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The Synthesis of New Aryl Boron-Dipyrromethene Compounds: Photophysical and pH Responsive Properties

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Abstract: In this work, 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. 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). We were interested in the electron transfer mechanism of compound $BDPNH_2$ which has amine subunit to alkyl substituted reference. The fluorescence enhancement of this compound in acidic media was associated with the inactivation of the acceptor type photoinduced electron transfer mechanism by fluorimetric measurements. Our results are helpful for designing new photosensitizers and for applications in the study of the molecular photochemistry.

Keywords: Aryl Borondipyrromethene, Pentaaryldipyrrin, BODIPY, pH Sensor

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INTRODUCTION

Investigating the photophysical properties of molecules provides convenient methods in various applications such as the determination of chemically or biologically important species (1-9), photodynamic therapy (10-14), TPA imaging microscopy (15-17), and organic photovoltaics (18-21). There are many studies in the literature about designing and synthesizing new molecules for these applications.

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. Actually, the widespread interest stems from their large molar absorption coefficients in the visible region, chemical robustness, solubility, high fluorescence quantum yields and photostability. Furthermore, photophysical properties of BODIPYs can be tailored and tuned by different substitution patterns on pyrrole rings and organic side, depending on application. Thus, many efforts have been devoted to engineer new BODIPY dyes and remarkable spectroscopic properties.

Alkyl substituted pyrrole derivatives such as 2,4-dimethylpyrrole and 2,4-dimethyl-3-ethylpyrrole are used as starting materials to obtain 4,4’-difluoro-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene derivatives known as 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 (22-24).

We note that, investigation of photophysical properties of arylated BODIPYs in terms of substitution patterns of aryl groups are lacking. The enhancement of the conjugation by direct linking and free rotation of aryl groups on the BODIPY core could change the photophysical absorption and fluorescence properties lead to fluorescence enhancement or quenching.

With these considerations, we designed and synthesized novel arylated BODIPY compounds by introducing 4-nitrophenyl and 4-aminophenyl moieties to investigate the pH sensor capability. We also synthesized 1,3,5,7-tetramethyl substituted BODIPY (TMB) to be able to compare the results and reveal the effect of substitution in terms of photophysical properties. The target compounds were isolated in higher yields compared to alkyl substituted analogue (TMB). In this work we showed the use of arylated BODIPYs as pH probe by explaining the fluorescence enhancement mechanism of the compound $BDPNH_2$ with an amine substituted by using fluorescence spectroscopy technique as well as steady state UV-vis measurements.

EXPERIMENTAL SECTION

Materials and measurement

All reagents were purchased from Sigma-Aldrich and Merck Chemical Companies and used as received without further purification. 2,4-diphenylpyrrole was prepared according to the literature procedure (2). Reactions were monitored by thin layer chromatography using Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was carried out on silica (230-400 mesh). Melting points were determined on a Barnstead Electrothermal IA9100 platform. UV-Visible spectra were recorded on a SHIMADZU UV-1800 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer. Mass spectral analyses were performed on an Agilent 6224 TOF LC/MS 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 (δ= 7.26 ppm) and DMSO (δ= 2.48 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.

Titration studies

Compound $BDPNH_2$ was dissolved in 2:1 CH_3CN-H_2O mixture and solution with $1x10^{-5}$ M concentration was prepared. Than 0.1 M solution of HCl were used to adjust the pH of the solutions by gradually adding a microliter of H^+ to the dye solution. Then fluorimetric titration was applied as a function of pH using the emission spectra. The recorded steady-state fluorescence data (F) was fitted to the following equation (Eq. 1) as a function of [H^+] yield value of K_a.

$$F = \frac{F_{max} H^{+n} + F_{min} K_a}{K_a + H^{+n}} \quad \text{(Eq. 1)}$$

Here, F_{min} and F_{max} denote fluorescence signals at minimal and maximal [H^+], respectively, and n denotes the number of protons bounded per fluorescent pH probe. n was kept fixed at 1 in the final curve fitting. Predicted an apparent pK_a value was obtained as 2.45 from the sigmoidal plot of pH versus fluorescence intensity.

Determination of fluorescence Quantum yields (Φ_F)

In order to determine the fluorescence quantum yields of the compounds $BDPNO_2$, $BDPNH_2$ and TMB, comparative method (Eq. 2) was applied.

$$\phi_F = \phi_F(Std)\frac{F\,x\,A_{Std}\,x\,n^2}{F_{Std}\,x\,A\,x\,n^2_{Std}} \quad \text{(Eq. 2)}$$

Where ϕ_F (Std) is the fluorescence quantum yield of Rhodamine B. 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 absorbance 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 in ethanol (Φ_f =0.65) was used as the fluorescence standard for fluorescence quantum yield calculations. The concentration of the dilute solutions at the excitation wavelengths fixed at 1 x 10^{-6} M in dichloromethane. All spectra were recorded at 25 ºC.

The synthesis of 4-difluoro-8-[4-nitrophenyl]-1,3,5,7-tetraphenyl-4-bora-3a,4a-diaza-s-indacene ($BDPNO_2$)

2,4-diphenylpyrrole (600 mg, 2.73 mmol) and 4-nitrobenzaldehyde (195 mg, 1.29 mmol) were dissolved in absolute CH_2Cl_2 (125 mL) under Ar atmosphere. Then one drop of trifluoroacetic acid (TFA) and tetrachloro-1,4-benzoquinone (0.48 g, 1.95 mmol) was added to the solution. The solution was stirred at room temperature for 6 h. The reaction mixture was condensed to 30 mL and filtered to provide a green solid. Without purification, the green solid and Hünig's base (1.50 mL, 9.12 mmol) were dissolved in 60 mL of CH_2Cl_2, the mixture was stirred at room temperature for 10 min; $BF_3.OEt_2$ (1.80 mL, 14.34 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 on silica gel (elution: benzene) to afford 291 mg (yield: 36%) Compound **$BDPNO_2$** in the form of purple powder. Mp = 315-318 ^oC. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.92-7.90 (4H, m, Ar-H), 7.46-7.44 (6H, m, Ar-H), 7.30 (2H, d, *J*=8.8 Hz, Ar-H), 6.99 (2H, d, *J*=8.8 Hz, Ar-H), 6.95-6.92 (2H, m, Ar-H), 6.86-6.83 (4H, m, Ar-H), 6.73-6.72 (4H, m, Ar-H), 6.56 (2H, s, Ar-H), ^{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 HRMS/TOF-ESI: Calculated as 617.20862, found: 640.20210 [M+Na]+, Δ=5.79 ppm.

The synthesis of 4,4-difluoro-8-[4-aminophenyl]-1,3,5,7-tetraphenyl-4-bora-3a,4a-diaza-s-indacene ($BDPNH_2$)

$BDPNO_2$ (225 mg, 0.36 mmol) was dissolved in THF (15 mL) and EtOH (80 mL) under nitrogen, 5% Pd/C (15 mg), and hydrazine monohydrate (0.54 mL, 80% v/v) were added. The resulting solution was refluxed for 3 h. TLC analysis showed complete consumption of the starting material and then cooled to room temperature. The catalyst was removed by filtration

and the solvent was removed by rotary evaporation. The target product was obtained by a column chromatography on silica gel using CH_2Cl_2:toluene (95:5 v/v) to afford the corresponding product **$BDPNH_2$**. Yield: 87 mg (41 %). Decomp.>300 ^oC. ^{1}H-NMR (400 MHz, DMSO, δ, ppm): 7.80-7.78 (4H, m, Ar-H), 7.43-7.41 (6H, m, Ar-H), 6.98-6.92 (6H, m, Ar-H), 6.86-6.84 (4H, m, Ar-H), 6.71 (2H, s, Ar-H), 6.55 (2H, d, *J*=8.4 Hz, Ar-H), 5.65 (2H, d, *J*=8.4 Hz, Ar-H), 5.27 (2H, s, -NH_2), ^{13}C-NMR (100 MHz, DMSO): 157.9, 147.5, 147.4, 142.4, 138.2, 135.0, 132.7, 132.2, 129.9, 129.5, 128.8, 128.3, 127.4, 126.9, 123.7, 123.6, 121.4. HRMS/TOF-ESI: Calculated as 587.23443, found: 588.24820 $[M+H]^+$, Δ=3.93 ppm

RESULTS AND DISCUSSION

The compound $BDPNO_2$ was obtained by a standard procedure starting from the 2,4-diphenylpyrrole and 4-nitrobenzaldehyde in the presence of trifluoroacetic acid catalyst as shown in Figure 1. In the first step, p-chloranil was used for the oxidation of dipyrromethanes. Then the treatment with hunig's base and boron trifluoride diethyl etherate gave the desired product.

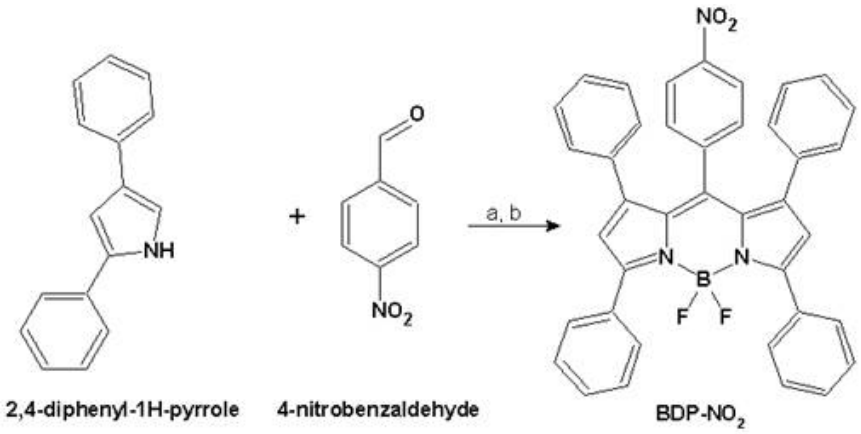

Figure 1: The synthesis of compound $BDPNO_2$ a) Tetrachloro-1,4-benzoquinone, Trifluoroacetic acid (cat.), CH_2Cl_2, 25 °C, a) 8-12 h. b) DIPEA, $BF_3.OEt_2$, 12 h.

In the first step of the reaction, oxidizing agent *p*-chloranil was added immediately after mixing pyrrole and aldehyde derivative. After adding the catalyst, the color of the reaction mixture turned to deep green. After the complexation with boron difluoride and isolation, yield for the synthesis was found to be as 36%. The compound $BDPNH_2$ was obtained by reducing of compound $BDPNO_2$ with hydrazine and palladium/carbon catalyst and reduction afforded in 41% yield (Figure 2).

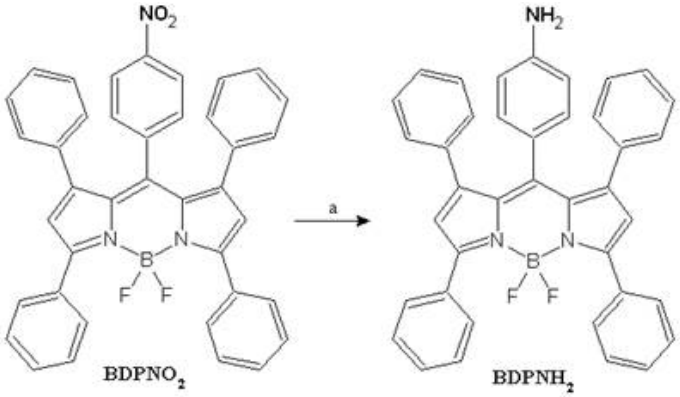

Figure 2: The synthesis of compound $BDPNH_2$ a) $(NH_2)_2$, Pd/C, THF:EtOH, reflux, 3h, Yield 41%

The identification of compounds was established by NMR spectroscopy. The most significant difference in the ^{1}H-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 $BDPNO_2$ and $BDPNH_2$ the chemical shifts observed in the higher values. For the comparison the chemical shifts of compounds TMB and $BDPNO_2$ were indicated in Figure. 3.

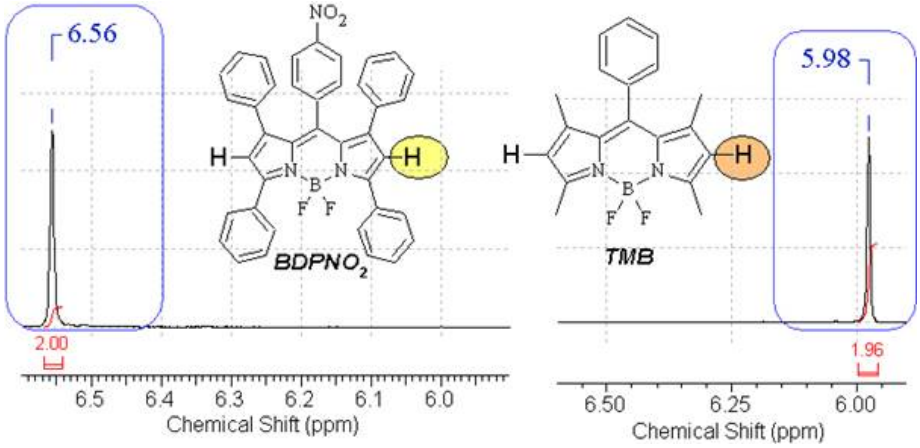

Figure 3: The scale of chemical shifts for compounds $BDPNO_2$ and TMB for pyrrolic protons in ^{1}H-NMR.

The downfield shifts of the aromatic pyrrole protons caused by the effect of aryl groups. In the series of compounds $BDPNO_2$ and $BDPNH_2$, there was a minor changes in chemical shifts of pyrrole protons when the meso substituents were changed from 4-nitrophenyl to 4-aminophenyl. Although these moieties have different donor or acceptor properties, no remarkable differences were observed in ^{1}H-NMR spectra. This is because the orthogonal geometry of meso (8) position of the indacene core.

The photophysical parameters of the dyes in dichloromethane are presented in Table 1. In general, the absorption spectra of synthesized BODIPY compounds show a similar shape as meso-substituted borondipyrromethene chromophores (Figure 4). UV-Vis absorption spectra of the compounds in DCM displayed an intense band between 553-565 nm assigned to the $S_0 \rightarrow S_1$ transitions along with high molar absorption coefficients. The broader absorption band localized between 350-400 nm is ascribed to the $S_0 \rightarrow S_2$ transitions of BODIPY moiety. Introducing aryl groups at 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 substituted counterpart. However, the molar absorption coefficients and fluorescence quantum yields were decreased.

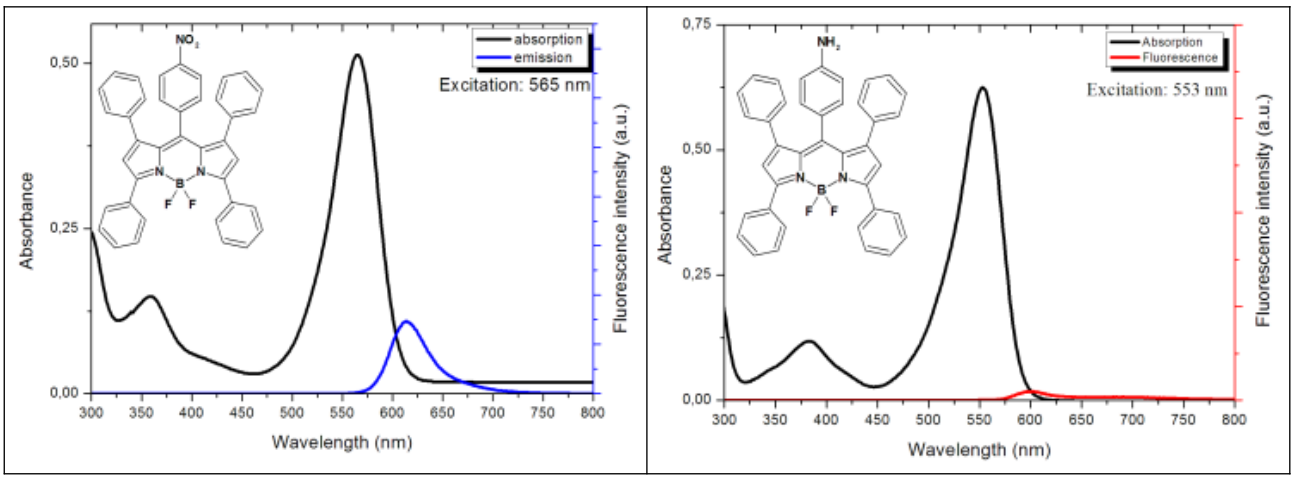

Figure 4: UV and Fluorescence spectrum of $BDPNO_2$ (left) and $BDPNH_2$ (right) in DCM.

Compounds with 4-nitrophenyl group on the 8 position of the BODIPY core showed a clear bathochromic shift in their absorption maxima, as compared to 4-aminophenyl substituted analogue $BDPNH_2$. For aryl substituted compounds, absorption bandwidths (FWHM) are 2-3 times broader than TMB counterpart. Furthermore, the fluorescence emission spectra display a Stokes-shifted (ca. 49 nm) for $BDPNO_2$, mirror-symmetrical bands relative to the absorption of BODIPY units. The stokes shift (expressed in nm) was measured as 49 nm.

Table 1. Photophysical data of synthesized compounds in DCM ($1x10^{-6}$ M)

Compound	λ_{Abs} max (nm)	λ_{Ems} max (nm)	ε ($M^{-1}cm^{-1}$)	FWHM (nm)	Stokes' shift (nm)	Φf
TMB	501	515	71400	21	14	0.36
$BDPNO_2$	565	614	51300	54	49	0.09
$BDPNH_2$	553	-	62500	51	-	-

A stokes-shifted band of perfect mirror image shape with minimum energy loss that shows the main absorption band corresponds to the $S_0 \rightarrow S_1$ transition. The diminishing fluorescence intensity for the compound $BDPNH_2$ can be attributed to the lone-pair electrons on the nitrogen atom that enables the photoinduced electron transfer. The decreasing fluorescence quantum yield of the compound $BDPNO_2$ is related with the same mechanism. 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 (23).

4-aminophenyl moiety of compound $BDPNH_2$ is sensitive to the pH and $-NH_2$ group can be protonated in acidic environments. The effect of pH was assessed by altering the solution pH from neutral to acidic environment through the addition of aq. HCl in $CH_3CN:H_2O$ (2:1). The pH dependent absorption and fluorescence graphs were given in Figure 5.

The spectroscopic data revealed that the main absorption band was nearly unchanged with a slight shift to longer wavelengths. This insignificant bathochromic shift in acidic solution may be caused by transpacer electronic interactions between the protonated $-NH_2$ subunit and the fluorophore that in agreement with the meso substitution. Besides, there is a bathochromic shift of band with higher energy in the range of 300-450 nm with decreasing pH indicate the formation of anilinium cation.

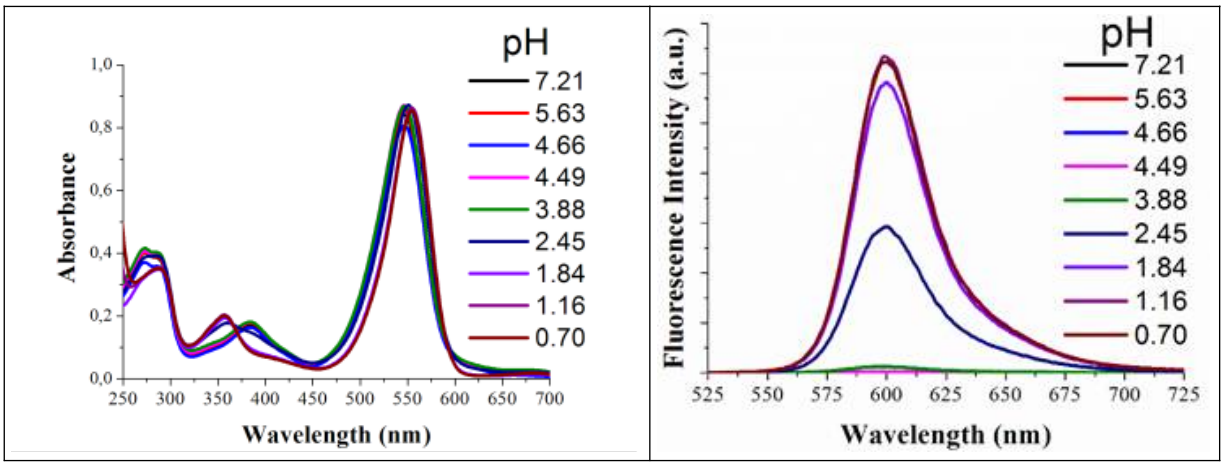

Figure 5. Dependence of the absorption (top) and fluorescence (bottom) of compound **$BDPNH_2$** on a change in pH upon addition of aq. HCl solution (excitation: 553 nm, dye concentration: 1x 10^{-5} M)

The corresponding emission features have also been investigated upon altering the pH. Although $BDPNH_2$ is not a fluorescent molecule in a neutral environment, upon protonation fluorescence signal showed drastic enhancement at a maximum emission wavelength at 600 nm. The studies were The nonlinear sigmoidal fitting of titration data was given in Figure 6. The reversibility experiments have been carried out and it was found that all changes are found to be fully reversible. The addition of pyridine to the acidic solution of compound $BDPNH_2$ resulted the fluorescence quenching as observed in the neutral solution.

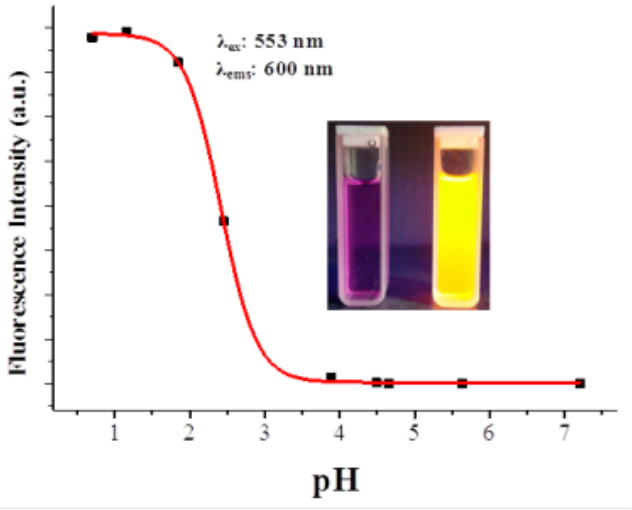

Figure 6: Nonlinear fitting of fluorescence intensity depends on decreasing pH for $BDPNH_2$, Figure inset shows Compound $BDPNH_2$ at neutral (left) and acidic (right) environment under UV irradiation**.**

hese observations can be explained by the inactivation of the acceptor type photoinduced electron transfer (PET) process between BODIPY core and the substituted group. The

intramolecular PET process strongly quenches the fluorescence of the compound $BDPNH_2$ in neutral media. The enhancement of fluorescence intensity shows that the inactivation of the PET process altered the energy level of the side group binding to the BODIPY core. This situation was depicted schematically in Figure. 7.

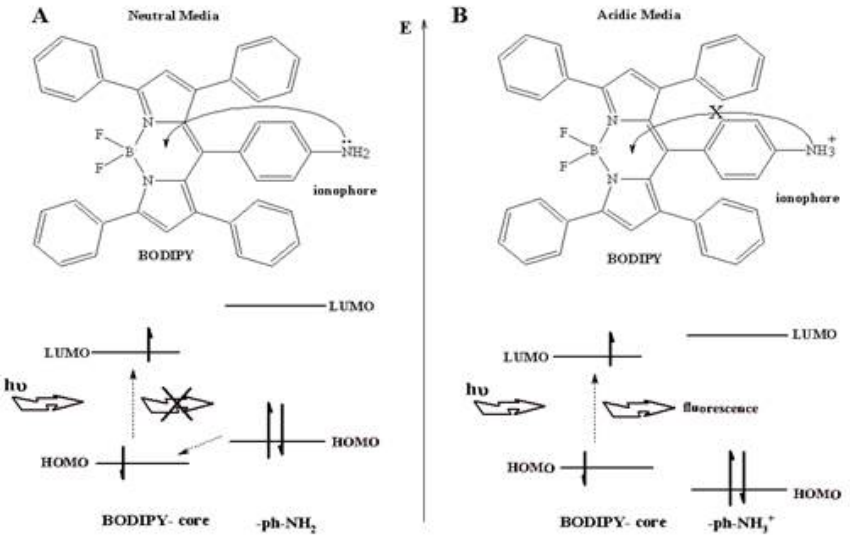

Figure 7: Proposed mechanism for fluorescence enhancement of $BDPNH_2$ in acidic media attributed by a-PET (a) quenching mechanism (b) fluorescence mechanism.

Coordination of the H^+ ion makes the ionophore electron poor and lowers the HOMO of the ionophore, so that PET from the excited BODIPY fluorophore to the ionophore becomes infeasible, leading to fluorescence enhancement.

CONCLUSION

In summary, we have synthesized new arylated BODIPY chromophores which show broadband absorption in visible spectral region. The photophysical studies exhibited that arylatedboron-dipyrromethenecompounds have the red-shifted absorption bands and 2-3 times higher stokes shifts and full width at half media (FWHM) values compared to alkyl substituted analogue (TMB). We performed the pH probe application of aminophenyl substituted $BDPNH_2$ compound which has showed drastic fluorescence enhancement upon increasing protonation. Coordination of the H^+ ion lowers the HOMO level of the ionophore. Therefore, electron transfer from ionophore to the excited BODIPY fluorophore becomes possible. This electron transfer leads to fluorescence enhancement. Our results are helpful for designing new photosensitizers and for applications in photodynamic therapy and for study of the molecular photochemistry**.**

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