

Two-photon absorption properties of a novel class of triarylamine compounds

E. Piovesan^a, L. De Boni^a, E. Ishow^b, C.R. Mendonça^{a,*}

^aInstituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

^bEcole Normale Supérieure de Cachan, PPSM CNRS UMR 8531, 61 av. Pdt Wilson, 94235 Cachan Cedex, France

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ABSTRACT

Two-photon absorption spectra of triarylamine compounds dissolved in toluene were measured using the well-known Z-scan technique, employing 120-fs laser pulse-width. According to the results, an extra band located at around 900 nm was observed only for triarylamine with azoaromatic units. On the other hand, a shift in the two-photon absorption band for triarylamine, with and without azoaromatic units, is observed when different electron donor/acceptor groups are changed. The fitting of the spectra, using sum-over-states model, allowed us to obtain the spectroscopic parameters of each molecule, which appears to be in reasonable agreement with molecules presenting similar structural moieties.

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1. Introduction

Processes related to two-photon absorption (2PA) have attracted attention in recent years owing to diverse applications in various fields, such as photodynamic therapy [1,2], optical-limiting [3–5], optical data storage [6,7], upconversion lasing [8,9], 3D microfabrication [10,11] and two-photon excited fluorescence microscopy [12,13]. 2PA occurs when molecules are exposed to intense laser pulses. In this regime, the molecule can absorb two photons, each one with half of the necessary energy to perform the electronic transition, resulting in an effect called two-photon absorption. This effect presents several interesting properties, such as the quadratic dependence of the excitation rate with laser irradiance, which results in high spatial selectivity and low photochemical damages owing to reduced excitation density [10,12,14–17].

Consequently, there is a great effort to obtain materials with remarkable 2PA cross-sections [18,19] and, in this context, organic compounds have presented great possibilities due to their flexibility in terms of structural engineering, allowing the development of molecules with tunable optical nonlinearities in accord with the targeted applications [18,20–24]. Consequently, the understanding of the nonlinear absorption spectrum is a fundamental subject for applications using two-photon absorption processes.

In this Letter, a study of the nonlinear optical properties of non-centrosymmetric push–pull triarylamine (TA) derivatives is presented, exploiting the electron-withdrawing effect of the azoaromatic units connected to the triarylamine derivatives [22,25–27]. Triarylamine compounds present interesting optical properties that can be exploited for applications such as, for exam-

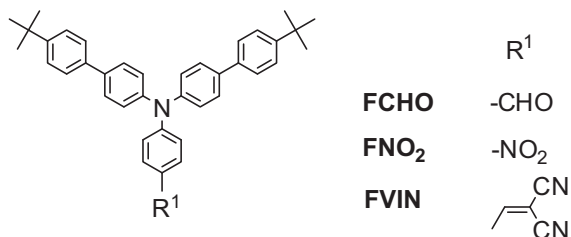
ple, active layers for two-photon holographic rewritable micropatterning [28], fluorescence photoswitching materials [29]. More recently, triarylamine compounds have also been used as electron donor for organic photovoltaic functional materials, leading to a reinforcement of the conversion efficiency of solar cells [30]. The molecular structures of the TA compounds we investigated in this work are presented in Scheme 1, for TA, and Scheme 2, for the azoaromatic triarylamine (AzoTA) derivatives. Similar compounds have been recently investigated for two-photon fluorescent holographic rewritable micropatterning [28]. For the nonlinear properties of the emitting TA and non-emitting AzoTA to be compared, we resorted to the open-aperture Z-scan technique [31,32] which represents a direct measurement of the two-photon absorption cross-sections by measuring the transmitted infrared red light after interaction with the samples in solution. The data were modeled by using a sum-over-states (SOS) approach considering a four-level-energy diagram. 2PA spectra reveal that the insertion of azoaromatic units results in the appearance of an additional band, related to a state allowed by both, one- and two-photon absorption, due to a charge symmetry breaking. These results shine light onto the nonlinear absorption of push–pull azoaromatic compounds the archetypical derivative of which, Disperse Red 1, is being much studied for electrooptics applications [33].

2. Experimental

A series of six compounds; three push–pull triphenylamines FCHO ($\epsilon^{400\text{ nm}} \approx 18\,000\text{ M}^{-1}\text{ cm}^{-1}$), FNO₂ ($\epsilon^{400\text{ nm}} \approx 25\,000\text{ M}^{-1}\text{ cm}^{-1}$), FVIN ($\epsilon^{450\text{ nm}} \approx 21\,000\text{ M}^{-1}\text{ cm}^{-1}$) and three azoaromatic triarylamine, AzocarbcN ($\epsilon^{470\text{ nm}} \approx 20\,000\text{ M}^{-1}\text{ cm}^{-1}$), AzocarbcNO₂ ($\epsilon^{490\text{ nm}} \approx 22\,000\text{ M}^{-1}\text{ cm}^{-1}$) and AzotBuCN ($\epsilon^{480\text{ nm}} \approx 21\,000\text{ M}^{-1}\text{ cm}^{-1}$) was studied. All photophysical experiments were carried out in toluene solutions. The UV–Vis absorption

* Corresponding author. Fax: +55 16 3373 9811.

E-mail address: crmendon@if.sc.usp.br (C.R. Mendonça).



Scheme 1. Structures of push-pull triarylamine derivatives FCHO, FNO₂ and FVIN.

spectra were measured using a Cary 17 spectrophotometer, with sample concentration of 10^{16} molecules per cm^3 (1.7×10^{-5} mol L^{-1}). The nonlinear absorption measurements were performed in solutions containing 10^{18} molecules per cm^3 (1.7×10^{-3} mol L^{-1}). Both, linear and nonlinear measurements were done in fused silica cuvettes with a 2 mm-long optical path.

The 2PA cross-section spectra were obtained using the open-aperture Z-scan technique [31,32]. 150-fs pulses from a commercial Ti:sapphire chirped pulse amplifier (775 nm and 1 kHz repetition rate) were employed to pump an optical parametric amplifier, allowing wavelength tuning from 460 up to 900 nm. To ensure a Gaussian profile of the laser beam, spatial filtering was performed before the Z-scan setup. Z-scan curves were obtained for each excitation wavelength, which, in the case of 2PA processes, corresponds to a decrease in the normalized sample transmittance at the focus. These curves, related to 2PA, were integrated over time t , assuming a Gaussian profile. The resulting normalized energy transmittance $T(z)$ can be expressed as:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z,t)e^{-t^2}] dt \quad (1)$$

where $q_0(z,t) = \beta I_0(t)L(1 + z^2/z_0^2)^{-1}$, L is the optical path, z_0 is the Rayleigh length, z is the sample position, and I_0 is the pulse irradiance [31,32]. Fitting the Z-scan signatures with Eq. (1), we obtained the two-photon absorption coefficient β . The 2PA cross-sections can be determined using $\delta = h\nu\beta/N$, where $h\nu$ is the excitation energy and N is the number of molecules per cm^3 . Usually δ is expressed in Göppert-Mayer (GM) units, being $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$ [34].

3. Results and discussion

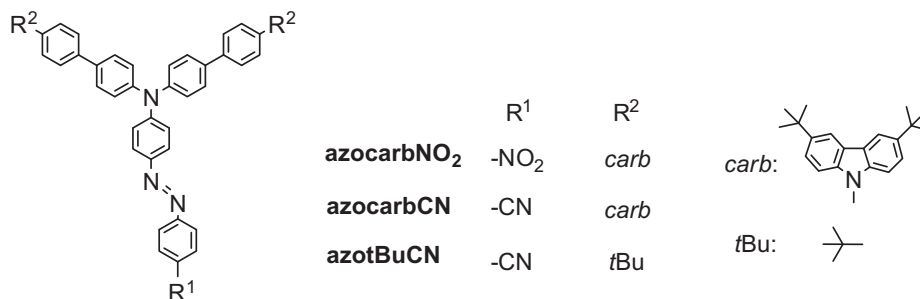
Figure 1 shows the linear (dotted lines) and nonlinear spectra (full circles) of TA derivatives, in the absence of the azoaromatic unit. Linear spectra (left axis) show two bands, one positioned around 320 nm, related to a $n\pi^*$ charge transfer from the amino core to the biphenyl substituents, and another one located from 370 nm to 450 nm according to the electronic influence of the electron donor-acceptor pairs. The 2PA spectra (right vertical axis in Figure 1) for FCHO, FNO₂ and FVIN present a band at ca. 550, 600 and 650 nm, respectively, and an increase as the excitation wavelength

approaches the linear absorption band (resonant enhancement of nonlinearity). One can notice that these spectra are also affected by the strength of the electron-withdrawing group.

The linear and nonlinear absorption spectra of AzoTA derivatives are presented in Figure 2. For all three compounds, the linear absorption spectra display a band around 340 nm. Compared to the previous compounds, an additional narrow band peaking around 340 nm could only be observed for AzocarbCN and AzocarbNO₂ and was attributed to $\pi\pi^*$ transitions located on the carbazole moieties. The band around 500 nm for all samples (AzotBuCN, AzocarbCN and AzocarbNO₂) stems from a charge transfer excited state involving the amino core and the azoaromatic unit, whose electron-withdrawing properties were reinforced by the terminal nitro and cyano substituents. The 2PA spectra (right vertical axis in Figure 2) exhibit a monotonous increase and a band around 650 nm, similarly to those obtained for the dipolar TA in Figure 1. However, there is also an additional 2PA band around 900 nm, which could be reasonably ascribed to the presence of the azoaromatic unit bringing a strong charge transfer within the molecules. This effect may relax the selection rules, enabling the existence of final states reached both by one- or two-photon absorption. Additionally, one can notice that the presence of different electron donor/acceptors groups substituting the azoaromatic unit also changes the position and the magnitude of the 2PA band centered around 900 nm, as expected from a change in the magnitude of the charge transfer. Similarly to the linear absorption spectra, the two-photon absorption maxima undergo a bathochromic shift.

To understand the 2PA spectra exhibited by TA and AzoTA derivatives, we applied the sum-over-states (SOS) approach, considering the four-energy-level diagram, depicted in the inset of Figures 1 and 2. The energy diagram used for the TA and AzoTA are slightly different because the latter present an extra band at 900 nm in their 2PA spectra. In that case, the extra two-photon transition can be represented by the first term on Eq. (2), which is considered to analyze the 2PA spectra of the dipolar AzoTA. To analyze the 2PA spectra of TA, Eq. (2) is used without the first term. In general, the SOS model describes transitions mediated by two-photon absorption from the ground state (0) to higher excited states (terms inside the brackets). When the photon energy approaches that of the first one-photon allowed transition leading to the first-excited state (1), the two-photon probability is enhanced by the resonance term (factor multiplying the square brackets). In this approach, the sum-over-state predicts a two-photon absorption cross-section (δ) spectrum (dotted lines in the 2PA spectra in Figures 1 and 2) varying as a function of the light frequency (ν) following the equation:

$$\delta(\nu) \propto \frac{A_1}{(\nu_{0-1} - 2\nu)^2 + \Gamma_{01}^2} + \frac{\nu^2}{(\nu_{0-1} - \nu)^2 + \Gamma_{01}^2} \times \left[\frac{A_2}{(\nu_{0-2} - 2\nu)^2 + \Gamma_{02}^2} + \frac{A_3}{(\nu_{0-3} - 2\nu)^2 + \Gamma_{03}^2} \right] \quad (2)$$



Scheme 2. Structures of the azoaromatics triarylamine derivatives AzocarbCN, AzocarbNO₂ and AzotBuCN.

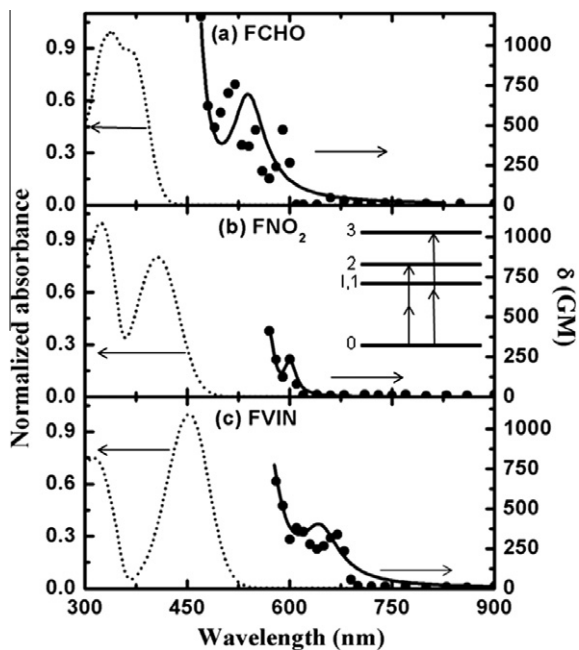


Figure 1. Linear (dotted lines) and two-photon (circles) absorption spectra of triarylamine derivatives. The line in the 2PA spectra represents the results obtained through SOS model.

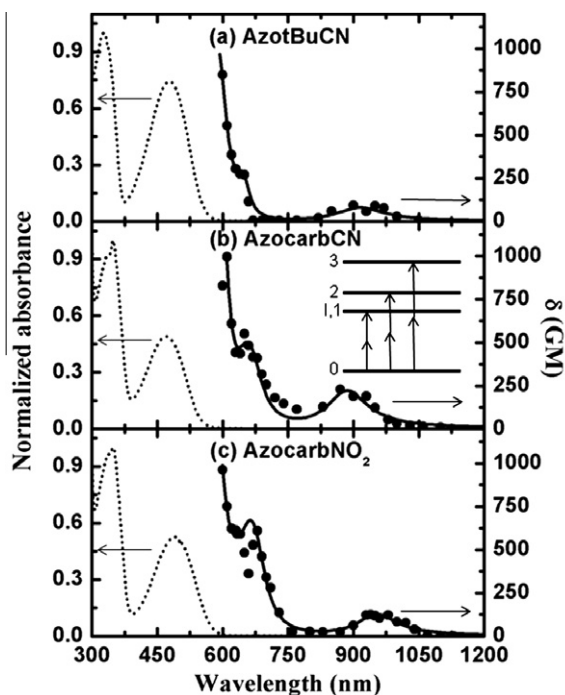


Figure 2. Linear (dotted lines) and two-photon (circles) absorption spectra of azoaromatic triarylamine derivatives. The line in the 2PA spectra represents the results obtained through SOS model.

where ν_{0-1} and Γ_{01} represent the frequency and the damping constant of the $0 \rightarrow 1$ transition respectively. The damping constant Γ_{01} (also Γ_{01}) was obtained from the first linear absorption transition. A_1 is proportional to $|\mu_{0-1}|^2 |\Delta\mu|^2 \Gamma_{01}$, where ν_{0-1} and $\Delta\mu$ are, respectively, the transition dipole moment and the difference between the permanent dipole moments between the ground and the first-excited states. A_2 and A_3 are described by $A_x = |\mu_{0-1}|^2 |\mu_{1-x}|^2 \Gamma_{0x}$, where μ_{1-x} (being x , 2 or 3) represent the

transition dipole moments between the first and the second (or third excited) states.

Most of the spectroscopic parameters used in Eq. (2) can be obtained from the linear and nonlinear absorption spectra, reducing the number of adjustable parameters. For example, the frequency of the intermediated state is represented by the position of the first one-photon allowed transition; also, the damping factor is obtained from the band width. The frequency of the transitions and the respective damping factors are obtained from the 2PA spectra. Additionally, to reduce even more the number of adjustable parameters, a complementary analysis was performed to determine the transition dipole moments of the compound using the linear absorption spectra. Having the first-excited state absorption in hand, one can calculate the transition dipole moment of the transition between the ground and the first-excited states using [35]:

$$\mu_{01} = \sqrt{\frac{3}{8\pi^2} \frac{c}{\sqrt{\pi N}} \frac{\ln(10^A)}{L} \frac{\omega}{2\sqrt{\ln(2)}} \frac{h}{\nu_{of}}} \quad (3)$$

in which c is the speed of light in cm s^{-1} , N is the number of molecules per cm^3 , A is the absorbance, L is the optical path in cm, ω is the full width band at half height in Hz, h is the Planck constant, and ν_{of} is the frequency in Hz of the respective transition. The value obtained from Eq. (3) is expressed in $\text{esu} \times \text{cm}$ ($1 \text{ Debye} = 1 \times 10^{-18} \text{ esu} \times \text{cm} = 3.33564 \times 10^{-30} \text{ C m}$).

To obtain the dipole moment of the excited states which is involved in the nonlinear absorption processes, we used Eq. (2) to determine the A_x values, which are proportional to the product between the dipole moments. Three terms are related to the nonlinear transition for the AzoTA ($\Delta\mu$, μ_{12} and μ_{13}) and two terms are related to the nonlinear transitions of the TA (μ_{12} and μ_{13}). The $\Delta\mu$ term is associated to the same final state, which in the case of the azoaromatic derivatives can be populated both by the 2PA and one-photon absorption. μ_{12} and μ_{13} are associated to transitions to higher states. At the end of this procedure, the parameters inferred from the SOS model are the transition dipole moments involving the higher excited states 2 and 3 and the position and damping factor of the third excited state, see Table 1. Since the position and magnitude of the 2PA band are not intertwined, the obtained parameters are in reasonable agreement with molecules presetting similar structural moieties [18,36,37].

In general, it is difficult to compare absolute 2PA cross-section values of different materials based on the available experimental results. It is justified, in part, by the different experimental conditions used. Therefore, in our case, the results can be compared taken into account experimental errors, specific molecular spectroscopic properties and solvent effects. Thus, in order to corroborate our 2PA modeled spectra and their spectroscopic parameters, we compared our results with those already published in the

Table 1
Electric dipole moment, frequency transitions and damping factor of TA and AzoTA derivatives.

	FCHO	FNO ₂	FVIN	AzotBuCN	AzoCarbCN	AzoCarbNO ₂
μ_{10} (Debye)	8.1	5.5	7.3	6.1	6.5	7.5
μ_{12} (Debye)	10.0	8.0	5.0	2.0	4.5	3.3
μ_{13} (Debye)	4.0	4.0	5.0	4.0	4.2	4.0
$\Delta\mu$ (Debye)	–	–	–	6.1	5.0	2.8
ν_{0-1} (cm ⁻¹)	–	–	–	10 900	11 200	10 500
ν_{0-2} (cm ⁻¹)	18 000	17 100	16 000	16 000	15 500	15 000
ν_{0-3} (cm ⁻¹)	27 000	25 000	22 500	21 500	21 500	21 000
Γ_{01} (cm ⁻¹)	–	–	–	4000	4500	3800
Γ_{02} (cm ⁻¹)	2000	1300	1500	800	1100	900
Γ_{03} (cm ⁻¹)	3500	3900	3000	2000	1600	1500

literature for similar compound [32–34]. First, according to the quantum chemistry calculations performed by Wang et al. [36], without considering solvent effects, dithienothiophene (DTT)-based chromophores with fluorene or *trans*-stilbene presented a lowest excited state that is allowed by two-photon absorption. In that case, they calculated a 2PA cross-section [32] about 340 and 450 GM for DTT fluorene containing the electron-withdrawing group NO₂ and donor–acceptor DTT stilbene, respectively, both centered at ca. 750 nm. Also, they calculated a transition dipole moment of the order of a few Debyes. Other important results were reported by Lin et al. [37] for different diphenylamino stilbenoids. In that work, they measured two-photon absorption cross-sections with maximum values between 50 and 150 GM, observed in the range from 700 to 1000 nm. According to the authors, the difference between the molecules was related to the conjugation length and donor–acceptor charge groups.

Several works [24,38] have reported 2PA cross-section in azoaromatic compounds with a 2PA band located at twice the wavelength of the first one-photon allowed transition [22,26,34]. The values of the 2PA cross-section δ were reported to be between 50 GM and 200 GM, and the changes in magnitude were related to the donor/acceptor groups. On the other hand, azoaromatic and diazoaromatic compounds [24,26], substituted by weak electron-donating or accepting groups, present no significant 2PA transition to the first-excited state, indicating that the strength of charge transfer is important to break the molecular symmetry [18], and increasing the probability of the 2PA process. Neves et al. [27] demonstrated that the 2PA cross-sections could be increased without having an increase in the conjugation length. In that work, a 2PA effect was measured in a molecule containing two phenyl azoaromatic units not connected by a conjugated bridge, and it was observed an enhancement of the 2PA cross-sections at 900 nm to twice the values for similar single azoaromatic units in the same region.

4. Conclusions

By using linear and two-photon absorption techniques, we have been able to observe the electronic effects brought by the presence of azoaromatic units on TA derivatives. The 2PA band, located at around 900 nm, is attributed to the azoaromatic moiety, and the variation of its magnitude and position to the electronic nature of the substituents. Changes in molecular symmetry brought about by the azoaromatic unit allow the first-excited state ($\pi\pi^*$) to be accessed by both one- and two-photon absorption, which was not observed for TA devoid of azoaromatic units. The characterization

and understanding of the 2PA spectrum of TA derivatives can help selecting the proper excitation wavelength for a given optical device, aiming at distinct applications such as, for instance, photoswitching and holographic micropatterning.

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