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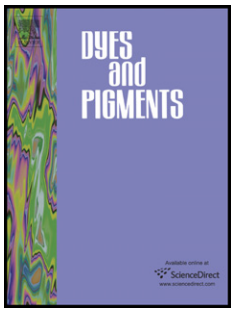

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Graphical Abstract

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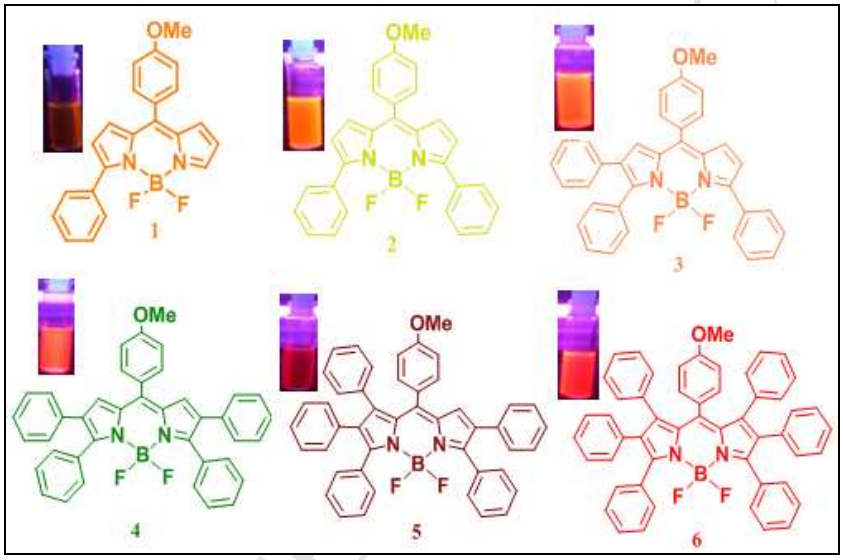

Synthesis, Spectral and Electrochemical Properties of Phenylated Boron-Dipyrromethenes

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Abstract:

The synthesis, absorption, electrochemical and fluorescence properties of boron-dipyrromethenes (BODIPYs) containing one to six phenyl groups at the pyrrole carbons are described. The phenylated BODIPYs were prepared by coupling of appropriate brominated BODIPY with phenyl boronic acid in THF/toluene/H_2O (1:1:1) mixture in the presence of catalytic amount of $Pd(PPh_3)_4/Na_2CO_3$ at 80 °C for overnight. The effect of the number of phenyl substituents at the pyrrole carbons of BODIPY framework on absorption, electrochemical and fluorescence properties were investigated. The absorption and fluorescence studies showed a bathochromic shift in absorption and emission bands, increase in quantum yield and singlet state lifetime upto the presence of four phenyl groups at the pyrrole carbons of BODIPY but the properties were reversed for five and six phenyl substituted BODIPYs. The electrochemical studies indicated that with the increase of number of phenyl groups at the pyrrole carbons of BODIPY framework, the electron rich nature of BODIPY increases.

Key words: Boron-dipyrromethenes, Phenylated BODIPYs, absorption, emission, electrochemical properties, electron rich systems.

1. Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacenes, commonly known as boron-dipyrromethenes or BODIPYs are prominent fluorescent dyes owing to their numerous applications in biological labeling and cell imaging, and also as artificial light harvesters, sensitizers for solar cells, fluorescent sensors, molecular photonic wires, and solid state dye lasers [1-4]. This is because of their excellent properties such as absorption and emission bands in the visible region, large molar absorption coefficients, relatively high fluorescence quantum yields and enhanced stability against chemicals and light [5-7]. Furthermore, the properties of BODIPYs can be fine tuned by introducing appropriate substituents at BODIPY framework as these dyes are amenable for easy modification [8-11]. Hence, the synthetic chemistry of BODIPY dyes has rapidly grown in recent years and several new types of BODIPYs have been synthesized by using functionalized BODIPYs. Specifically, the pyrrole substituted and pyrrole fused BODIPY systems possesses excellent photophysical properties [12-18]. One approach to synthesize pyrrole substituted BODIPYs is by using substituted pyrroles as key synthons [12-16]. However, the substituted pyrroles are not easily accessible. Alternately, the functionalized BODIPY dyes such as halogenated BODIPYs can be used to synthesize pyrrole substituted BODIPYs [19-22]. Although several reports are available on pyrrole substituted BODIPYs, to the best of our knowledge, there is no systematic study of the effect of increasing the number of aryl groups at the pyrrole carbons of BODIPY core on the spectral, electrochemical and photophysical properties of BODIPY. In this paper, we report synthesis, spectral and electrochemical properties of pyrrole phenylated BODIPYs **1-6** where the number of phenyl groups on the BODIPY core has been varied from one to six. Our studies indicated that spectral and electrochemical properties were varied systematically upto introduction of four phenyl

groups but the properties were reversed upon introduction of five and six phenyl groups at the pyrrole carbons of BODIPY.

2. Experimental Section

2.1. General

THF and toluene were dried over sodium benzophenone ketyl and chloroform, ethyl-acetate, methanol, acetonitrile were dried under calcium hydride. $BF_3{\cdot}OEt_2$ 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).

2.2. 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 Varian and spectrometer operating at 282.2 MHz. ^{11}B NMR spectra were recorded on Varian spectrometer operating at 96.3 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 Perkin–Elmer Lambda-35, Varian 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 Rhodamine 6G (Φ_f = 0.88) as standard [23]. 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^{+}) = 0.42 V, vs SCE [24].

2.4 General method for the synthesis of 8-(4-methoxyphenyl)-mono to hexaphenyl-4-bora-3a,4a-diaza-*s*-indacenes (1-6)

Samples of **7-12** (100 mg, 0.13 mmol), phenylboronic acid (387 mg, ~ 2.6 mmol) and Na_2CO_3 (256 mg, 2.44 mmol), water/ THF / toluene (1:1:1) 15 ml were taken in a 100 ml round bottomed flask fitted with a reflux condenser, stirred under N_2 for 5 min. A catalytic amount of $Pd(PPh_3)_4$ (68 mg, ~ 5-10 mol%), was added and the reaction mixture was refluxed at 80 ^{o}C for 1 h to 6 h depending on the number of phenyl groups on the BODIPY. After completion of the reaction as judged by TLC analysis, the reaction mixture was diluted with water (5 ml) and extracted with diethyl ether. The combined organic layers were washed with water, brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified on a silica gel column using petroleum ether/ethyl acetate (95:5) to afford phenylated BODIPYs **1- 4** in 50-55% yield.

2.4.1. 4,4-Difluoro-8-(4-methoxyphenyl)-3-phenyl-4-bora-3a,4a-diaza-*s*-indacene (1)

Yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.91 (s, 3H, -OCH_3), 6.52 (m, 1H) 6.68 (d, 1H, ^{3}J(H,H) = 4.3 Hz, Py), 6.90 (d, 1H, ^{3}J(H,H) = 3.8 Hz, Py), 7.01 (d, 1H, , ^{3}J(H,H) = 4.3 Hz,

Py), 7.05 (d, 2H, , ^{3}J(H,H) = 8.68 Hz, Ar), 7.48 (m, 3H, Ph), 7.55 (d, 2H, , ^{3}J(H,H) = 8.69 Hz, Ar), 7.82 (s, 1H, Py), 7.95 (m, 2H, Ph); ^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -139.01 (q, ^{3}J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 0.92 (t, ^{3}J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.68, 114.13, 118.08, 120.89, 126.72, 128.47, 129.57, 129.67, 130.01, 132.53, 132.77, 134.22, 137.21, 141.94, 145.89, 159.88, 161.93. HR-MS calcd for $C_{22}H_{17}BF_2N_2O$ 355.1418 $(M\text{-}F)^+$, found 355.1434 $(M\text{-}F)^+$.

2.4.2. 4,4-Difluoro-8-(4-methoxyphenyl)-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (2)

Yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.93 (s, 3H, -OCH_3), 6.62 (d, 2H, ^{3}J(H,H) = 4.3 Hz, Py), 6.95 (d, 2H, ^{3}J(H,H) = 3.8 Hz, Py), 7.07 (d, 2H, , ^{3}J(H,H) = 8.6 Hz, Ar), 7.41 (m, 6H, Ph), 7.56 (d, 2H, , ^{3}J(H,H) = 8.69 Hz, Ar), 7.87(m, 4H, Ph);^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -132.39 (q, ^{3}J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 1.48 (t, ^{3}J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.68, 114.13, 118.08, 120.89, 126.72, 128.47, 129.57, 129.67, 130.01, 132.53, 132.77, 134.22, 137.21, 141.94, 145.89, 159.88, 161.93. ES-MS calcd for $C_{28}H_{21}BF_2N_2O$ 431.1731 $(M\text{-}F)^+$, found 431.1747 $(M\text{-}F)^+$.

2.4.3 4,4-Difluoro-8-(4-methoxyphenyl)-2,3,5-triphenyl-4-bora-3a,4a-diaza-*s*-indacene (3)

Yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.90 (s, 3H, -OCH_3), 6.64 (d, 1H, ^{3}J(H,H) = 4.3 Hz, Py), 6.95 (d, 1H, ^{3}J(H,H) = 3.8 Hz, Py), 7.05 (m, 5H, Ph), 7.14(m, 3H, Py+ Ph), 7.36 (m, 6H, Ph), 7.49 (d, 2H, , ^{3}J(H,H) = 8.69 Hz, Ar), 7.59 (d, 2H, , ^{3}J(H,H) = 8.69 Hz, Ar), 7.84(m, 2H, Ph);^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -132.50 (q, ^{3}J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 1.26 (t, ^{3}J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.68, 114.09, 114.23, 120.99, 126.95, 127.97, 128.38, 129.14, 129.56, 130.60, 131.27, 132.15,

132.55, 132.71, 134.13, 134.34, 134.50, 136.75, 144.33, 155.54, 159.01, 161.73. HR-MS calcd for $C_{34}H_{35}BF_2N_2O$ 507.2044 $(M-F)^+$, found 507.2046 $(M-F)^+$.

2.4.4. 4,4-Difluoro-8-(4-methoxyphenyl)-2,3,5,6-teraphenyl-4-bora-3a,4a-diaza-*s*-indacene (4)

Yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.92 (s, 3H, -OCH_3), 7.05 (m, 9H, Ph + Py) 7.14 (m, 6H, Ph), 7.31 (m, 6H, Ar), 7.48(m, 4H, Ph), 7.65 (d, 2H, Ar); ^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -132.63 (q, ^3J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 1.08 (t, ^3J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.71, 114.20, 127.02, 128.34, 128.34, 128.46, 128.76, 129.20, 130.58, 132.02, 132.64, 134.15, 134.54, 134.79, 156.12, 161.84. HR-MS calcd for $C_{40}H_{29}BF_2N_2O$ 583.2357, found 583.2358 $(M-F)^+$.

2.4.5. 4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (5)

Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.72 (s, 3H, -OCH_3), 6.51 (d, 2H, ^3J(H,H) = 6.8 Hz, Ar), 6.66 (m, 4H, Ph + Py), 6.91 (m, 10H, Ph), 7.14 (m, 4H, Ph), 7.32 (m, 6H, Ph), 7.41(m, 2H, Ph), 7.49 (d, 2H, Ar);^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -131.88 (q, ^3J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 1.17 (t, ^3J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.68, 114.13, 118.08, 120.89, 126.72, 128.47, 129.57, 129.67, 130.01, 132.53, 132.77, 134.22, 137.21, 141.94, 145.89, 159.88, 161.93. HR-MS calcd for $C_{46}H_{33}BF_2N_2O$ 659.2670 $(M-F)^+$, found 659.2699 $(M-F)^+$.

2.4.6. 4,4-Difluoro-8-(4-methoxyphenyl)1,2,3,5,6,7-hexaphenyl-4-bora-3a,4a-diaza-*s*-indacene (6)

Yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.51 (s, 3H), 5.89 (d, 2H, ^{3}J(H,H) = 8.76 Hz), 6.54-6.56 (m, 8H), 6.70-6.79 (m, 8H), 6.89-6.93 (m, 6H), 7.28-7.39 (m, 6H), 7.42 (d, 4H, ^{3}J(H,H) = 5 Hz); ^{19}F NMR (376.49 MHz, $CDCl_3$, δ in ppm) -131.30 (q, ^{3}J(B,F) = 64.0 Hz); ^{11}B NMR (128.38 MHz, $CDCl_3$, δ in ppm) 1.20 (t, ^{3}J(B,F)= 30.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 55.22, 112.4, 123.9, 125.5, 125.7, 126.3, 127.2, 127.5, 127.6, 128.4, 128.8, 129.2, 130.4, 130.9, 131.9, 132.4, 133.3, 133.6, 134.7, 134.9, 144.2, 156, 160; HRMS calcd for $C_{52}H_{37}BF_2N_2O$ 735.2983 $(M-F)^+$, found 735.3001 $(M-F)^+$.

3. Results and Discussion:

Although the synthesis of phenylated BODIPYs containing one to six phenyl groups at pyrrole carbons of BODIPY have been reported earlier in different reports [25-31], we realized that the synthetic routes which adopted were different and there is no single report that describes the synthesis and properties of all BODIPYs **1-6** containing one to six phenyls at pyrrole carbons. To provide complete synthetic information in one report, in this paper, we describe the synthesis of all BODIPYs **1-6** containing one to six phenyl groups which were prepared from their corresponding brominated BODIPYs **7-12** by coupling with phenylboronic acid under Pd(0) coupling conditions. The BODIPYs containing one to six bromines **7-12** were prepared as reported by us earlier [32]. The phenylated BODIPYs **1-6** were synthesized by coupling of their corresponding brominated BODIPY compounds **7-12** with appropriate equivalents of phenylboronic acid in THF/toluene/H_2O (1:1:1) mixture in the presence of catalytic amount of $Pd(PPh_3)_4/Na_2CO_3$ at 80 °C for overnight as shown in the Scheme 1. The reflux time was varied from 1 h to 6 h depending on the number of phenyl groups on the BODIPY. For one and two phenylated BODIPYs, the reaction was completed in 1 h whereas in case of three and four

phenylated compounds, the reaction requires 3 h but for penta and hexaphenylated BODIPYs, longer reaction times upto 6 h are required. The progress of the reaction was followed by TLC analysis which clearly showed the spot corresponding to the required phenylated BODIPY along with one or two minor spots corresponding to lower and higher analogues of phenylated BODIPYs. For example, compound **10** on reaction with four equivalents of phenyl boronic acid under Pd(0) coupling conditions showed four spots on tlc within 1 h corresponding to mono, di, tri and tetraphenylated BODIPYs. However, as the reaction was progressed, the spots corresponding to other phenylated BODIPys were almost disappeared and a spot corresponding to tetraphenylated BODIPY was clearly appeared. Furthermore, we also noted that the bromo groups present at the 3 and 5-positions of BODIPY were more reactive compared to bromines present at the 2- and 6-positions of BODIPY. The penta and hexaphenylated BODIPYs requires longer reaction times due to steric hindrance. The crude compounds were purified by silica gel column chromatography and afforded pure fluorescent solids **1-6** in 60-80% yields. The compounds **1-6** were freely soluble in common organic solvents and characterized by mass and various spectroscopic techniques. The HR-MS mass spectra showed the corresponding expected molecular ion peak confirming the identity of compounds **1-6**.

The compounds **1-6** were characterized in detail by ^{1}H, ^{19}F and ^{11}B NMR. ^{1}H-^{1}H COSY also recorded for couple of compounds to identify all the signals in ^{1}H NMR. The representative ^{1}H NMR and ^{1}H-^{1}H COSY NMR spectra for compound **3** are shown in Figure 1. In ^{1}H NMR of pyrrole unsubstituted *meso*-anisyl BODIPY **13** [33], the six pyrrole protons appeared as three sets of signals. The compounds **1-6** showed signals for pyrrole protons as well as for substituted phenyl groups. However, the number of pyrrole signals in compounds **1-6** are either more or less depending on the symmetric nature of the compound as well as on the number of phenyl groups.

No pyrrole signal was observed for compound **6** due to presence of six phenyl groups at six pyrrole carbons. The comparison of ^{19}F and ^{11}B NMR spectra of compounds **1-6** along with compound **13** is shown in Figure 2 and the relevant data is tabulated in Table 1. Compounds **1-6** showed a typical quartet in ^{19}F and triplet in ^{11}B NMR due to coupling with each other. However, compounds **1-6** exhibited slight shifts in ^{19}F and ^{11}B NMR compared to **13** indicating that the π-delocalization is altered in the boron-dipyrrin core due to presence of phenyl groups at the pyrrole carbons.

The absorption spectra of pyrrole phenylated BODIPYs **1-6** were recorded in five different solvents of varying polarity and the data are presented in Table 2. The comparison of absorption spectra of pyrrole phenylated BODIPYs **1-6** along with unsubstituted BODIPY **13** [33] recorded in toluene is shown in Figure 3. The pyrrole phenylated BODIPYs **1-6** showed absorption features of typical of BODIPYs such as a strong band in the 500-600 nm region corresponding to $S_0 \rightarrow S_1$ transition with a vibronic transition on the higher energy side as a shoulder and an ill-defined, weak band corresponding to the $S_0 \rightarrow S_2$ transition at about 400 nm. The introduction of phenyl group at the pyrrole carbons of BODIPY core resulted in bathochromic shift compared to unsubstituted *meso*-anisyl BODIPY **13** [33] and the magnitude of red shift of absorption band depends on the number of phenyls substituted at the BODIPY core However, this systematic red shift was observed only upto the presence of four phenyls at the pyrrole carbons in compounds **1** to **4**. In case of five and six phenyls substituted compounds **5** and **6** respectively, the absorption band was slightly blue shifted. This indicates that the phenyl substituents at 1 and 7 positions induce steric crowding resulting in the decrease of effective π-conjugation in the BODIPY core.

A comparison of steady state fluorescence spectra of compounds **1-6** along with **13** in toluene using same concentration is shown in Figure 4. Compounds **1-6** showed one single broad emission band in the region of 540-650 nm. The emission band of compounds **1-4** experiences bathochromic shift with the increase of number of phenyl groups upto four compared to **13** but the emission band shifts towards blue for compounds **5** and **6** containing five and six phenyl groups respectively at the pyrrole carbons of BODIPY (Table 2). The quantum yield Φ_f of compounds **1-6** calculated by comparative method [23] indicated a steady increase in the quantum yield on the increase of number of phenyl groups at the pyrrole carbons of BODIPY compared to **13**. Surprisingly, compound **5** showed a weak fluorescence with low quantum yield compared to other phenylated BODIPYs which needs further investigation. The singlet state lifetimes τ of compounds **1-6** along with compound **13** in toluene were measured using time-correlated single photon counting (TCSPC) technique (Table 2). The fluorescence decays of compounds **1-6** were fitted to single exponential and a representative fluorescence decay profile for compound **4** is shown in Figure 5. The singlet state lifetimes of compounds **1-6** were in agreement with their fluorescence quantum yields. The lifetimes τ of weakly fluorescent compounds **1** and **5** were not obtained due to limitation of our instrument. Using the experimental Φ_f and τ values, we calculated the radiative k_r and nonradiative k_{nr} rate constants which are in agreement with the quantum yield and singlet state life time data. The absorption and fluorescence properties of compounds **1-6** were also investigated by changing the polarity of the solvent. With the increase of solvent polarity, the absorption and emission bands of compounds **1-6** experienced slight blue shift and the quantum yields and singlet state lifetimes were decreased (Table 2).

The redox properties of phenylated BODIPYs **1-6** are probed through cyclic voltammetric and differential pulse voltammetric studies using tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) in dichloromethane as solvent. The comparison of cyclic voltammograms and diffential pulse voltammograms of **1-6** are presented in Figure 6 and redox potential data are tabulated in Table 3. In general, BODIPYs such as compound **13** show one irreversible oxidation and one reversible reduction indicating that BODIPYs are electron deficient. Since compounds **1-6** contain electron rich phenyl groups, we expected that compounds **1-6** are stable under oxidation conditions. As clear from the Figure 6, the compounds **1-3** exhibited an irreversible oxidation but compounds **4-6** showed one reversible oxidation supporting that the electron rich nature of BODIPY core increases with the increase of number of phenyl groups. Furthermore compounds **1-6** showed one reversible reduction. However, the reduction potential did not alter much with the increase of the number of phenyl groups in compounds **1-6**.

3. Conclusion

In conclusion, we synthesized BODIPYs containing one to six phenyl groups at the pyrrole carbons of BODIPY framework to study the effect of number of phenyl groups on spectral and electrochemical properties of BODIPY. The absorption and fluorescence bands experienced systematic bathochromic shifts on introduction of phenyl groups but the systematic trend was observed only upto introduction of four phenyl groups. However, BODIPYs containing five and six phenyl groups showed hypsochromically shifted absorption and emission bands. The fluorescence quantum yields and singlet state lifetimes were also follow same trend. The electrochemical studies indicated that BODIPY core which is normally electron deficient in

unsubstituted BODIPY changes to electron rich with the increase of number of phenyl groups at the pyrrole carbons of BODIPY framework.

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Table 1: The ^{19}F and ^{11}B NMR spectra data of compounds **1-6** along with **13** recorded in $CDCl_3$ (δ in ppm)

Compound	^{19}F	^{11}B
13	-145	0.34
1	-139	0.91
2	-132.4	1.49
3	-132.5	1.26
4	-132.6	1.06
5	-131.9	1.19
6	-131.3	1.19

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Table 2: The photophysical data of compounds **1-6** along with **13** in different solvents.

		λ_{abs}	λ_{em}	*log* ε	Φ_f	τ [ns]	K_r	k_{nr}
Compd	Solvent	[nm]	[nm]				$10^9 s^{-1}$	$10^9 s^{-1}$
13	Toluene	501	517	4.76	0.11	0.72	0.16	1.23
	$CHCl_3$	499	515	4.76	0.097	0.72	0.14	1.25
	THF	497	515	4.74	0.052	0.41	0.13	2.3
	EtOAc	495	511	4.75	0.035	0.32	0.18	1.93
	MeCN	494	511	4.71	0.0013	0.24	0.13	4.04
1	Toluene	529	553	4.69	0.05	---	---	---
	$CHCl_3$	527	550	4.65	0.043	---	---	---
	THF	526	548	4.67	0.029	---	---	---
	EtOAc	523	545	4.69	0.023	---	---	---
	MeCN	520	545	4.57	0.015	---	---	---
2	toluene	555	587	4.84	0.46	2.5	0.18	0.22
	$CHCl_3$	552	586	4.82	0.29	2.2	0.13	0.32
	THF	552	585	4.84	0.27	1.8	0.15	0.41
	EtOAc	547	581	4.82	0.29	1.5	0.19	0.47
	MeCN	543	580	4.78	0.17	1.0	0.17	0.83
3	Toluene	570	604	4.79	0.49	3.4	0.14	0.15
	$CHCl_3$	568	603	4.79	0.34	3.7	0.09	0.15
	THF	566	600	4.67	0.36	2.9	0.12	0.22
	EtOAc	562	598	4.78	0.32	2.7	0.12	0.25
	MeCN	556	598	4.73	0.22	2.0	0.11	0.39
4	toluene	586	616	4.52	0.66	3.8	0.17	0.09
	$CHCl_3$	582	616	4.51	0.48	4.1	0.12	0.13
	THF	580	614	4.51	0.39	3.3	0.12	0.18
	EtOAc	576	611	4.48	0.37	3.2	0.11	0.19
	MeCN	569	611	4.45	0.34	2.5	0.14	0.26
5	toluene	580	613	4.81	0.11	---	---	---
	$CHCl_3$	577	612	4.79	0.075	---	---	---
	THF	574	609	4.82	0.037	---	---	---
	EtOAc	570	606	4.80	0.049	---	---	---
	MeCN	562	605	4.76	0.033	---	---	---
6	toluene	575	609	4.68	0.41	2.2	0.19	0.27
	$CHCl_3$	573	607	4.67	0.39	2.5	0.17	0.25
	THF	570	604	4.65	0.22	1.6	0.14	0.48
	EtOAc	566	601	4.67	0.25	2.2	0.11	0.34
	MeCN	555	596	4.63	0.26	1.9	0.14	0.39

Table 3: Electrochemical data of compounds **1-6** recorded in CH_2Cl_2, measured with n-$Bu_4N^+P(ClO_4)_6^-$ (0.1 M) as a electrolyte at a scan rate of 50 mV s^{-1}. [a]Irrversible oxidation.

Compound	Oxidation Potential (V vs SCE)	Reduction Potential (V vs SCE)
13	1.68[a]	-0.81
1	1.46[a]	-0.83
2	1.33[a]	-0.84
3	1.33[a]	-0.81
4	1.32	-0.79
5	1.32	-0.80
6	1.32	-0.86

Figure Captions

Figure 1: (a) ^1H NMR (b) ^1H-^1H COSY NMR spectra of compound **3** recorded in $CDCl_3$

Figure 2: Comparison of (a) ^{19}F and (b) ^{11}B NMR spectra of compounds **1-6** along with **13**.

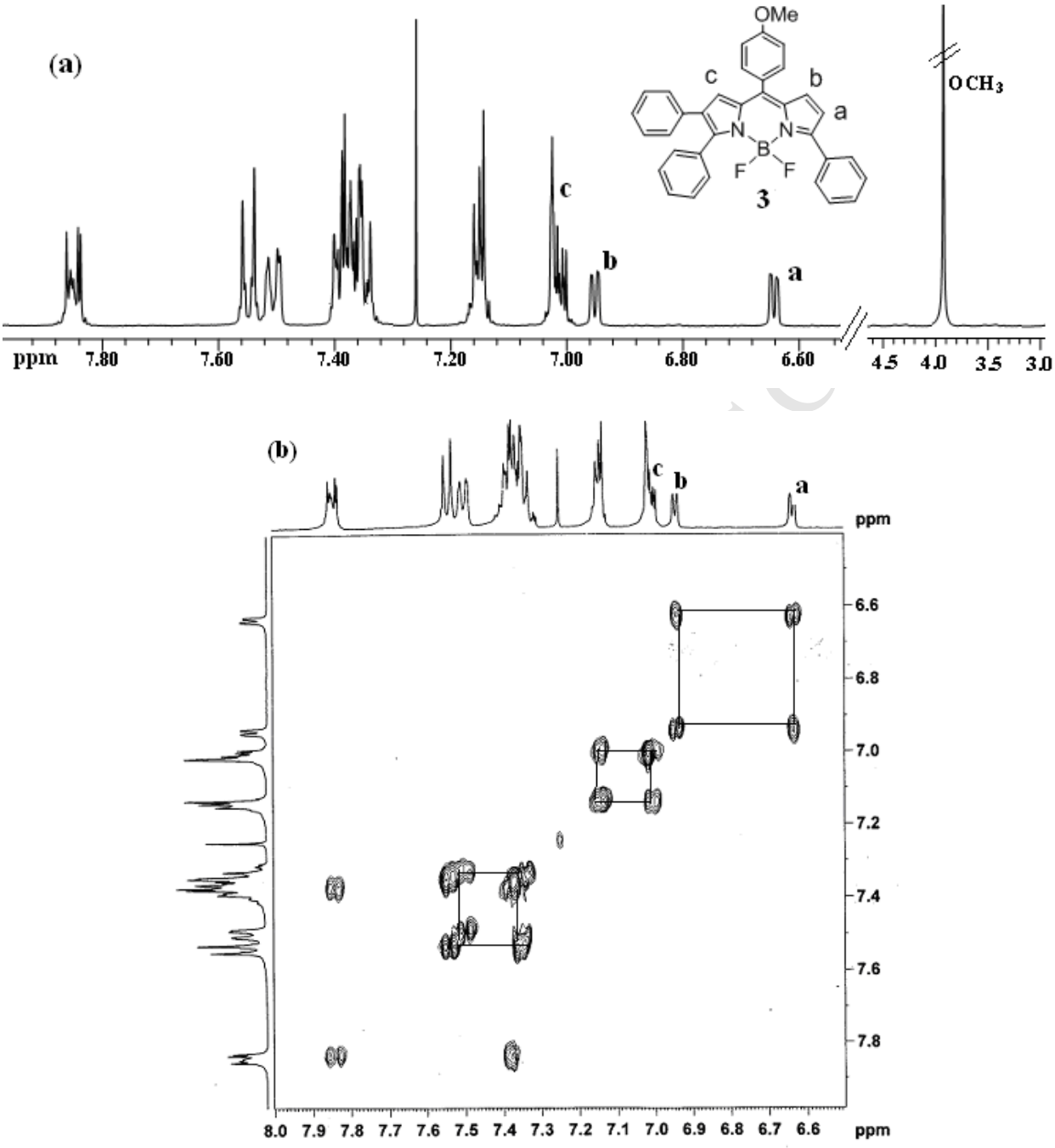
Figure 3: The comparison of normalized absorption spectra of phenylated compounds **1-6** along with **13** recorded in toluene

Figure 4: The comparison of normalized emission spectra of compounds **1-6** along with **13** recorded in toluene

Figure 5: A representative fluorescence decay profile and weighted residual distribution fit of **4** in toluene. The excitation wavelength used was 440 nm and emission was detected at 616 nm

Figure 6: The cyclic Voltammogram (solid line) and differential pulse voltammogram (dotted line) of compounds **1-6** recorded in CH_2Cl_2 containing 0.1 M $Bu_4N^+P(ClO_4)_6^-$ as supporting electrolyte recorded at 50 mV s^{-1} scan speed.

Scheme 1: Synthesis of phenylated BODIPY compounds **1-6**. [a]$Pd(PPh_3)_4$, Na_2CO_3, phenylboronic acid; toluene, THF, water (1:1:1)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b
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Figure 1

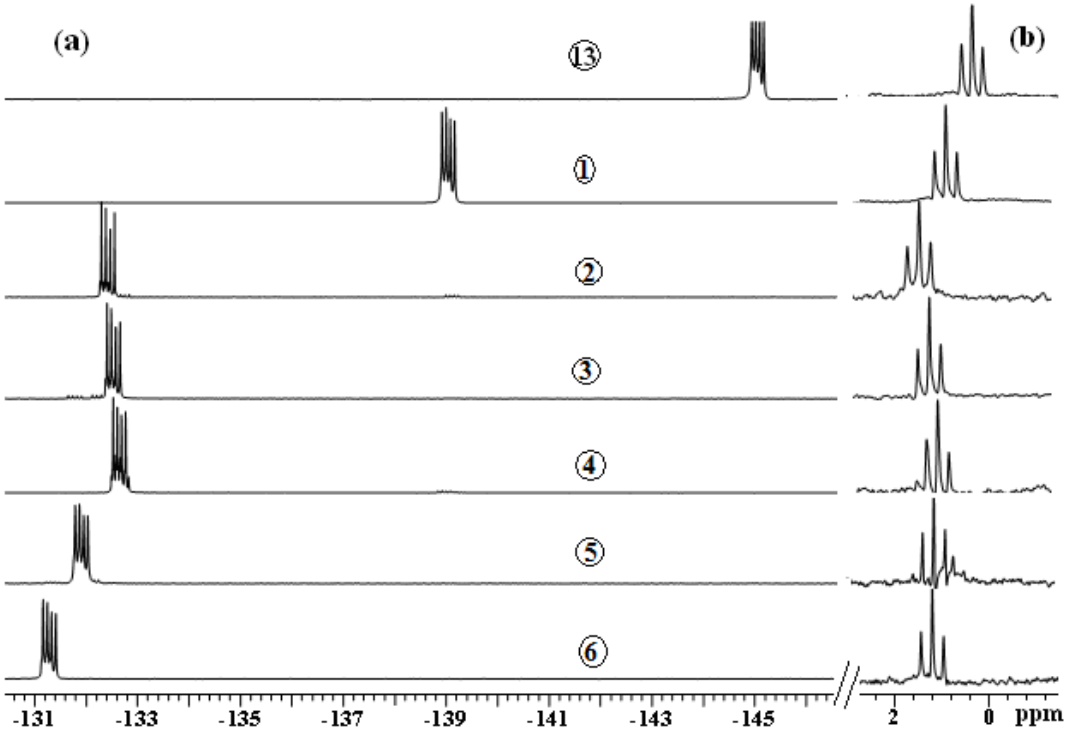


Figure 2

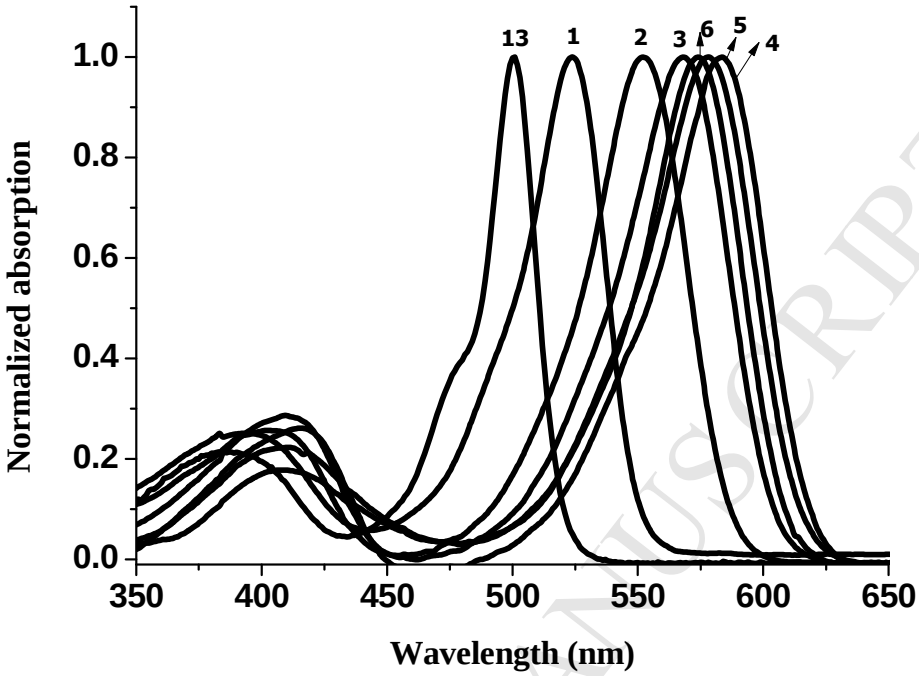
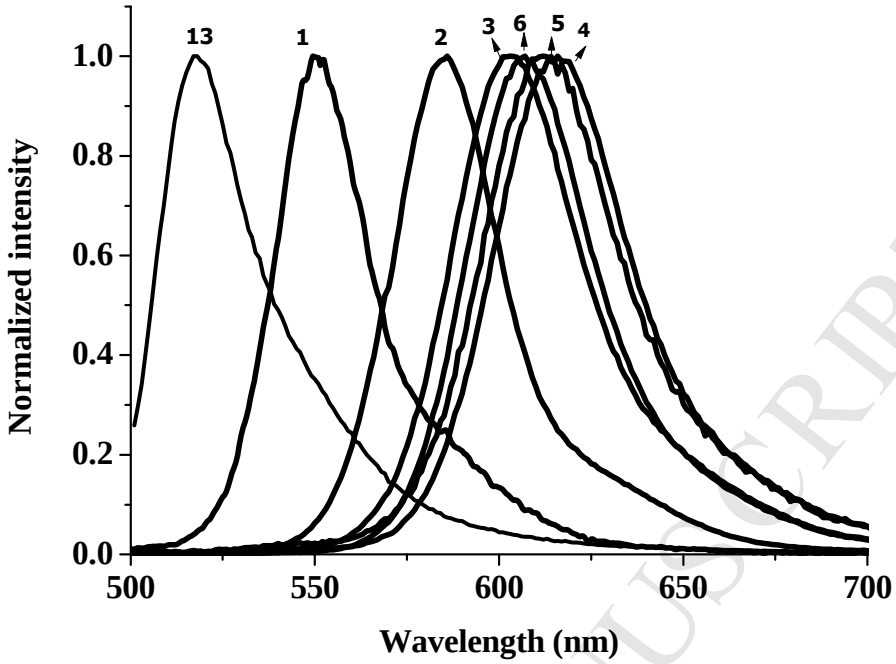


Figure 3



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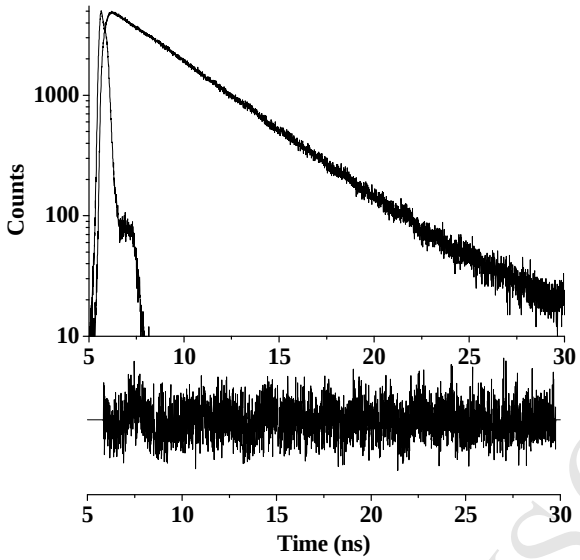

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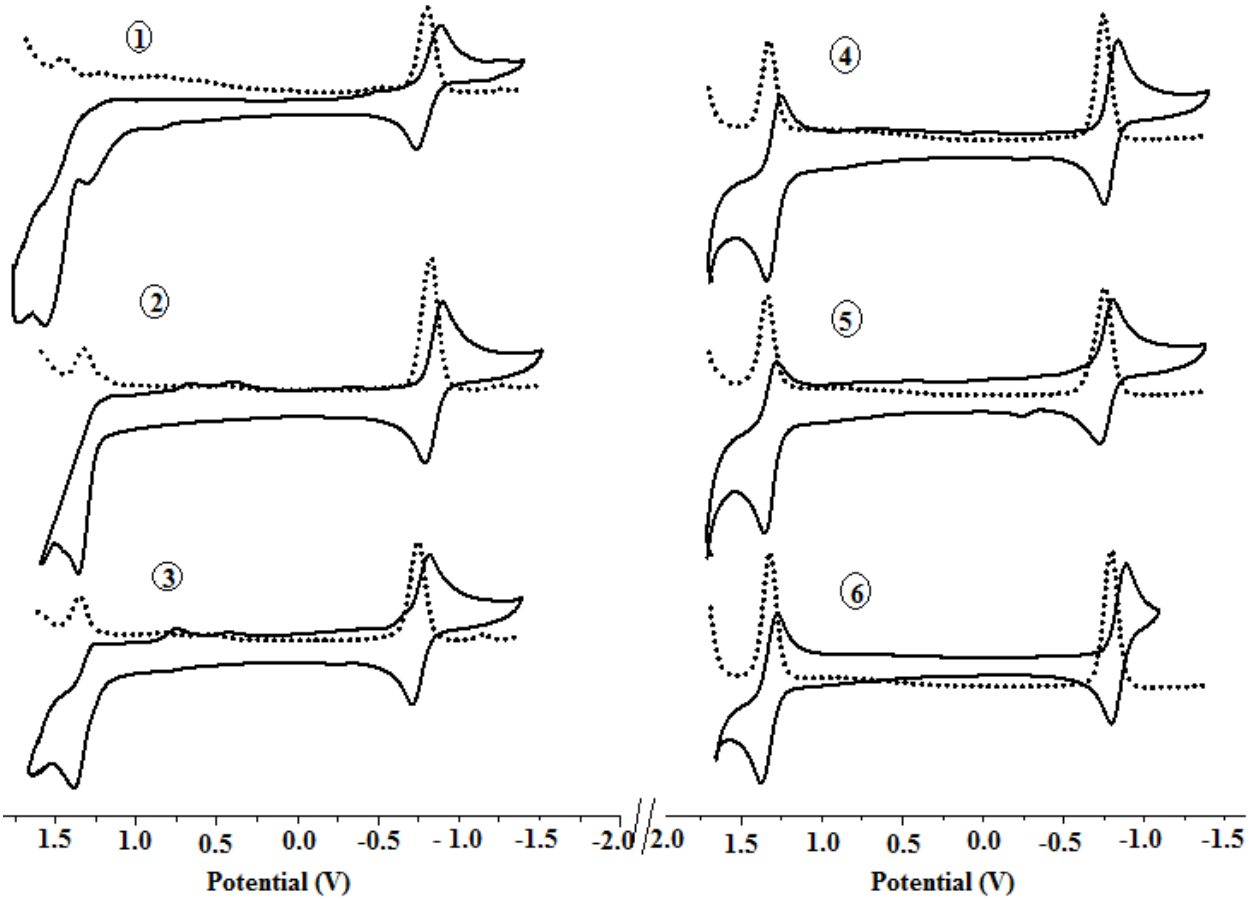
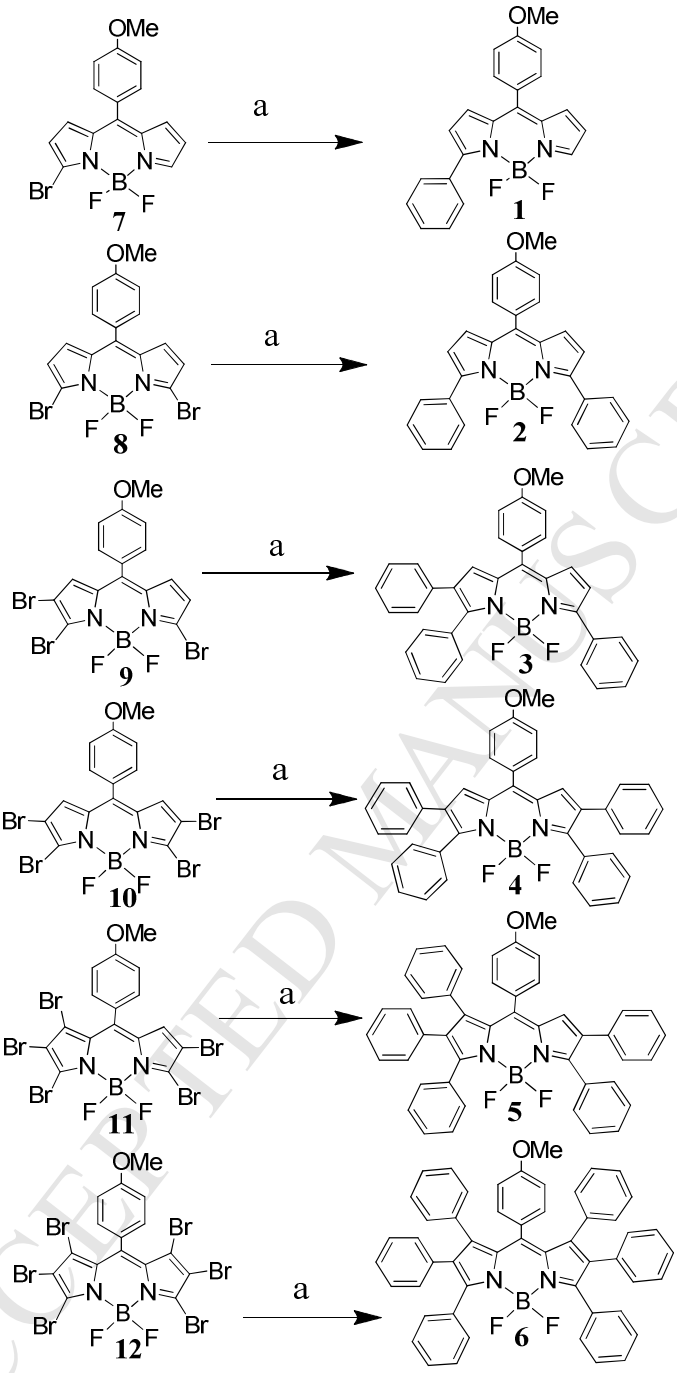


Figure 6



Scheme 1

Research Highlights

- Synthesized a series of boron dipyrromethenes containing phenyl groups at the pyrrole carbons.
- The introduction of phenyl groups at the pyrrole carbon of the BODIPY core alters the electronic properties.
- Absorption and emission properties were systematically altered upto introduction of four phenyl groups.
- BODIPY core becomes electron rich and oxidation becomes easier with the increase of number of phenyl groups.