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Synthesis, optical properties and ultrafast dynamics of aza-boron-dipyrromethene compounds containing methoxy and hydroxy groups and two-photon absorption cross-section

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ABSTRACT

In this work, aza-boron-dipyrromethene (aza-BODIPY) compounds containing methoxy and hydroxy groups were synthesized. The effects of substitution and intramolecular charge transfer on linear and nonlinear optical absorptions (especially two photon absorption) of these BODIPY derivatives were investigated. Drastic spectral changes of aza-BODIPY compounds containing hydroxy group were observed in linear absorption spectra depending on basicity of solution. New bands in linear absorption spectra of phenolate form of these compounds appeared bellow 500 nm and above 700 nm in THF solution. These findings were caused by occurrence of the intramolecular charge transfer state in the phenolate form. Ultrafast pump probe spectroscopy experiments revealed that phenolic form shows only bleaching signal around 600 nm. On the other hand, the phenolate form showed fast growing nonlinear absorption signals bellow 500 nm and above 700 nm regions in addition to the bleaching signal around 600 nm. Intramolecular charge transfer state occurs above 700 nm and the lifetime of this state is found on the order of ultrafast time scales. Since the excitation of the fluorescence experiments is at 600 nm there is no fluorescence signal due to the relaxation of the energy through intramolecular charge transfer state. Aza-BODIPY compounds containing methoxy group did not show any two photon absorption properties due to weak electron-donating strength of methoxy group while aza-BODIPY compounds containing hydroxyl showed two photon absorption properties in wide spectral range (1200-1450 nm). Our results also indicated that intramolecular charge transfer enhances two photon absorption properties.

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1. Introduction

Materials with large two photon absorption (TPA) properties have attracted increasing attention in relation with a wide range of potential applications including optical limiting [1,2], TPA imaging microscopy [3], three-dimensional microfabrication [4,5], optical data storage [6,7], photodynamic therapy [8] and TPA upconversion lasing [9]. Therefore, design and synthesis of molecules with large TPA cross-sections (TPCS) has received a lot of attention [10,11]. Many organic materials have been developed for TPA applications [12]. However, emitting and two photon active wavelengths of these organic materials are mostly located around 400–600 nm and 700–1100 nm spectral ranges, respectively [12].

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Near-infrared (NIR) spectral range has been less studied although there is an increasing need for devices presenting TPA properties in this spectral range such as signal processing in the telecommunication wavelengths $(1.30-1.55 \,\mu m)$. Boron-dipyrromethene (BODIPY) dyes are novel organic dyes with high fluorescence quantum yields, excellent photo stability, good solubility [13-15] and high TPCS [16–18]. It was found that linear absorption wavelength of BODIPY dyes can be tuned to NIR (above 600 nm) by a derivatization reaction with benzaldehyde derivatives [19-21]. One of the various strategies to design and synthesize highly efficient two photon active compounds is manipulating electron-donor and/or acceptor properties and their incorporation in a molecular architecture [22–26]. In general, increasing electron-donor strength leads to increasing TPCS [12]. Recently, Bouit et al. reported that functionalized aza-BODIPY dyes exhibit strong TPA properties in the telecommunications spectral range [27]. Intramolecular charge transfer (ICT) within BODIPY has also attracted considerable attention due to its effect on linear absorption and fluorescence properties [28].

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Scheme 1. Structures of newly synthesized methoxy (MABDP) and hydroxy (HABDP) substituted aza-BODIPY in the present study.

In this work, we investigate ICT properties of newly synthesized aza-BODIPY compounds containing methoxy and hydroxy groups and study the effect of ICT on the TPA properties in the telecommunication spectral range. Therefore, we introduce various phenolic and phenolate forms of aza-BODIPY molecules with different electron-donating strength to study the effects of substitution and ICT on linear and nonlinear absorptions (especially TPA).

2. Experimental

2.1. Synthesis of aza-BODIPY

The syntheses of methoxy (MABDP), hydroxyl (HABDP) aza-BODIPY and phenolate ABDPⁿ⁻ forms of aza-BODIPY compounds involved a multistep approach as shown in Scheme 1, and the details are given in the supplementary material. 3-(4-Methoxyphenyl)-1-phenylpropenone (1a) and 3-(3,4dimethoxyphenyl)-1-phenylpropenone (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 3-(4-methoxyphenyl)-4-nitro-1-phenylbutan-1-one (**2**a) and 3-(3,4-dimethoxyphenyl)-4-nitro-1-phenylbutan-1-one (**2b**). [3-(4-Methoxvphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(4-methoxyphenyl)-5phenylpyrrol-2-ylidene]amine (3a) and [3-(3,4-dimethoxvphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(3,4-dimethoxyphenyl)-5-phenylpyrrol-2-ylidene]amine (3b) were synthesized by reactions of 2a and 2b with ammonium acetate in ethanol. Then, BF2-chelated-[3-(4-methoxyphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(4-methoxyphenyl)-5-phenylpyrrol-2-ylidene]amine (DMABDP) and BF₂-chelated-[3-(3,4-dimethoxyphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(3,4-dimethoxyphenyl)-5-phenylpyrrol-2-ylidene]amine)

(TMABDP) were synthesized by reactions of **3a** and **3b** with diisopropylethylamine and boron trifluoride diethyl etherate in dry CH₂Cl₂. Finally, hydroxy derivatives of aza-BODIPY, BF₂-chelated-[3-(4-hydroxyphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(4-methoxyphenyl)-5-phenylpyrrol-2-ylidene]amine (MHABDP), BF₂-chelated-[3-(4-hydroxyphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(4-hydroxyphenyl)-5-phenylpyrrol-2-ylidene]amine (DHABDP) and BF₂-chelated-[3-(3,4-dihydroxyphenyl)-5-phenyl-1H-pyrrol-2-yl][3-(4-dihydroxyphenyl)-5-phenylpyrrol-2-ylidene]amine (THABDP) were obtained from methoxy derivatives of corresponding aza-BODIPY's via hydrolyses with BBr₃ than purified by flash column chromatographic purification. The structural identification of the newly synthesized compounds was established from ¹H, ¹³C NMR, mass, and optical techniques (see supplementary material).

2.2. Optical measurement

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

Wavelength dependent pump probe measurements were performed using Ti:Sapphire laser amplifier–optical parametric amplifier system with 45 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS). In order to investigate intramolecular charge transfer nature of derivatives, pump probe experimental setup (Spectra Physics, Helios) with white light continuum was used. Experiments were conducted with 600 nm pump wavelength and 120 fs pulse duration inside pump probe setup.

Nonlinear optical absorption properties of aza-BODIPY derivatives were investigated by using open aperture Z-scan technique [29]. Laser source is mode-locked Ti:Sapphire laser amplifier system with 45 fs pulse duration and 1 kHz repetition rate. Laser beam



Fig. 1. Absorption spectra of aza-BODIPY in THF solution.

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 measurement are 0.056 M.

3. Results and discussion

3.1. Steady-state absorption and fluorescence measurement

UV–Vis absorption spectra of aza-BODIPY containing methoxy and hydroxy groups in THF are shown in Fig. 1. All of the absorption spectra of studied aza-BODIPY molecules reveal strong $S_0 \rightarrow S_1$ transition with maximum absorbance wavelength varying between

Table 1

Spectroscopic absorbance properties of aza-BODIPY with concentration $5\times 10^{-6}\,\text{M}$ in THF.

Compound	R_1	<i>R</i> ₂	<i>R</i> ₃	λ_{abs} (max/nm)	$FWHM_{abs}$ (cm ⁻¹)
DMABDP	−OCH ₃	-H	-	664	1304
TMABDP	-OCH ₃	-OCH ₃	-	662	1604
MHABDP	–OCH ₃	-H	-OH	664	1615
DHABDP	-OH	-H	-OH	660	2251
THABDP	-OH	-OH	-0H	654	3968

654 and 664 nm, depending on the substituent group. When the electron-donating group is at the para position of the phenyl rings (α) attached to pyrrole in aza-BODIPY, significant bathochromic shift is observed in the absorption spectra. On the other hand, when the electron-donating group is at the β position of pyrrole ring, there is no considerable change in the absorption maxima as observed in Fig. 1 [30]. Full width half maximum (FWHM) values of the absorption bands and maximum absorption wavelengths are given in Table 1.

In an attempt to introduce photoinduced ICT, we added NaH to phenolic solution and obtained ionic phenolate form. In order to check whether chemical degradation occurs upon addition of base, we checked the reversibility of the compounds by adding trifluoroacetic acid. We also checked the formation of the phenolate form by adding dropwise KOH solution (in THF). Depending on the amount of KOH, a gradual change between phenol and phenolate form was observed. Fig. 2a–c shows the absorption spectra of the investigated phenolic/phenolate compounds in THF. Upon increasing the amount of KOH solution for DHABDP, the most intensive peak located at 666 nm decreased while new bands below 500 nm and above 700 nm appeared (Fig. 2e). New bands were also observed in the literature [31,32]. Killoran et al. studied the effect of pH changes on absorption spectrum of dimethylamino



Fig. 2. (a-c) Normalized absorption spectrum of phenol and phenolate forms of aza-BODIPY, (d) fluorescence spectrum, (e) spectral changes of DHABDP derivative depending on NaH saturated solution (in THF).



Fig. 3. Femtosecond transient absorption spectra at different time intervals: (a) DHABDP, (b) ABDP²⁻. The figure inset indicates fast decay of transient bands corresponding to intramolecular charge transfer state.

derivatives of aza-BODIPY [31]. It was found that by decreasing the pH of dimethylamino derivatives of aza-BODIPY, absorption band around 800 nm also decreased due to decreasing electrondonating properties of amine group [31]. Very recently, Amin et al. investigated electrochemistry and photodynamics of ferroazadipyrromethane (ADP) donor–acceptor dyads and triads [32]. They observed spectral changes due to formation of charge separation during the first reduction of aza-BODIPY compound ADP in benzonitrile using a thin layer spectroelectrochemical cell. During the course of reduction, the peak located at 658 nm diminished in intensity with concurrent appearance of new bands at 446 and 820 nm. Observed new bands were assigned to aza-BODIPY radical anion (ADP^{*–}) and confirmed charge separation [32].

While methoxy derivatives of aza-BODIPY showed sharp absorption band, hydroxy derivatives of aza-BODIPY showed broader absorption band (Figs. 1 and 2). Oxy form of aza-BODIPY especially di- and tetra-oxy derivatives (phenolate ABDPⁿ⁻) showed the most broadened absorption band (Fig. 2).

It was previously shown that aza-BODIPY structures showed high extinction coefficients and fluorescence quantum yields [13-15]. Phenolic form of MHABDP and DHABDP revealed a single fluorescence band at 730 nm (Fig. 2d). However, steadystate fluorescence was not observed for the phenolate form of MHABDP and DHABDP. Besides, there is no fluorescence signal for the phenol form of THABDP as well. THABDP compound is more ionic than MHABDP and DHABDP. Therefore, charge transfer may occur in the phenol form of THABDP. Recently, phenol/phenolate dependent fluorescence quenching was observed for BODIPY [33-36]. Fluorescence quenching was attributed to photoinduced electron transfer between phenolate and BOD-IPY subunit. It was also found that significant fluorescence quenching in BODIPY occurs by intramolecular energy transfer [37]. This property was used as highly sensitive fluorescent probe.

Phenolate form of aza-BODIPY including high electron-donating moiety that is $-O^-$ (oxy) results in ICT. Observed new bands above 700 nm in absorption spectra (Fig. 2e) during phenol/phenolate transition correspond to ICT state. Presence of nonradiative decay of such state can be very fast and hence fluorescence will not be able to compete efficiently with the nonradiative decay. In an attempt to understand the relationship between fluorescence properties and ICT state we have performed ultrafast pump probe spectroscopy experiments.

3.2. Ultrafast pump probe spectroscopy studies

Ultrafast wavelength-dependent pump probe spectroscopy technique was used to investigate photodynamics and nonlinear optical properties of DHABDP (phenol) and ABDP^{2–} (phenolate). Femtosecond transient absorption spectra for phenol/phenolate forms show different characteristics as shown in Fig. 3. While phenol form shows only bleaching signal around 600 nm, fast growing nonlinear absorption signals appear bellow 500 nm and above 700 nm regions in phenolate form in addition to the bleach signal around 600 nm. The signals at upper and lower wavelengths correspond to ICT states of aza-BODIPY as observed in Fig. 2e.

Upon excitation of the deprotonated molecules the aza-BODIPY band shifts (now the S_2 state) slightly hypsochromically as can be seen best for DHABDP while at the same time there appears another band above 700 nm corresponding to the direct excitation of this ICT state (the S_1 state) (Fig. 2). As seen in Fig. 3, the excited state absorption (positive signal) is formed immediately after excitation and it decays at the same rate as the ground state depletion (bands around 600 and 675 nm). There is actually a isosbestic point close to 530 nm indicating that we have only two species: The extremely



Fig. 4. Effects of different number of phenol substituent on transient absorption spectra at 681 nm probe wavelength. The figure inset indicates slow decay time between 2 and 3 ns time scales.



Fig. 5. (a) Experimental results (filled circle) and theoretical fits (solid line) of open aperture Z-scan experiments for MHABDP, ABDP⁻, DHABDP and ABDP²⁻ in THF, using 1200 nm femtosecond pulses. (b) TPCS σ_2 comparison for phenol and phenolate form of ABDP.

fast (by internal conversion following excitation in the S_2 state) populated ICT state decays directly to the ground sate on a ps time scale (inset of Fig. 3b). Since the excitation of the fluorescence experiments is at 600 nm there is no fluorescence signal (Fig. 2b) due to the relaxation of the energy through ICT state above 700 nm.

In general, BODIPY [38] and aza-BODIPY [39] structures have singlet-triplet transition with intersystem crossing (ISC) mechanism. Adarsh et al. measured the triplet lifetimes in the order of microseconds with nanosecond laser flash photolysis study [39]. We have observed three decay times in Fig. 4: The fast decay (less than 1 ps), the middle decay (around couple hundred ps) and slow decay time (on the order of μ s). The measured long lifetime may be related to the lifetime of the triplet state in phenol form for MHABDP, DHABDP, THABDP in Fig. 4. Upon increasing electrondonating property, relative lifetime shortened as observed in the literature [32].

BODIPY and aza-BODIPY compounds exhibit strong TPA behavior [18,27]. Therefore, it is interesting to investigate TPA properties and the effect of ICT.

3.3. Two photon absorption properties

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TPA properties were investigated by open aperture (OA) Z-scan technique [18,29] 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), we used the following equations [40]:

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

$$T(I_0) = \frac{1}{1 + I_0 bl}$$
(1)

where *l* is optical path length. σ_2 (1 GM = 10⁻⁵⁰ cm⁴ s photon⁻¹) is obtained from the following equation,

$$\sigma_2 = \frac{n\nu\beta}{N_A d_0 \times 10^{-3}} \tag{2}$$

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

By using electron-donating moiety as a functional group for BODIPY structure the absorption spectrum can be shifted into NIR and nonlinear optical properties can be enhanced [40]. DMABDP and TMABDP compounds did not show any TPA properties due

to weak electron-donating strength of methoxy group. OA Z-scan experimental results at 1200 nm wavelength and 2.61×10^{15} W/m² peak intensity are shown in Fig. 5a and b. MHABDP, DHABDP and THABDP samples show TPA properties in wide spectral range (1200–1450 nm) and σ_2 increases with increasing electrondonating strength (Fig. 5b). Fig. 5a and b also shows the effect of ICT on the TPA properties in the phenolate form. MHABDP and ABDP⁻ have approximately the same σ_2 values (Fig. 5b). On the other hand, ABDP²⁻ has larger σ_2 than DHABDP. Zhang et al. studied effects of various groups such as phenyl, carbazole and triphenylamino on TPCS [41]. They found that σ_2 increases with the strength of electron-donating properties. Formation of the phenolate form of THABDP causes broadening of linear absorption peak, thus we could not observe nonlinear optical absorption at investigated wavelength range. We obtained maximum σ_2 value for THABDP derivative with 12.8 GM at 1200 nm wavelength due to strength of electron-donating property.

4. Conclusion

In summary, we synthesized new aza-BODIPY compounds containing methoxy and hydroxy group. Obtaining phenolate forms of aza-BODIPY containing hydroxyl group caused drastic changes in linear absorption spectra. New bands in phenolate form of these compounds appeared bellow 500 nm and above 700 nm in linear absorption spectra in THF solution. No fluorescence signals were observed with 600 nm excitation for phenolate forms. Ultrafast pump probe spectroscopy experiments confirmed occurrence of intramolecular charge transfer state above 700 nm with ultrafast lifetime. Therefore, 600 nm excitation in steady-state fluorescence experiments did not reveal any fluorescence signal due to the relaxation of the energy through intramolecular charge transfer state above 700 nm. The investigated aza-BODIPY compounds containing hydroxy group (HABDP) reveal two photon absorption properties in 1200-1450 nm spectral range. Two photon absorption cross-section values increase with increasing electron-donating strength. Our results also indicated that intramolecular charge transfer enhances two photon absorption properties. These findings may open the path to synthesize new BODIPY compounds with good two photon absorption properties in telecommunication wavelength range.

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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.2012.08.003.

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