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Synthesis and spectroscopic properties of a novel “turn off” fluorescent probe: Thienyl-pyridine substituted BODIPY

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ABSTRACT

We report the synthesis and photophysical properties of a new fluorophore compound **TPy-BDP**, containing thienyl-pyridine group in meso position of dipyrrin ligand. UV–Vis spectroscopy and steady state fluorimetric methods have been utilized to determine the photophysical features of this chromophore in variety of solvents. The photostability of the chromophore has been examined in solution and the dependence of spectral shifts upon solvent parameter has been studied. Also, pH sensitivity of the compound was evaluated in aqueous solutions. On binding to H^+ ions fluorescence quenching was observed by an approximately 94% reduction in the emission intensity within the pH range of 7.6–1.0 in solution. However, no obvious fluorescence change could be observed in the basic conditions. To identify the underlying mechanism of the probe depending on pH, ultrafast pump probe experiments have been performed. The results indicate that fast electron transfer known as photoinduced electron transfer between boron-dipyrromethene scaffold to the appended group are responsible to the fluorescence quenching. Experimental results proved the capability of **TPy-BDP** in terms of using under strongly acidic conditions as a pH indicator.

1. Introduction

Investigating the photophysical features of fluorescent molecules provide convenient methods in chemically or biologically important species [1–5] due to several advantages such as high sensitivity and quick response times [6]. Among the selective fluorescent sensors, difluoroborondipyrromethene compounds (derivatives of the well-known fluorophore BODIPY) are good candidates as a signaling unit with their high fluorescence quantum yields, high absorption coefficients for visible light, relative ease of preparation [7–9]. When these versatile molecules are utilized, a variety of substituents which have selective fluoroionophoric features are bonded to BODIPY core. Various substituents at BODIPY core can lead to large differences on their photophysical features [10,11]. Therefore spectroscopic changes upon selective binding of guests can be employed as a platform for the recognition of ions. Elucidating the underlying mechanism of fluorescence signaling is important and gives useful data about the designing of novel molecules with increased advantages.

In the main, spectroscopic methods have been continually published for the confirmation of the fluorescence and quenching process [12]. Additionally, computational methods such as density functional theory calculations could be informative [13,14]. However, with the development of technology, ultrafast spectroscopy can be more elucidatory because it makes possible to analyze for femto and nano scale events such as absorption and emission [15].

In the present study, we synthesized a new probe containing a novel thienyl-pyridine group. The investigation of slight structure variations influence on photophysical features can give promising results. From this point of view, we have performed ultrafast spectroscopic measurements to determine the mechanism of quenching associated with the protonation of thienyl-pyridine substituted BODIPY (**TPy-BDP**) in aqueous solution. It was seen that binding of H^+ ions resulting in quenching of its fluorescence. The response H^+ is rapid upon addition of acid. In order to better understand the pH effect on the fluorescence features on **TPy-BDP**, we have undertaken a detailed pump and probe study as a function of the H^+ ion addition. In general, researches have

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been focused on the colorimetric pH probes. However, relatively less effort has been made to obtain fluorimetric ones that sensitive in strongly acidic media. With this consideration in mind, We have successfully designed and synthesized a fluorescent molecular probe for sensing pH. We have also investigated photostability and solvent dependent photophysical properties of the probe for its practical applications.

2. Experimental

2.1. Synthesis and characterization

All solvents and chemicals were of reagent grade quality, were obtained commercially (Merck Co.) and were used without further purification. Column chromatography was used on Merck silica gel 60, 40–60 µm size). Shimadzu Infınıty FT-IR Spectrometer (equipped with ATR unit) was used for IR spectra of the compounds in the range 400–4000 cm-1 "^{1}H NMR spectra were recorded on a Varian Mercury spectrometer (400 MHz). Chemical shifts (δ) were given in ppm downfield from TMS standard, determined by chloroform (δ = 7.26 ppm). Chemical shift multiplicities were reported as s:singlet, d:dublet, dd: doublet of doublets, t:triplet and q:quartet. Hz unit were used as coupling constants. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer (Varian Mercury). ^{13}C NMR chemical shifts were reported in ppm unit with internal $CDCl_3$ (δ:77.0 ppm) as standard. Mass spectra of the compounds were performed on an Alliance Micromass MS spectrometer [12,16]."

2.2. The steady state UV–visible absorption and emission measurements

UV–visible absorption measurements were performed by Shimadzu UV-1800 spectrophotometer with 1 cm quartz cells. Perkin Elmer LS55 model Fluorescence spectrometer was used to steady state emission measurements. Both absorption and emission measurements were performed at 25 °C. Dilute solutions with an absorbance below 0.1 at the excitation wavelength (λ_{ex} = 530 nm) were used in order to obtain fluorescence quantum yields (Φ_f). In order to calculate the fluorescence quantum yield of the **TPy-BDP**, Rhodamine B was based as a standard compound in ethanol solution ((Φ_f = 0.65). In order to determine the fluorescence quantum yields of the **TPy-BDP** in different solutions, comparative method was applied [16]. Fluorescence measurements in different pH values were applied in CH_3CN-H_2O (2:1, v/v) by adding 10^{-4} M of HCl to the **TPy-BDP** dye solution (c = 3.0×10^{-6} M). The final pH values were measured using the Ohaus ST 300 pH-meter.

2.3. Photostability

The photostability experiments of **TPy-BDP** (c = 3.0×10^{-6} M in acetonitrile) were performed as shown schematically in Fig. 1. The solution was irradiated with a 125 W mercury lamp at room temperature. 3 M $NaNO_2$ solution (c = 3 M) was set up between the quartz cell and the mercury lamp for eliminating the absorption of short wavelength light and the heat. The distance between the lamp and cell was 10 cm. The decreasing of the absorption maxima at 530 nm was recorded as a function of time.

2.4. Pump probe studies

"Ultrafast pump probe spectroscopy measurements were performed by using Ti:Sapphire laser amplifier system (Spectra Physics, Spitfire Pro XP) together with optical parametric amplifier (Spectra Physics, TOPAS) and commercial pump probe setup (Spectra Physics, Helios)" [12]. Pulse duration was determined as 100 fs The excitation wavelengths (pump beam wavelength) were chosen according to the absorption band of BODIPY unit as 530 nm for **TPy-BDP** compound. The white light continuum was used as a probe beam.

2.5. Synthesis

3-oxo-3-(thiophen-2-yl)propanenitrile [17], 4,6-Dimethyl-2-(thiophen-2-yl)nicotinonitrile (TPy-nitrile) [18], 4,6-Dimethyl-2-(thiophen-2-yl)nicotinaldehyde (TPy-ald) were synthesized according to the method described in literatüre [19]. The synthesis of the target molecules were given in Schemes 1 and 2.

2.5.1. Synthesis of 4,6-Dimethyl-2-(thiophen-2-yl)nicotinonitrile (TPy-nitrile)

A mixture of 3-oxo-3-(thiophen-2-yl)propanenitrile (1.81 g, 12.0 mmol), ammonium acetate (1.85 g, 24.0 mmol) and acetylacetone (1.20 g, 12.0 mmol) was dissolved in glacial acetic acid (20 mL). The resulting mixture was refluxed 24 h. After cooling to room temperature, the reaction mixture was poured over cold water and the precipitate was collected by filtration. Crystallization from EtOH afforded a pale yellow solid (2.05 g, 80%, mp: 104–105 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3H), 2.57 (s, 3H), 6.98 (s, 1H), 7.15 (dd, 1H, J = 5.2, 4.0 Hz), 7.50 (dd, 1H, J = 5.2, 1.2 Hz), 8.22 (dd, 1H, J = 4.0, 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 20.8, 25.0, 102.1, 117.5, 122.4, 128.6, 128.8, 130.3, 142.5, 152.7, 153.7, 162.0. LC-MS, m/z (%): 215.3 ([M $+$H]$^+$,100).

2.5.2. Synthesis of 4,6-Dimethyl-2-(thiophen-2-yl)nicotinaldehyde (TPy-ald)

Diisobutyl aluminum hydride (6 mL, 6.0 mmol, 1 M solution in toluene) was slowly added under nitrogen atmosphere to a solution of **TPy-nitrile** (0.92 g, 4.3 mmol) in dichloromethane (30 mL). The mixture was heated at reflux for 4 h. After this period, the reaction mixture was treated with a mixture of ice and 10% sulphuric acid and extracted with dichloromethane. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated. The crude product was purified by chromatography using ethyl acetate/hexane (1:5) as the eluent to afford as a yellow solid (0.46 g, 53%, mp: 53 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.59 (s, 3H), 2.60 (s, 3H), 7.01 (s, 1H), 7.14 (d, 2H, J = 3.2 Hz), 7.55 (t, 1H, J = 3.2, 1.2 Hz), 10.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCI_3$) δ: 20.8, 24.7, 125.0, 126.3, 127.8, 129.5, 131.4, 141.4, 149.4, 155.7, 161.7, 193.0. ES/MS, m/z (%): 218.0 ([M+H]$^+$, 100). FT-IR (Atr, cm^{-1}): 2960, 2924, 2852, 1672 (CO), 1583, 1537, 1429, 1406, 1375, 1344, 1247, 1219, 1149, 1029, 852, 812,790, 752, 719.

2.5.3. Synthesis of 8-[4,6-dimethyl-2-(2-thiophen-2yl)pyridin-3-yl]-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (TPy-BDP)

2,4-Dimethyl-3-ethylpyrrole (0.37 g, 3.0 mmol) and **TPy-ald** (0.30 g, 1.4 mmol) was mixed with 200 mL CH_2C1_2 in a flat bottom flask. The reaction mixture was purged with argon bubbles for 5 min. Then, one drop of trifluoroacetic acid was added as a catalyst at room temperature. The red colored solution was stirred for 15 h. After this period, the oxidizing agent 2,3,5,6-tetrachloro-1,4-benzoquinone (0.51 g, 2.1 mmol), then 6 h later N,N-diisopropylethylamine (DIPEA) (1.24 g, 9.7 mmol) and finally $BF_3.Et_2O$ (2.16 g, 15.2 mmol) were added respectively. After stirring for 3 h, the reaction solution was washed by extraction with water, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography using ethyl acetate/hexane (1:2) solution to afford **TPy-BDP** in the form of brown-green powder (0.16 g, 23%, mp: 155 $^{\circ}$C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, 6H, J = 7.6 Hz), 1.34 (s, 6H), 2.15 (s, 3H), 2.24 (q, 4H, J = 7.6 Hz), 2.55 (s, 6H), 2.62 (s, 3H), 6.90 (dd, 1H, J = 4.8; 4.0 Hz), 7.03 (s, 1H), 7.27 (dd, 1H, J = 5.2; 1.2 Hz), 7.33 (dd, 1H, J = 4.0; 1.2 Hz). ^{13}C NMR (100 MHz, $CDCI_3$) δ: 158.5, 154.6, 149.1, 146.9, 143.7, 137.5, 136.5, 133.0, 130.1, 128.5, 128.3, 127.7, 125.1, 123.3, 24.6, 19.6, 17.3, 14.9, 12.9, 11.4. ES/MS, m/z (%): 492.2 ([M $+$H]$^+$,100). FT-IR (Atr, cm^{-1}): 2962, 2926, 2870, 1585, 1541 (B-N), 1473, 1406, 1317, 1267, 1190 (B-F), 1114, 1074, 977, 862, 796, 731.

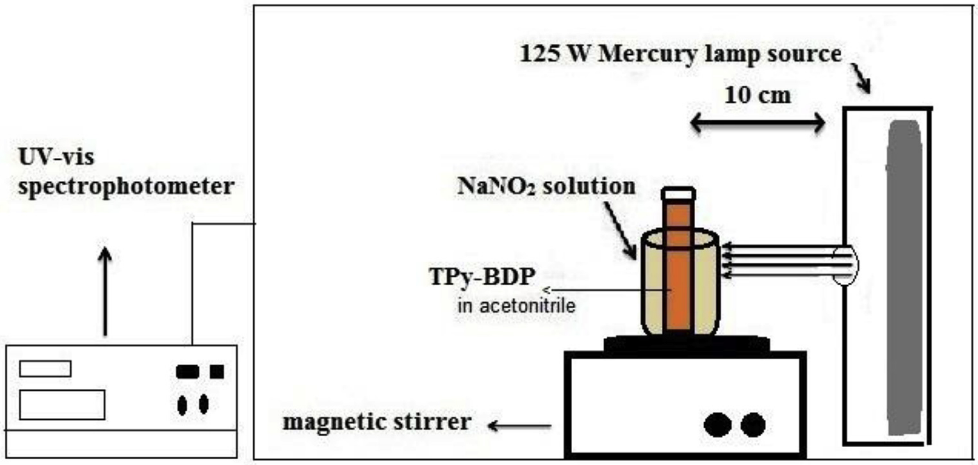
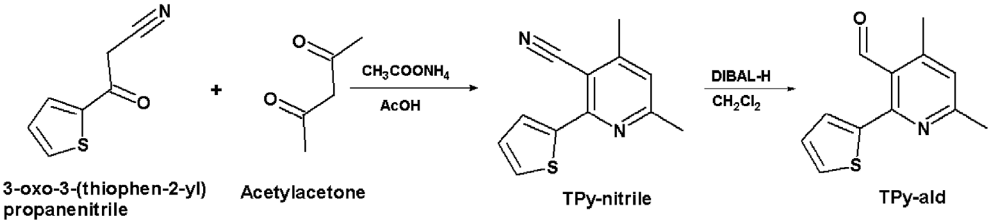
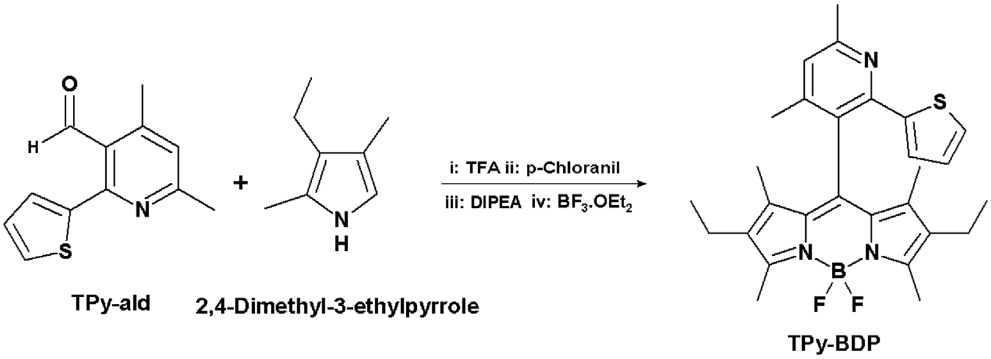


Fig. 1. Experimental setup for the determination of photostability of **TPy-BDP**.



Scheme 1. The synthesis of the starting aldehyde; **TPy-ald**.



Scheme 2. The synthesis of the target molecule; **TPy-BDP**.

Anal. Calc. (%) for $C_{28}H_{32}BF_2N_3S$: C, 68.43; H, 6.56; N, 8.55. Found: C, 68.41; H, 6.58; N, 8.53.

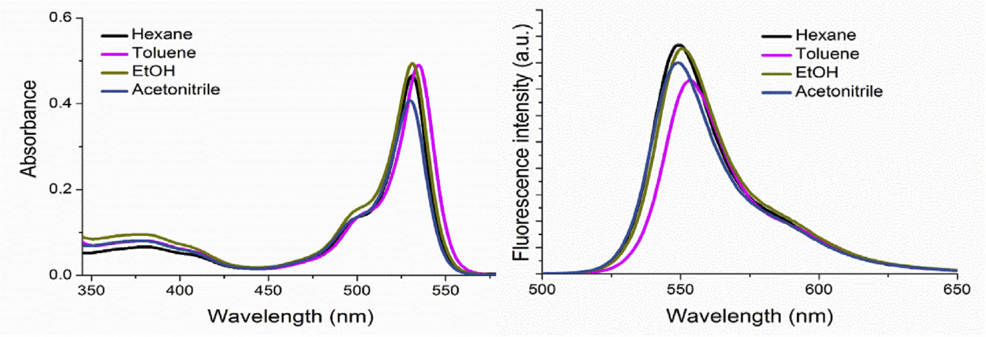
3. Results and discussion

3.1. Photophysical properties

The absorption spectra of **TPy-BDP** in several solvents are shown in Fig. 2a, and the photophysical data are compiled in Table 1.

TPy-BDP in various solvents show intense and narrow absorption band at 534 ± 4 nm, which is attributed to the effective S_0-S_1 transition with molar extinction coefficient on the order of 140,000 $M^{-1}cm^{-1}$. A shoulder at 504 ± 4 nm is assigned to the vibrational band of the same S_0-S_1 transition. A considerably weaker and broader absorption band at about 375 nm corresponding to the S_0-S_2 transition of the BODIPY core with a high energy level was also seen in all solvents studied.

As can be seen clearly from Table 1, the absorption spectra of **TPy-BDP** is similar to those of the classical meso-substituted BODIPY dyes [20] in pure solvents. Besides, minority of the solvent dependent shifts indicates a weak charge transfer (the absence of donor-acceptor interaction) for the S_0-S_1 excitation. This is due to indacene plane and meso substituent is practically vertical to each other as has been observed in BODIPY dyes [20,21]. To confirm the effect of solvent polarity on transition energies, emission spectra of the dye in various solvents and the summary was presented in Table 1. **TPy-BDP** showed the typical emission characteristics of meso-substituted BODIPYs [22] (Fig. 2b). A slightly Stokes-shifted band gave mirror image shape with minimum energy loss that shows the absorption band at 530 nm corresponds to the S_0-S_1 transition. In terms of the fluorescence quantum yields the maximum value was obtained in cyclohexane solution ($\Phi_f = 0.53$) and the yields show a tendency to decrease as the polarity of solvents increase. Furthermore, the Stokes shifts ($\Delta\bar{\upsilon}$; expressed in cm^{-1}) ranged 611 to 678 cm^{-1}. The fluorescence excitation spectra of **TPy-BDP** overlap the UV/Vis spectra (see supporting information). In order to describe the solvent effect as a function of Stokes shifts ($\Delta\bar{\upsilon}$), we used to Lippert-Mataga expression [23]. To this end, we measured the dependence of spectral shifts upon Lippert solvent parameter (Δf) [24] and plotted to $\Delta\bar{\upsilon}$ values as a function of Δf (Fig. 3) by studying with various solvents which have different refractive indices (n) and dielectric



(a) (b)

Fig. 2. (a) Absorption and (b) Fluorescence spectra of **TPy-BDP** (3×10^{-6} M) in hexane, toluene, ethanol and acetonitrile. The limited number of spectra were shown to a better clarity because all spectra have similar shape.

constants (ε). The Δf values were calculated according to equation (1) [25].

$$\mathbf{\Delta f = f(\varepsilon) -\ f}\left(\mathbf{n}^2 = \frac{\varepsilon-1}{2\ \varepsilon+1} - \frac{\mathbf{n}^2-1}{2\mathbf{n}^2+1}\right) \tag{1}$$

As is evident from Fig. 3, there is a poor linearity (correlation coefficient r = 0.032) between the Stokes shift $\Delta\bar{\upsilon}$ versus Δf for the solvents indicated in Table 1. The independence between Stokes shift and Δf proves the presence of minor solvatochromism that, the dyes permanent dipole moment are similar both in the ground and excited states [26].

It is known that, the low magnitude of Stokes shift indicates the independence of the excited state geometry with the ground state geometry. Furthermore, an increase in the polarity of the solvent with the Stokes shifts implies the increment in the dipole moment of the molecule [27]. Thus, a conclusion can be drawn from results that, the permanent dipole moment of the **TPy-BDP** is similar and solvent independent in the ground and excited states which is supported by the minority of the spectral shifts.

BODIPY dyes are known with their stability against light [20]. This is a crucial feature for applications of fluorescent compounds. The fluorescence properties of these dyes have been extensively studied. However, little work has been reported on the photostability of these dyes, which included the different substituted subunits. Because, the fact that, generally, photostability is influenced by substituents on a large scale. Therefore, we intended to measure the degree of photofading. The photofading process of **TPy-BDP** was researched by measuring the decrease of main absorption wavelength in acetonitrile upon irradiation for 8 h. The effect of light to the main absorption band of **TPy-BDP** has shown in Fig. 4 versus the time.

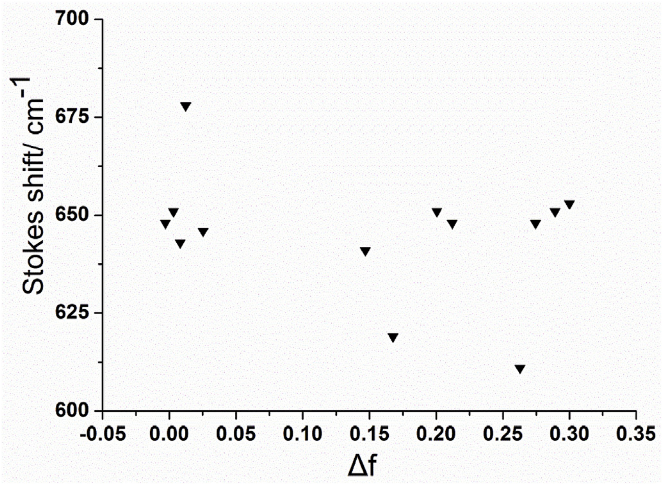


Fig. 3. The Correlation graph of Stokes shifts for **TPy-BDP** in various solvents against the Lippert solvent parameter Δf.

Based on the following equation, which describes the first-order kinetics, we plotted the $\ln(A_0/A_t)$ versus irradiation time [28].

$$\mathbf{In}\frac{\mathbf{A_0}}{\mathbf{A_t}} = \mathbf{k.\ t} \tag{2}$$

A_0 and A_t are the absorbance maximum in the main absorption band of **TPy-BDP** at 530 nm before and after irradiation respectively. The plot gave a straight line which slope equals the apparent first-order rate constant k, as 0.29×10^{-2} mol min^{-1} and the chromophore has decayed in the rate of 5% upon irradiation for 8 h. This result shows that, **TPy-BDP** has been affected by light moderately. It also gives

Table 1
Photophysical data of **TPy-BDP** in several solvents.

Solvent	Abs. Max (nm)	Ems. max (nm)	ε (M^{-1} cm^{-1}) x 10^4	FWHM (nm)	Stokes shift (cm^{-1})	Refractive index (n)	Dielectric Constant (ε)	Lippert parameter (Δf)	Φ_f
Cyclohexane	532	551	7.6	23	648	1.43	2.02	0.00	0.53
Hexane	531	550	7.0	23	651	1.37	1.90	0.00	0.52
CCl_4	534	553	8.2	24	643	1.47	2.24	0.01	0.50
Toluene	533	553	7.4	24	678	1.50	2.38	0.01	0.49
1,4 Dioxane	533	552	7.5	25	646	1.42	2.25	0.03	0.49
Chloroform	535	554	7.6	24	641	1.45	4.81	0.15	0.49
Et_2O	530	548	5.7	24	619	1.35	4.33	0.17	0.50
Ethyl acetate	531	550	7.8	25	651	1.37	6.02	0.20	0.47
THF	532	551	7.2	24	648	1.40	7.58	0.21	0.46
DMSO	534	552	6.0	27	611	1.48	46.70	0.26	0.44
DMF	532	551	7.2	26	648	1.43	36.70	0.27	0.44
EtOH	531	550	7.4	25	651	1.36	24.50	0.29	0.47
CH_3CN	530	549	6.1	25	653	1.34	27.50	0.30	0.45

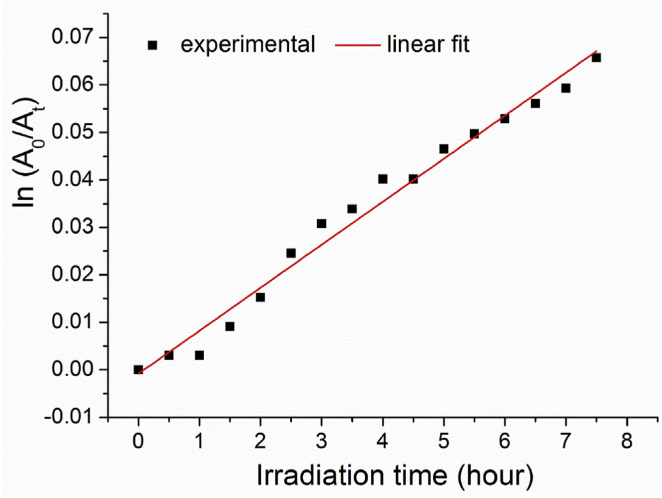


Fig. 4. The effect of light on the main absorption band of **TPy-BDP** at 530 nm.

information about the fluorescence quantum yield (Φ_f). Because, There is an inverse proportion between photostability and the fluorescence quantum yields in BODIPY compounds [28] and consequently **TPy-BDP** with value of fluorescence quantum yield as 0.45 could be assumed to have a moderate photostability in solution.

3.2. Acid-base titration studies

The thienyl-pyridine moiety of **TPy-BDP** is sensitive to the pH and can be protonated in acidic environment. Determining the effect of the environmental acidity in solution was performed by altering the pH through the addition of HCl in acetonitrile-water (2:1, v/v) and the UV spectra were given in Fig. 5. When the pH of the solution was decreased a slight shift on the main absorption band of the compound was observed. This minor shift may be due to interactions between the protonated thienyl-pyridine subunit and the BODIPY core in acidic media [29]. Apart from the main absorption band shifted from 532 to 539 nm, there is a broader absorption between 290 and 325 nm localized at 304 nm. This transition which was not observed on the reference BODIPY compound (see supporitng information) can be attributed to meso-substituted, thienyl pyridine group that shifts the longer wavelength upon protonation.

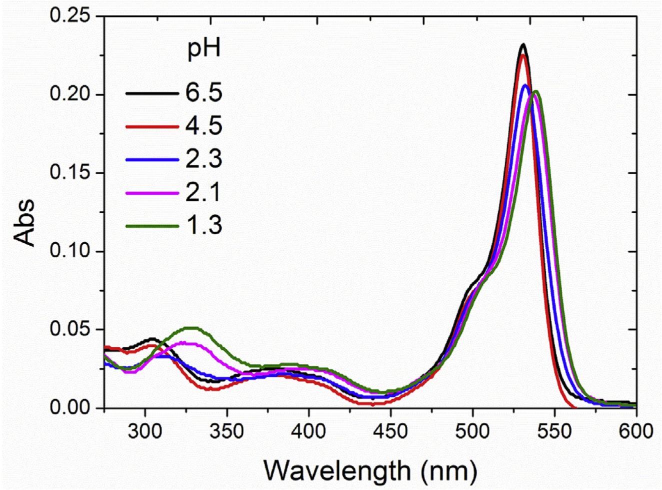


Fig. 5. Absorption spectra of **TPy-BDP** in acetonitrile-H_2O (2:1, v/v). The limited number of spectra were shown to a better clarity.

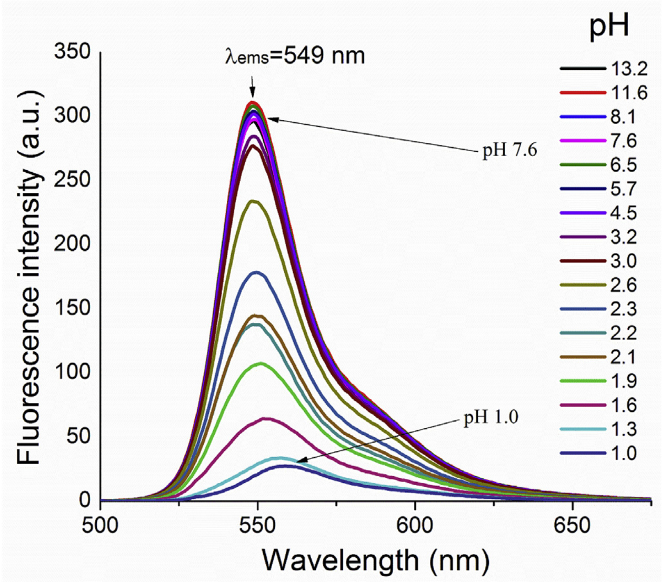


Fig. 6. Fluorescence spectra, excited at 530 nm using 3.0×10^{-6} M solution of **TPy-BDP** in acetonitrile-H_2O mixture (2:1, v/v). pH values are in order of decreasing intensity.

The corresponding emission features have also been investigated upon pH. **TPy-BDP** exhibits drastic fluorescence quenching in acetonitrile-H_2O (2:1, v/v) solution upon addition of HCl. Although there is a slight shift of emission wavelength (Fig. 6), fluorescence intensity was observed to be drastically quenched at 549 nm. In addition, the reversibility experiments have been carried out that all changes are found to be fully reversible. The similar fluorescence intensity at neutral media was obtained depending on the addition of pyridine to a protonated forms of the fluorophore in solution. Although the fluorescence emission of **TPy-BDP** was quenched in acidic media, upon addition of base to a neutral solution, no changes were observed. The acidity constant k_a of the dye was determined by direct fluorimetric titration using the fluorescence emission spectra as described in the previous study [12] that the apparent pK_a value was obtained as 2.50. The titration plot was shown in Fig. 7.

These results indicate that, **TPy-BDP**, having a thienyl-pyridine receptor part, has a big affinity and serves as a highly sensitive fluorescent probe for the measurement of pH. Although there is no intramolecular

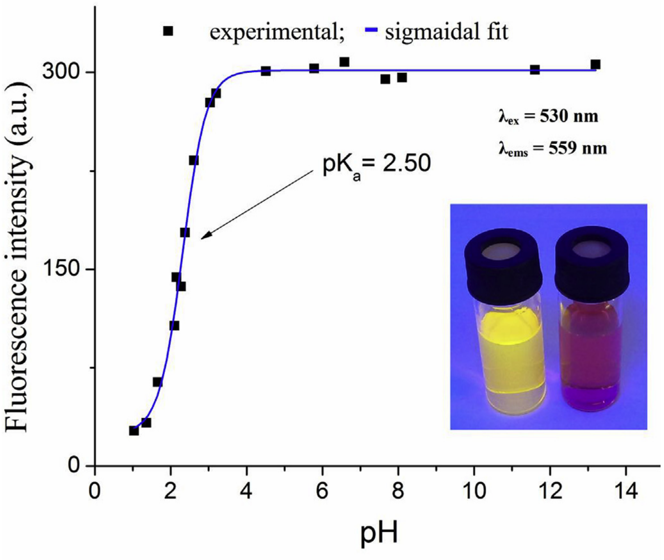


Fig. 7. Fluorescence intensity-pH profiles of the **TPy-BDP.** Figure inset shows **TPy-BDP** at neutral (left) and acidic (right) environment under UV irradiation.

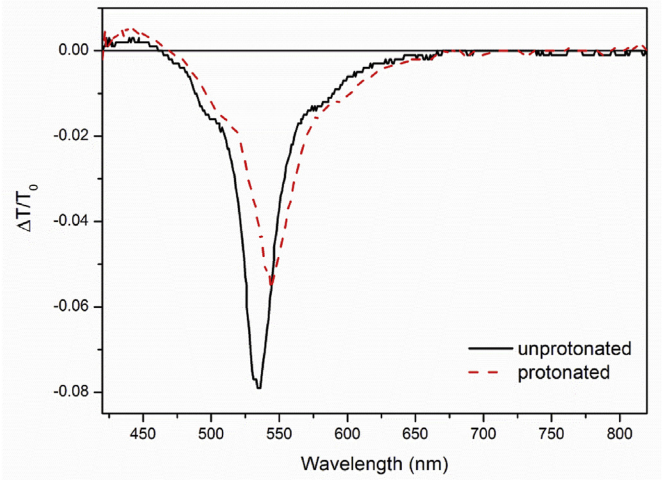


Fig. 8. Femtosecond transient absorption spectra of protonated and unprotonated **TPy-BDP** compound.

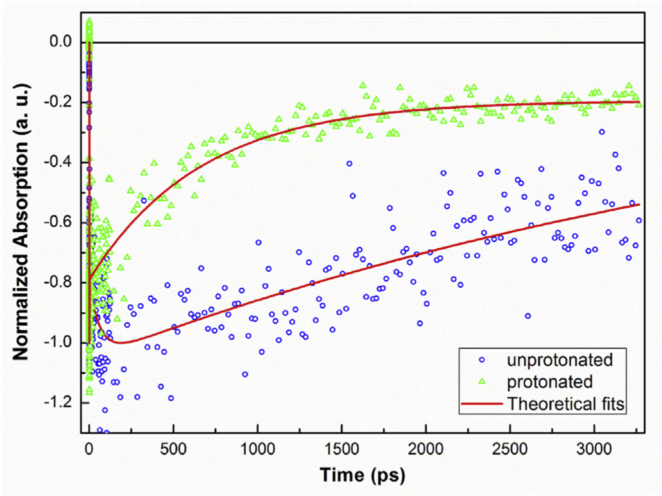


Fig. 9. The decay curves of protonated and unprotonated **TPy-BDP** compounds.

electron transfer in neutral media between BODIPY core and thienyl-pyridine group proved by the slight changes on fluorescence quantum yields depend on the polarity of the solvents (Φ_f: 0.52 and 0.47 in hexane and ethanol for **TPy-BDP**, respectively), the fluorescence quenching in acidic media could be caused by the activation of photoinduced electron transfer process between BODIPY core and the substituted group. In an attempt to make sure that the quenching mechanism in TPy-BDP is related to the PeT, we performed utrafast pump probe spectroscopy measurements under the neutral and protonated form.

3.3. Pump probe spectroscopy studies

In order to clarify fluorescence quenching process, the ultrafast pump probe experiments were performed for both neutral and the acidic form of the **TPy-BDP** in solution. 530 nm which was corresponding the main absorption band of the compound was used as the pump beam for the neutral and acidic solution. The spectra of compound for both in neutral and acidic media show strong single bleach signal at 535 nm and 545 nm, respectively (Fig. 8). The stimulated emission and ground state bleach absorption of the fluorophore group may cause the related negative signals which were also observed some pyrromethene–BF_2 fluorophores [30]. The ground state bleach signals for protonated and unprotonated compounds were fitted to the multi-exponential decay functions. Bleach signal of the unprotonated compound can be fitted with biexponential decay which gives tens of ps, and around a couple of ns lifetimes. Although the signal for the protonated compound has similar decay components, it has an additional ultrafast component as ~600 fs as seen in Fig. 9. That means, the ground state bleach signal decays faster while protonation.

The ultrafast component might be explained with electron transfer from LUMO level of the BODIPY moiety to some other state (charge transfer state) which might be LUMO energy level of thienyl-pyridine moiety in **TPy-BDP** compound. Since the energy level of the charge transfer state is very close to the LUMO energy level of the BODIPY, there is no extra bleach signal at longer wavelengths than the ground state bleach signal as an indication of the saturation of the LUMO energy level of thienyl-pyridine moiety (Fig. 8). The possible extra signal might be coverd with ground state bleach signal. The ultrafast electron transfer from the LUMO level of the BODIPY moiety to the charge transfer state causes dramatic decreasing of the fluorescence intensity for protonated **TPy-BDP** compound as seen in fluorescence quenching figure (Fig. 6).

These results, evidently indicate the activation of the photoinduced electron transfer process in acidic media. The electron transfer at the femtosecond scale from the LUMO level of the fluorophore to the substituted thienyl pyridine part depending on the excitation leads fluorescence quenching.

4. Conclusions

A novel compound (TPy-Ald) including thienyl-pyridine group was synthesized and characterized from the starting nicotinonitrile derivative (TPy-nitrile). A novel Borondipyrromethene molecule (TPy-BDP) was synthesized, characterized and examined as fluorescent sensor for pH. Photophysical properties in various solvents and photostability of this compound has been investigated. Solvent dependent measurements confirmed that meso substitution did not alter the characteristic photophysical features of the synthesized BODIPY chromophore significantly. The chromophore has decayed in the rate of 5% upon irradiation, showed the influence by light moderately. The binding study showed fluorescence quenching in the presence of H^+ ions. Such a high proton induced fluorescence quenching makes **TPy-BDP** sensitive probe for these ions. Findings from the pump probe spectroscopy measurements suggest that, the main quenching mechanism in the meso-substituted BODIPY dyes causes on/off type fluorescence quenching which is named PET (photoinduced electron transfer). Obtained results extend the scope of borondipyrromethene chromophores available as sensors and the **TPy-BDP** can be used as a pH probe in the strongly acidic media.

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Appendix A. Supplementary data

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