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Carbazole Substituted Boron Dipyrromethenes

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Abstract : *Meso*-substituted BODIPY with N-butylcarbazole (**1**) was prepared and derivatized. Dibromo BODIPY **2**, α -formyl BODIPY **3** and β -formyl BODIPY **4** were synthesized. All compounds were characterized by HRMS mass, NMR, UV-vis absorption, electrochemical and fluorescence techniques. Crystal structure of BODIPY **1** and its dibromoderivative **2** were also solved. In both the X-ray structures, the dihedral angle between the *meso*-carbazole group and dipyrroin plane was decreased, suggesting the increased interaction between the two units. *Meso*-substitution with N-butylcarbazole group on BODIPY core, rendered huge Stokes shifts (111-168 nm) and higher quantum yields as compare to *meso*-aryl BODIPY. An efficient energy transfer from carbazole unit to BODIPY core was observed by fluorescence spectroscopy for all the compounds **1-4**. CV studies of compounds **1-4** showed anodic shifts of the reduction and oxidation potentials, suggesting that *meso*-carbazole group is affecting the electronic properties of the BODIPY core and making them easier to reduce.

Keywords: Carbazole BODIPY, Stokes Shifts, Carbazole Dipyrroin, BODIPY Crystals

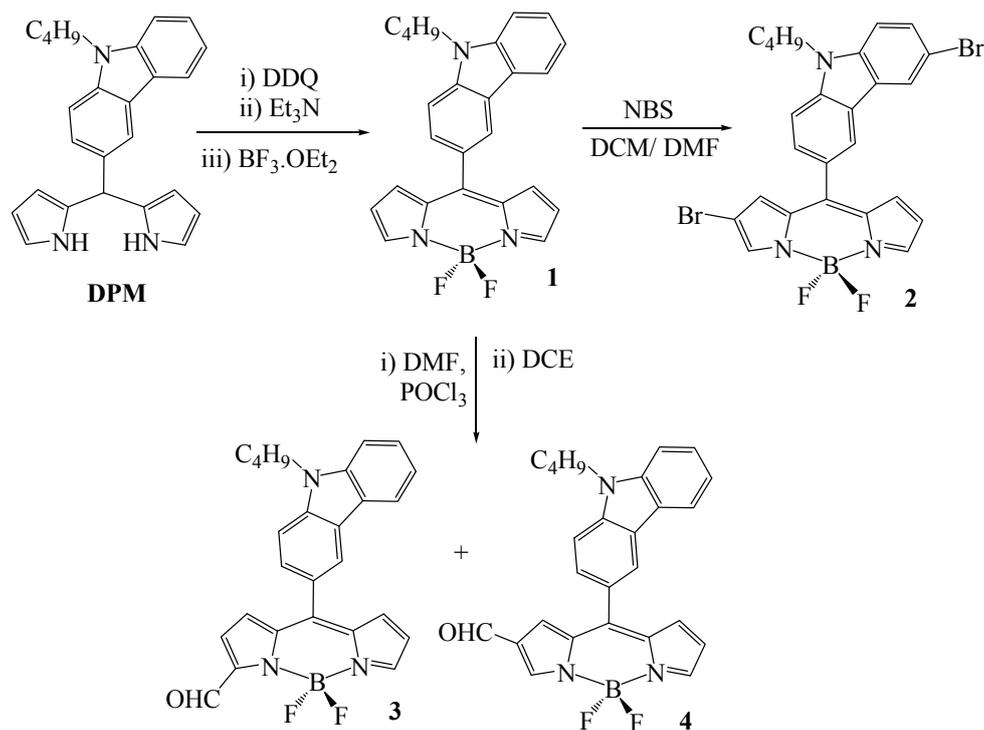
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Introduction

The BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) dyes were first discovered by Treibs and co-workers in 1968.¹ The BODIPY (Boron dipyrrens) are a class of boron chelates with dipyrin units. This fluorescent dye has remarkable photophysical properties like: intense absorption in the 480-600 nm region, high quantum yield, negligible triplet-state formation, good thermal and photochemical stability.² Good solubility and easy functionalization of the BODIPY core has made them very popular among chemists. Due to their photo-stable nature and insensitivity towards the environmental pH they gained attention as fluorescent labels³ (proteins and DNA) inside the cell.⁴ BODIPYs have been shown useful for variety of applications such as chemosensors,⁵ laser dyes,⁶ fluorescent switches⁷ etc. Halogenated BODIPY derivatives are also used for the treatment of cancerous cells in PDT (photo dynamic therapy)⁸ due to low dark toxicity and less photo-bleaching and good ISC (inter system crossing). Numerous reports are available on BODIPY derivatives substituted with halogens,⁹ alkyl groups,¹⁰ aryl groups,¹¹ extended π systems,¹² crown ether based sensors¹³ etc. In spite of having variety of applications, the major limitations of such dyes are the emission range (about 600 nm) and small Stokes shifts (5-15 nm). In order to make them emit far in red region one has to either attach other chromophores with the BODIPY core or make their dimers and higher oligomers to get good Stokes shift (80 nm).¹⁴ Covalently linked BODIPY dimers¹⁵ (linked at α - α and β - β position) have gained interest due to their good Stokes shift and red shifted absorption and emission bands. Another simple way to induce bathochromic shift in their absorption and emission bands is the introduction of electron donor moieties at the various position of BODIPY core.¹⁶ Its a known fact, that carbazole is a good electron donor and that's why its derivatives have been used for various photovoltaic (OLEDs) and photosensitizers applications.¹⁷ Carbazole is popular among chemists due to its facile functionalization, stability and its derivatives exhibits good absorption and efficient emissive properties.¹⁸ Recently, Ooyama *et al.* have synthesized D-A BODIPYs having diphenylaminocarbazole group attached to the *meso*-phenyl position of boron dipyrin core for DSSC (dye sensitized solar cells) application.^{19, 20} BODIPY based nano-cars containing carbazole and *p*-carborane groups have been prepared by Tour *et al.*²¹ NIR fluorescent BODIPYs with two carbazole groups attached to their α -pyrrole position, exhibiting reasonable two-photon absorption cross section were also reported.^{22, 23} In this paper, we report the synthesis and studies of four Boron dipyrrens **1-4** having N-butylcarbazole group at their *meso* (C8) position. It is

anticipated that substitution by electron rich carbazole moiety at the *meso*-position should affect the electronic, photophysical and electrochemical properties of the BODIPY dyes. The first X-ray crystal structures of BODIPYs **1** and **2** containing *meso*-N-butylcarbazole group at C8 position and its dibromo derivative are also reported.



Scheme 1. Synthesis of Carbazole substituted BODIPYs

Results and Discussion

The carbazole substituted dipyrane, **DPM** was synthesized by condensation of pyrrole and 3-formyl carbazole in the presence of TFA (ESI). BODIPY **1** was synthesized from **DPM** as shown in the Scheme 1. **DPM** was oxidized by DDQ and the resultant dipyrin was complexed with BF₃·OEt₂ as per the literature reported method.¹¹ Silica gel column chromatographic purification in 35% DCM / Pet ether afforded **1** as orange solid in 50% yield. BODIPY **2** was prepared by reacting **1** with NBS at room temperature for couple of hours in DCM/ DMF mixture.²⁴ Silica gel column purification in 25% DCM / Pet ether produced **2** as dark-orange solid in 75% yield. Vilsmeier Haack formylation of **1** produced mixture of α-formyl BODIPY **3** and β-formyl BODIPY **4** in 25% and 50% yield respectively (ESI).²⁵

All BODIPYs **1-4** were characterized by HRMS, ^1H , ^{19}F , ^{13}C , ^1H - ^1H COSY spectroscopy (ESI). **DPM** was confirmed by molecular ion peak at 366.1825 in HRMS. In ^1H NMR of **DPM**, four β -pyrrole protons showed up as two singlets at 6.17 and 5.98 ppm and two α -pyrrole protons showed up as singlet at 6.68 ppm. The *meso*-carbazolyl proton showed up as singlet at 5.66 ppm and seven carbazole aromatic protons appeared as four sets of multiplets between 8.02 to 7.17 ppm. The N-butyl aliphatic protons showed up as four set of signals ranging from 4.29 to 0.93 ppm. Compounds **1-4** were confirmed by molecular ion peak in HRMS mass in the positive ion mode. In ^1H NMR of BODIPY **1**, four β -pyrrole protons showed up as two singlets at 7.04 and 6.58 ppm and two α -pyrrole protons showed up as singlet at 7.95 ppm. The seven carbazole aromatic protons appeared as five sets of signals between 8.02 to 7.17 ppm. The N-butyl aliphatic protons showed up as four set of signals ranging from 4.29 to 0.93 ppm. The electronic properties of the BODIPY core were affected by the introduction of N-butylcarbazole group at the *meso*-position which resulted in the downfield shifts of β -pyrrolic protons in ^1H NMR compared to the *meso*-tolyl BODIPY.²⁶ The two β -pyrrolic protons in ^1H NMR of *meso*-tolyl BODIPY appeared at 6.89 and 6.55 ppm.²⁶ The X-ray crystal structure of **1** clearly shows that aromatic carbazole group is more in plane with the BODIPY core, thereby increasing the π -electron delocalization in the molecule. In ^1H NMR of BODIPY **2** due to one bromination at β -pyrrole position, the two α -pyrrole protons showed up as two separate signals at 8.01 and 7.80 ppm and the remaining three β -pyrrole protons showed up as three singlets at 7.08, 6.96 and 6.63 ppm respectively. The six carbazole aromatic protons were slightly downfield shifted w. r. t. compound **1** and showed up as five sets of signals between 8.37 to 7.38 ppm. The N-butyl aliphatic protons were also slightly downfield shifted and showed up as four set of signals ranging from 4.37 to 1.01 ppm. In BODIPY **3** and **4**, the formyl proton appeared as singlet at 10.43 and 9.88 ppm respectively. The chemical shifts for the rest of carbazole aromatic protons and alkyl protons in BODIPY **3** and **4** were similar to compound **2**. The ^{19}F NMR spectra of BODIPYs **1-4** were recorded in CDCl_3 and the fluorine resonance signals splits into quartet due to the coupling with adjacent boron atom (^{11}B , $I = 3/2$). In ^{19}F NMR spectra of compounds **1** and **2**, the ^{19}F quartet appeared around -145.96 ppm whereas, in compound **3** the ^{19}F signals appeared at -137.75 ppm. This downfield shift in the ^{19}F NMR of compound **3** is in accordance with the literature reported BODIPYs having α -formyl groups.²⁷ The authors, reasoned that due to the H-

bonding between F and H (of α -CHO group) in CDCl_3 , ^{19}F signal experienced this downfield shift.²⁷ In the case of BODIPY **4** having formyl group at the β -position, the ^{19}F signal appeared at -144.98 ppm, here H-bonding between F and β -CHO group is not possible.

Single Crystal X-ray Diffraction Studies

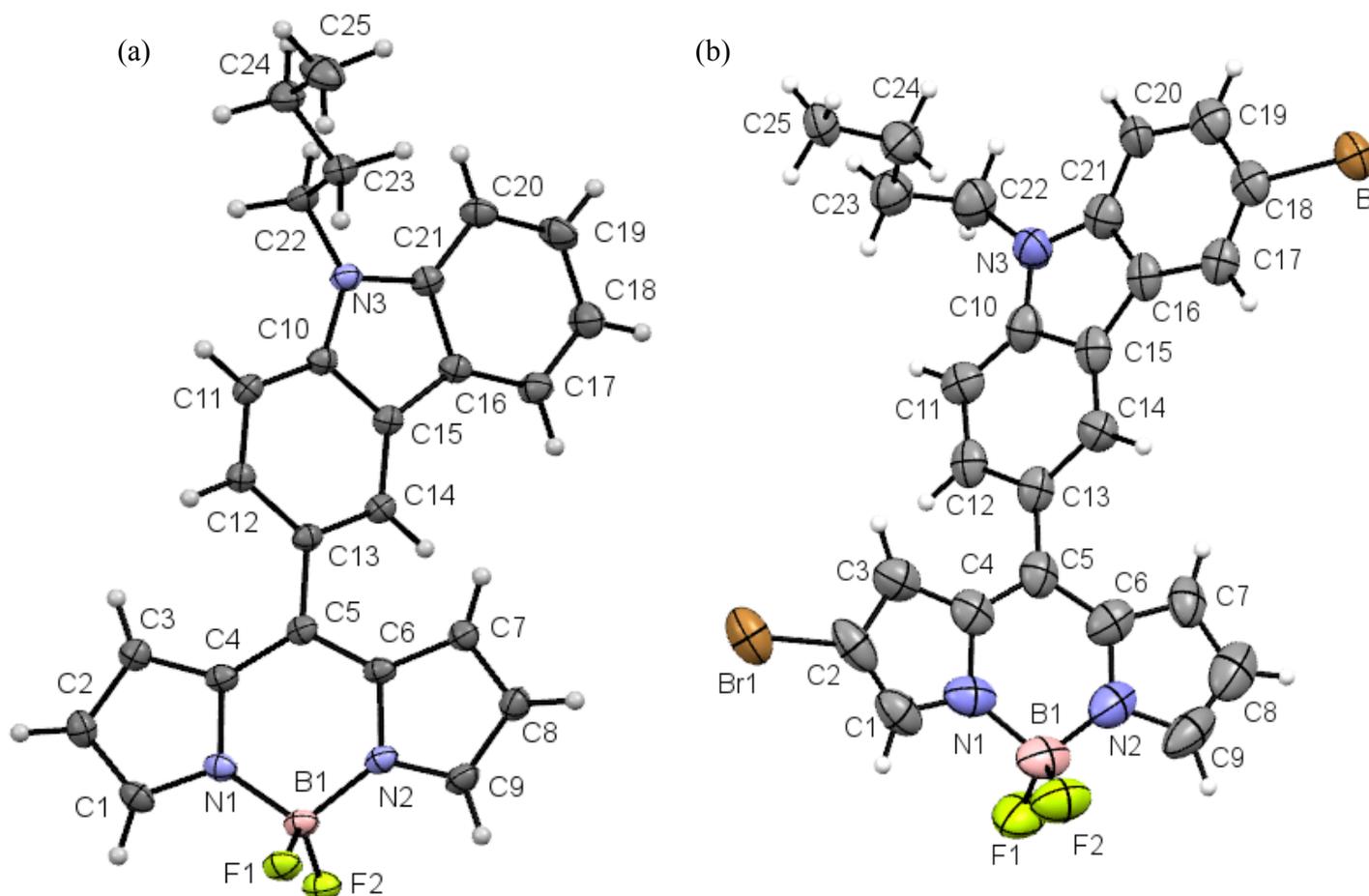


Figure 1. X-ray crystal structures of (a) BODIPY **1** and (b) BODIPY **2**, thermal ellipsoids are shown at 50% probability level in Ortep diagrams.

The single crystals of compound **1** and **2** were obtained by slow evaporation of the *n*-heptane/chloroform solution over a period of 10-12 days. Compound **1** gave orange needle shape crystals in monoclinic form and compound **2** gave orange platelets in orthorhombic form (ESI). The X-ray structures of compound **1** (CCDC **982777**) and **2** (CCDC **979461**) are shown in Figure 1 and relevant data are given in ESI. The orientation of *meso*-*N*-butylcarbazole group towards the plane of BODIPY core is clearly evident from both the crystal structures. In

agreement with the previously reported crystal data of *meso*-aryl BODIPYs,²⁸ the X-ray structures of **1** and **2** showed that the boron containing central six membered ring is coplanar with the dipyrin plane. Also the plane defining BF₂ unit is perpendicular to the core BODIPY plane. The interesting feature of X-ray structures of **1** and **2** is that the dihedral angle (C6-C5-C13-C14) between *meso*-carbazole group and dipyrin plane is 46°, which is much lesser to that of *meso*-phenyl BODIPY crystal structure (reported value 60°). In both the crystal structures the C5-C13 bond lengths (the bond between dipyrin and *meso*-carbazole group) are also affected (ESI) and are slightly shorter than that of *meso*-phenyl BODIPY crystal structure (the reported value is 1.481Å).²⁸ The bond lengths such as C1-C2, C2-C3, B-N, B-F, C-N and bond angles such as N1-B1-N2 and C4-C5-C6 are also slightly altered compared to the *meso*-phenyl BODIPY. Overall, the X-ray parameters revealed increased interactions between *meso*-carbazole group and dipyrin unit in both the compounds.

Photophysical Properties

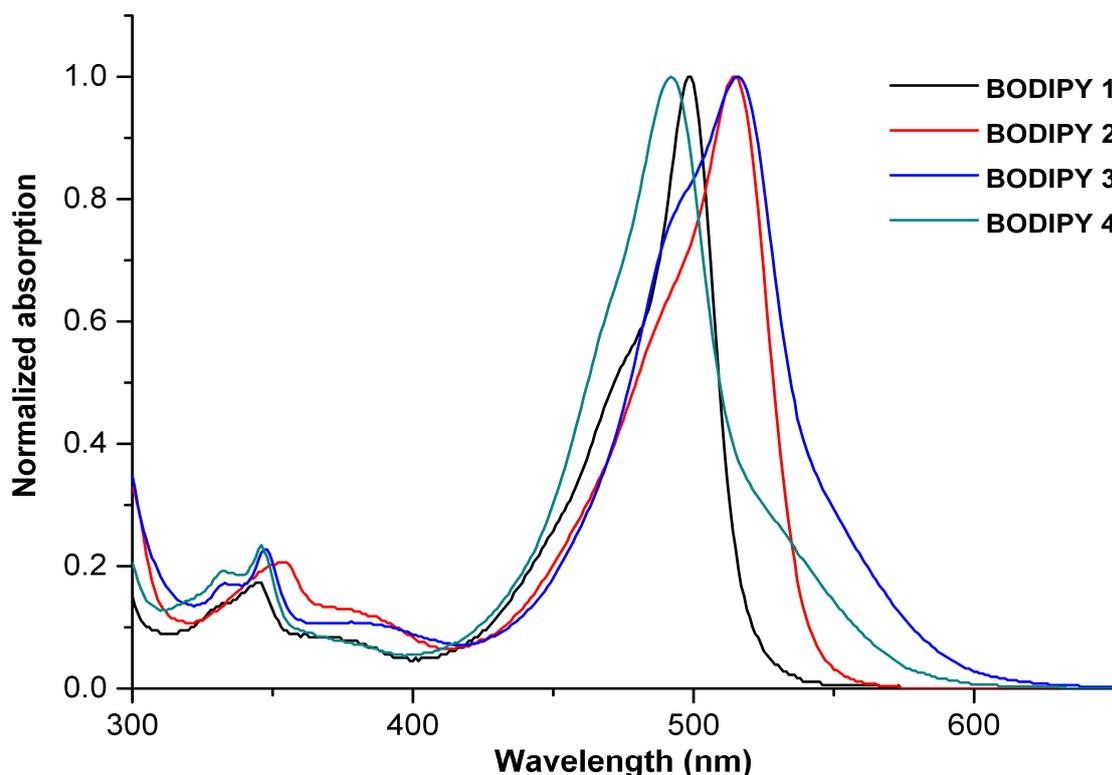


Figure 2. Comparison of normalized absorption spectra of compounds **1-4** in chloroform.

Table 1. Photophysical data of BODIPYs **1-4** in different solvents. The concentration used was 2.4×10^{-6} M and excitation wavelength was 488 nm.

Compound	Solvent	λ_{abs}	$\log \epsilon$ (nm)	fwhm_{abs} (nm) (cm^{-1})	λ_{em} (nm)	$\Delta\nu_{\text{st}}$ (nm) (cm^{-1})	ϕ_f
BODIPY 1	Chloroform	498, 345	4.87, 4.12	37 1563	583	85 2928	0.18
	Toluene	499, 343	5.35, 4.57	37 1556	519	20 772	0.33
	DCM	497, 345	4.99, 4.27	40 1656	618	21 3939	0.06
	THF	496, 343	4.83, 4.12	38 1598	602	106 3549	0.09
BODIPY 2	Chloroform	515, 354	5.04, 4.36	49 1934	588	74 2411	0.051
	Toluene	515, 355	4.87, 4.08	48 1843	539	24 864	0.11
	DCM	512, 354	4.76, 4.09	50 2007	631	119 3683	0.017
	THF	510, 352	5.05, 4.38	50 2023	621	111 3504	0.022
BODIPY 3	Chloroform	516, 347	5.18, 4.54	57 2255	643	127 3828	0.07
	Toluene	518, 347	5.18, 4.54	52 2020	602	84 2693	0.085
	DCM	512, 347	4.56, 3.82	61 2388	671	159 4628	0.002
	THF	511, 345	5.00, 2.39	59 2327	665	153 4531	0.004
BODIPY 4	Chloroform	492, 346	4.57, 4.03	47 1995	621	129 4222	0.05
	Toluene	498, 345	5.11, 4.46	44 1825	588	90 3074	0.17
	DCM	491, 346	4.87, 4.18	48 2046	659	168 5192	0.012
	THF	492, 345	4.82, 4.24	46 1979	660	168 5174	0.011

The UV/vis absorption, fluorescence spectra and fluorescence lifetimes of BODIPY **1-4** were measured in chloroform. The absorption spectra of compounds **1-4** are presented in Figure 2 and photophysical properties are summarized in Table 1. BODIPYs **1-4** showed two absorption bands, shorter wavelength band corresponding to the carbazole unit gave absorption maxima between 347-354 nm. The longer wavelength band corresponding to the $^1\pi-\pi^*$ transition of BODIPY core appeared between 498-516 nm in all the compounds **1-4**. This longer wavelength band is blue shifted in compound **1** as compare to the *meso*-phenyl BODIPY²⁹ and slightly red shifted for compounds **2-4**. The extinction coefficients were quite higher than the *meso*-phenyl BODIPY (Table 1) for lower energy absorption band in all the compounds **1-4** and the absorption maxima varied very little (2-4 nm) upon changing the solvent polarity from toluene to THF (ESI), reflecting the typical behavior of BODIPY chromophores.¹⁶ The fwhm_{abs} (full width at half maxima of major absorption band) and quantum yields of all the compounds **1-4** were calculated in different solvents (Table 1). Solvent polarity affected the broadening of the absorption band and fwhm_{abs} values were lower in non-polar solvent (toluene) and higher in polar solvents (DCM, THF) for our compounds. This trend is in agreement with the *meso*-aryl BODIPYs. The *meso*-tolyl and *meso*-anisyl BODIPYs exhibited fwhm_{abs} in the range of 697 cm^{-1}

in non-polar solvents to 819 cm^{-1} in polar solvents.^{29b} Whereas the fwhm_{abs} of mono- and di-bromo derivatives of *meso*-anisyl BODIPYs were in the range of 975 cm^{-1} in non-polar solvents to 1390 cm^{-1} in polar solvents.^{29c} The fwhm_{abs} values of BODIPYs **1-4** were quite higher than the reported *meso*-aryl BODIPYs, indicating that significant changes occurred in bond lengths / bond angles upon excitation.^{29b}

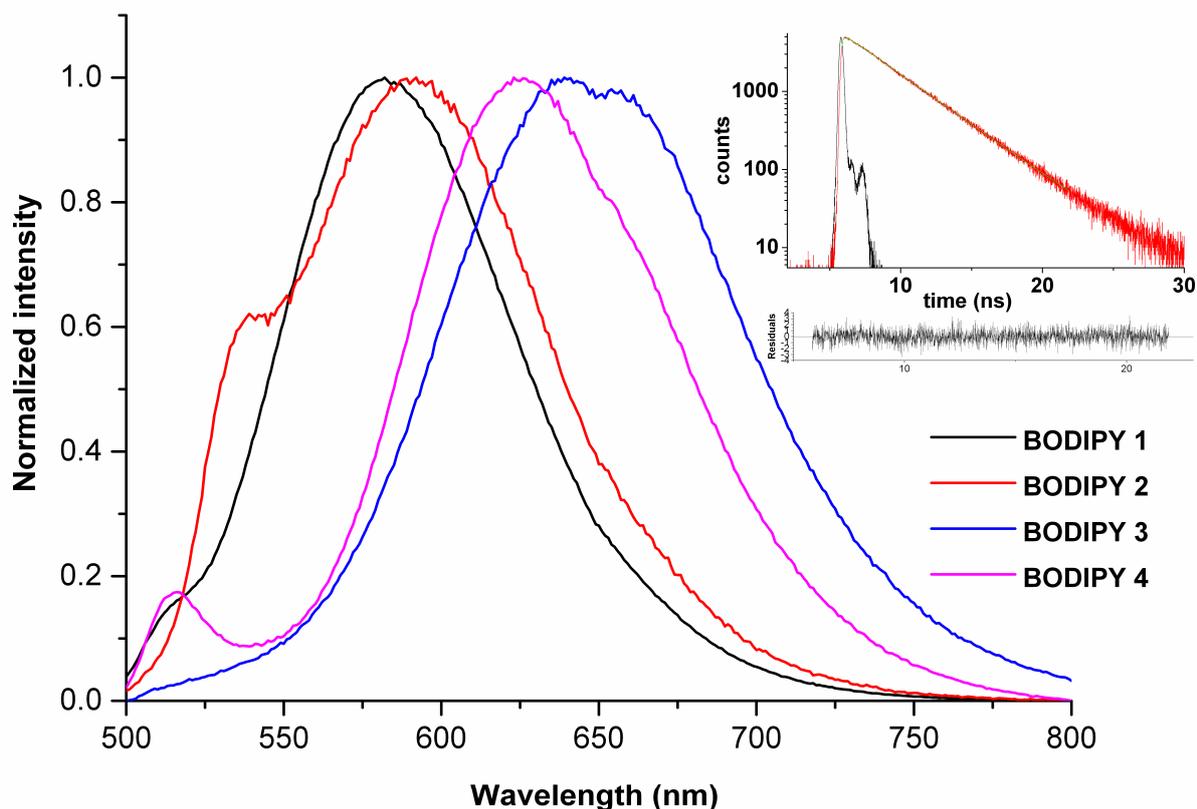


Figure 3. Comparison of normalized emission spectra of BODIPYs **1-4** in CHCl_3 ($\lambda_{\text{ex}} = 488\text{ nm}$). Inset shows the fluorescence decay profile and weighted residuals, distribution fit of compound **1** in chloroform. The excitation wavelength used was 440 nm , collected at 583 nm .

The fluorescence properties of compounds **1-4** were investigated in chloroform by both steady state and time resolved fluorescence techniques. A comparison of emission spectra of **1-4** is shown in Figure 3 and solvatochromism data is given in Table 1. The typical mirror-image relationship was observed for the lowest energy absorption band and emission spectra of all the compounds **1-4**. The emission maxima for compounds **1-4** were red shifted as compare to that of *meso*-phenyl BODIPY.²⁹ Compounds **1** and **2** showed 67 nm red shift w. r. t. *meso*-phenyl BODIPY and compound **3** and **4** showed 120 nm red shifted emission bands. The large shift in

emission maxima could be attributed to the carbazole group present at their *meso* position and formyl group on the BODIPY core. Solvatochromic studies revealed that BODIYP **2** showed less shifts (14- 29 nm) in emission maxima by changing the solvents polarity (Table 1). Whereas change in the solvent polarity, resulted in significant shifts (45-70 nm) in the emission maxima for BODIPYs **1**, **3** and **4**.

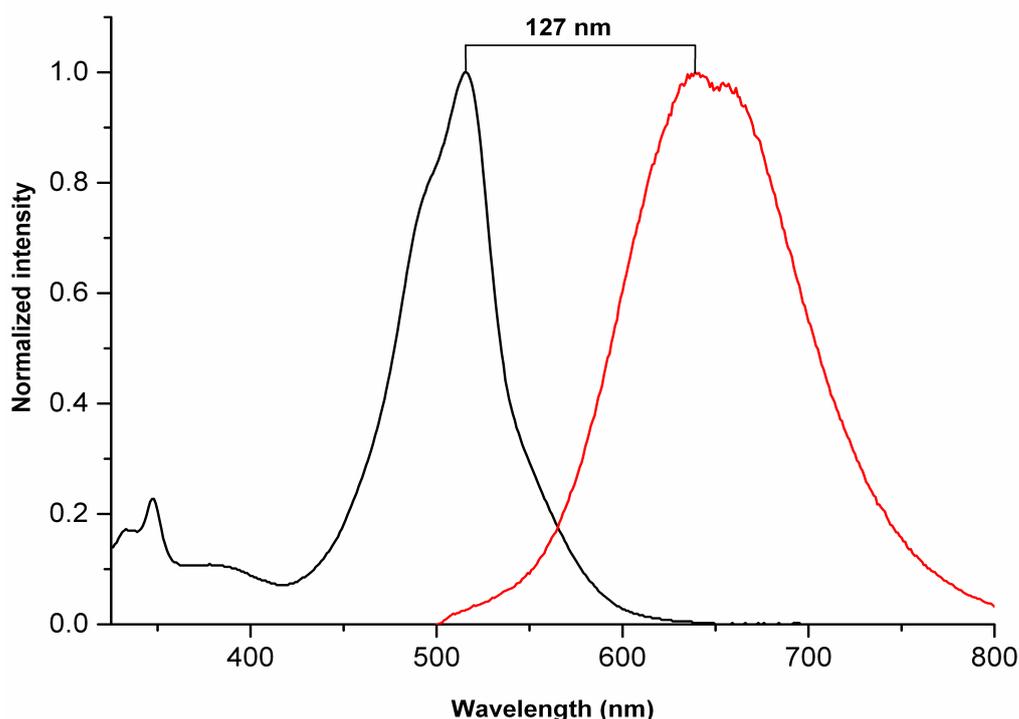


Figure 4. Normalized absorption (black) and emission (red) spectra of BODIPY **1** in CH₂Cl₂.

For all the compounds **1-4** Stokes shifts were small (20- 80 nm) in toluene and chloroform (Table 1), whereas large Stokes shifts (111-168 nm) were observed in polar solvents like DCM and THF. A comparison of absorption and emission spectra of BODIPY **1** is shown in Figure 4. Usually the *meso*-aryl BODIPYs shows 10-15 nm Stokes shifts.¹⁶ For example, the Stokes shift of *meso*-tolyl BODIPY^{29b} in CHCl₃ was 482 cm⁻¹; whereas for the mono- and di-bormo derivatives of *meso*-anisyl BODIPYs^{29c} Stokes shifts were 526 cm⁻¹ and 394 cm⁻¹ respectively. The observed Stokes shifts for compound **1-4** were ranging from 2411 to 4222 cm⁻¹ (Table 1). The red shifted emission maxima in polar media indicate larges dipoles of the CT excited states. This is in agreement with the report by N. Boens et al.^{29b} of the BODIPY having N,N-dimethyl -amoniophenyl group at C-8 position, which showed Stokes shift of 3199 cm⁻¹ in

CHCl₃. Recent reports on BODIPYs having phenylcarbazole-diphenylamine^{19a} and theinylcarbazole-diphenylamine^{19b} groups at C-8 positions showed Stokes shifts of 388 cm⁻¹ and 490 cm⁻¹ in 1,4-dioxane. Another report on *meso*-iodophenyl BODIPYs having one and two N-enthynylcarbazole moieties at their C-3 and C-6 positions showed Stokes shifts of about 538 cm⁻¹ and 365 cm⁻¹ respectively in CHCl₃.²² Thus, the substitution at C-8 position of BODIPY with carbazole moiety is affecting the Stokes shifts more than the substitution at C-3 and C-6 positions. The large Stokes shifts could be due to the effect of electron rich carbazole, which acts an electron donor moiety in BODIPYs.²² The fluorescence quantum yields Φ_f in CHCl₃ for BODIPY **1** (0.18) and **3** (0.07) were three and 1.2 times higher respectively than the *meso*-phenyl BODIPY.²⁹ The fluorescence quantum yields Φ_f for BODIPY **2** and **4** were slightly lesser than the *meso*-phenyl BODIPY. The higher quantum yield of compounds **1** and **3** could be due to the bulky nature of carbazole group at their *meso*-position, which hinders the free rotation in the BODIPY molecules. The lower quantum yields for compounds **2** and **4** suggests, higher intersystem crossing from S₁ to T₁ in these compounds. The quantum yields of compound **1-4** were higher in non-polar solvent (toluene) and lower in polar solvents (DCM, CHCl₃); this is due to the large dipole moment difference between CT excited state and ground state which in turn facilitate internal conversion in polar media.^{29b} The time-correlated single photon counting technique was used to measure the singlet state life times τ of BODIPYs **1-4**. The fluorescence decay of compounds **1-4** were fitted to a single exponential decay. The singlet state life times τ , the decrease in radiative decay constant k_r and the increase in non-radiative decay constant k_{nr} are in line with the quantum yield data.

Table 2. Quantum yields and lifetime data of BODIPYs **1-4** in CHCl₃.

Compound	Φ_f^a	Φ_f^b	$\Phi\tau$ (ns)	k_r (10 ⁹ s ⁻¹)	k_{nr} (10 ⁹ s ⁻¹)
BODIPY 1	0.18	0.163	3.37	0.053	0.24
BODIPY 2	0.045	0.038	1.08	0.042	0.88
BODIPY 3	0.07	0.062	1.47	0.047	0.63
BODIPY 4	0.043	0.037	3.15	0.014	0.30
<i>Meso</i> -Phenyl BODIPY ^c	0.06	–	0.45	0.14	2.08

$k_r = \Phi_f/\tau$ and $k_{nr} = (1 - \Phi_f)/\tau$; a: $\lambda_{ex} = 488$ nm; b: $\lambda_{ex} = 347$ nm; c: in toluene, taken from ref. (29)

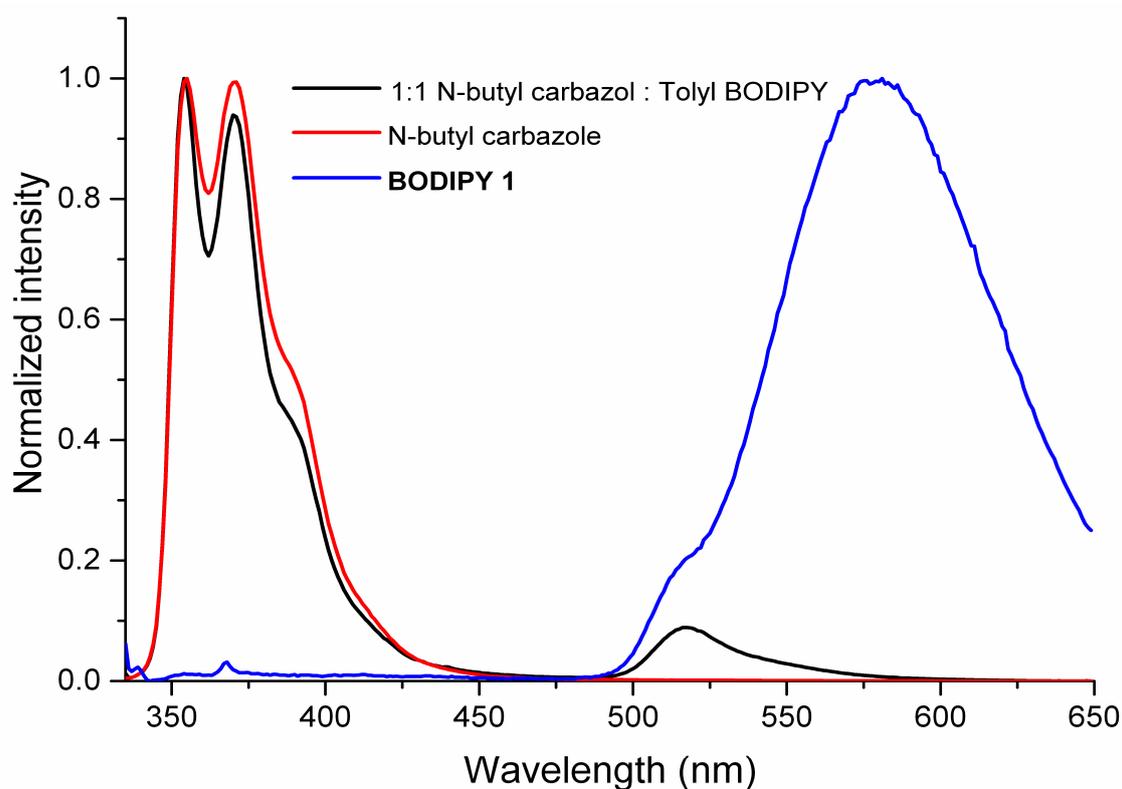


Figure 5. Comparison of normalized emission spectra of BODIPY **1**, a 1:1 mixture of N-butyl Carbazole and *meso*-Tolyl BODIPY and only N-butyl carbazole in CHCl_3 ($\lambda_{\text{ex}} = 347$ nm).

Since carbazole moiety absorbs between 300-450 nm and BODIPY dyes absorb around 500-600 nm, an energy transfer from carbazole moiety to BODIPY core is expected. Indeed, all the compounds **1-4** exhibited energy transfer phenomenon from carbazole unit to BODIPY core. A comparison of emission spectra of BODIPY **1**, N-butylcarbazole and a 1:1 mixture of N-Butyl carbazole and *meso*-tolyl BODIPY is shown in Figure 5.²⁵ In our systems, the *meso*-carbazole unit acts as energy donor and the BODIPY core acts as energy acceptor. Therefore, upon excitation of carbazole unit at 347 nm in all the compounds **1-4**, the dominant emission was observed from the BODIPY core in the range of 500-650 nm. N-butylcarbazole molecule emits in the range of 340-450 nm. It is very clear from Figure 5, that upon excitation of a 1:1 mixture of N-butylcarbazole and *meso*-tolyl BODIPY at 347 nm, where N-butylcarbazole absorbs strongly, emission was observed exclusively from N-butylcarbazole around 340 nm and no emission was observed from the BODIPY core. However, in the case of BODIPY **1** the excitation of N-butylcarbazole unit at 347 nm resulted in exclusive emission from BODIPY unit around 583 nm

and carbazole emission was drastically quenched (Figure 5). The large Stokes shifts could possibly be due to the through bond energy transfer from donor (*meso*-carbazole) to acceptor (BODIPY unit).³⁰ The “energy transfer efficiency” (ETE, %) is a measure of through bond energy transfer and it can be calculated as follows:

$$\text{ETE \%} = \frac{\phi_f \text{ of acceptor in the molecule excited at the donor}}{\phi_f \text{ of acceptor in the molecule excited at the acceptor}} \times 100$$

The quantum yields of BODIPY unit in all the compounds **1-4** were calculated at two different wavelengths i. e. excited at donor (*meso*-carbazole, 347 nm) and excited at acceptor (BODIPY core, 488 nm) and data is given in Table 2. ETE gives the idea of the extent of energy transfer including the loss in energy by nonradiative process during the energy transfer.³⁰ The calculated values of ETE (%) were: BODIPY **1** (90 %), BODIPY **2** (85 %), BODIPY **3** (88 %) and BODIPY **4** (86 %). X-ray crystal structure also support the fact that in the compounds **1** and **2**, the *meso*-carbazole (donor) and boron-dipyrrin core (acceptor) are not coplanar, therefore possibility of energy transfer through other mechanism is not very favorable. However, more detailed photophysical and electrochemical studies will be required to understand the mechanism of energy transfer in these compounds. The ETE (%) values are between 85% to 90% indicating, an efficient energy transfer from donor to acceptor in all the BODIPY **1-4**.

Electrochemical Properties

Table 3. Electrochemical redox data (V) of compounds **1-4** in dichloromethane, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed.

Compound	E _{ox} (V vs SCE)		E _{red} (V vs SCE)	
	I	II	I	II
1	1.29	1.03	-0.705	-1.79
2	1.32	1.05	-0.56	-1.60
3	1.44	1.17	-0.37	-1.23
4	1.41	1.15	-0.51	-1.53

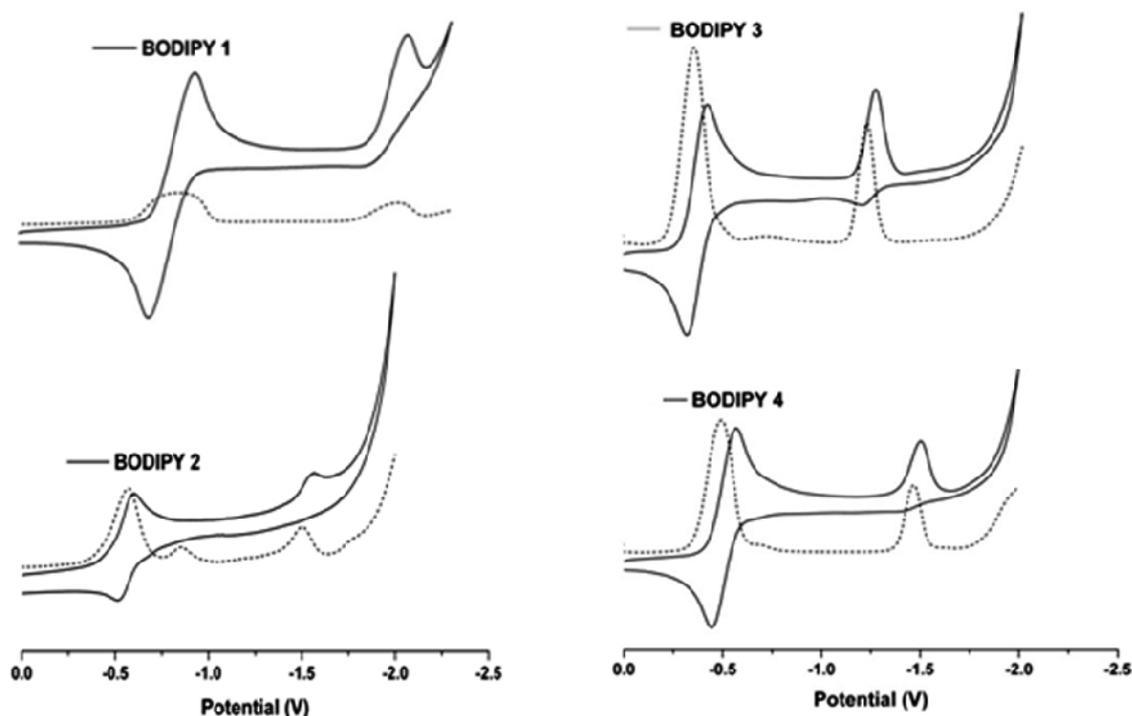


Figure 6. Comparison of cyclic voltammograms of compounds **1-4** in dichloromethane, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed (V vs. SCE).

The cyclic voltammetry measurements of BODIPYs **1-4** were carried out at the scan rate of 50 mV/s using tetrabutylammonium perchlorate as supporting electrolyte. The redox potential data and a comparison of reduction waves are shown in the Table 3 and Figure 6 respectively. The BODIPYs typically shows one reversible reduction and one quasi reversible reduction along with one irreversible oxidation. Compounds **1-4** showed one reversible and one irreversible reduction wave. The reduction potentials are showing anodic shift as compare to that of *meso*-tolyl-BODIPY, indicating that compounds **1-4** are easier to reduce compare to the *meso*-tolyl-BODIPY.²⁶ Compounds **1** and **2** showed two irreversible oxidations, whereas compound **3** showed two quasi-reversible oxidations. Compound **4** showed one quasi-reversible oxidation at 1.52 V and one irreversible oxidation at 1.15 V. The oxidation and reduction potential values of compound **3** are very different from the parent BODIPY **1**, suggesting that substitution by formyl group at the α -pyrrolic position affected the electronic properties of the compound more than the substitution at β -pyrrolic position. The oxidation potential values are more positive than the

typical *meso*-aryl BODIPY, suggesting that all the compounds **1-4** are difficult to oxidize compared to their *meso*-aryl analogues.

Conclusion

In conclusion, we have synthesized and characterized four boron-dipyrrins containing *meso*-carbazole group. Their absorption, emission, electrochemical and time resolved fluorescence studies were carried out. Also, the X-ray crystal structures of two BODIPYs were solved. The reduced dihedral angle between the *meso*-carbazole group and dipyrrin core in the both the crystal structures revealed better interaction between the two moieties. It was found that, the *meso*-carbazole group altered the electronic properties of the four BODIPYs which were reflected in the higher extinction coefficient, red shifted emission maxima, increased quantum yields and large Stokes shifts. Fluorescence studies indicated an efficient energy transfer from *meso*-carbazole moiety to boron-dipyrrin core in all the compounds. Due to increased conjugation with the electron donor *meso*-carbazole group, anodic shifts were observed in the redox potentials of all four BODIPYs.

Experimental Section

Instrumentation and Reagents

Unless otherwise mentioned, all the reagents and solvents were purchased from Aldrich, Acros Organics or Merck and used without further purification. Pyrrole was distilled under vacuum prior to use. Silica gel (60-120 mesh size) and neutral alumina (Brockmann Grade I-II) used for column chromatography were procured from Merck. The dipyrrmethanes were visualized upon exposure of TLC plate to Br₂ vapors. The solution NMR spectra of compounds were recorded with Bruker Avance III 500 MHz NMR spectrometer. The HRMS data for all the compounds was recorded (in positive ion mode) with Waters Synapt-G2S ESI-Q-TOF Mass instrument. Absorption spectra were recorded with Shimadzu UV-1700 and Fluorescence emission studies were performed using Horiba-Jobin Yvon Fluorolog-3 Spectrofluorometer at IIT Gandhinagar. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm using Rhodamine 6B ($\Phi_f = 0.49$) in methanol as standard. The time-resolved fluorescence decay measurements were carried out at the magic angle using a pico-second-diode-laser-based, time-correlated, single-photon counting

(TCSPC) fluorescence spectrometer from IBH, UK. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary 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 vs. saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.51 \text{ V vs. SCE}$. The elemental analysis was done on Thermo Quest Microanalysis instrument at IIT Bombay.

Synthesis and Characterization

9-butyl-9H-carbazole: It was synthesized as reported before and the spectral data matches with the reported one.³¹ Carbazole (16.7 g, 1mol) was taken in benzene (20 mL) and tetrabutylammonium iodide (TABI, 1.11g, 3 mmol) was added. 1-Bromo butane (17.13 g, 125 mmol) and 50% NaOH aqueous solution (120 mL) were mixed in the RB. Reaction mixture was stirred at 80°C for 2 h. Solvent was removed under reduced pressure on rotary evaporator. The residue was extracted with DCM. The organic layer was dried over Na₂SO₄ and filtered. After removal of the solvent, product was recrystallized from ethanol to afford 9-butyl-9H-carbazole in 83% yield (18.5g).

9-butyl-9H-carbazole-3-carbaldehyde: It was synthesized as reported before and the spectral data matches with the reported one.³² Phosphoril chloride (6.12 g, 40 mmol) was added slowly to dry DMF (5 mL) at 0°C and the mixture was stirred for 1 h at RT then a solution of compound **1** (5.6 g, 20 mmol) in dichloroethane was added and stirred for 1 hr. After this, reaction mixture was refluxed for 15 h. Finally the solution was cooled and poured into water. The organic layer was extracted with dichloromethane, dried with sodium sulfate and the solvent was removed under reduced pressure. Desired compound was isolated via silica gel column chromatography using ethyl acetate/ petroleum ether (5:95) mixture to afford 9-butyl-9H-carbazole-3-carbaldehyde in 43% yield (4.32 g) ¹H NMR (500 MHz, CDCl₃, δ ppm): 10.07 (s, 1H), 8.5 (s, 1H), 8.13 (d, *J* = 7 Hz, 1H), 7.9 (d, *J* = 8 Hz, 1 H), 7.5 (m, 4H), 4.2 (t, ³*J* = 7.3 Hz, 2 H), 1.81 (q,

$J = 7.3$ Hz, 2H), 1.28 (m, 2H), 0.91 (t, $^3J = 7.3$ Hz, 3H). HRMS (ESI-Q-TOF): $C_{17}H_{17}NO^+$ $[M+H]^+$: calcd. m/z 252.131 found. m/z 252.1418.

9-butyl-carbazole dipyrromethane (Carbazole DPM)

9-butyl-9*H*-carbazole-3-carbaldehyde (1g, 3.97 mmol) was dissolved in pyrrole (2.75 mL, 39.6 mmol) under nitrogen atmosphere. After 5 min. TFA (0.1 eq, 30 μ L) was added and reaction mixture was allowed to stir for half an hour. By vacuum distillation the excess pyrrole was removed. Desired compound was isolated via silica gel column chromatography using dichloromethane/petroleum ether (50:50) to afford Carbazole DPM in 54.8% (800 mg). 1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.01 (m, 4H, Ar-*H*), 7.45 (m, 2H, Ar-*H*), 7.34 (m, 2H, pyrrole N-*H*), 7.19 (t, $^3J = 7$ Hz, 1H, Ar-*H*), 6.68 (s, 2H, pyrrole α -*H*), 6.17 (s, 2H, pyrrole β -*H*), 5.98 (s, 2H, pyrrole β -*H*), 5.66 (s, 1H, meso-*H*), 4.29 (t, $^3J = 6.5$ Hz, 2H, N- CH_2 -C-), 1.85 (q, $J = 7.5$ Hz, 2H, C- CH_2 -C-), 1.42 (m, 2H, -C- CH_2 - CH_3), 0.95 (t, $^3J = 7$ Hz, 3H, -C- CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 140.78, 139.57, 133.36, 132.44, 126.26, 125.69, 122.9, 122.56, 120.43, 119.96, 118.75, 117, 108.83, 108.72, 108.38, 107.06, 43.98, 42.89, 31.15, 20.54, 13.87. HRMS (ESI-Q-TOF): $C_{25}H_{24}N_3^-$ $[M-H]^-$ calcd. m/z 366.2048 found. m/z 366.1825. Anal. Calcd. (%) for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 81.79; H, 6.80; N, 11.23.

BODIPY 1: Carbazole DPM (100 mg 0.32 mmol) was dissolved in dichloromethane (38 mL) and oxidized with DDQ (87.17 mg, 0.384 mmol) at RT under air. The reaction mixture was allowed to stir at room temperature for 30 min. Triethyl amine (1.78 mL), followed by $BF_3 \cdot Et_2O$ (2.03 mL) was added to the reaction mixture successively without any time delay. The stirring was continued at room temperature for an additional 30 min., the reaction mixture was evaporated and the crude product was purified by using silica gel column chromatography and eluted with dichloromethane/ petroleum ether (35:65) mixture to afford **BODIPY 1** as orange solid in 50.1% yield (66.3 mg). 1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.35 (s, 1H, Ar-*H*), 8.14 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.94 (s, 2H, pyrrole α -*H*), 7.72 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.56 (m, 3H, Ar-*H*), 7.32 (t, $^3J = 7$ Hz, 1H, Ar-*H*), 7.04 (s, 2H, pyrrole β -*H*), 6.57 (s, 2H, pyrrole β -*H*), 4.4 (t, $^3J = 7$ Hz, 2H, N- CH_2 -C-), 1.94 (t, $^3J = 5$ Hz, 2H, -C- CH_2 -C-), 1.49 (m, 2H, -C- CH_2 - CH_3), 1.01 (t, $^3J = 7$ Hz, 3H, -C- CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 142.85, 142.09, 141.1, 135.2, 131.81, 128.71, 126.72, 124.71, 123.55, 123, 122.53, 120.72, 119.93, 118.16, 109.29, 108.67,

43.22, 31.15, 20.6, 13.87. ^{19}F NMR (470.4 MHz, CDCl_3 , δ ppm): -145.96 (q, 2F). HRMS (ESI-Q-TOF): $\text{C}_{25}\text{H}_{22}\text{BF}_2\text{N}_3^+[\text{M}^+]$: calcd. m/z 413.266 found. m/z 413.1875. Anal. Calcd. (%) for $\text{C}_{25}\text{H}_{22}\text{BF}_2\text{N}_3$: C, 72.66; H, 5.37; N, 10.17. Found: C, 72.32; H, 5.07; N, 10.07.

BODIPY 2: A solution of **BODIPY 1** (50 mg, 0.12 mmol) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (3:3) was taken in RB and a solution of NBS (51.24 mg, 2.4 eq) in CH_2Cl_2 (1.8 mL) was added to it. The mixture was stirred at room temperature for 2 h. The reaction mixture was washed with water and organic layer was extracted with dichloromethane and dried over sodium sulfate. Evaporation of solvent mixture under reduced pressure gave crude compound. Desired compound was isolated via silica gel (100-200 mesh) column chromatography using dichloromethane/petroleum ether (25:75) mixture to afford **BODIPY 2** as dark orange solid in 75% yield (51.7 mg) ^1H NMR (500 MHz, CDCl_3 , δ ppm): 8.27 (d, $J = 5.5$ Hz, 2H, Ar-*H*), 8.0 (s, 1H, pyrrole α -*H*), 7.8 (s, 1H, pyrrole α -*H*), 7.72 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.64 (d, $J = 8.5$ Hz, 1H, Ar-*H*), 7.55 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.38 (d, $J = 8.5$ Hz, 1H, Ar-*H*), 7.08 (s, 1H, pyrrole β -*H*), 6.96 (s, 1H, pyrrole β -*H*), 6.63 (s, 1H, pyrrole β -*H*), 4.37 (t, $^3J = 6.5$ Hz, 2H, N- CH_2 -C-), 1.92 (t, $^3J = 6.5$ Hz, 2H, -C- CH_2 -C-), 1.46 (m, 2H, -C- CH_2 - CH_3), 1.01 (t, $^3J = 7$ Hz, 3H, -C- CH_3). ^{13}C NMR (125.7 MHz, CDCl_3 , δ ppm): 145, 142.43, 141.20, 139.77, 135.47, 134.50, 133.3, 130.47, 129.61, 129.22, 124.65, 124.16, 123.70, 123.58, 122.11, 119.31, 112.96, 110.81, 109.19, 43.41, 31.08, 29.69, 20.55, 13.82. ^{19}F NMR (470.4 MHz, CDCl_3 , δ ppm): -145.96 (q, 2F). HRMS (ESI-Q-TOF): $\text{C}_{25}\text{H}_{20}\text{BBr}_2\text{F}_2\text{N}_3^+[\text{M}^+]$: calcd. m/z 569.0085 found. m/z 569.3715. Anal. Calcd. (%) for $\text{C}_{25}\text{H}_{20}\text{BBr}_2\text{F}_2\text{N}_3$: C, 52.58; H, 3.53; N, 7.36. Found: C, 52.32; H, 3.07; N, 7.23.

Synthesis of Mono-formyl BODIPYs 3 & 4

Phosphoril chloride (5 g, 32.6 mmol) was added slowly to dry DMF (3g) at 0°C and the mixture was stirred for 5 min. under N_2 atmosphere. The mixture was warmed to room temperature and stirred for additional 30 min. **BODIPY 1** (100 mg, 0.24 mmol) in 1,2-DCE was added to the mixture and the resulting solution was stirred for 2 hours at 50°C . Then the reaction mixture was cooled to room temperature and poured into saturated aqueous NaHCO_3 solution at 0°C . After this, the mixture was warmed to room temperature and stirred for further 30 min. Reaction mixture was washed with water and the organic layer was collected, dried over Na_2SO_4 .

Removal of solvent on rotary evaporator gave pure compounds. **BODIPY 3** and **4** were separated as first and second fraction respectively using silica gel column chromatography. **BODIPY 3** was eluted with 50% dichloromethane/petroleum ether and **BODIPY 4** was eluted with 80% dichloromethane/petroleum ether.

BODIPY 3: Dark pink solid in 23% yield (25 mg) ^1H NMR (500 MHz, CDCl_3 , δ ppm): 10.43 (s, 1H, -CHO), 8.35 (s, 1H, Ar-*H*), 8.19 (s, 1H, pyrrole α -*H*), 8.15 (d, $J = 7.5$ Hz, 1H, Ar-*H*), 7.73 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.58 (t, $^3J = 6.5$ Hz, 2 H Ar-*H*), 7.51 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.34 (t, $^3J = 7$ Hz, 1H, Ar-*H*), 7.24 (d, $J = 4$ Hz, 1H, pyrrole β -*H*), 7.15 (d, $J = 5$ Hz, 1H, pyrrole β -*H*), 6.98, (d, $J = 4$ Hz, 1H, pyrrole β -*H*), 6.76 (d, $J = 4$ Hz, 1H, pyrrole β -*H*), 4.41 (t, $^3J = 6.5$ Hz, 2H, N- CH_2 -C-), 1.96 (m, 2H, -C- CH_2 -C-), 1.55 (m, 2H, -C- CH_2 - CH_3), 1.01 (t, $^3J = 7$ Hz, 3H, -C- CH_3). ^{13}C NMR (125.7 MHz, CDCl_3 , δ ppm): 184.57, 151.73, 147.99, 146.96, 142.53, 141.17, 137.1, 136.83, 135.34, 129, 128.91, 127.06, 124.32, 124.07, 123.28, 122.43, 121.23, 120.81, 120.29, 118.1, 109.49, 109.03, 52.33, 43.30, 31.15, 29.70, 20.6, 13.87. ^{19}F NMR (470.4 MHz, CDCl_3 , δ ppm): -137.75 (q, 2F). HRMS (ESI-Q-TOF): $\text{C}_{26}\text{H}_{23}\text{BF}_2\text{N}_3\text{O}^+ [\text{M}+\text{H}]^+$ m/z : 442.1902 found. m/z 442.1822. Anal. Calcd. (%) for $\text{C}_{26}\text{H}_{22}\text{BF}_2\text{N}_3\text{O}$: C, 70.77; H, 5.03; N, 9.52. Found: C, 70.47; H, 5.09; N, 9.29.

BODIPY 4: Reddish maroon solid in 54% (57 mg) ^1H NMR (500 MHz, CDCl_3 , δ ppm): 9.88 (s, 1H, CHO), 8.36 (s, 1H, Ar-*H*), 8.29 (s, 1H, pyrrole α -*H*), 8.15 (m, $J = 6$ Hz, 2H, pyrrole α -*H* + Ar-*H*), 7.74 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.58 (t, $^3J = 8.5$ Hz, 2H, Ar-*H*), 7.51 (d, $J = 8$ Hz, 1H, Ar-*H*), 7.41 (s, 1H, pyrrole β -*H*), 7.34 (t, $^3J = 7$ Hz, 1H, Ar-*H*), 7.25 (d, $J = 8$ Hz, 1H, pyrrole β -*H*), 6.75 (d, $J = 3$ Hz, 1H, pyrrole β -*H*), 4.41 (t, $J = 7$ Hz, 2H, N- CH_2 -C-), 1.95 (m, 2H, -C- CH_2 -C-), 1.48 (m, 2H, -C- CH_2 - CH_3), 1.02 (t, $^3J = 7$ Hz, 3H, -C- CH_3). ^{13}C NMR (125.7 MHz, CDCl_3 , δ ppm): 185.03, 151.75, 151.15, 147.45, 142.62, 142.1, 141.18, 136.87, 135.14, 135.06, 131.74, 128.87, 127.06, 124, 123.93, 123.34, 122.41, 120.89, 120.27, 109.49, 109.15, 43.30, 31.14, 20.60, 13.88. ^{19}F NMR (470.4 MHz, CDCl_3 , δ ppm): -144.98 (q, 2F). HRMS (ESI-Q-TOF): $\text{C}_{26}\text{H}_{23}\text{BF}_2\text{N}_3\text{O}^+ [\text{M}+\text{H}]^+$ m/z : 442.1902 found. m/z 442.1893. Anal. Calcd. (%) for $\text{C}_{26}\text{H}_{22}\text{BF}_2\text{N}_3\text{O}$: C, 70.77; H, 5.03; N, 9.52. Found: C, 70.53; H, 5.14; N, 9.41.

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Supporting Information

The characterization data like ESI-MS, ^1H , ^{13}C , ^{19}F , ^1H - ^1H COSY NMR spectra, Fluorescence and absorption spectra of reported compounds are available as supporting information.

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