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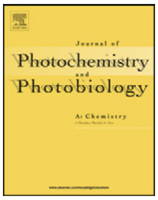

Enhancement of two photon absorption properties by charge transfer in newly synthesized aza-boron-dipyrromethene compounds containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties

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ABSTRACT

The effects of substitution and charge transfer on linear and nonlinear optical absorption (especially two photon absorption) properties of aza-BODIPY containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties were investigated by ultrafast pump probe spectroscopy technique. Fluorescence and ultrafast pump probe spectroscopy experiments revealed that aza-BODIPY compounds with good electron donating moieties (triphenylamine and 4-ethynyl-*N*,*N*-dimethylaniline moieties) have charge transfer from electron donating parts of the molecules to aza-BODIPY core. The two photon absorption cross sections increase with the electron donating strength. Maximum two photon absorption cross section is obtained as 126 GM at telecommunication wavelength (1310 nm) for aza-BODIPY compound containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline. Our results indicate that charge transfer enhances two photon absorption properties.

1. Introduction

Two-photon absorption (TPA) is an instantaneous nonlinear process, in which a atoms or molecule absorbs two photons simultaneously. A particular property of the TPA is that the rate of the absorption increases as the square of the incident light intensity [1]. Such a quadratic dependence supplies the capability to localize the excitation with high three dimensional spatial resolution in the focus of laser beam. Molecules with large TPA coefficient are now in great demand for a various applications; including optical limiting applications [2,3], TPA imaging microscopy [4], three-dimensional micro fabrication [5,6], optical data storage [7,8], photodynamic therapy [9] and TPA up conversion lasing [10]. Therefore, the design of efficient compounds with TPA response is one of the most important challenges. Two photon active wavelengths of these organic materials are mostly located around 700–1100 nm spectral ranges [1]. There is an increasing need for devices presenting TPA properties in near-infrared (NIR) spectral range for applications such as signal processing in the telecommunication wavelengths. Boron-dipyrromethene (BODIPY) dyes are novel organic dyes with high fluorescence quantum yields, excellent photo stability, good solubility [11–13] and high two photon absorption cross sections (TPCS) [14–16]. Although two photon absorption properties of BODIPY compounds are widely studied in the literature [15–17], there are only a few studies on TPA properties of aza-BODIPY compounds [18,19]. Recently, Bouit et al. [18] reported that functionalized aza-BODIPY dyes with electron donating substituent exhibit strong TPA properties in the telecommunications spectral range. In our previous work, we introduced various phenolic and phenolate forms of aza-BODIPY molecules with different electron-donating strength to study the effects of substitution and intramolecular charge transfer (ICT) on TPA properties. Our previous results indicated that two photon absorption cross-section values increase with electron donating strength and intramolecular charge transfer enhances two photon absorption properties in the telecommunications spectral range [19].

Based on our previous results, we synthesized new aza-BODIPY compounds containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties to enhance TPA properties in this work. Triphenylamine and 4-ethynyl-*N*,*N*-dimethylaniline moieties are known with their strong electron donating strengths. Absorption spectrum of aza-BODIPY compounds containing triphenylamine are greatly red shifted. Electron-donating strength [19,20] and molecule conjugation

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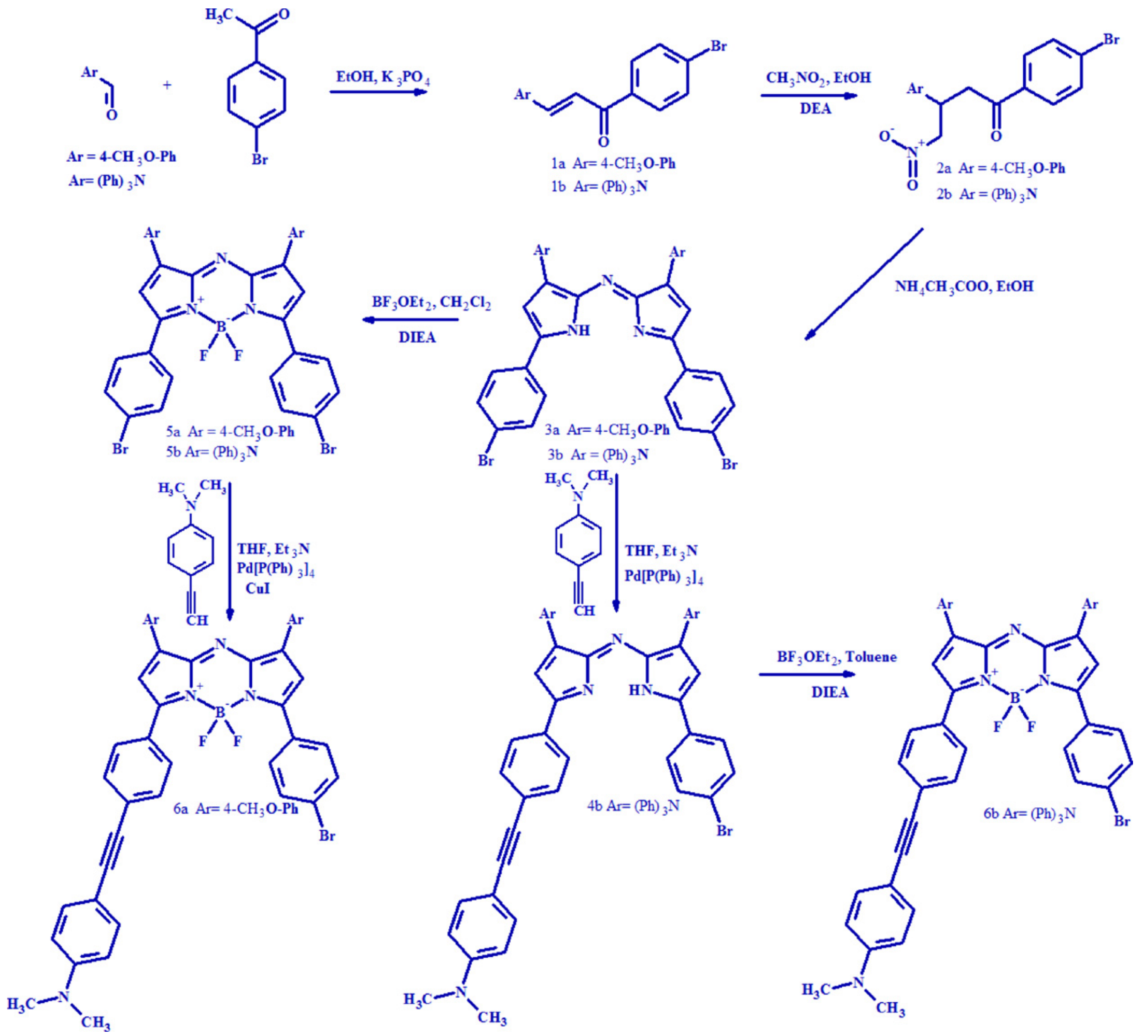


Scheme 1. Structures of newly synthesized and investigated compounds.

length [1] enhance TPA properties i.e. σ_2 (TPCS) in wide spectral range (1200–1450 nm). In this work, we investigated the effect of different electron-donating strength of different moieties on TPA properties.

2. Experimental

2.1. Synthesis of aza-BODIPY

The syntheses of compounds **5a**, **5b**, **6a** and **6b** involved multistep approach as shown in Scheme 1. 1-(4-Bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**1a**) and 1-(4-bromophenyl)-3-(4-(*N*,*N*-diphenylamino)phenyl)prop-2-en-1-one (**1b**) were synthesized from a reaction of the corresponding benzaldehyde, acetophenone, and potassium phosphate. These compounds were subsequently reacted with nitromethane and diethylamine in dry ethanol to obtain respective 1-(4-bromophenyl)-3-(4-methoxyphenyl)-4-nitrobutan-1-one (**2a**) and 1-(4-bromophenyl)-3-(4-(*N*,*N*-diphenylamino)phenyl)-4-nitro-butan-1-one (**2b**). The [5-(4-bromophenyl)-3-(4-methoxyphenyl)-1H-pyrrol-2-yl]-[5-(4-bromophenyl)-3-(4-methoxyphenyl)-pyrrol-2-ylidene]amine (**3a**) and [5-(4-bromophenyl)-3-(4-(N,N-diphenylamino)phenyl)-1H-pyrrol-2-yl]-[5-(4-bromophenyl)-3-(4-(N,N-diphenylamino) phenyl) pyrrol-2-ylidene]amine (**3b**) were synthesized by reactions of **2a** and **2b** with ammonium acetate in ethanol. After that, BF$_2$-chelated-[5-(4-bromomphenyl)-3-(4-methoxyphenyl)-1H-pyrrol-2-yl]-[5-(4-bromophenyl)-3-(4-methoxyphenyl) pyrrol-2-ylidene] amine (**5a**) and BF$_2$-chelated-[5-(4-bromomphenyl)-3-(4-(N,N-diphenylamino)-phenyl)-1H-pyrrol-2-yl]-[5-(4-bromophenyl)-3-(4-(N,N-diphenylamino) phenyl) pyrrol-2-ylidene]amine (**5b**) were synthesized by reactions of **3a** and **3b** with diisopropylethylamine and boron trifluoride diethyl etherate in dry CH$_2$Cl$_2$.

Table 1
Optical properties of compounds **5a**, **5b**, **6a** and **6b** in THF solutions.

Compound	λ^a_{abs} (nm)	λ^b_{fluo} (nm)	λ^c_{fluo} (nm)	$\sigma_2{}^d$ (GM)
5a	675	710	710	–
5b	660/770	–	450	37
6a	700	–	410	25
6b	680/770	–	450	83

[a] The peak wavelength of absorption spectra.
[b] The peak wavelength of one-photon fluorescence with excitation wavelength λ_{abs}.
[c] The peak wavelength of one-photon fluorescence with excitation wavelength 340 nm.
[d] TPA cross section at wavelength of 1200 nm.

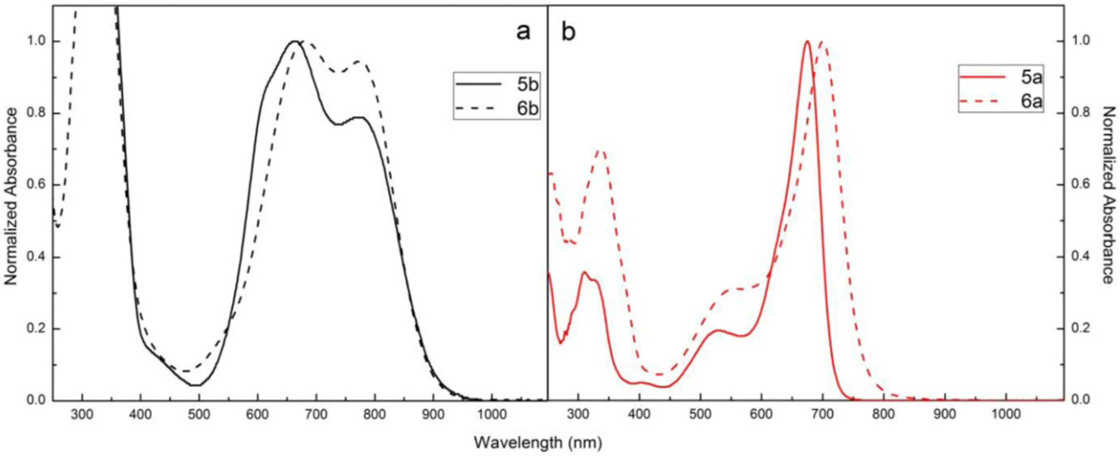


Fig. 1. Absorption spectrum of (a) compounds **5b** and **6b**, (b) compounds **5a** and **6a** in THF solution.

BF_2-chelated-[5-(4-bromomphenyl)-3-(4-methoxyphenyl)-1H-pyrrol-2-yl]-[5-(4-N,N-dimeyhlamino) ethenylphenyl-3-(4-methoxyphenyl) pyrrol-2-ylidene]amine (**6a**) were obtained from compound **5a** and [5-(4-bromophenyl)-3-(4-(N,N-diphenylamino)phenyl)-1H-pyrrol-2-yl]-[5-(4-N,N-dimeyhl-amino)ethenylphenyl)-3-(4-(N,N-diphenylamino)phenyl) pyrrol-2-ylidene]amine (**4b**) were synthesized from corresponding boron free ligands of these aza-BODIPY (**3b**). After obtaining this free ligand **4b** than BF_2 complexation were done and obtained compound **6b**. Experimental details were given in supporting information.

2.2. Optical measurement

UV–vis absorption spectra of aza-BODIPY derivatives were recorded by using a scanning spectrophotometer (Shimadzu UV-1800). Uncorrected emission and corrected excitation spectra in the fluorescence measurements were obtained with Perkin Elmer model LS 55 Fluorescence spectrometer.

Nonlinear optical absorption properties of aza-BODIPY derivatives were investigated by using open aperture (OA) Z-scan technique [21]. Laser source is mode-locked Ti:Sapphire laser amplifier system with 1200 nm and 1310 nm wavelength, 45 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS). Laser beam was focused on solution in 1 mm thick cell by a lens with 20 cm focal length. Concentrations of the solutions for two photon absorption measurements were 0.01 M.

Wavelength dependent ultrafast pump probe spectroscopy measurements were performed by using Ti:Sapphire laser amplifier-optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) and commercial setup (Spectra Physics, Helios). Pulse duration was measured as 100 fs. Wavelengths of the pump beam were chosen according to the peak of the absorption spectra as 700 nm for **5b**, **6b** and 650 nm for **5a**, **6a**. White light continuum was used as a probe beam.

3. Results and discussion

3.1. Absorption and fluorescence measurement

UV–vis absorption and fluorescence spectra of aza-BODIPY compounds (in THF) containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties are shown in Figs. 1 and 2. Optical parameters were summarized in Table 1. When 4-ethynyl-*N*,*N*-dimethylaniline moiety is at position 5 of aza-BODIPY core, bathochromic shift (about 20 nm) is observed in the absorption spectra as observed previously in the literature [18]. All of the absorption spectra of studied aza-BODIPY molecules reveal strong $S_0 \rightarrow S_1$ transition with maximum absorbance wavelength varying between 600 and 700 nm (Table 1), depending on the electron donating moieties. The absorption peak around 770 nm in Fig. 1a may be attributed to charge transfer state as observed in our previous study [19]. Our previous results revealed that there is no fluorescence signal when charge transfer occurs due to electron donor property of phenolate form of hydroxyl groups in compounds. Therefore, we have performed fluorescence measurement at various excitation wavelengths to investigate relationship between fluorescence quenching and charge transfer.

In the literature, there are many aza-BODIPY structures which have high fluorescence quantum yield and high extinction coefficient [11–13]. However, fluorescence signal was not observed for studied compounds except **5a** when aza-BODIPY core was excited due to charge transfer mechanism (Fig. 3 and Table 1). Fluorescence property and charge transfer relation will be discussed in detail Section 3.2. On the other hand, absorption bands of triphenylamine moieties are around 350 nm. In attempt to clarify whether the fluorescence signal comes from aza-BODIPY core or not when triphenylamine is excited, we chose 340 nm as excitation wavelength. The results of measurements show that the fluorescence signal was not observed from aza-BODIPY instead signal came from triphenylamine moiety itself. There is strong fluorescence signal around 450 nm for **5b**, **6a** and **6b** upon excitation of triphenylamine and 4-ethynyl-*N*,*N*-dimethylaniline moieties with 340 nm wavelength (Fig. 2). This fluorescence signal was not observed for **5a**. Compound **5a** has single fluorescence signal at 710 nm for both 340 nm and 675 nm excitation wavelengths (Fig. 2). As seen in Fig. 3 for compound **5a**, we observed fluorescence signal from singlet state of aza-BODIPY core when aza-BODIPY core (675 nm excitation) or methoxy group (340 nm excitation) was excited.

In an attempt to obtain deep insight on charge transfer mechanism and to investigate relationship between charge transfer and excited state lifetime for aza-BODIPY compounds containing triphenylamine and 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moiety we have performed ultrafast pump probe spectroscopy experiments.

3.2. Ultrafast pump probe spectroscopy experiments

Ultrafast pump probe spectroscopy with white light continuum experiment was used to investigate the optical dynamics and decay processes of excited states of aza-BODIPY derivatives containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties. The aza-BODIPY core in the absorption spectra (Fig. 1) has an

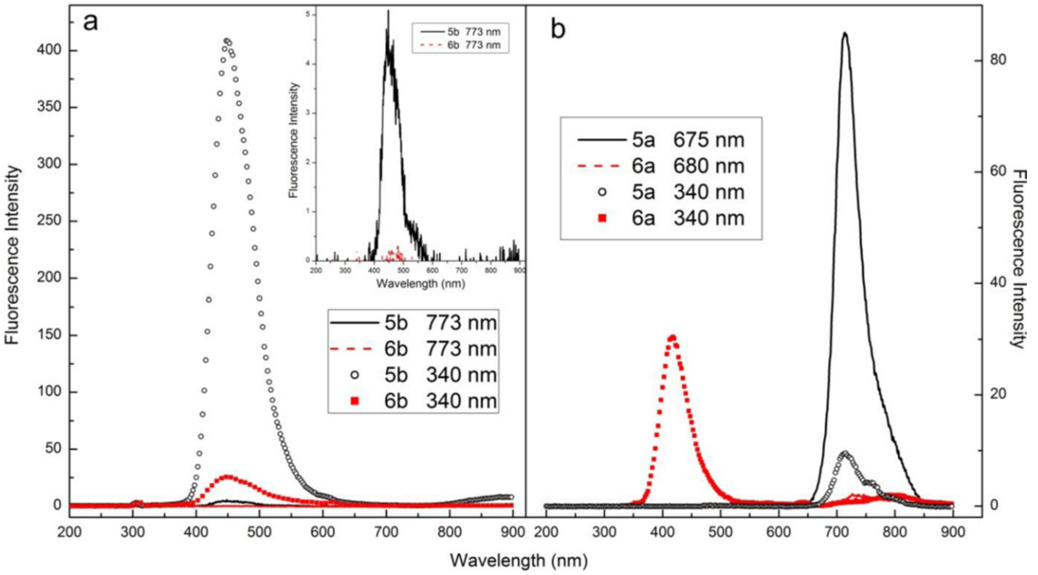


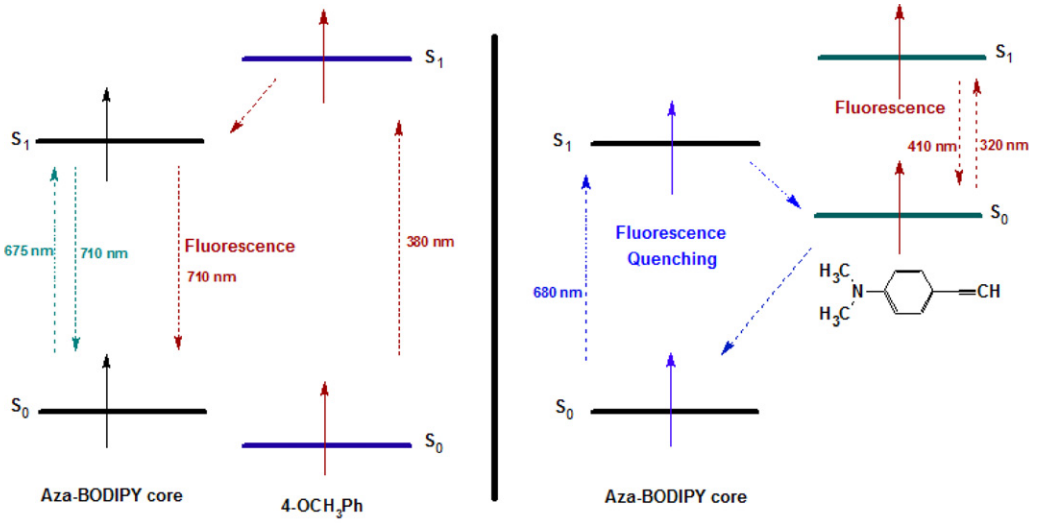
Fig. 2. Fluorescence spectrum of (a) compounds **5b** and **6b**, (b) compounds **5a** and **6a** in THF solution (1×10^{-5} M). The excitation wavelengths are given in figure legends. The figure inset indicates small fluorescence intensity scale between 0 and 5 for compounds **5b** and **6b** with excitation wavelength 773 nm.

intense maximum at approximately 700 nm for **5b**, **6b** and 650 nm for **5a**, **6a**. Therefore, these wavelengths were used for the pump beam to populate the excited states (S_1) of aza-BODIPY.

Transient absorption data versus wavelength for various time delays are shown in Fig. 4 for aza-BODIPY derivatives containing triphenylamine moieties. **5b** and **6b** compounds show positive signal bellow 575 nm and negative bleach signal above 575 nm in transient absorption spectra (Fig. 4). The positive signal is attributed to electron transition from S_1 state of aza-BODIPY to singlet state of the moieties. Compound **5b** has a single and broad bleach signal between 600 and 800 nm and single and broad nonlinear absorption signal around 500 nm. Since linear absorption spectrum of this compound is broadened, the observed broad nonlinear bleach signal corresponds to singlet state of moieties as seen in Fig. 3. Time evolution of the nonlinear absorption of **5b** and **6b** at 490 nm probe wavelength were given in Fig. 5a. Compounds **5b** and **6b** have similar decay processes. We have observed two decay times in Fig. 5a: the fast decay time (less than 3 ps) and the slow decay time (around couple hundred ps).

Compound **5a** shows bleach signal around 660 nm (Fig. 6) which corresponds to $S_0 \rightarrow S_1$ transition in absorption spectra. Besides, three nonlinear absorption signals can be observed around 440 nm, 565 nm and 780 nm wavelengths for compound **5a**. These signals represent excited state absorptions to higher energy levels (Fig. 3a). Compounds **5a** and **6a** have similar transient absorption data with 30 nm shifts on wavelength scale (Fig. 6). This shift is compatible with the absorption spectra of **5a** and **6a**.

Two aza-BODIPY compounds containing methoxy groups have different excited state lifetimes (Fig. 5b). While compound **5a** has a slow decay process (around thousand ps), compound **6a** has faster



5a

(a)

6a

(b)

Fig. 3. Energy level diagrams for compounds (a) **5a** and (b) **6a**.

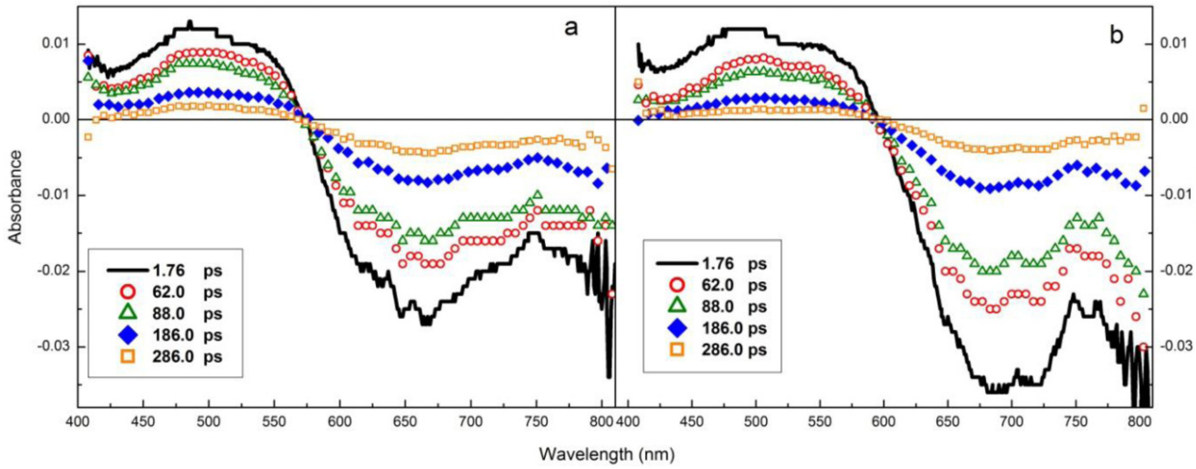


Fig. 4. Transient absorption data versus wavelength for various time delays (a) compound **5b** and (b) compound **6b** in THF solution.

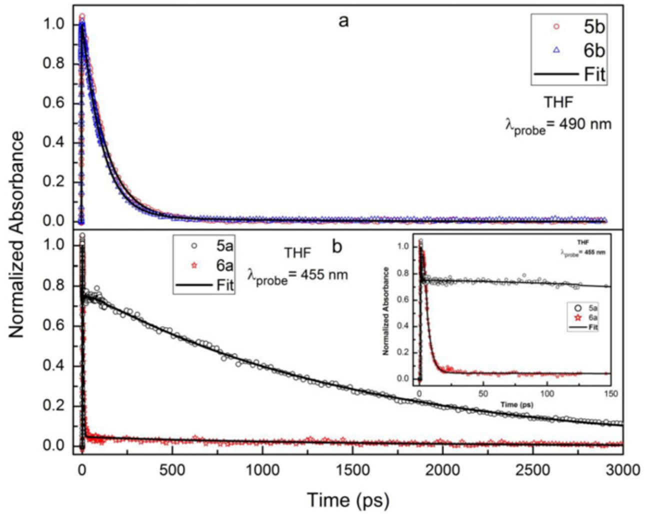


Fig. 5. Time evolution of the nonlinear absorption of (a) compounds **5b** and **6b** at a probe wavelength of 490 nm and (b) compounds **5a** and **6a** at a probe wavelength of 455 nm. The figure inset indicates slow decay time between 0 and 150 ps time scales for compounds **5a** and **6a**.

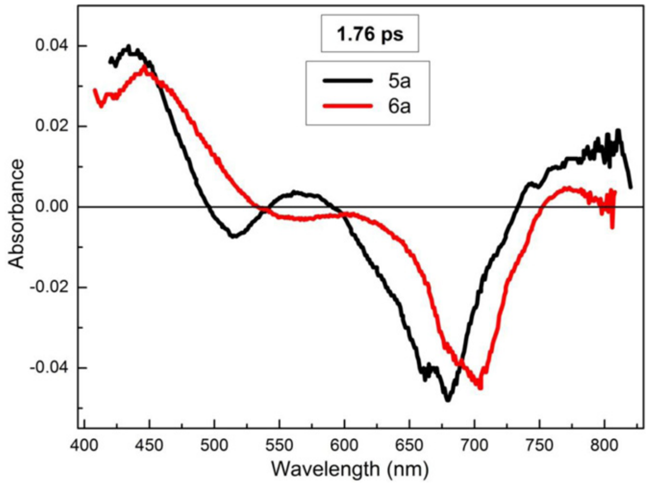


Fig. 6. Transient absorption data versus wavelength for compounds **5a** and **6a** at 1.76 ps.

decay process (on the order of ultrafast time scales). This fast transition can be attributed to charge transfer from S_1 state of aza-BODIPY core to S_0 state of 4-ethynyl-*N*,*N*-dimethylaniline group [19,22]. This leads to fluorescence quenching for compound **6a**.

3.3. Two photon absorption properties

TPA properties were enhanced upon increasing charge transfer for BODIPY and aza-BODIPY compounds [16,18,19]. We investigated TPA properties of these compounds by OA Z-scan technique [16] using mode-locked Ti: Sapphire laser amplifier system with 45 fs pulse duration and 1 kHz repetition rate. In order to calculate TPA coefficient (β) and TPCS (σ_2), Eq. (1) was used [20].

Nonlinear transmittance T is given in terms of laser intensity I_0,

$$T(I_0) = \frac{1}{1 + I_0 \beta l} \qquad (1)$$

where l is optical path length. TPCS value σ_2 ($1\,\text{GM} = 10^{-50}\,\text{cm}^4\,\text{s photon}^{-1}$) is obtained from the following equation,

$$\sigma_2 = \frac{h\nu\beta}{N_A d_0 \times 10^{-3}} \qquad (2)$$

where N_A is the Avogadro number and d_0 is molar concentration of the solution.

OA Z-scan experimental results at 1200 nm wavelength and $6 \times 10^{15}\,\text{W/m}^2$ peak intensity are shown in Fig. 7. It is known that absorption spectrum can be shifted into NIR and nonlinear optical properties can be enhanced by using electron donating moiety as a functional group for BODIPY structure [20]. Triphenylamine is a strong electron donor moiety and absorption spectrum of compounds containing triphenylamine is greatly red shifted. Thus, TPA properties can be seen in wide spectral range (1200–1450 nm) and σ_2 increases with increasing electron donating strength [19,20] and molecule conjugation length [1]. Compounds **5b** and **6b** have better nonlinear optical absorption (Fig. 7 and Table 1) and higher TPCS (σ_2) values than compounds **5a** and **6a** at the same pulse intensities due to increasing electron donating strength. TPCS (σ_2) values of compound **5b** for 1200 nm and 1310 nm wavelengths are 37 GM and 83 GM respectively. In order to enhance TPCS value, functional groups were introduced with strong electron donating property and long conjugation length. Therefore, by using 4-ethynyl-*N*,*N*-dimethylaniline group as a functional group, we obtained maximum σ_2 values for **6b** as 83 GM and 126 GM at 1200 nm and 1310 nm wavelengths respectively. Similar effect was observed for aza-BODIPY containing methoxy groups as well. It is

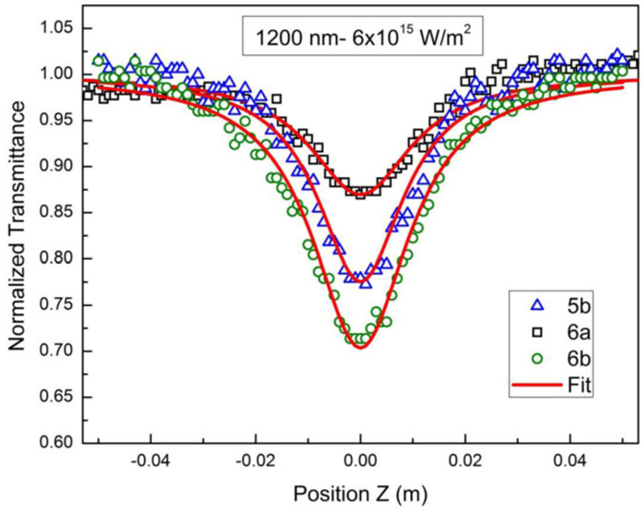


Fig. 7. Experimental results (filled circle) and theoretical fits (solid line) of open aperture Z-scan experiments for compounds **5b**, **6a** and **6b** in THF, using 1200 nm femtosecond pulses.

well known that methoxy group is less donating than triphenylamine moiety, therefore there is no TPA property for compound **5a**. If electron donating property of this compound is be improved by 4-ethynyl-*N*,*N*-dimethylaniline moiety with longer conjugation length TPA behavior can be observed (σ_2 value for **6a** with 25 GM) (Table 1). There are only a few studies about TPA properties of aza-BODIPY compounds in the literature [18,19]. Therefore, obtaining high TPCS values are valuable for the applications such as optical communication.

4. Conclusion

In summary, we synthesized new aza-BODIPY compounds containing triphenylamine, 4-ethynyl-*N*,*N*-dimethylaniline and methoxy moieties. The effects of substitution and charge transfer on linear and nonlinear optical absorption especially two photon absorption properties were investigated by femtosecond laser spectroscopic techniques. The two photon absorption cross sections are obtained as 25, 37 and 83 GM at 1200 nm for **6a**, **5b** and **6b**, respectively. Maximum two photon absorption cross section is obtained as 126 GM for compound **6b** at telecommunication wavelength (1310 nm). Fluorescence and ultrafast pump probe spectroscopy experiments revealed that aza-BODIPY compounds with good electron donating moieties (triphenylamine and 4-ethynyl-*N*,*N*-dimethylaniline) show charge transfer from moiety to aza-BODIPY core. The observed strong two photon absorption property can be attributed to charge transfer. On the other hand, the charge transfer leads to decreasing of fluorescence signal of compounds **5b**, **6a** and **6b**. These findings may open the path to synthesize new aza-BODIPY compounds with good two photon absorption properties in telecommunication wavelengths.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2013.02.002.

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