time, relatively low cost, excellent processability, high laser tolerance and stability [13–15].

Although the relationship of structure and property for organic third-order nonlinear optical (NLO) materials is still under exploration, it is well known that a large electron-delocalization is the prerequisite for achieving large third-order NLO response in organic system. Strong delocalization of π-electrons in the organic backbone determines a high molecular polarizability and thus remarkable third-order optical nonlinearity. Recently, it has been reported that the multi-branched molecules displayed large third-order NLO response, especially large two-photon absorption (TPA), due to the coupling effect among the branches (cooperative enhancement) [16–23]. However, to the best of our knowledge, every branch in the multi-branched molecule is the same, and little attention has been put into the third-order NLO property of multi-branched molecules with different branches, i.e., non-identical multi-branched molecules. We are interested in investigating whether introducing different branches into multi-branched molecules will have strong influence on the nonlinear optical response. And the research of nonlinear optical property in non-identical multi-branched molecules might be helpful to deepen the understanding of the relationships between the molecular structure and the nonlinear optical properties in multi-branched molecules and provides some guidelines for the design and synthesis of new nonlinear optical materials.

Herein, we wish to report the synthesis and third-order NLO properties of a series of non-identical three-branched molecules based on triphenylamine as a core (Scheme 1). The three branches are not all the same in these molecules, and they are of two D–π–D′ and one D–π–A motif, where D is the nitrogen atom in triphenylamine at the core, D′ and A is periphery donor and acceptor, respectively. Diethylamino group is stronger donor than diphenylamino group [24] and the strength of acceptor reduces from —NO_2, —SO_2Et to —CN ($a > b \approx c$) [25,26].

2. Experimental

^1H NMR spectra were recorded on Varian Mercury VX300 FT-NMR spectrometer in $CDCl_3$ (Varian, USA) operating at 298 K. Elemental analysis was performed by Vario EL III (German). Mass spectra were recorded on Finnigan Trance Mass spectrometer. UV–vis spectra were obtained using a Schimadzu 160A spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. All chemicals are commercially available and were used as received unless stated otherwise. Third-order nonlinear optical responses were determined by

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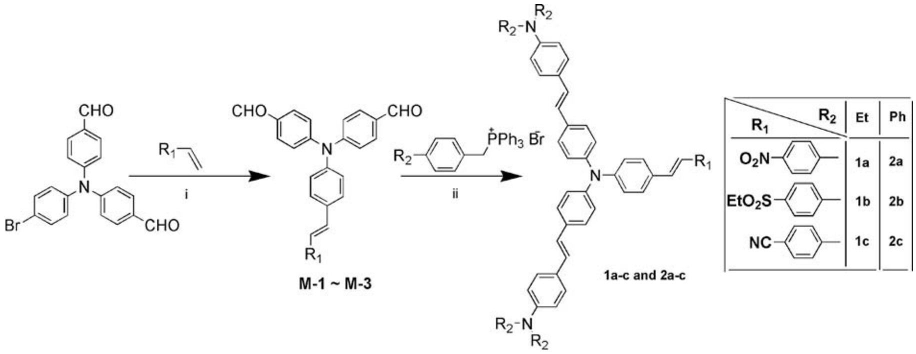
doi:10.1016/j.molstruc.2009.06.023



Scheme 1. The synthetic routes of the non-identical three-branched molecules. (i) $Pd(AcO)_2$, PPh_3, Et_3N, DMF, 140 °C, 12 h. (ii) t-BuOK, THF, 12 h.

Z-scan measurement in chloroform ($\sim 1 \times 10^{-3}$ M) at 800 nm with Ti: Sapphire laser (Mira 900, Coherent) with a pulse width of 2.5 ps and a repetition rate of 76 MHz. The NLA and NLR were measured by open- and closed-aperture Z-scanning, respectively. The polarization of the laser pulses incident to the samples was adjusted by a HWP. The samples were scanned around the waist of the focused Gaussian laser beam along *Z*-axis. The cell used in the Z-scan measurement is $10 \times 1 \times 30$ mm, and the thickness of the samples is 1 mm. To minimize thermal effects during measurement of the NLA and NLR, the peak irradiance of the laser pulses was kept weak, 0.18 GW cm^{-2}.

Details of the preparation and characterization of these compounds and the open-aperture and close/open-aperture Z-scan curve of solvent are available in the Electronic Supplementary materials.

3. Results and discussion

3.1. Synthesis and structural characterization

The synthetic routes of the multi-branched molecules are shown in Scheme 1. Triphenylamine was functionalized first by Vilsmeiler reaction and subsequently bromation. The synthesis of aryl ethylenes were operated facilely in a formalin solution (aq., 37%) with a good yield by Wittig reaction. The D–π–A motifs were obtained by a palladium-catalyzed Heck reaction between 4-bromophenyl-bis-(4-formylphenyl)-amine and aryl ethylenes. And D–π–D′ motif can be introduced easily into molecules through Wittig reaction since there are aldehyde groups on triphenylamine. All compounds were purified by column chromatography and recrystallization. The structures of these molecules were confirmed by ^{1}H NMR, Mass spectra and elemental analysis.

3.2. Linear absorption and single-photon-excited fluorescence

The linear absorption and fluorescence emission spectra of the six molecules in chloroform are shown in Figs. 1 and Fig. 2 respectively, and the corresponding spectroscopic properties are listed in Table 1.

The absorption band at about 250–360 nm is assigned to absorption of the phenylene ring, whereas the longer wavelength region absorption band is attributed to the π–π^* transition [27]. The strong shoulder peak in the UV–vis absorption spectra at long wavelength originates from the absorption of D–π–A motif. The shoulder peak reduces gradually with the strength of peripheral acceptor weakening. All the maximum absorption wavelength (λ_{max}^{ab}, the strongest peak of each molecule) of these non-identical molecules are adjacent. It seems that the λ_{max}^{ab} is red-shifted slightly with the strength of periphery acceptor or donor weakening.

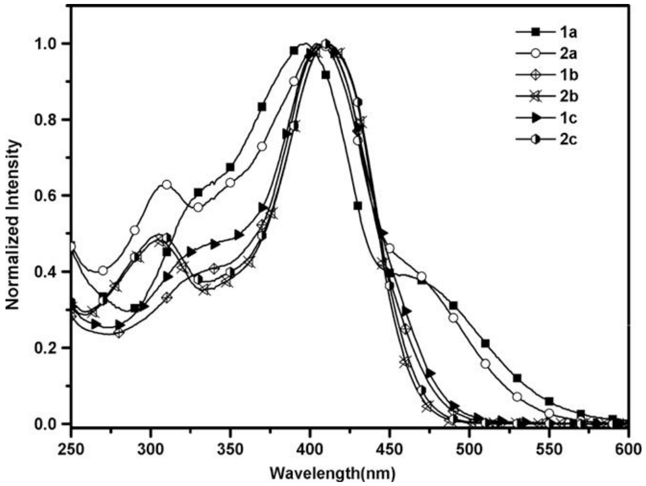


Fig. 1. The linear absorption spectra of the six compounds.

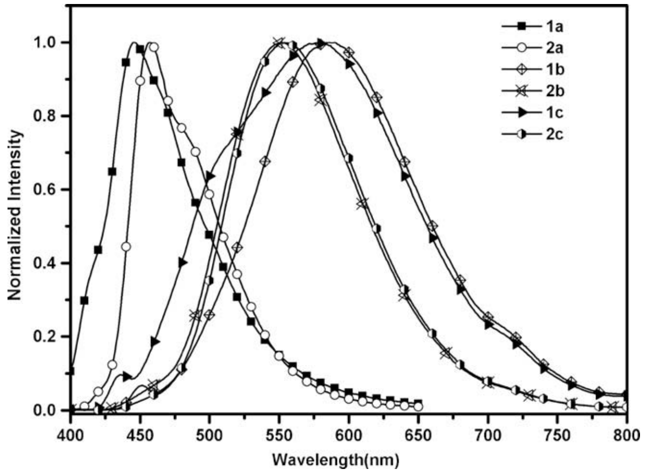


Fig. 2. The fluorescence spectra of the six compounds.

Table 1
The single-photon optical properties of the six molecules.

	1a	2a	1b	2b	1c	2c
λ_{max}^{ab} (nm)	397	404	409	410	408	411
λ_{max}^{fl} (nm)	445[a]	457[a]	584	551	578	554
Δv^{b} (cm^{-1})	2720	2870	7320	6240	7200	6280

[a] The fluorescence spectra were collected by increasing the slit width of emission and excition.

[b] Stokes shift ($\Delta v = 1/\lambda_{max}^{ab} - 1/\lambda_{max}^{fl}$).