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The synthesis of −1, −3, −5, −7, −8 aryl substituted boron-dipyrromethene chromophores: Nonlinear optical and photophysical characterization

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ABSTRACT

A convenient protocol enabled the synthesis of novel Arylated Borondipyrromethene (BODIPY) compounds was applied that synthesis yields found to be higher than classical alkyl substituted analogues. The nonlinear properties of the target molecules were investigated systematically in terms of aryl substitution to the pyrrole side and the meso substitution on the indacene core. It was found that, −3, −5 positions of the indacene core are effective positions for charge transfer, which is essential for two photon absorption (TPA). The greatest two photon cross section (TPCS) value (178 GM) is obtained for BDP3 compound, while TPCS value of BDP4 compound is 27 GM at near infrared wavelength (800 nm). Arylated chromophores exhibited the broader red-shifted absorption and fluorescence bands with higher stokes shifts with regard to reference Borondipyrromethene compound (4,4′-difluoro-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene, TMB). Our results are helpful for designing new photosensitizers and for applications in the study of the molecular photochemistry.

1. Introduction

The researches on the photophysical and nonlinear optical features of molecules may lead to obtaining convenient methods in various applications such as the determination of chemically or biologically important species [1–9], photodynamic therapy [10–14], two photon absorption imaging microscopy [15–17], organic photovoltaics [18–21] and two photon absorption (2 PA) properties [22–27]. In this way, dipyrrin based boron complexes known as BODIPY dyes have appeared as a fascinating class of luminescent molecules since their relative ease of preparation and modification over the past two decades [28,29]. Actually, the widespread interest stems from their large molar absorption coefficients in the visible region, chemical robustness, solubility, high fluorescence quantum yields and photostability [30–33]. Furthermore, the photophysical properties of the BODIPYs can be tailored and tuned by different substitution patterns on the pyrrole rings and organic side, depending on application. Thus, many efforts have been devoted to engineering new BODIPY dyes and remarkable spectroscopic properties.

In general, alkyl substituted 1*H*-Pyrrole derivatives such as 2,4-Dimethylpyrrole and 2,4-Dimethyl-3-ethylpyrrole are used as starting materials to obtain BODIPY dyes. Although there are many studies for the photophysical properties of these types of dyes in the literature, only a few examples of arylated BODIPY derivatives on the −1, −7, - 3, - 5 positions of the indacene core were reported [34–36]. We note that, investigation of nonlinear optical properties of arylated BODIPYs in terms of substitution patterns of aryl groups are lacking. Generally, BODIPY chromophores do not present efficient two photon cross-sections and typically have a value in the range of 50–130 GM [37–40]. However, since their promising photophysical properties as mentioned above, new approaches were devoted to enhancing their non-linear features. In this direction, for instance changing the electron density of the indacene core by extending the π-conjugation lengths have provided the more efficient two photon absorption activity [39,40]. It can be said that, the bathochromic shifts in the absorption of the BODIPYs

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towards near IR region have brought the positive outcomes in terms of two photon absorption. For this reason, a variety of chemical modifications have performed on the BODIPY scaffold in order to enhance the 2 PA cross sections. The enhancement of the conjugation by direct linking and free rotation of aryl groups on the BODIPY core could change the photophysical and nonlinear absorption properties. With these considerations, we have previously studied on the arylated 2,4-Diphenylpyrrole derivatives to obtain novel BODIPY compounds in order to get improved two photon absorption properties. Furthermore, we previously applied Suzuki-miyaura cross coupling reactions to get higher conjugation [36].

In this work, our main purpose is to investigate meso substitution effect by using different electron donating and accepting moieties in terms of two photon cross section. Secondly, we investigated to substitution patterns as positional on the −1, −7, -3, −5 and −8 positions of the indacene core. The Purpose of this work to clarify structure and two photon absorption features in terms of electron releasing or accepting capabilities and conjugation lengths to obtain ultimately two photon active BODIPY chromophores.

With these considerations, we designed and synthesized arylated BODIPYs by introducing 4-methoxyphenyl, 4-nitrophenyl, 4-(diphenylamino)phenyl and 4-bromophenyl moieties systematically with various electron donating/withdrawing properties and π-conjugation lengths to investigate two photon absorption properties. We synthesized −1, −7, - 3, - 5 tetramethyl substituted BODIPY (**TMB**) to be able to compare the results and evaluate the effect of substitution in terms of photophysical properties of the chromophores. The target compounds were isolated in higher yields compared to alkyl substituted analogue. In an attempt to study photophysical properties of the compounds **BDP1-BDP5**, steady state absorption and emission properties were measured. Open aperture (OA) Z-scan experiments were performed to reveal two photon absorption (2 PA) properties of the compounds.

2. Experimental Section

2.1. Materials and characterization

Reagents were obtained by Merck Co. 2,4-diarylpyrrole derivatives were prepared according to the literature procedure [8]. TLC Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator were used in monitoring the reactions and Silica column chromatography was carried out in purification. The Barnstead Electrothermal IA9100 device was used for melting point determination. Fluorescence measurements were carried out on a PerkinElmer LS55 Fluorescence Spectrometer and absorption spectra were recorded on a Shimadzu UV1800 spectrophotometer. Mass spectral analyses were performed on an Agilent 6224 HRMS spectrometer. ^{1}H NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by chloroform ($\delta = 7.26$ ppm. ^{13}C NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer. ^{13}C NMR chemical shifts (δ) are reported in ppm with the internal $CDCl_3$ δ 77.0 ppm as standard [36]. Perkin−Elmer 100 spectrometer (equipped with ATR unit) was used for FT-IR spectra of the compounds in the range 650−4000 cm^{-1}.

2.2. Determination of fluorescence quantum yields (Φ_F)

In order to determine the fluorescence quantum yields of the compounds **BDP1-BDP5** and **TMB**, comparative method Eq. (1) was applied.

$$\Phi_F = \Phi_F(Std)\ \frac{F\ .\ A_{Std}\ .\ n^2}{F_{Std}\ .\ A\ .\ n^2_{Std}} \tag{1}$$

where ϕ_F (Std) is the fluorescence quantum yield of the reference compound. F and F_{Std} denote the areas under the fluorescence emission curves of samples and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard compound at the excitation wavelenghts. n^2 and $n^2{}_{std}$ are the refractive indices of the solvents used for the sample and standard, respectively. Rhodamine B solution in ethanol was prepared and used as the fluorescence standard ($\Phi_f = 0.65$) for fluorescence quantum yield calculations. The concentration of the dilute solutions at the excitation wavelengths fixed at 1×10^{-6} M in dichloromethane. All spectra were recorded at 25 °C.

2.3. Synthesis

2.3.1. Synthesis of compound 4,4-difluoro-8-[4-methoxyphenyl]-1,3,5,7-tetraphenyl-4-bora-3a,4a-diaza-s-indacene (***BDP1***)

2,4-diphenylpyrrole (400 mg, 1.82 mmol) and 4-methoxybenzaldehyde (118 mg, 0.87 mmol) were dissolved in absolute CH_2Cl_2 (150 mL) under argon atmosphere, one drop of Trifluoroacetic acid (TFA) and tetrachloro-1,4-benzoquinone (*p*-chloranil) (320 mg, 1.30 mmol) was added. The reaction mixture was stirred for 8 h at 25 °C. Then, the reaction mixture was concentrated to 25 mL and filtered. The filtrate solid and N,N-diisopropylethylamine (hunig's base, DIPEA, 1.01 mL, 6.08 mmol) were dissolved in 100 mL CH_2Cl_2, the resulting solution was stirred at room temperature for 10 min; $BF_3\cdot OEt_2$ (1.21 mL, 9.55 mmol) were then added and stirring was continued overnight. The resulting solution was washed with water and dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was chromatographed (elution: benzene) to afford 0.35 g (yield: 67%). m. p: 330−334 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm]: 3.55 (s, 3H), 6.00 (d, $J = 8.4$ Hz, 2H), 6.55 (s, 2H), 6.79−6.75 (m, 6H), 6.95−6.90 (m, 6H), 7.45−7.43 (m, 6H), 7.90 (d, $J = 7.6$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 156.7, 147.8, 146.4, 135.9, 133.4, 132.7, 132.6, 129.5, 129.4, 128.8, 128.1, 127.2, 126.1, 123.8, 123.3, 112.4, 55.1; FT-IR (Atr, cm^{-1}): 3013, 2994, 2961, 1613, 1690, 1613, 1590, 1570 (B−N), 1504, 1468 (C=N), 1438, 1227, 1166 (B−F), 1143, 1108, 1009, 821, 760, 702; HRMS/TOF-ESI: Theoretical calculation: 602.23411 ($C_{40}H_{29}BF_2N_2O$) and experimental value: 625.22719 [M+Na]$^+$, $\Delta = 5.29$ ppm.

2.3.2. 4,4-difluoro-8-[4-nitrophenyl]-1,3,5,7-tetraphenyl-4-bora-3a,4a-diaza-s-indacene (***BDP2***)

By utilizing the above described procedure used to prepare compound **BDP2**. 2,4-diphenylpyrrole (200 mg, 0.91 mmol), 4-nitrobenzaldehyde (65 mg, 0.43 mmol), CH_2Cl_2 (75 mL), tetrachloro-1,4-benzoquinone (160 mg, 0.65 mmol), hunig's base (0.50 mL, 3.04 mmol) and $BF_3\cdot OEt_2$ (0.60 mL, 4.78 mmol) were used in this reaction. The residue was chromatographed (elution: benzene) to afford 97 mg (yield: 36%). m. p: 315−318 °C; ^{1}H NMR (400 MHz, $CDCl_3$):δ[ppm]: 6.56 (s, 2H), 6.72 (d, $J = 7.2$ Hz, 4H), 6.85 (t, $J = 7.6$ Hz, 4H), 6.94 (t, $J = 6.4$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.46−7.44 (m, 6H), 7.92−7.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.9, 147.5, 147.4, 142.4, 138.2, 135.0, 132.7, 132.2, 129.9, 129.5, 129.5, 128.8, 128.3, 127.4, 126.9, 123.6, 121.40; FT-IR (Atr, cm^{-1}): 3068, 2958,1597, 1539 (B−N), 1521, 1493, 1471 (C=N), 1395, 1349, 1227, 1166 (B−F), 1143, 1103, 849, 755, 696; HRMS/TOF-ESI: Theoretical calculation: 617.20862 ($C_{39}H_{26}BF_2N_3O_2$), found: 640.20210 [M+Na]$^+$, $\Delta = 5.79$ ppm.

2.3.3. *4,4-difluoro-8-[4-bromophenyl]-1,3,5,7-[4-methoxyphenyl]-4-bora-3a,4a-diaza-s-indacene (**BDP3**)*

Compound **BDP3** was synthesized by utilizing the procedure above as that used to obtain compound **BDP1**. 2,4-bis(4-methoxyphenyl)-1H-pyrrole (473 mg, 1.69 mmol), 4-bromobenzaldehyde (150 mg, 0.81 mmol), CH_2Cl_2 (80 mL), tetrachloro-1,4-benzoquinone (0.99 g. 4.03 mmol), hunig's base (0.94 mL, 5.67 mmol) and $BF_3 \cdot OEt_2$ (1.13 mL, 8.92 mmol) were used in this reaction. The residue was chromatographed (elution: benzene) to afford 250 mg (yield: 40%). m. p: 308–310 °C; ^1H NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.72 (s, 6H), 3.86 (s, 6H), 6.44 (d, $J = 8.8$ Hz, 4H), 6.49 (s, 2H), 6.63 (d, $J = 8.8$ Hz, 4H), 6.65 (s, 4H), 6.96 (d, $J = 8.8$ Hz, 4H), 7.89 (d, $J = 9.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.7, 158.4, 156.5, 143.3, 142.5, 133.5, 131., 130.8, 129.9, 129.6, 127.8, 125.1, 122.7, 122.6, 118.9, 113.7, 112.9, 55.4, 55.3; FT-IR (Atr, cm^{-1}): 3005, 2974, 2955, 1608, 1511 (B–N), 1471 (C=N), 1285, 1232, 1136 (B–F), 1105, 1029, 828, 762, 669; HRMS/TOF-ESI: Theoretical calculation: 770.17633 ($C_{43}H_{34}BBrF_2N_2O_4$), found: 809.14240 $[M+K]^+$, $\Delta = 2.92$ ppm.

2.3.4. *4,4-difluoro-8-[4-bromophenyl]-1,7-[4-methoxyphenyl]-3,5-[4-bromophenyl]-4-bora-3a,4a-diaza-s-indacene (**BDP4**)*

Compound **BDP4** was synthesized by utilizing the procedure above as that used to obtain compound **BDP1**. 2-(4-bromophenyl)-4-(4-methoxyphenyl)-1H-pyrrole (556 mg, 1.69 mmol), 4-bromobenzaldehyde (150 mg, 0.81 mmol), CH_2Cl_2 (80 mL), tetrachloro-1,4-benzoquinone (0.99 g. 4.03 mmol), hunig's base (0.94 mL, 5.67 mmol) and $BF_3 \cdot OEt_2$ (1.13 mL, 8.92 mmol) were used in this reaction. The residue was chromatographed (elution: benzene) to afford 400 mg (yield: 43%). m. p: 319–321 °C; ^1H NMR (400 MHz, $CDCl_3$): δ[ppm]: 3.72 (s, 6H), 6.44 (d, $J = 8.8$ Hz, 4H), 6.48 (s, 2H), 6.63 (d, $J = 9.2$ Hz, 4H), 6.67 (s, 4H), 7.57 (d, $J = 8.4$ Hz, 4H), 7.74 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.7, 133.3, 131.5, 131.3, 131.0, 130.9, 130.8, 130.6, 130.4, 129.9, 129.7, 127.3, 124.3, 123.0, 122.9, 122.9, 113.0, 55.4; FT-IR (Atr, cm^{-1}): 3013, 2950, 2912, 2833, 1613, 1590, 1570, 1504 (B–N), 1468 (C=N), 1438, 1227, 1166, 1143 (B–F), 1108, 1009, 821, 760, 702, 668; HRMS/TOF-ESI: Theoretical calculation: 867.97416 ($C_{41}H_{28}BBr_3F_2N_2O_2$), found: 868.98232 $[M+H]^+$, $\Delta = 0.38$ ppm.

2.3.5. *4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-bromophenyl]-4-bora-3a,4a-diaza-s-indacene (**BDP5**)*

Compound **BDP5** was synthesized by utilizing the literatured procedure [36]. 2-(4-bromophenyl)-4-(4-methoxyphenyl)-1H-pyrrole (975 mg, 2.98 mmol), 4-(diphenylamino)benzaldehyde (390 mg, 1.42 mmol), CH_2Cl_2 (150 mL), tetrachloro-1,4-benzoquinone (1.76 g. 7.14 mmol), hunig's base (1.65 mL, 9.98 mmol) and $BF_3 \cdot OEt_2$ (1.99 mL, 15.69 mmol) were used in this reaction. The residue was chromatographed (elution: toluene) to afford 637 mg (yield: 47%). m. p: 305–306 °C; ^1H NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.81 (s, 6H), 6.24 (d, $J = 8.4$ Hz, 2H), 6.48 (s, 2H), 6.65 (d, $J = 8.4$ Hz, 4H), 6.77 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 4H), 6.86 (d, $J = 8.4$ Hz, 4H), 7.09 (t, $J = 7.2$ Hz, 2H), 7.29 (t, J = , 8.0 Hz, 4H), 7.56 (d, $J = 8.8$ Hz, 4H), 7.73 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.2, 155.1, 148.6, 147.8, 147.1, 146.6, 133.3, 132.6, 131.6, 131.4, 130.9, 130.1, 129.3, 128.6, 125.8, 124.2, 124.2, 124.0, 123.1, 118.3, 113.0, 55.2; FT-IR (Atr, cm^{-1}): 3034, 2962, 2904, 2847, 1609, 1587, 1501 (B–N), 1486, 1463 (C=N), 1285, 1232, 1166, 1148 (B–F), 1105, 1011, 844, 821, 760, 699; HRMS/TOF-ESI: Theoretical calculation: 957.13715 ($C_{53}H_{38}BBr_2F_2N_3O_2$), found: 980.13117 $[M+Na]^+$, $\Delta = 4.34$ ppm.

3. Results and Discussion

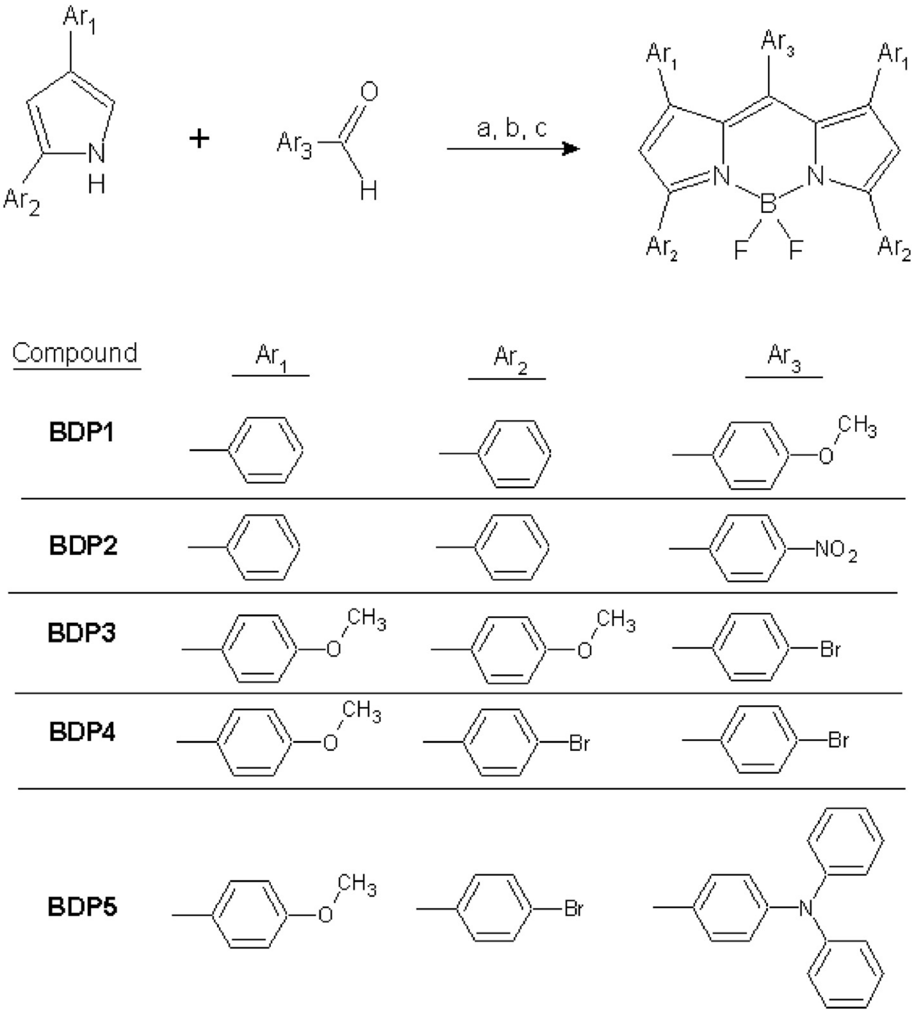
3.1. *The synthesis of the compounds BDP1-BDP5*

The compounds **BDP1-BDP5** were obtained by a standard procedure starting from the 2,4-diphenylpyrrole derivatives and aromatic aldehydes in the presence of trifluoroacetic acid catalyst to obtain dipyrromethane intermediates as shown in Scheme 1. In the second step *p*-chloranil was used for the oxidation of dipyrromethanes. Then the treatment with hunig's base and boron trifluoride diethyletherate gave the desired products. For the compounds **BDP1** and **BDP2,** isolated yields were very poor than classical BODIPY synthesis procedure. After some experimentation, we made a modification to standard procedure. In the first step of the reaction, oxidizing agent *p*-chloranil was added immediately after mixing pyrroles and aldehydes. After adding catalyst, the color of the reaction mixture turned deep green. After the complexation with boron difluoride and isolation, yields for the synthesis were found to be higher than expected and lies between 36% and 67%.

The identification of compounds was established by NMR spectroscopy. Primarily, the singlet peaks observed for the pyrolic protons are evidence the symmetrical structures. Furthermore the most significant difference in the ^1H NMR spectrum is the chemical shift of aromatic pyrrole protons. While the signal at 5.98 ppm is assigned to pyrrole protons of reference alkyl substituted compound **TMB,** for the aryl substituted compounds **BDP1-BDP5** the chemical shifts observed in the higher values. For the comparison, the chemical shifts of the compounds were indicated in Fig. 1. The downfield shifts of the aromatic pyrrole protons may be caused by the effect of aryl groups. In the series of compounds **BDP1-BDP5**, there was a minor changes in chemical shifts of pyrrole protons when the meso substituents were changed such as 4-methoxypheyl, 4-nitrophenyl, 4-bromophenyl and triphenylamine. Although these moieties have different donor or acceptor properties, no remarkable differences were observed in ^1H NMR spectra. For instance, the chemical shift values are 6.54 and 6.56 ppm for the meso (8) methoxyphenyl and nitrophenyl substituted compounds, respectively. This is because the orthogonal geometry of the meso position. Although the nitro group is a strong electron withdrawing group and the methoxy is an electron donor, the chemical shifts which were found very close to each other are due to the fact that the meso position has minor effect on the BODIPY indasen ring. Such that, orthogonal position of the aromatic groups on the BODIPY core structure in the meso position limits the conjugation [7,28]. This perspective is used to describe the PET mechanisms commonly seen in meso-substituted BODIPY compounds [29]. The same result is observed not only in absorption and fluorescence but also in the ^1H NMR.

3.2. *UV–Vis absorption and fluorescence studies*

The electronic absorption and emission spectra of the studied compounds in dichloromethane are given in Fig. 2. In general, the absorption spectra of all synthesized arylated BODIPY compounds show a similar shape as meso substituted borondipyrromethene chromophores. UV–Vis absorption spectra of the chromophores **BDP1-BDP5** displayed intense bands between 555 and 586 nm assigned to the $S_0 \rightarrow S_1$ transitions along with high molar absorption coefficients. The broader absorption band localized between 350 and 400 nm is ascribed to the $S_0 \rightarrow S_2$ transitions of BODIPY moiety. Introducing aryl groups in the −1, −3, −5, −7 positions of the BODIPY core showed significant bathochromic shifts compared to alkyl substituted analogue due to the extended conjugation. Additionally, the absorption bands of the compounds are relatively broader and the Stokes shifts are larger compared to those of alkyl



Scheme 1. The synthesis of compounds **BDP1-BDP5** a) Trifluoroacetic acid (cat.), CH_2Cl_2, 25 °C 8–12 h. b) Tetrachloro-1,4-benzoquinone, 8–12 h c) DIPEA, $BF_3 \cdot OEt_2$, 12 h.

substituted counterpart. However, the molar absorption coefficients and fluorescence quantum yields were decreased.

Compounds with 4-methoxyphenyl group on the −3, −5 positions of the BODIPY core showed a clear bathochromic shifts in their absorption maximas, as compared to phenyl substituted analogues**.** This is due to the electron releasing effect of methoxy groups that, unpaired electrons of the methoxy group became a part of Π system [41]. For all aryl substituted compounds, absorption bandwidths (FWHM) are 2–3 times broader than **TMB** counterpart. Furthermore, the fluorescence emission spectra display a Stokes-shifted (ca. 41 nm), mirror-symmetrical bands relative to the absorption of BODIPY units. The stokes shifts (expressed in nm) ranged 41–49 nm. The main absorption band corresponds to the $S_0 \rightarrow S_1$ transition that shows a perfect mirror image shape with minimum energy loss. The compound **BDP5**, which has triphenyl group at the meso position of the BODIPY core have quenching effect of fluorescence signal. It seems that, charge transfer occurs easily by incorporation of triphenylamine group to the BODIPY core. It is obvious that, extended Π conjugation and free rotation of aryl groups around Ar–Ar bonds have responsible the both absorption and fluorescence properties of the compounds [34].

3.3. *Nonlinear absorption properties*

BODIPY and Aza-BODIPY compounds are known to have improved two-photon absorption properties in case of the increased charge transfer properties [25,26,42–45]. Since the BDP3 -BDP5 compounds have substituent groups which can provide an intramolecular charge transfer they might display two photon absorption features as well. Therefore, open aperture Z-scan technique was used to investigate two photon absorption properties of the compounds. The 800 nm laser source is a mode-locked Ti:Sapphire laser amplifier system with 1 ps pulse durations and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS). The laser beam was focused on solution in a 1 mm thick cell by using biconvex lens with a focal length of 20 cm. All these measurements were performed for all investigated compounds at 800 nm wavelength in 0.0025 M tetrahydrofuran solution.

In order to calculate the two photon absorption coefficient (β) and two photon cross section (σ_2) values from the experimental results the given equations (equations (1) and (2)) have been used. Nonlinear transmittance T is defined in terms of laser intensity I_0 [25].

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

where, l represents optical path length. β value is obtained from the curve fitting the open aperture Z-scan data to equation (1). TPCS value (1 GM = 10^{-50} cm^4 s photon-1) is obtained by using β value in

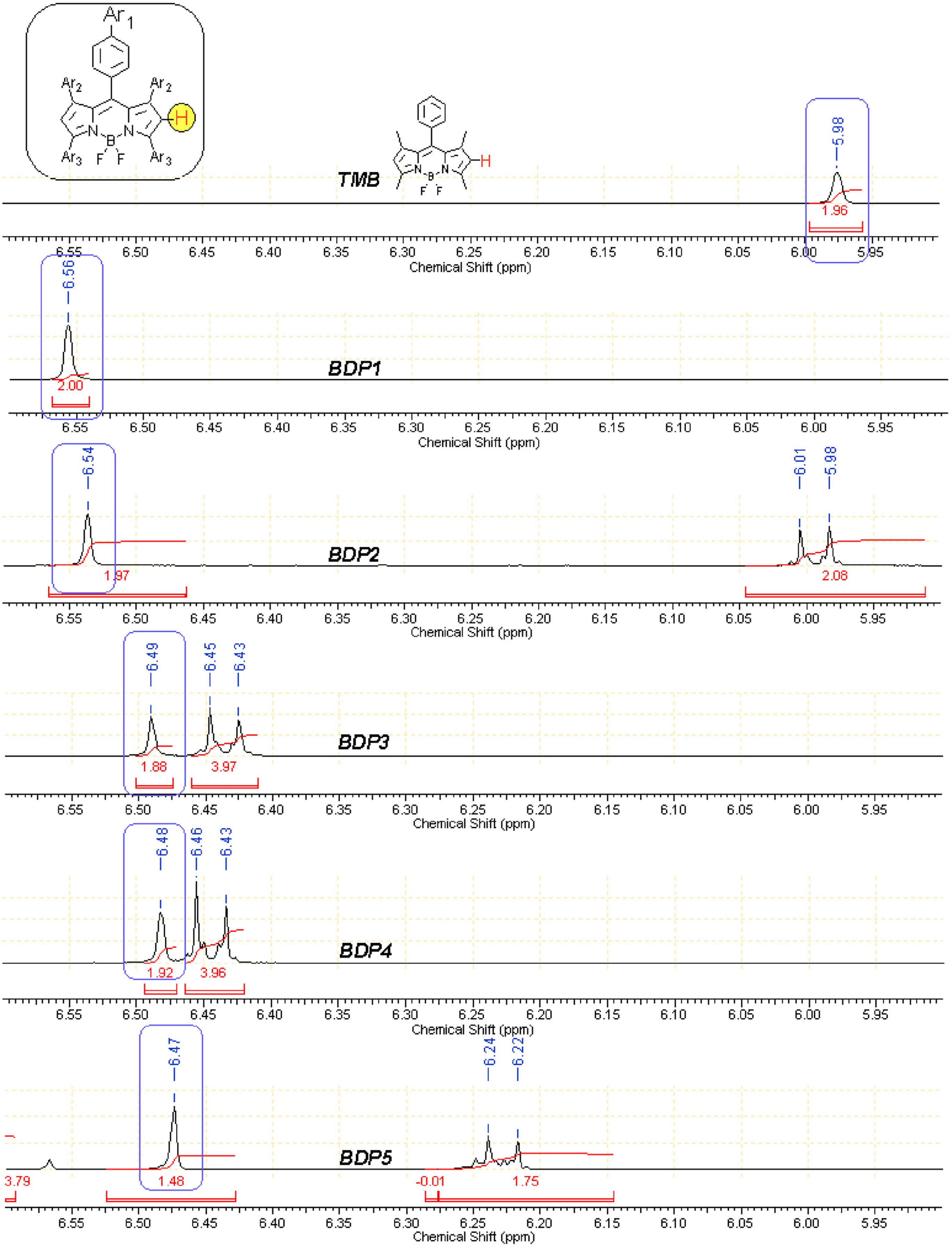


Fig. 1. The scale of chemical shifts for the reference compound **TMB** and compounds **BDP1-BDP5** for pyrrolic protons in ^{1}H NMR (for clarity, the corresponding peaks were enclosed in a blue rectangle).

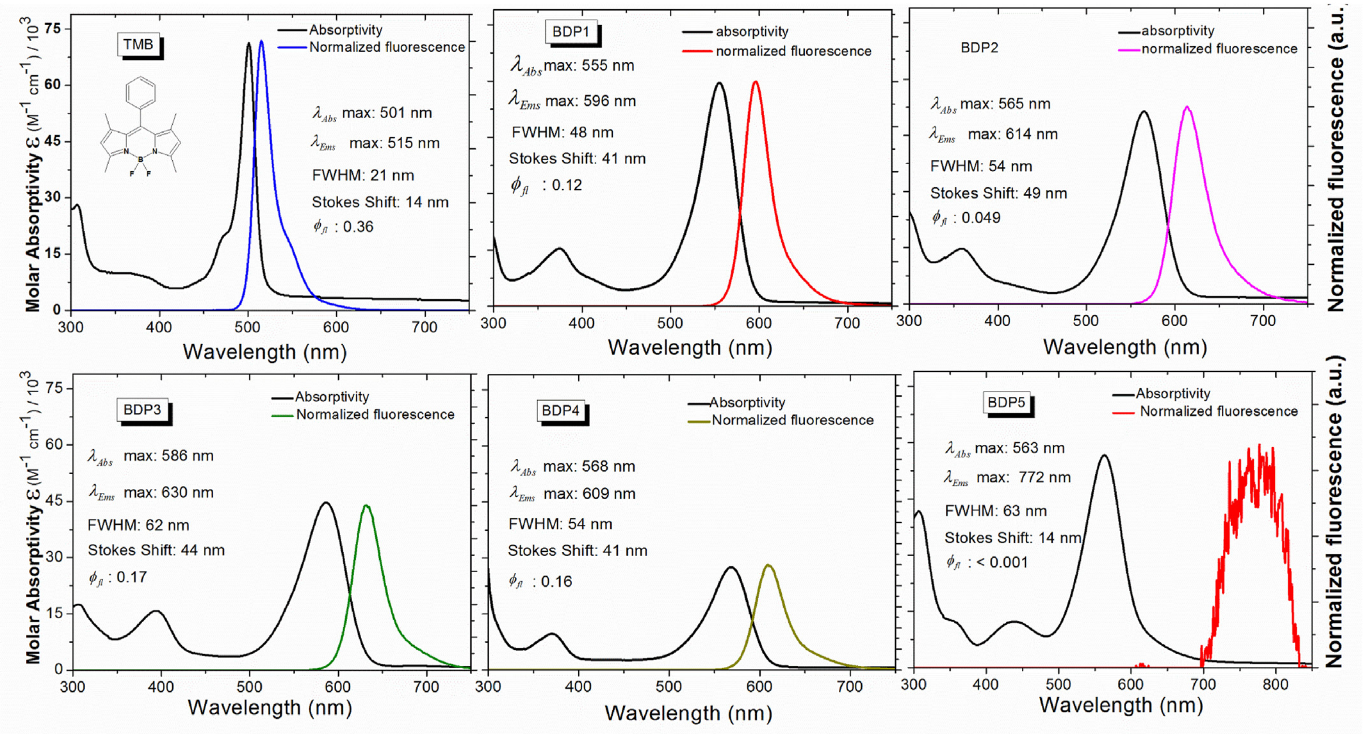


Fig. 2. UV/Vis and fluorescence spectra of the compounds **BDP1-BDP** and **TMB** as reference in dichloride methane.

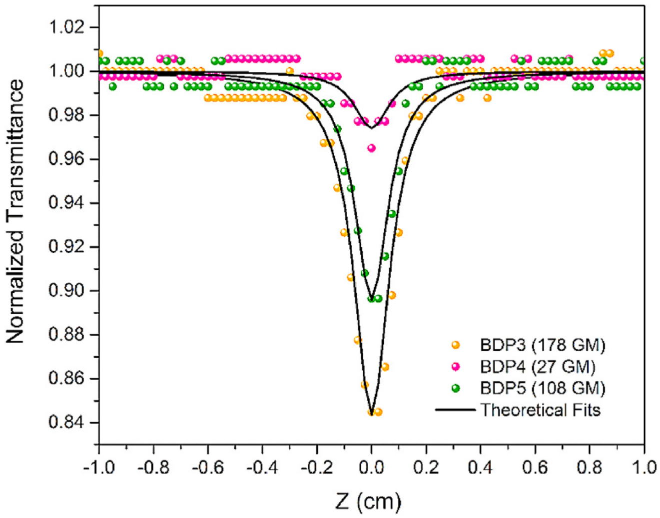


Fig. 3. Open aperture Z-scan experimental results of **BDP3**, **BDP4** and **BDP5** compounds at 800 nm wavelength in tetrahydrofuran.

the second equation,

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

where, N_A represents the Avogadro number and d_0 represents molarity of the solution.

OA Z-scan experimental results of **BDP3, BDP4** and **BDP5** compounds and their theoretical fits at 76 GW/cm^2 peak intensities for 800 nm wavelength are represented in Fig. 3 together with the calculated TPCS values. **BDP1** and **BDP2** compounds did not show any TPA properties.

It is known that two photon absorption features of chromophores closely related with the charge transfer and conjugation lengths of moieties. In an attempt to enhance intermolecular charge transfer of the molecules, electron donating moieties bind to efficient positions of BODIPY core. Although, **BDP1** contains electron donor moiety (i.e. methoxy) at meso position of the BODIPY core, we could not observe TPA properties due to the ineffective position (meso position) of BODIPY core for charge transfer. **BDP3** compound contains two more methoxy moieties at para position of the phenyl groups at the −3, −5 positions of the BODIPY core, compared to **BDP4** compound. Therefore, the greatest TPCS value (178 GM) is obtained for **BDP4** compound, while TPCS value of **BDP4** compound is 27 GM. It can be concluded that, −3, −5 positions of BODIPY core are effective positions for charge transfer mechanism and also methoxyphenyl groups are efficient enhancers for the two photon absorption activity of the molecules, especially when linked at the −3, −5 positions of the BODIPY core. TPCS value of **BDP5** compound containing diphenylamine moiety at para position of the phenyl group at the meso position is obtained as 108 GM. TPA properties of **BDP5** compound [36] is stronger than **BDP4** compound, due to containing diphenylamine moiety which has long conjugation length and more electron donating nature. Based on the results from literature, BODIPY compounds generally show 2 PA values between 50 and 130 GM, typically 50 GM [37–39]. The compound BDP5 also has the values within the range specified (108 GM). However, the BODIPY BDP1 and BDP2 with phenyl groups on the −1, −7, - 3, - 5 positions have no 2 PA properties. It can be drawn from the results that donor substituted phenyl groups extend the π-electron system of the BODIPYs to make them intermediate two-photon absorbers. Furthermore, the arylation of BODIPY core at the −1, −7, - 3, - 5 positions, has a moderate effect in respect to two photon absorption. However, it should be noted that, there is approximately 7-fold enhancement in the 2 PA cross section for the BDP3 with methoxyphenyl groups compared to bromophenyl substituted BDP4 compound.

4. Conclusions

In summary, we synthesized new arylated BODIPY chromophores which show broadband absorption and fluorescence in the visible spectral region. The photophysical studies exhibited that, all arylated boron-dipyrromethene compounds have the red-shifted absorption and fluorescence bands and 2–3 times higher stokes shifts and full width at half media (FWHM) values compared to alkyl substituted analogue (**TMB**). Open aperture Z-scan experiments revealed that; although there is electron accepting or donating substituent on the −8 (meso) position of the BODIPY core structure, −1, −3, −5, −7 phenyl substituted BODIPYs (**BDP1** and **BDP2**) has no remarkable two photon absorption properties. We attributed this the ineffective meso (−8) position of the BODIPY core for charge transfer, while −3, −5 positions of the BODIPY core are more feasible for the charge transfer mechanism. The compounds **BDP3**, **BDP4** and **BDP5** showed two photon absorption properties at 800 nm wavelength. Two photon cross section values for **BDP3** and **BDP4** compounds were 178 and 27 GM, respectively. Besides, two photon absorption property of the **BDP5** compound (108 GM) is stronger than that's of **BDP4** compound (27 GM). Our findings indicate that diphenylamine moiety which has longer conjugation and electron donating nature can enhance the two photon absorption cross section even if it is on the meso position on the core structure. In particular, the studied molecules revealed that, methoxyphenyl groups are efficient two photon absorption enhancers. The BODIPY compounds which contain extended π-electron systems enable the polarizable of the molecules that increase the dipole moment 2 PA cross section [46]. From point of this view, all synthesized compounds with aryl groups should be able to have efficient 2 PA values. However the results indicate that auxochrome donor group or groups dynamize the 2 PA cross sections as well as the extension of the π conjugation. Although the existence of direct linkage of the aryl groups have been found to increase the 2 PA activities of the BODIPYs to some extent, the organic reactions such as Knoevenagel condensation reactions and Pd catalyzed reactions may be more feasible to obtain BODIPY compounds bearing π-extended auxochrome groups. On the other hand, these reactions involve multiple-steps resulting in poor synthetic yields along with the purification difficulties. The usage of the 2,4-aryl substituted pyrrole derivatives as starting materials make the synthesis yields higher significantly (e.g. 67% and 40% for the compounds BDP1 and BDP3, respectively). Though BDP3-BDP5 have not significant nonlinear properties compared to BODIPYs in literature, the ease of preparation and higher synthetic yields can enable to the relevant compounds to be used in further reactions as a starting material in order to enhance the 2 PA features of them. In accordance with this purpose, appropriate synthetic modifications may be performed, such as multiple methoxy groups can be employed though functionalization of the BODIPY core from the positions of −3, −5, −8, as a subject of future study.

CRediT authorship contribution statement

Gökhan Sevinç: Conceptualization, Methodology, Investigation, Writing - review & editing. **Betül Küçüköz:** Investigation, Writing - review & editing, Data curation. **Ayhan Elmalı:** Supervision, Methodology. **Mustafa Hayvalı:** Supervision, Methodology.

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Appendix A. Supplementary data

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