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ORIGINAL PAPER

Synthesis and Properties of *Meso*-unsubstituted 3-Pyrrolyl Boron Dipyrromethene

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Abstract We report the synthesis of *meso*-free 3-pyrrolyl boron dipyrrin (3-pyrrolyl BODIPY) and fully unsubstituted *meso*-free boron dipyrrin (parent BODIPY) in one pot under simple reaction conditions by treating *meso*-free dipyrromethane with pyrrole in $CHCl_3$ followed by oxidation with DDQ, neutralization with triethylamine and complexation with $BF_3.OEt_2$. The compounds were separated by column chromatography on silica and isolated in 6–10 % yields. The compounds are characterized by HR-MS mass, NMR, absorption, electrochemical and fluorescence techniques. The *meso*-free 3-pyrrolyl BODIPY exhibit red shifted absorption and emission bands compared to *meso*-free BODIPY. The *meso*-free BODIPY exhibit green fluorescence and *meso*-free 3-pyrrolyl BODIPY exhibit orange fluorescence in solution. Furthermore, compared to *meso*-phenyl 3-pyrrolyl BODIPY, the *meso*-free 3-pyrrolyl BODIPY is more strongly fluorescent with nearly 41 % increase in quantum yield. Electrochemical studies showed that *meso*-free 3-pyrrolyl BODIPY exhibit one irreversible reduction and one ill-defined oxidation indicating that the compound is not stable under redox conditions. Computational studies revealed that *meso*-free pyrrolyl BODIPY has reduced HOMO-LUMO gap compared to parent *meso*-free BODIPY. Furthermore, the *meso*-free 3-pyrrolyl BODIPY exhibit much higher quantum yield compared to *meso*-aryl analogue of 3-pyrrolyl BODIPY.

Keywords *meso*-free BODIPY · *mes*-free 3-pyrrolyl BODIPY · Bright fluorescence · High quantum yields · Red shifted absorption and emission bands · Large singlet-state lifetime

Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) chromophores containing the monoanionic, conjugated dipyrromethene ligands are highly fluorescent compounds and known for their small Stokes shifts, high quantum yields, sharp excitation and emission peaks [1–3]. These properties render them very useful for various applications including their use as fluorescent labels in biological systems and as laser dyes [4, 5]. However, the photophysical properties such as large quantum yields and singlet state lifetimes of these dyes are extremely sensitive to the type of substituents present at the BODIPY core and in general, the β-substituted BODIPYs exhibit intense fluorescence with high quantum yields and large singlet state lifetimes compared to *meso*-substituted BODIPYs [6, 7]. This is attributed to the *meso*-aryl group rotation which enhances the distortions in boron dipyrrin framework leading to an excited-state conformer with low radiative probability and facile nonradiative deactivation to the ground state. However, the recent studies showed that the quantum yields and lifetimes of *meso*-substituted BODIPYs can be exponentially increased by providing internal steric hindrance toward *meso*-aryl group which reduces aryl ring rotation and thereby prevents nonradiative decay channels. Thus, the *meso*(8-phenyl) boron dipyrromethene **1** bearing no internal steric hindrance exhibits Φ_f=0.062 and τ_f=0.45 ns whereas the *meso*(o-tolyl) boron dipyrromethene **2** (Fig. 1) bearing strong internal hindrance

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exhibits Φ_f=0.93 and τ_f=5.8 ns [6]. Thus, by suitable modifications on the BODIPY framework, the fluorescence properties particularly high quantum yields and lifetimes can be obtained [8–10]. Furthermore, it is very recently shown that the fully unsubstituted BODIPY **3** with no substituents at *meso* as well as at pyrrole carbons exhibit high fluorescence yield (0.95) and singlet state lifetime (6.89 ns). However, the synthesis of completely unsubstituted BODIPY is reported only in 2009 by oxidising the dipyrromethane with DDQ followed by complexation with $BF_3{\cdot}OEt_2$ at -78 °C [11]. The reason for the failure to prepare the completely unsubstituted BODIPY until recently was due to the unstable nature of the dipyrromethene intermediate which decomposes even at -40 °C. Alternately, the fully unsubstituted BODIPY **3** was also prepared at the same time in nearly quantitative yield by treating 8-thiomethyl BODIPY with triethylsilane in the presence of a catalytic amount of Pd and a stoichiometric amount of copper(I) thienyl-2-carboxylate in THF at 55 °C [12]. Furthermore, it was also shown recently that the compound **3** can be prepared by condensing 2-pyrrole carboxaldehyde and pyrrole in 1:1 ratio in CH_2Cl_2 in the presence of catalytic amount of trifluoroacetic acid at room temperature followed by deprotonation with diethyldiisopropylamine and subsequent complexation with $BF_3{\cdot}OEt_2$ [13]. All these approaches now allow us to prepare the parent BODIPY **3** to explore its potential use for various applications. Recently, we reported the synthesis of *meso*-phenyl substituted 3-pyrrolyl boron dipyrromethene **4** by carrying out the nucleophilic substitution reaction on *meso*-aryl dipyrromethene with pyrrole followed by complexation with $BF_3{\cdot}OEt_2$ [14]. The 3-pyrrolyl *meso*-phenyl BODIPY **4** absorbs and emits at much longer wavelengths and possesses decent quantum yield and high singlet state lifetime compared to *meso*-phenyl BODIPY **1**. Thus, the pyrrole at 3-position of BODIPY significantly enhances the photophysical properties of compound **4** hence useful for biological studies. Infact, the chemical company, Invitrogen (formerly Molecular Probes) markets the 3-pyrrolyl BODIPY complexes which have been used as biological labels because of their excellent photophysical properties and biocompatibility [15]. However, the 3-pyrrolyl BODIPYs are very expensive and available in small quantities. Interestingly, completely *meso* and pyrrole unsubstituted parent 3-pyrrolyl BODIPY such as compound **5** is not available commercially and to the best of our knowledge, there is no approach available to synthesize the parent 3-pyrrolyl BODIPY **5**. This may be because of the unstability of precursors and intermediate compounds involved in the preparation of this type of compound. Here in, we report the synthesis of fully unsubstituted parent 3-pyrrolyl BODIPY **5** under room temperature conditions using readily available precursors. Furthermore, the fully unsubstituted parent BODIPY **3** also obtained as a side product in decent yield under room temperature conditions which indicates that low temperature conditions used earlier is not necessary to obtain parent BODIPY **3**. Thus, we report the synthesis of two novel fully unsubstituted parent BODIPYs **3** and **5** prepared in one flask under simple room temperature conditions.

Experimental Section

General

THF and toluene were dried over sodium benzophenone ketyl and chloroform, ethyl-acetate, methanol, acetonitrile dried over calcium hydride distilled prior to use. $BF_3{\cdot}OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Sigma-Aldrich (USA) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh).

Instrumentation

^{1}H NMR spectra (δ in ppm) were recorded using Varian VXR 300 & 400 MHz and Bruker 400 MHz NMR spectrometer. ^{13}C NMR spectra were recorded on Varian and Bruker spectrometer operating at 100.6 MHz. ^{19}F NMR spectra were recorded on Bruker operating at 376.4 MHz. ^{11}B NMR spectra were recorded on Bruker operating at 128.4 MHz. TMS was used as an internal reference for recording ^{1}H (of residual proton; δ 7.26) and ^{13}C (δ 77.0 signal) in $CDCl_3$. Absorption and steady-state fluorescence spectra were obtained with Varian Cary Eclipse and PC1 Photon Counting Spectrofluorometer manufactured by ISS, USA instruments respectively. Fluorescence spectra were recorded at 25 °C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm in ethanol using

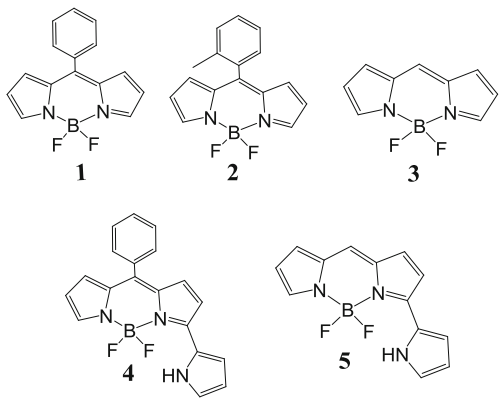


Fig. 1 Molecular structures of boron-dipyrromethenes **1–5**

Rhodamine 6 G (Φ_f=0.88) [16] as standard. High-resolution mass spectrum was obtained from Q-TOF instrument by electron spray ionization (ESI) technique.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}$ (Fc/Fc^+)= 0.48 V, vs SCE [17].

Computational Studies

The computational studies were performed with Gaussian 03 [18] installed on windows operating system. The structures of compounds **3** and **5** were generated with Chem3D utility in Chemoffice. The structures were subjected to simple molecular dynamics simulation for 10 fs time length to identify local minima. The last structure from trajectory was taken up and were energy optimized using quantum mechanics with density functional theory (DFT) and B3LYP gradient corrected correlation functional method in conjugation with standard 6-31 G(p,d) basis set and parameters. For the optimized structures, complete population analyses studies were done. Electron affinity and ionization potentials were also predicted computationally.

General Procedure for the Synthesis of BODIPYs 3 and 5

A sample of *meso*-free dipyrromethane **6** (1.38 mmol) was dissolved into $CHCl_3$ (30 mL) and oxidized with DDQ (4.14 mmol) at room temperature for 10 min. Pyrrole (4.0 mmol) was added and the reaction mixture stirred for an additional 10 min. During this period, the reaction mixture turned from yellow to red. Triethylamine (55.2 mmol) followed by $BF_3{\cdot}Et_2O$ (69 mmol) was added, and the reaction mixture was heated at 50 °C for an additional 30 min. The TLC analysis of crude compound showed two spots; the first spot corresponding to the required *meso*-free pyrrolyl BODIPY **5** and the second spot corresponding to the unsubstituted *meso*-free BODIPY **3**. The crude compound was subjected to silica gel column chromatography and the required BODIPYs were collected using of petroleum ether/ethylacetate (94:4) as brown solids.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (3)

Yield 10 %. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm) 6.6 (d, ^3J=4.1 Hz, 2H), 7.2 (d, ^3J=4.0 Hz, 2H), 7.4 (s, 1H), 7.9 (br s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ in ppm) 119.0, 131.5, 131.7, 135.4, 145.3. ^{19}F NMR ($CDCl_3$, 282.4 MHz, δ in ppm) -145.2 (q, $J_{B\text{-}F}$=56.5 Hz). ^{11}B ($CDCl_3$, 96.3 MHz, δ in ppm) 0.31(t, $J_{B\text{-}F}$=29.5 Hz). HR-MS mass calcd. for (C_9H_7BF): 173.0686 $[M\text{-}19]^+$ found: 173.0683 $[M\text{-}19]^+$.

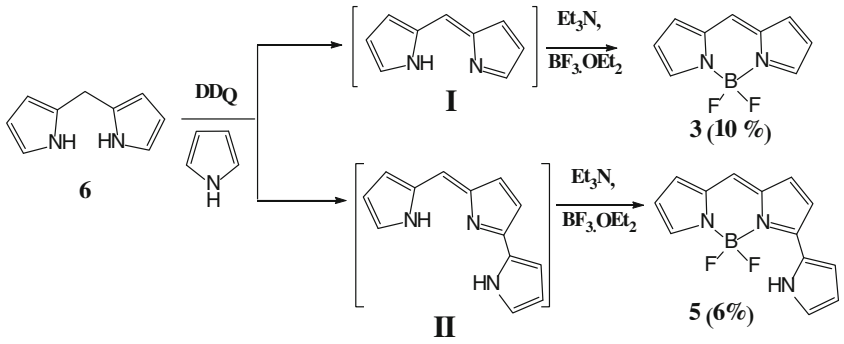
4,4-Difluoro-3-(2-pyrrolyl)-4-bora-3a,4a-diaza-*s*-indacene (5)

Yield 5–7 %. ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm) 6.39–6.41 (m, 1H; py), 6.45–6.46 (m, 1H; py), 6.88 (d, 1H, ^3J(H,H)= 3.6 Hz; py), 6.93 (d, 1H, ^3J(H,H)=4.7 Hz; py), 7.05–7.07 (m, 1H; Py), 7.09 (s, 1H; CH), 7.13 (d, 1H, ^3J(H,H)=4.7 Hz; py), 7.20–7.21 (m, 1H; py), 7.61 (s, 1H; py), 10.51 (s, 1H; -NH). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ in ppm) 112.1, 116.3, 119.3, 121.5, 123.7, 123.9, 124.7, 127.1, 133.2, 137.1, 138.8. ^{19}F NMR ($CDCl_3$, 282.4 MHz, δ in ppm) -141.2 (dq, J(B,F), J(H, F), $J_{B\text{-}F}$=56.5 Hz). ^{11}B ($CDCl_3$, 96.3 MHz, δ in ppm) 1.34(t, $J_{B\text{-}F}$=29.5 Hz). HR-MS mass calcd. for ($C_{13}H_{10}BFN_3$): 238.0950 $[M\text{-}19]^+$ found: 238.0952 $[M\text{-}19]^+$.

Results and Discussion

The fully unsubstituted 3-pyrrolyl BODIPY **5** along with unsubstituted BODIPY **3** were prepared in one flask starting with *meso*-unsubstituted dipyrromethane **6** as shown in Scheme 1. The *meso*-unsubstituted dipyrromethane **6** was prepared by following the literature procedure [19]. Upon treatment of one equivalent of formaldehyde with excess pyrrole in acetic acid under mild room temperature conditions followed by work-up and column chromatographic purification afforded **6** as white solid in 40 % yield. The compound **6** was treated with one equivalent of DDQ in $CHCl_3$ at room temperature in air for maximum period of 10 min and then three equivalents of pyrrole was added. The reaction mixture was stirred for additional 10 min. Triethylamine followed by $BF_3{\cdot}OEt_2$ were added to the reaction mixture and stirred in air at room temperature for 30 min. TLC analysis at this stage showed two clear major spots corresponding to the required compound **5** along with **3**. The crude compound was subjected to column chromatography on silica and the first band corresponding to the required compound **5** followed by the band corresponding to parent BODIPY **3** were collected. The solvent was removed on rotary evaporator and afforded dark solids of **5** and **3** in 6–10 % yields. To optimize the reaction, we carried

Scheme 1 Synthesis of compounds **3** and **5**



out the reaction under the following conditions: (1) the oxidation of dipyrromethane **6** to dipyrromethene in the presence of DDQ was carried out for longer than 10 min at room temperature. We noted that the yields of compounds **5** and **3** were reduced to greater extent indicating that the dipyrromethene intermediate formed in this reaction is not stable for longer time. (2) The yields were also reduced when we used mild oxidizing agents such as 2,3,5,6-tetrachloro *p*-benzoquinone to oxidize dipyrromethane to dipyrromethene. This indicates that the strong oxidizing agents like DDQ is required for complete oxidation of dipyrromethane to dipyrromethene in short time. We also carried out the reaction without adding pyrrole to confirm the formation of stable parent BODIPY **3** at the room temperature conditions. We obtained **3** in decent yields which indicate that the low temperature conditions are not required to obtain compound **3** as reported in the literature [11]. Furthermore, we propose a tentative oxidative nucleophilic substitution mechanism for the formation of compound **5** as shown in the Supporting information. In the first step, the *meso*-free dipyrromethane was oxidised with three equivalents of DDQ to obtain dipyrromethene **I** which undergoes nucleophilic substitution reaction with pyrrole to form *meso*-free pyrrolyl dipyrromethene **II**. The *meso*-free pyrrolyl dipyrromethene **II** was stabilized in solution due to aromatization in the presence of excess DDQ leading to the extension of π-conjugation. In the last step, the dipyrromethenes **I** and **II** upon complexation with $BF_3{\cdot}OEt_2$ led to the formation of compounds **3** and **5** respectively.

Compounds **5** and **3** are freely soluble in common organic solvents and characterized by mass, 1D and 2D NMR, absorption and fluorescence studies. The molecular ion peak for compound **5** was observed at 238.0950 $[M\text{-}F]^+$ and for compound **3** was observed at 173.0686 $[M\text{-}F]^+$ in HR-MS mass spectra confirmed the identities of the compounds **5** and **3**. The complete structure of compound **5** was deduced from ^1H, ^{19}F, ^{11}B and ^1H-^1H COSY NMR studies. Comparison of ^1H NMR spectra of compound **5** with 3-pyrrolyl *meso*-phenyl BODIPY **4** is shown in Fig. 2a and ^1H-^1H COSY NMR spectrum of compound **5** is shown in Fig. 2b. As clear from Fig. 2 that the eight protons (a-h) of three pyrrole groups are chemically inequivalent and appeared as eight sets of signals in 6.4–7.7 ppm region like *meso*-phenyl BODIPY **4**. The multiplet observed at 7.5 ppm region for *meso*-aryl group of compound **4** was absent in compound **5** but a singlet corresponding to *meso*-proton is present at 7.04 ppm confirming the molecular structure of compound **5**. The NH proton in compound **5** was observed at more downfield (10.6 ppm) indicating a possibility of intramolecular hydrogen bonding between NH proton and fluoride ion of the BF_2 group in compound **5**. Furthermore, the absence of *meso*-phenyl group resulted in downfield shift of protons of type 'c' and 'd' which are adjacent to *meso*-position compared to the equivalent protons in *meso*-phenyl BODIPY **4**. The other BODIPY core protons in compound **5** did not experience much shifts compared to compound **4**. The presence of intramolecular hydrogen bonding between pyrrole NH and fluoride ions of BF_2 group in compound **5** was also clearly evident in ^{19}F NMR spectrum which showed a clear doublet of quartets at~-141 ppm due to coupling with NH proton. In ^{11}B NMR, the compound **5** showed a triplet due to coupling with two fluoride ions and appeared at 1.30 ppm like compound **4**. Thus, the NMR studies clearly indicated that compound **5** showed similar NMR features like *meso*-phenyl BODIPY **4** except slight shifts of type 'c' and 'd' protons due to the absence of *meso*-phenyl group in compound **5**.

The absorption and fluorescence properties of **3** and **5** were studied in different solvents of varying polarity and the data for compounds **3** and **5** along with their respective *meso*-aryl analogues **1** and **4** in $CHCl_3$ are presented in Table 1. A comparison of the absorption spectra of compounds **3**, **4** and **5** recorded in $CHCl_3$ is presented in Fig. 3. All three compounds showed similar absorption spectral features exhibiting one strong absorption band corresponding to $S_0 \rightarrow S_1$ transition with a shoulder at higher energy side corresponding to vibronic transition which is clearly separated in compounds **4** and **5**. Compared to compound **3**, the absorption band of compound **5** experienced a bathochromic shift of ~70 nm indicating an enhancement in the π-electron delocalization because of the additional pyrrole moiety in compound **5**. However, the absorption band is slightly blue shifted in compound **5** compared to compound **4** because of absence of *meso*-phenyl group in compound **5**. Furthermore, the absorption properties of compounds **3** and **5** do not show major variations with solvent polarity. On the other hand, the

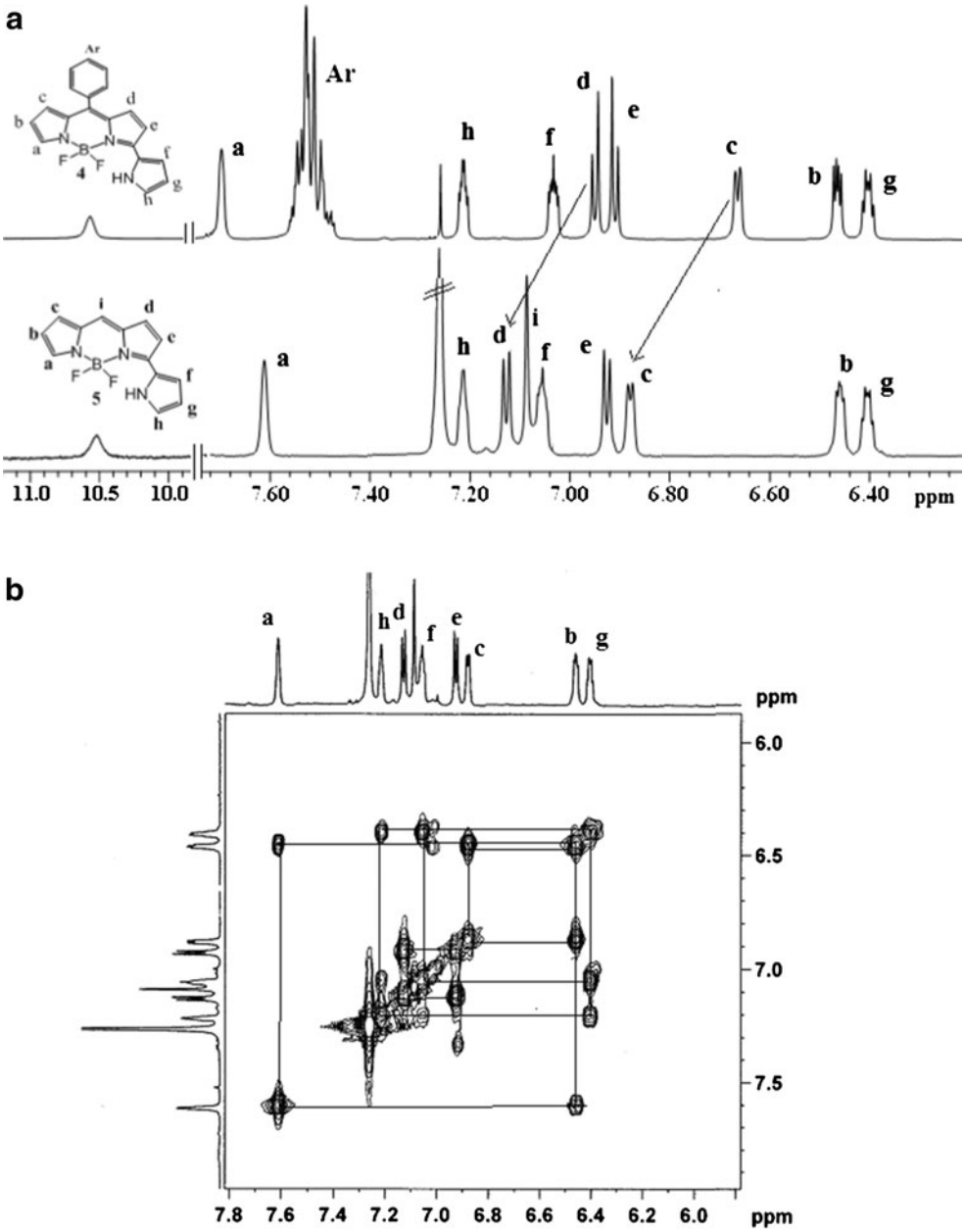


Fig. 2 **a** Comparison of ^{1}H NMR spectra of compounds **5** and **4**. **b** ^{1}H-^{1}H COSY NMR spectrum of compound **5** recorded in $CDCl_3$ (δ in ppm)

emission properties of compounds **3** and **5** are quite impressive. The comparison of normalized steady state emission spectra of compounds **3**, **4** and **5** in $CHCl_3$ is shown in Fig. 4. Tram et al. showed recently [6] that compound **3** exhibit fluorescence features like compound **1** with slightly hypsochromically shifted fluorescence band but exhibits very high quantum yield (0.95) compared to weakly fluorescent compound **1**. This is attributed to the absence of *meso*-aryl group in compound **3** which decrease the non-radiative decay channels and increase the fluorescence yield. Thus, their studies concluded that compound **3** is highly fluorescent unlike compound **1**. We anticipated similar changes in fluorescence

Table 1 Photophysical data of BODIPYs **3** and **5** along with associated reference compounds recorded in toluene

Compound	λ_{abs} (nm)	λ_{emi} (nm)	Δvst (cm-1)	log ε_{max}	Φ_f	τ (ns)	k_f ($10^9 s^{-1}$)	k_{nr} ($10^9 s^{-1}$)
1	504	521	620	4.76	0.06	0.45	0.14	2.08
3	504	512	311	4.13	0.70	5.0	0.12	0.03
4	584	608	676	4.66	0.35	3.2	0.10	0.21
5	574	586	356	4.71	0.50	4.4	0.11	0.09

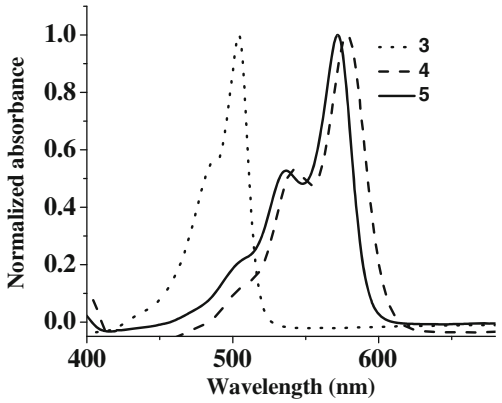


Fig. 3 Comparison of absorption spectra of compounds **3** and **5** along with **4** recorded in $CHCl_3$

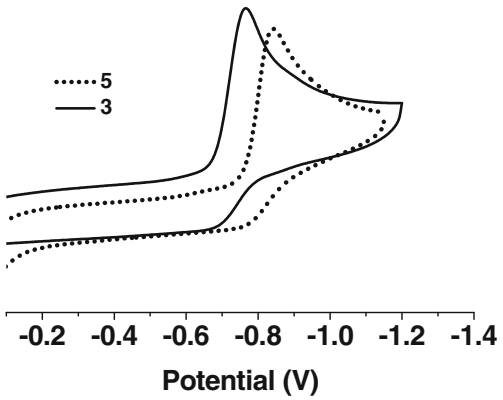


Fig. 5 Comparison of reduction waves of compounds **3** and **5** in CH_2Cl_2, measured using n-$Bu_4N^+P(ClO_4)_6^-$ (0.1 M) as supporting electrolyte at a scan rate of 50 $mV\,s^{-1}$

properties on moving from *meso*-aryl 3-pyrrolyl BODIPY compound **4** to *meso*-free 3-pyrrolyl BODIPY **5**. As clear from the data in Table 1 that compound **5** showed slightly blue shifted and less Stokes shifted fluorescence band compared to **4**. However, the *meso*-free analogue **5** is more strongly fluorescent with nearly 41 % increase in quantum yield compared to **4**. This is also clearly evident in their solution colors under UV lamp. The fluorescence lifetimes were measured for compounds **1**, **3**, **4** and **5** by time-correlated single photon counting method and the fluorescence decay profiles were fitted to single exponential. The singlet state lifetime increased from compound **1** to compound **3** as well as from compound **4** to compound **5** which is in agreement with their quantum yield data. Using the experimental Φ_f and τ values, we calculated radiative (k_f) and non-radiative rate (k_{nr}) constants which are higher and lower respectively for compounds **3**/**5** compared to compounds **1**/**4**. Thus, the fluorescence measurements supported strong fluorescence behaviour of *meso*-free BODIPY compounds **3**/**5** compared to *meso*-aryl substituted BODIPYs **1**/**4**.

The electrochemical properties of compounds **3** and **5** were determined by cyclic voltammetry at a scan rate of 50 mV/s using tetrabutyl ammonium perchlorate as supporting electrolyte. Both compounds **3** and **5** showed only one irreversible reduction (-0.73 V and -0.89 V) and one ill-defined oxidation (1.61 V and 1.00 V) indicating that the *meso*-free BODIPYs **3** and **5** are not stable under redox conditions. A comparison of reduction waves of compounds **3** and **5** is presented in Fig. 5. It is clear from Fig. 5 that the compound **5** is relatively less easier to reduce compared to compound **3** which supports the electron rich nature of compound **5** due to the presence of additional pyrrole ring at 3-position.

Unfortunately, we failed to obtain the single crystal of compound **5** for X-ray structure analysis. Hence, we performed the quantum mechanics calculations using DFT method with a standard basis set to obtain some structural information. The calculations resulted in a structure with a lowest energy having an intramolecular hydrogen bond between the NH of appended pyrrole and fluoride of BF_2 group. The presence of hydrogen bond was confirmed with further calculations like Atoms in Molecules, plot of Reduced Density Gradient (RGD) vs Sign(λ^2)*ρ and Density of States (Supporting information). The presence of intramolecular hydrogen bonding between the pyrrole NH and fluoride ion of BF_2 group was also noted earlier in the X-ray structure solved for compound **4**. Furthermore, the DFT calculations also revealed that the appended pyrrole group lies almost in the

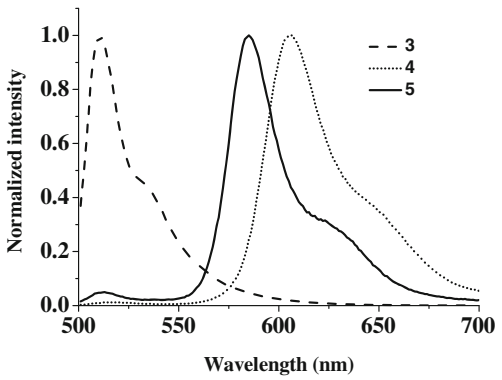


Fig. 4 Comparison of fluorescence spectra of compounds **3** and **5** along with **4** recorded in $CHCl_3$. The excitation wavelength used was 488 nm

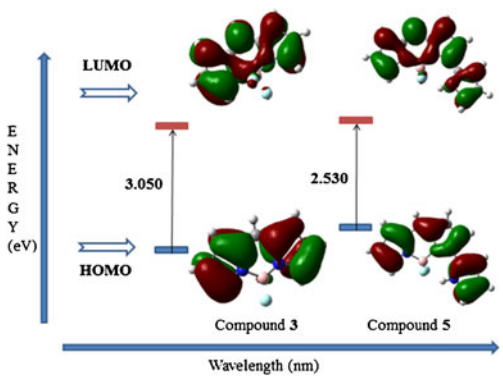


Fig. 6 Energies and electron distribution pattern in HOMO and LUMO states of compounds **3** and **5**

same plane as the BODIPY core with a deviation of 11.1° supporting that the orbitals are oriented parallel to each other for extension of π-electron conjugation. The presence of pyrrole ring at 3-position in compound **5** destabilizes both HOMO and LUMO states resulting in the decrease of 0.5 eV energy gap compared to compound **3** (Fig. 6). Furthermore, the computational studies also indicated that the compound **5** was found to be less easily reducible compared to compound **3** (Supporting information). Thus, the computational studies are in agreement with the experimental observations.

Conclusions

In conclusion, we synthesized *meso*-free 3-pyrrolyl BODIPY as well as fully unsubstituted BODIPY in one pot under simple room temperature conditions. The compounds are stable, soluble in common organic solvents and show excellent photophysical properties. The *meso*-free BODIPY and *meso*-free 3-pyrrolyl BODIPY are brightly fluorescent in solution with high quantum yields and singlet state lifetimes. We are currently investigating the functionalization of the *meso*-free 3-pyrrolyl BODIPY to prepare biologically important new BODIPY derivatives.

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