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Polyarylated Boron-Dipyrromethenes Containing Three Different Types of Aryl Groups

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Abstract

We report the synthesis and properties of first examples of four novel multiply hexaarylated boron-dipyrromethenes (BODIPYs) containing three different types of aryl groups on each pyrrole ring of BODIPY. The BODIPYs were synthesized over sequence of steps of bromination followed by Suzuki coupling with arylboronic acids. All reactions worked smoothly and we isolated the multiply polyarylated BODIPYs as stable fluorescent solids in high yields. The hexaarylated BODIPYs and associated reference compounds were confirmed by HR-MS and characterized by NMR, absorption, fluorescence and electrochemical techniques. The multiply polyarylated BODIPYs absorb strongly in 550-600 nm region and emits in 590-640 nm region with decent quantum yields and singlet state lifetimes. The polyarylated BODIPYs are very stable under redox conditions.

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Introduction

Sterically crowded boron difluoride dipyrrin complexes (BODIPYs) are brightly fluorescent in the solid state[1] and have potential use in the field of optoelectronics, such as high performance electroluminescent devices, light-emitting field-effect transistors and lasers.[2] The sterically crowded BODIPYs can be prepared by introducing bulkier aryl groups at the pyrrole carbons of BODIPY.[3] The sterically crowded polyarylated BODIPYs can be prepared either by using aryl substituted pyrroles[1,3] or by using the functionalized BODIPYs[4] as key precursors. The aryl substituted pyrroles are not easily accessible and their synthesis involves several steps.[1,5] In recent times, the functionalized BODIPYs have been used as building blocks to synthesize a variety of substituted BODIPYs.[6] However, the functionalization at all six pyrrole carbons of BODIPY is also not easy task and a perusal of literature revealed that there are very few reports available in literature which deals with the synthesis of sterically crowded BODIPYs using the functionalized BODIPYs.[4] Recently, we developed a rapid synthetic route for sterically crowded polyarylated symmetrical BODIPYs by coupling hexabromo BODIPY with arylboronic acids under Pd(0) coupling conditions.[4a] The symmetrical polyarylated BODIPYs exhibits very interesting photophysical and electrochemical properties[7] and show good fluorescence in the solid state.[1] Thus, our synthetic strategy is now well established for the synthesis of sterically crowded polyarylated BODIPYs having one type of aryl group at all pyrrole carbons. However, no reports are available if one wants to introduce three different types of aryl groups on BODIPY i.e. each pyrrole of BODIPY unit having three different types of aryl groups. The presence of three different types of aryl groups on six pyrrole carbons of BODIPY helps in tuning the electronic properties of BODIPY and makes them ideal compounds for wide range of applications. However, the extensive halogenation reactions carried out on

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BODIPY made clear about the regioselectivity of halogenations on BODIPY.[4b] This helps in introducing halogens selectively at the desired positions and the halogenated BODIPYs are useful for coupling with desired aryl boronic acids under Pd(0) coupling conditions to prepare polyarylated BODIPYs having different types of aryl groups. Thus, we adopted step-wise approach to synthesize such novel sterically crowded multiply polyarylated BODIPYs. In this paper, we describe our successful attempts towards the synthesis of sterically crowded multiply polyarylated BODIPYs **1-4** containing three different types of aryl groups (Figure 1) on each pyrrole ring by coupling of bromo BODIPYs with three different types of arylboronic acids over sequence of steps. These multiply polyarylated BODIPY compounds **1-4** are difficult to synthesize by other rational methods and our approach is very convenient and high yielding. Furthermore, the required precursors, bromo functionalized BODIPYs[8] can be prepared readily in good quantities. The spectral and electrochemical properties of multiply polyarylated BODIPYs **1-4** (Figure 1) are also described.

Results and Discussion

The multiply polyarylated BODIPYs **1-4** were prepared over sequence of steps. We started with 3,5-dibromo BODIPY **5** as key precursor which was prepared in good quantity by following the reported procedure.[9] The 3,5-dibromo BODIPY **5** was coupled with two equivalents of 4-phenylboronic acid in the presence of $Pd(PPh_3)_4/Na_2CO_3$ in THF/toluene/water (1:1:1) at 80 °C for 1 h followed by column chromatographic purification afforded 3,5-diphenyl BODIPY[8a] **6** in 87% yield (Scheme 1). The BODIPYs **5** and **6** were characterized by mass and various spectroscopic techniques and the data was in agreement with the reported data.[8a,9] The 3,5-diphenyl BODIPY **6** was treated with 2.2 equivalents of Br_2 in CH_2Cl_2 at room tempearture

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under inert atmosphere for 1.5 h. TLC analysis showed the desired 3,5-diphenyl-2,6-dibromo BODIPY **7** as major pink coloured spot accompained by less polar faint spot corresponding to the unidentified higher homologue of brominated BODIPY and more polar minor spot corresponding to the starting compound **6**. Column chromatographic purification on silica afforded BODIPY **7** in 85% yield. The molecular ion peak in ESI-MS spectrum confirmed the identity of compound **7** (Figure S21). In ^{1}H NMR, the resonance corresponding to 2,6-protons which appeared at 6.62 ppm in compound **6** was completely disappeared in compound **7** due to substitution by bromines (Figure S22). In absorption spectrum, the absorption band at 551 nm in compound **6** experienced bathochromic shift and appeared at 562 nm in compound **7** due to presence of two bromines at 2- and 6-pyrrolic carbons. It is known in the literature[4b] that the halogenation first occurs on BODIPY at 2 and 6-pyrrolic carbons followed by other pyrrolic carbons. Thus, we obtained compound **7** in good yield which is the key synthon to prepare multiply polyarylated BODIPYs **1-4**.

Towards the synthesis of compound **1**, first we prepared the tetraarylated BODIPY **8** by treating compound **7** with *p*-tolylboronic acid in the presence of $Pd(PPh_3)_4/Na_2CO_3$ in THF/toluene/water (1:1:1) at 80 °C for 3 h (Scheme 1). Column chromatographic purification on silica gel of crude reaction mixture afforded compound **8** in 81% yield. In ^{1}H NMR spectrum of compound **8**, the signal at 2.27 ppm corresponding to six protons of CH_3 group and more number of signals in the aromatic region were observed (Figure S27). In absorption spectrum, the band at 562 nm in **7** was shifted bathochromically by 22 nm and appeared at 584 nm in compound **8.** In the next step, compound **8** was treated with six equivalents of Br_2 in CH_2Cl_2 at room temperature for 2 h (Scheme 1). The crude reaction mixture was subjected to silca gel column chromatographic purification and afforded compound **9** in

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89% yield. We optimized the bromination conditions for the synthesis of compound **9** and the best yields were obtained when we used six equivalents of Br_2. The molecual ion peak in HR-MS spectrum and the disappearance of resonance at 7.02 ppm corresponding to 1 and 7-pyrrolic protons in ^{1}H NMR confirmed the identity of the compound **9** (Figure S32). The compound **9** showed hypsochromically shifted absorption band at 562 nm compared to compound **8**. In the last step, the compound **9** was reacted with 4-fluorophenylboronic acid in the presence of $Pd(PPh_3)_4/Na_2CO_3$ in THF/toluene/water (1:1:1) at 80 °C for 5 h. The crude reaction mixture was subjected to silica gel column chromatography and afforded the desired BODIPY **1** containing three different types of aryl groups on each pyrrole of BODIPY unit in 85% yield. To prepare the multiply polyarylated BODIPY **2**, we first prepared the tetrasubstituted BODIPY **10** by treating compound **7** with *p*-anisylboronic acid under similar Suzuki coupling conditions. The compound **10** was subjected to bromination by treating compound **10** with six equivalents of Br_2 in CH_2Cl_2 at room temperature and afforded brominated compound **11** in 88% yield. The brominated compound **11** was further reacted with two equivalents of 4-biphenylboronic acid under same Pd(0) coupling conditions (Scheme 1) and the resulted crude compound was subjected to silica gel column chromatographic purification to afford pure compound **2** in 86% yield.

The compound **3** was also synthesized similarly by reacting compound **7** with *o*-tolyl boronic acid under Suzuki coupling conditions and the resulted tetraraylated BODIPY **12** was subjected to bromination to afford dibromo tetraraylated BODIPY **13** in 91% yield (Scheme 2). The compound **13** was then coupled with 4-ethenylphenylboronic acid under similar Pd(0) coupling conditions and obtained compound **3** in 83% yield. To obtain compound **4**, we first reacted compound **7** with 4-*tert*-butylphenylboronic acid under Pd(0) coupling conditions and

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the resulted tetraarylated BODIPY **14** was treated with Br_2 in CH_2Cl_2 to room temperature to afford compound **15** in 78% yield (Scheme 3). The reaction of compound **15** with 4-phenoxyphenylboronic acid under same Suzuki coupling conditions afforded the compound **4** in 61% yield.

The compounds **1-4** are freely soluble in common organic solvents and the identities of the compounds were confirmed by correponding molecular ion peak in their respective HR-MS mass spectra. The compounds **1-4** were characterized in detail by ^{1}H, ^{1}H-^{1}H COSY, ^{11}B and ^{19}F NMR spectroscopy. The ^{1}H and ^{1}H-^{1}H COSY NMR spectra of compound **1** are presented in Figure 2. The cross peak correlations observed in ^{1}H-^{1}H COSY NMR were used to identify and assign all resonances observed in ^{1}H NMR. The detailed NMR spectral analysis of compound **1** is explained as follows: We attempted first to identify the aryl signals corresponding to *meso*-tolyl group. The CH_3 signal (*type I*) of *meso*-tolyl group observed at 2.02 ppm showed cross peak correlation with a doublet signal at 6.28 ppm which we identified as *type a* protons of *meso*-tolyl group. The *type a* protons at 6.28 ppm showed cross peak correlation with a doublet at 6.64 ppm (Figure 2b) which we assigned as *type b* protons of *meso*-tolyl group. The CH_3 signal (*type II*) of tolyl groups present at the 2 and 6-positions of BODIPY **1** observed as singlet at 2.14 ppm showed cross peak correlation with a doublet at 6.73 ppm (Figure 2b) which we identified as *c-type* protons. The multiplet in 6.45-6.52 ppm region was assigned as *d-type* protons as this resonance showed cross-peak correlation with resonance at 6.73 ppm (*c-type,* Figure 2c). The aryl signals of *p*-fluorophenyl groups at 1- and 7-positions of BODIPY were also identified similarly. The *e-type* protons were appeared as triplet at 6.73 ppm which showed correlation with multiplet resonance appeared in 6.45-6.52 ppm region which we assigned to *f-type* of protons (Figure 2c). The *g-type* protons of phenyl groups at 3- and 5-positions were appeared as

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doublet at 7.40 ppm which showed cross-peak correlation with a multiplet appeared in 7.21-7.30 ppm region which we assigned to *h*- and *i-type* protons of phenyl groups respectively. Similarly, all resonances in ^{1}H NMR of BODIPY **2** were also identified and assigned. However, in case of BODIPYs **3** and **4**, the three different aryl signals appeared as overlapping resonances and no efforts have been made to identify all resonances.

Absorption, Fluorescence and Electrochemical Properties

The absorption properties of multiply polyarylated BODIPYs **1-4** along with their associated reference compounds were studied in CH_2Cl_2 and the data are tabulated in Table 1. The comparison of absorption spectra of BODIPYs **1-4** is presented in Figure 3a. All compounds showed a characteristic strong band corresponding to a $S_0 \rightarrow S_1$ transition in 550-600 nm region with one vibronic component on the higher energy side. In addition, an ill-defined band at ~400 nm corresponding to a $S_0 \rightarrow S_2$ transition is also present. The close inspection of Table 1 clearly reveals that the substituents at pyrrole carbons of BODIPY influences the electronic properties of the BODIPY which reflects in the shifts in absorption band. Thus, introduction of every substituent/functional group shifts the absorption band position which we discussed here by taking BODIPY **1** and its associated reference compounds as examples. The 3,5-diphenyl BODIPY **6** showed the absorption band at 551 nm which was bathochromically shifted and appeared at 562 nm upon introduction of two bromines at 2- and 6-positions in BODIPY **7** (Figure 3b). When *p*-tolyl groups were introduced at 2- and 6-positions in place of bromines of BODIPY **7**, the resulted tetraaryl BODIPY **8** showed bathochromically shifted absorption band at 584 nm. Upon introduction of two bromines at 1- and 7-positions of tetraraylated BODIPY **8**, the resulted BODIPY **9** showed hypsochromically shifted absorption band at 562 nm. Finally, when the bromines of BODIPY **9** were converted to *p*-fluorophenyl

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groups at 1- and 7-positions, the resulted hexaraylated compound **1** showed a bathochromically shifted absorption band at 574 nm. All other hexararyl BODIPYs **2**-**4** also showed similar shifts in absorption band compared to their associated reference compounds (Figure 3a). Furthermore, the introduction of functional groups/aryl substituents at 1,7-positions causes hypsochromic shift compared to 2,3,5,6-tetrasubstituted BODIPYs which is attributed to the steric hindrance between the 1,7-substituents and *meso*-aryl group leading to the distortion of the BODIPY. The BODIPYs **1**-**4** showed slight shifts (10-15 nm) in their absorption peak maxima compared to each other. However, compared to our previously reported symmetrical polyarylated BODIPYs,[4a] the absorption properties were altered slightly and the properties were sensitive to the type of aryl groups present at the pyrrole carbons of BODIPY.

The steady state fluorescence spectra of BODIPYs **1**-**4** and their associated reference compounds were recorded in CH_2Cl_2 using excitation wavelength of 530 nm and the relevant data is included in the Table 1. The comparison of fluorescence spectra of BODIPYs **1**-**4** is shown in Figure 4a. Generally, the BODIPYs show one single broad fluorescence band and the position of the fluorescence band is sensitive to the substituents present at pyrrole carbons of BODIPY. The 3,5-diphenyl BODIPY **6** showed one fluorescence band at 585 nm with quantum yield (ϕ_f) of 0.29 which was slightly bathochromically shifted to 592 nm in its 2,6-dibromo BODIPY **7** derivative but the ϕ_f was reduced to 0.11 because of heavy halogen effect (Figure 4b). However, the tetraaryl BODIPY **8** showed bathochromically shifted fluorescence band at 626 nm and the ϕ_f was increased to 0.19. The corresponding dibromo BODIPY derivative **9** showed hypsochromically shifted fluorescence band at 603 nm and ϕ_f was significantly decreased to 0.029. The hexaarylated BODIPY **1** showed a fluorescence band at 616 nm with decent ϕ_f of 0.26 (Table 1). Thus, the fluorescence spectra followed similar trend like

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absorption spectra. Furthermore, depends on the nature of aryl groups, the fluorescence band position was varied and BODIPY **2** showed maximum red shifted fluorescence band at 640 nm and BODIPY **4** showed higher quantum yield (ϕ_f) of 0.53 compared to the other three hexaarylated BODIPYs. The maximum red shifted fluorescence band for BODIPY **2** was tentatively attributed to the presence of electron donating anisyl groups at 2,6-positions and the large quantum yield noted for BODIPY **4** was due to the presence of bulkier aryl substituents at the 2,6-positions which decreases non-radiative decay channels. The Stoke's shifts measured for all BODIPYs were in the range of 900-1750 cm^{-1} which are much higher than the regular BODIPYs known in the literature.[50] Furthermore, the Stokes shifts observed for multiply polyarylated BODIPYs **1-4** were found to be higher than the symmetrical polyarylated BODIPYs.[4a] The large Stokes shifts would help in eliminating the spectral overlap between absorption and emission bands and such dyes gives strong signal when we used for biological imaging. The singlet state lifetimes of BODIPYs and associated reference compounds were measured by time correlated single photon counting method (Table 1). The singlet excited state lifetimes of BODIPYs **1-4** and their associated reference compounds were measured using an excitation wavelength of 560 nm and emissions were collected at their corresponding emission wavelength maxima. The fluorescence decays of all BODIPYs were fitted to single exponential functions and the fluorescence decay profiles of BODIPYs **1-4** are shown in Figure 5. The fluorescence lifetimes (τ_f) of all BODIPYs were in agreement with the quantum yield (ϕ_f) data and the BODIPY **4** showed the longest lifetime of 4.4 ns among BODIPYs **1-4** which is in agreement with its quantum yield data. The solid state absorption (Figure S66, S67)and emission spectra (Figure S68) of BODIPYs **1-4** were recorded and the data was included in Table 1. The absorption and emission spectra of BODIPYs in films were broad and red shifted

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compared to their solution spectra. Surprisingly, BODIPY **3** is non-emissive in the solid state. Thus, the preliminary investigations revealed that the BODIPYs **1, 2** and **4** appear to be strongly fluorescent in the solid state, which will be investigated in due course of time.

The redox properties of BODIPYs **1-4** and associated reference compounds were probed through cyclic voltammetric and differential pulse voltmmetric studies using tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) in CH_2Cl_2 as solvent. A comparison of first oxidation and first reduction waves of BODIPYs **1-4** is shown in Figure 6 and the data for all compounds are presented in Table 2. However, in general BODIPYs are electron deficient and exhibit only one reversible reduction and an ill-defined irreversible oxidation. As clear from the Figure 6 that BODIPYs **1-4** showed one reversible oxidation and one reversible reduction. However, all other associated reference compounds also showed one reversible oxidation and one reversible reduction but in some cases, we noted an additional irreversible oxidation/reduction (Table 2). Thus, the multiply polyarylated BODIPYs showed reversible oxidation and reduction indicating that the BODIPYs **1-4** are stable under redox conditions.

Conclusions

In conclusion, we synthesized the first examples of multiply hexaarylated BODIPYs containing three different types of aryl substituents on each pyrrole ring of BODIPY over sequence of steps in high yields. All reactions worked smoothly and required straight-forward chromatographic purifications to isolate the pure desired multiply polyarylated BODIPYs. Prior to this work, the reports on hexaarylated BODIPYs are very few[19,23-29] and to the best of our knowledge, such types of multiply hexarylated BODIPYs reported here are not known in the

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literature. These hexaarylated BODIPYs possesses very interesting photophysical and electrochemical properties. The multiply hexaarylated BODIPYs absorbs and emits strongly in the visible region with decent quantum yields and singlet state lifetimes. These compounds exhibit reversible oxidation and reduction and are highly stable under redox conditions. Thus, the properties of BODIPY can be fine-tuned by selectively introducing the aryl groups at the designated sites of the BODIPY core. The hexaarylated BODIPYs are brightly fluorescent in solid state and we presently exploring the solid state fluorescence properties of these BODIPYs.

Experimental Section

General

All NMR spectra (δ values, ppm) were recorded with 400 or 500 MHz spectrometers. Tetramethylsilane (TMS) was used as an internal reference for recording ^{1}H (of residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.2 ppm) spectra in $CDCl_3$. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. The HRMS spectra were recorded using eletron spray ionization method, TOF analyser. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon (working) electrode, platinum wire (auxiliary) electrode, and a saturated calomel (reference) electrode. The experiments were performed in dry CH_2Cl_2 with 0.1 M tertabutylammonium perchlorate (TBAP) as the supporting electrolyte. Half-wave potentials ($E_{1/2}$) were measured with 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^{+}) = 0.45 V, vs SCE. The photophysical data for all the compounds has been done in CH_2Cl_2 solvent with 5 μM concentration. The films of compounds

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1-4 were prepared by drop-casting method by evaporation of dichloromethane solution on the quartz plates, and their absorption and emission spectra were recorded directly measured. The quantum yields were calculated using Sulforhodamine B reference (ϕ = 0.69 in ethanol, λ_{exc} = 530 nm).[10] All ϕ are corrected for changes in refractive index of solvent.

2,6-Dibromo-4,4-difluoro-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (7)

The CH_2Cl_2 (3 mL) solution of liquid bromine (0.026 mL, 0.51 mmol) and $NaHCO_3$ (43 mg, 0.51 mmol) was added to a solution of compound **6** (100 mg, 0.23 mmol) in dry CH_2Cl_2 (10 mL) at room temperature under N_2 atmosphere. The mixture was left stirring for 2 h at room temperature, washed with an aqueous solution of sodium thiosulfate and extracted with CH_2Cl_2 (3x50 mL) . The organic layers were combined, dried over Na_2SO_4, and evaporated on rotary evaporator to dryness under vacuum. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (95:5) and afforded the desired product **7** as pink solid in 85% yield (116 mg). M.p. 231 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 2.50 (s, 3 H) 7.04 (s, 2 H) 7.38 (d, *J*=8.03 Hz, 2 H) 7.41 - 7.46 (m, 6 H) 7.50 (d, *J*=7.78 Hz, 2 H) 7.61 (dd, *J*=6.27, 2.51 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 21.7, 109.5, 127.9, 128.0, 128.5, 129.4, 129.6, 130.0, 130.1, 130.4, 130.5, 130.7, 131.9, 134.4, 141.7, 144.9, 156.3; ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm) -133.42 (q); ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm) 0.61; HRMS calcd. for $C_{28}H_{19}BBr_2F_2N_2K$ 628.9613 $[M+K]^+$ found 628.9584.

4,4-Difluoro-3,5-diphenyl-2,6-ditolyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (8)

Samples of **7** (100 mg, 0.168 mmol), *p*-tolylboronic acid (69 mg, 0.51 mmol) and Na_2CO_3 (54mg, 0.51 mmol) in 15 mL of water/THF/toluene (1:1:1) were added to two neck 50 mL round

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bottom flask fitted with a reflux condenser and the mixture were degassed with N_2 for few minutes. A catalytic amount of $Pd(PPh_3)_4$ (6 mol%) was added and the reaction mixture was refluxed at 80°C for 3h. The TLC analysis of the reaction mixture showed the disappearance of spot corresponding to compound 7 and formation of new spot corresponding to compound **8**. The reaction mixture was diluted with water and extracted with diethyl ether (1x50 mL). The combined organic layers were washed with water, brine and dried over $NaSO_4$. The solvent was evaporated on rotary evaporator under vacuum and the crude product was purified on a silica gel column using petroleum ether/ethyl acetate 97:3 to afford the desired compound **8** as brownish red solid. Yield 81% (84 mg). M.p. 233 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 2.27 (s, 6 H) 2.51 (s, 3 H) 6.89 (d, *J*=8.12 Hz, 4 H) 6.96 (d, *J*=8.04 Hz, 4 H) 7.02 (s, 2 H) 7.29 - 7.40 (m, 6 H) 7.38 (d, *J*=7.80 Hz, 2 H) 7.49 (d, *J*=6.78 Hz, 4 H) 7.59 (d, *J*=8.03 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 21.3, 21.7, 115.3, 127.0, 128.0, 128.3, 128.4, 129.0, 129.1, 129.2, 129.3, 129.6, 130.2, 130.5, 130.9, 131.1, 131.8, 132.1, 134.5, 134.8, 136.8, 140.9, 144.1, 156.3; ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm) -132.76 (q); ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm) 1.09. HRMS calcd. for $C_{42}H_{33}BF_2N_2Na$ 637.2604 $[M+Na]^+$ found 637.2604.

1,7-Dibromo-4,4-difluoro-2,6-ditolyl-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (9)

The dry CH_2Cl_2 (3 mL) solution of liquid bromine (0.025 mL, 0.49 mmol) and $NaHCO_3$ (41 mg, 0.49 mmol) were added to a solution of compound **8** (50 mg, 0.081 mmol) in dry CH_2Cl_2 (10 mL) at room temperature under N_2 gas conditions and stirred for 2 h. After work-up, the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (98:2) to afford the desired product **9** as purple solid in 89% yield (56 mg).

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M.p. 248 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 2.26 (s, 6 H) 2.47 (s, 3 H) 6.88 (d, *J*=8.08 Hz, 4 H) 6.99 (d, *J*=8.03 Hz, 4 H) 7.18 - 7.25 (m, 8 H) 7.32 - 7.37 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 21.5, 21.9, 120.9, 127.7, 128.8, 129.1, 129.3, 129.4, 129.9, 130.7, 131.3, 136.2, 139.8, 145.3, 156.5; ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm) -130.70 (q); ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm) 0.84; HRMS calcd. for $C_{42}H_{31}BBr_2F_2N_2K$ 809.0554 $[M+K]^+$ found 809.0557.

4,4-Difluoro-1,7-bis(4-fluorophenyl)-3,5-diphenyl-2,6-ditolyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (1)

Samples of **9** (50 mg), 4-fluorophenylboronic acid (5 equiv.) and Na_2CO_3 (5 equiv.) in water/THF/toluene (1:1:1) 15 mL was stirred under N_2 for 5 min in two necked round bottom flask fitted with condenser. The coupling was initiated by addition of catalytic amount of $Pd(PPh_3)_4$ (6 mol%) and the reaction was stirred at 80 °C for 5 h. After standard work-up, the crude reaction mixture was subjected to silica gel column chromatography using petroleum ether/ethyl acetate (97:3) and afforded the desired compound **1** as red solid in 85% yield (44 mg). M.p. >280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm) 2.02 (s, 3 H) 2.14 (s, 6 H) 6.28 (d, *J*=7.82 Hz, 2 H) 6.37 - 6.43 (m, 4 H) 6.45 - 6.52 (m, 8 H) 6.64 (d, *J*=7.89 Hz, 2 H) 6.73 (d, *J*=8.04 Hz, 4 H) 7.21 - 7.30 (m, 6 H) 7.40 (d, *J*=7.23 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 20.9, 21.2, 114.0, 114.2, 127.3, 127.6, 128.4, 128.9, 129.9, 130.6, 130.8, 131.8, 131.9 (d), 132.0, 132.4, 134.8, 136.1, 139.1, 142.9, 147.1, 156.2, 160.0, 162.4; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -131.44 (q), -116.7 (s); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.03; HRMS calcd. for $C_{54}H_{39}BF_4N_2Na$ 825.3044 $[M+Na]^+$ found 825.3062.

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2,6-Bis(4-anisyl)-4,4-difluoro-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (10)

Treatment of **7** (100mg, 0.169 mmol) with *p*-anisylboronic acid (77 mg, 0.51 mmol) under Pd(0) coupling conditions for 4h followed by silica gel column chromatographic purification using petroleum ether/ethyl acetate (93:7) afforded **10** in 79% yield (86 mg). M.p. 278 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 2.51 (s, 3 H) 3.74 (s, 6 H) 6.69 (d, *J*=8.78 Hz, 4 H) 6.92 (d, *J*=8.78 Hz, 4 H) 6.97 (s, 2 H) 7.28 - 7.35 (m, 6 H) 7.37 (d, *J*=8.03 Hz, 2 H) 7.47 (d, *J*=6.27 Hz, 4 H) 7.58 (d, *J*=7.78 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 21.7, 55.3, 113.8, 126.6, 128.0, 129.3, 129.6, 130.6, 130.9, 131.8, 132.2, 134.2, 134.8, 140.8, 143.9, 156.1, 158.7; ; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -132.87 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.23; HRMS calcd. for $C_{42}H_{33}BF_2N_2O_2K$ 685.2242 $[M+K]^+$ found 685.2243.

2,6-Bis(4-anisyl)-1,7-dibromo-4,4-Difluoro-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (11)

Following the procedure of compound **9**, the addition of the CH_2Cl_2 (3 mL CH_2Cl_2) solution of liquid bromine (0.024 mL, 0.464 mmol) and $NaHCO_3$ (39 mg, 0.464 mmol) to a solution of compound **10** (50 mg, 0.077 mmol) in dry CH_2Cl_2 followed by silica gel column chromatographic purification afforded compound **11** in 88% yield (55 mg). M.p. 262 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 2.48 (s, 3 H) 3.74 (s, 6 H) 6.72 (d, *J*=8.78 Hz, 4 H) 6.92 (d, *J*=8.53 Hz, 4 H) 7.18 - 7.25 (m, 6 H) 7.30 - 7.38 (m, 8 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 21.8, 55.2, 113.5, 120.8, 124.6, 127.7, 129.1, 129.3, 129.4, 129.9, 130.4, 130.6, 131.3, 131.8, 135.9, 139.7, 156.5, 159.0; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -130.70 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.03; HRMS calcd. for $C_{42}H_{31}BBr_2F_2N_2KO_2$ 841.0452 $[M+K]^+$ found 841.0435.

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2,6-Bis(4-anisyl)-1,7-bis(4-biphenyl)-4,4-difluoro-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (2)

Following the procedure of compound **1**, the reaction of **11** (50 mg, 0.062 mmol) with 4-biphenylboronic acid (37 mg, 0.186 mmol) under Suzuki Pd(0) coupling conditions for 3h followed by silica gel column chromatographic purification by using petroleum ether/ethyl acetate (96:4) afforded **2** in 86% yield (51 mg). M.p. >280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm) 1.72 (s, 3 H) 3.63 (s, 6 H) 6.19 (d, *J*=7.78 Hz, 2 H) 6.48 (d, *J*=8.85 Hz, 4 H) 6.55 - 6.59 (d, *J*=8.85 Hz, 4 H) 6.61 (d, *J*=8.09 Hz, 4 H) 6.71 (d, *J*=7.93 Hz, 2 H) 6.94 (d, *J*=8.24 Hz, 4 H) 7.24 - 7.29 (m, 8 H) 7.32 - 7.39 (m, 8 H) 7.43 (d, *J*=6.71 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 21.2, 55.1, 113.1, 125.5, 125.8, 126.9, 127.2, 127.5, 127.7, 128.7, 128.7, 128.8, 129.0, 130.8, 130.9, 131.9, 132.0, 132.1, 132.5, 134.0, 134.1, 138.3, 138.9, 141.1, 143.6, 156.1, 158.0; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -129.51 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.36; HRMS calcd. for $C_{66}H_{49}BF_2N_2NaO_2$ 973.3758 $[M+Na]^+$ found 973.3755.

4,4-Difluoro-3,5-diphenyl-2,6-bis(3-tolyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (12)

Following the procedure of compound **8**, the reaction of **7** (100mg, 0.169 mmol) with *o*-tolylboronic acid (69 mg, 0.51 mmol) under pd(0) Suzuki coupling conditions for 4h followed by column chromatography with petroleum ether/ethyl acetate (98:2) afforded **12** in 79% yield (82 mg). M.p. 269 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, *δ* in ppm) 1.94 (s, 6 H) 2.46 (s, 3 H) 6.93 (s, 2 H) 6.97 - 7.03 (m, 2 H) 7.03 - 7.09 (m, 4 H) 7.09 - 7.15 (m, 2 H) 7.18 -7.25 (m, 6 H) 7.32 (d, *J*=7.78 Hz, 2 H) 7.43 (d, *J*=7.03 Hz, 4 H) 7.58 (d, *J*=8.03 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) 20.5, 21.6, 125.6, 127.7, 127.8, 128.4, 129.1, 129.3, 130.2, 130.3, 130.8, 130.9, 131.0,

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131.7, 132.1, 134.1, 134.7, 134.9, 136.7, 140.9, 144.4, 156.9; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -129.94 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.50; HRMS calcd. for $C_{42}H_{33}BF_2N_2Na$ 637.2604 $[M+Na]^+$ found 637.2605.

1,7-Dibromo-4,4-difluoro-3,5-diphenyl-2,6-bis(3-tolyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (13)

Following the procedure of compound **9**, the addition of the CH_2Cl_2 (3 mL CH_2Cl_2) solution of liquid bromine (0.025 mL, 0.49 mmol) and $NaHCO_3$ (41 mg, 0.49 mmol) to a solution of compound **12** (50 mg) in dry CH_2Cl_2 afforded compound **13** in 91% yield (57 mg). M.p. 247-253 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) 1.95 - 2.02 (d, 6 H) 2.46 (s, 3 H) 6.93 (d, *J*=8.03 Hz, 2 H) 7.01 - 7.10 (m, 4 H) 7.12 - 7.24 (m, 8 H) 7.32 - 7.37 (m, 8 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 20.4, 22.8, 122.4, 125.6, 127.6, 128.3, 128.9, 129.3, 129.4, 129.9, 130.0, 130.7, 131.2 (t), 132.4, 136.7, 137.5, 137.6, 139.8, 145.2, 156.4 (d); ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -128.62 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.16; HRMS calcd. for $C_{42}H_{31}BBr_2F_2N_2Na$ 793.0814 $[M+Na]^+$ found 793.0820.

4,4-Difluoro-1,7-bis(4-ethenylphenyl)-3,5-diphenyl-2,6-bis(3-tolyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (3)

Following the procedure of compound **1**, the reaction of **13** (50 mg, 0.065 mmol) with 4-vinylphenylboronic acid (29 mg, 0.194 mmol) under pd(0) coupling conditions for 3h followed by column chromatographic purification by using petroleum ether/ethyl acetate (94:6) afforded **3** in 83% yield (44 mg). M.p. 265 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm) 1.99 (d, *J*=6.78 Hz, 6 H) 2.57 (s, 3 H) 5.90 (q, *J*=16.56 Hz, 4 H) 6.49 - 6.55 (m, 4 H) 6.97 - 7.01 (m, 2 H) 7.06 (d,

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J=7.53 Hz, 4 H) 7.08 - 7.13 (m, 8 H) 7.15 - 7.20 (m, 6 H) 7.33 - 7.40 (m, 4 H) 7.47 (d, *J*=7.78 Hz, 2 H) 7.57 (d, *J*=8.03 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 20.2, 21.5, 121.5 (d), 125.9 (d), 126.6, 127.4, 127.7, 127.9, 128.4, 128.7, 130.0, 130.1, 130.3, 130.5, 130.7, 131.4, 131.5, 131.6, 131.9, 133.0 (d), 133.4, 134.3, 137.2 (d), 137.4, 139.9, 143, 156; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -129.01 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.36; HRMS calcd. for $C_{58}H_{45}BF_2N_2Na$ 841.3546 $[M+Na]^+$ found 841.3546.

4,4-Difluoro-2,6-(4-*tert*-butylphenyl)-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (14)

Following the procedure of compound **8**, the reaction of **7** (100 mg, 0.169 mmol) with 4-*tert*-butylphenylboronic acid (90 mg, 0.51 mmol) under pd(0) coupling conditions for 4h followed by column chromatography with petroleum ether/ethyl acetate (96:4) afforded **14** in 74% yield (87 mg). M.p. 277 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, *δ* in ppm) 1.28 (s, 18 H) 2.53 (s, 3 H) 6.97 (d, *J*=8.39 Hz, 4 H) 7.06 (s, 2 H) 7.19 (d, *J*=8.39 Hz, 4 H) 7.32 - 7.41 (m, 8 H) 7.52 (d, *J*=7.63 Hz, 4 H) 7.60 (d, *J*=7.93 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 21.7, 31.4, 34.6, 114.9, 125.3, 126.6, 127.9, 128.0, 128.5, 129.2, 129.3, 130.6, 131.0, 131.1, 131.8, 132.2, 134.4, 134.8, 140.9, 144.1, 150.0, 156.3; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -132.80 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.25; HRMS calcd. for $C_{48}H_{45}BF_2N_2K$ 737.3284 $[M+K]^+$ found 737.3283.

1,7-Dibromo-2,6-bis(4-*tert*-butylphenyl)-4,4-difluoro-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (15)

Following the procedure of compound **9**, the addition of the CH_2Cl_2 (3 mL CH_2Cl_2) solution of liquid bromine (0.022 mL, 0.43 mmol) and $NaHCO_3$ (36 mg, 0.43 mmol) to a solution of

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compound **14** (50 mg, 0.072 mmol) in dry CH_2Cl_2 afforded compound **15** in 78% yield (48 mg). M.p. 253 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm) 1.24 (s, 18 H) 2.47 (s, 3 H) 6.92 (d, *J*=8.39 Hz, 4 H) 7.17 (d, *J*=8.24 Hz, 5 H) 7.20 (d, *J*=7.63 Hz, 4 H) 7.25 - 7.26 (m, 2 H) 7.31 - 7.37 (m, 9 H) 7.23 - 7.27 (m, 4 H) 7.31 - 7.37 (m, 6 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 21.9, 31.4, 34.7, 120.8, 124.9, 127.6, 129.2, 129.3, 129.5, 129.9, 130.2, 130.5, 130.7, 131.3, 136.1, 139.7, 145.2, 150.5, 156.6; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ ppm) -130.63 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.05; HRMS calcd. for $C_{48}H_{43}BBr_2F_2N_2Na$ 877.1754 $[M+Na]^+$ found 877.1789.

2,6-Bis(4-*tert*-butylphenyl)-4,4-difluoro-1,7-bis(4-phenoxyphenyl)-3,5-diphenyl-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4)

Following the procedure of compound **1**, the reaction of **15** (50 mg, 0.058 mmol) with 4-phenoxyphenylboronic acid (38 mg, 0.175 mmol) under pd(0) coupling conditions for 5h followed by column chromatography with petroleum ether/ethyl acetate (98:2) afforded **4** in 61% yield (37 mg). M.p. >280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm) 1.16 - 1.21 (m, 18 H) 1.86 (s, 3 H) 6.09 (d, *J*=8.24 Hz, 2 H) 6.15 (d, *J*=7.78 Hz, 2 H) 6.25 (d, *J*=7.93 Hz, 2 H) 6.36 (t, *J*=7.48 Hz, 2 H) 6.49 (d, *J*=8.39 Hz, 2 H) 6.51 - 6.55 (m, 2 H) 6.66 (dd, *J*=7.71, 1.45 Hz, 2 H) 6.70 - 6.75 (m, 2 H) 6.85 - 6.91 (m, 3 H) 6.97 (d, *J*=7.32 Hz, 2 H) 7.00 - 7.04 (m, 2 H) 7.05 - 7.11 (m, 3 H) 7.17 - 7.25 (m, 5 H) 7.37 - 7.44 (m, 3 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ in ppm) 22.8, 31.4, 31.5, 114.7, 115.9, 120.4, 120.6, 121.0, 121.6, 123.5, 123.7, 124.3, 125.2, 125.9, 127.2, 127.3, 127.4, 128.6, 129.4, 129.5, 129.9, 130.1, 130.3, 130.6, 130.9, 131.0, 131.1, 132.2, 132.9, 133.1, 139.0, 138.7, 139.9, 147.0, 148.9, 149.0, 154.8, 155.1, 155.7, 156.0, 156.2; ; ^{19}F

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NMR (470.5 MHz, $CDCl_3$, δ ppm) -129.01 (q); ^{11}B NMR (160.5 MHz, $CDCl_3$, δ ppm) 1.41; HRMS calcd. for $C_{72}H_{61}BF_2N_2NaO_2$ 1057.4698 $[M+Na]^+$ found 1057.4644.

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Supporting Information Available. Characterization data for all new compounds.

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Legends

Figure 1. Multiply polyarylated BODIPYs **1-4.**

Figure 2. (a) The ^{1}H NMR spectrum of compound **1**. (b) ^{1}H-^{1}H correlation spectrum of compound **1.** (c) ^{1}H-^{1}H NMR correlation spectrum in the selected region recorded in $CDCl_3$.

Figure 3. The comparison of normalized absorption spectra of compounds (a) **1** (square)**, 2** (circle), **3** (star) and **4** (triangle) (b) associated reference compounds **6** (square), **7** (circle), **8** (triangle), **9** (star) along with compound **1** (diamond) in CH_2Cl_2**.**

Figure 4. The comparison of normalized emission spectra of compounds (a) **1** (square), **2** (circle), **3** (triangle) and **4** (star) (b) associated reference compounds **6** (triangle), **7** (circle), **8** (triangle), **9** (star) along with compound **1** (diamond) in CH_2Cl_2**.**

Figure 5. Fluorescence decay profile of compounds **1** (black), **2** (red), **3** (green) and **4** (purple) in CH_2Cl_2.

Figure 6. Comparison of cyclic voltamogramms (solid line) and differential pulse voltamogramms (dotted line) of compounds (a) oxidation waves (i) **1**, (ii) **2**, (iii) **3** and (iv) **4.** (b) Reduction waves (v) **1** (vi) **2** (vii) **3** and (ix) **4** recorded in CH_2Cl_2 using TBAP as supporting electrolyte at 50 mV/sec scan rate.

Scheme 1. Synthesis of compounds **1** and **2**

Scheme 2. Synthesis of compound **3**

Scheme 3. Synthesis of compound **4**

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Table 1. The optical properties of compounds **1-15**.

Compd	λ_{abs} (log ε_{max})[a] [nm]		λ_{em} [nm]		$\Delta\nu_{st}$	ϕ_f[c]	τ_f[d]
	CH_2Cl_2	Film[b]	CH_2Cl_2	Film[b]	[cm^{-1}]		[ns]
7	562 (4.86)		592		902	0.11	1.1
8	584 (4.73)		626		1149	0.19	3.3
9	562 (4.60)		603		1210	0.029	0.3
1	574 (4.84)	611	616	683	1188	0.26	3.5
10	601(4.76)		659		1464	0.11	2.2
11	570 (4.80)		633		1746	0.015	---
2	582 (4.75)	632	640	687	1557	0.23	3.2
12	566 (4.88)		603		1084	0.22	1.4
13	549 (4.85)		587		1179	0.15	0.7
3	587 (4.88)	620	627	---	1087	0.25	1.8
14	591(4.66)		636		1197	0.29	3.5
15	565 (4.76)		610		1306	0.041	0.3
4	580 (4.80)	595	621	669	1138	0.53	4.4

[a]Molar absorption (log ε_{max} , ± 0.1). [b]Recorded in solid state. [c]Excited at 530 nm. Fluorescenc quatum yileds were measured using sulforhodamine B in ethanol (ϕ, ± 0.05). [d]Fluorescence lifetime (τ, ± 0.05 ns).

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Table 2. The electrochemical data of compounds **1-15** recorded in CH_2Cl_2.

Compound	$E_{1/2ox}$ (V *vs* SCE)		$E_{1/2red}$ (V *vs* SCE)	
	I[a]	II	I	II[b]
7	1.54	---	-0.61	-1.53
8	1.27	---	-0.80	-1.72
9	1.47	---	-0.67	-1.65
1	1.30	---	-0.85	---
10	1.19	1.57	-0.80	-1.73
11	1.41	1.71	-0.68	-1.62
2	1.21	---	-0.87	---
12	1.32	---	-0.86	-1.76
13	1.46	---	-0.71	-1.68
3	1.28	---	-0.78	---
14	1.26	---	-0.83	-1.72
15	1.46	---	-0.71	-1.66
4	1.24	---	-0.94	---

[a]irreversible oxidation, [b]irreversible reduction

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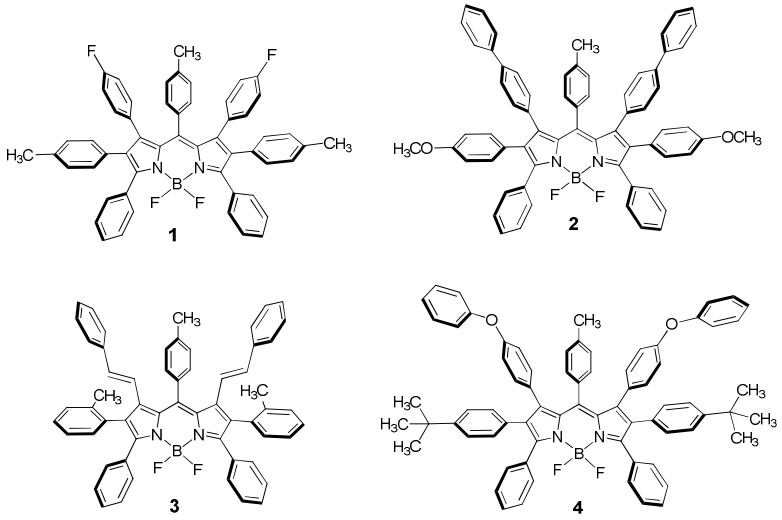

Figure 1

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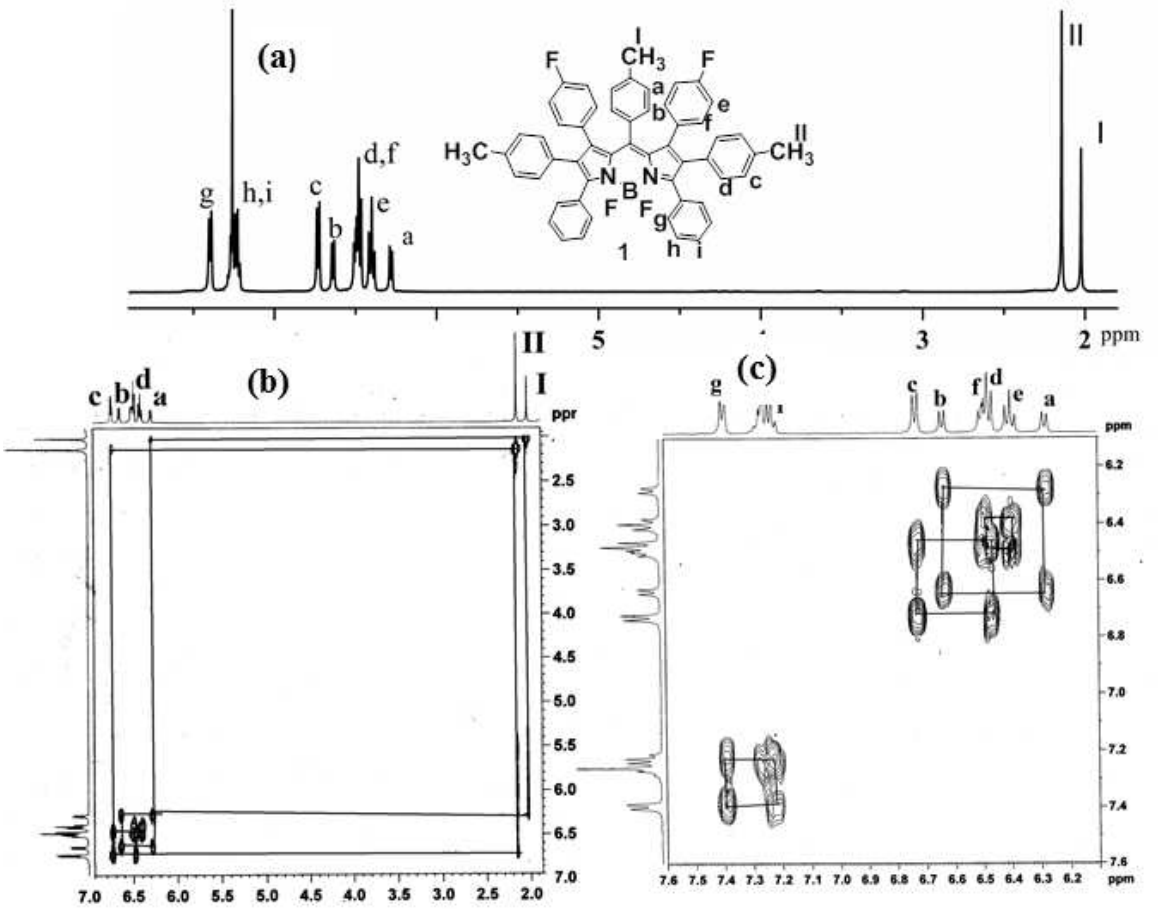

Figure 2

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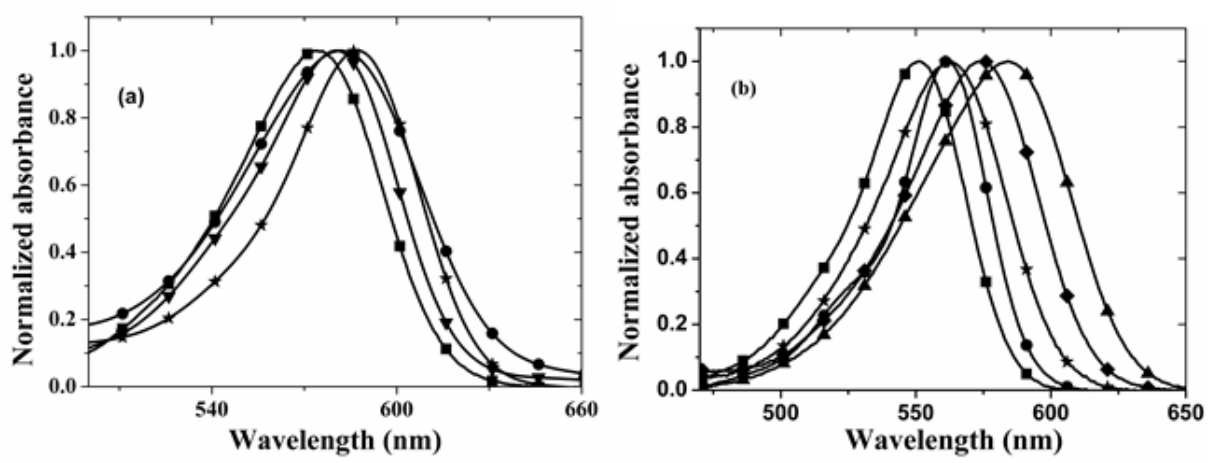

Figure 3

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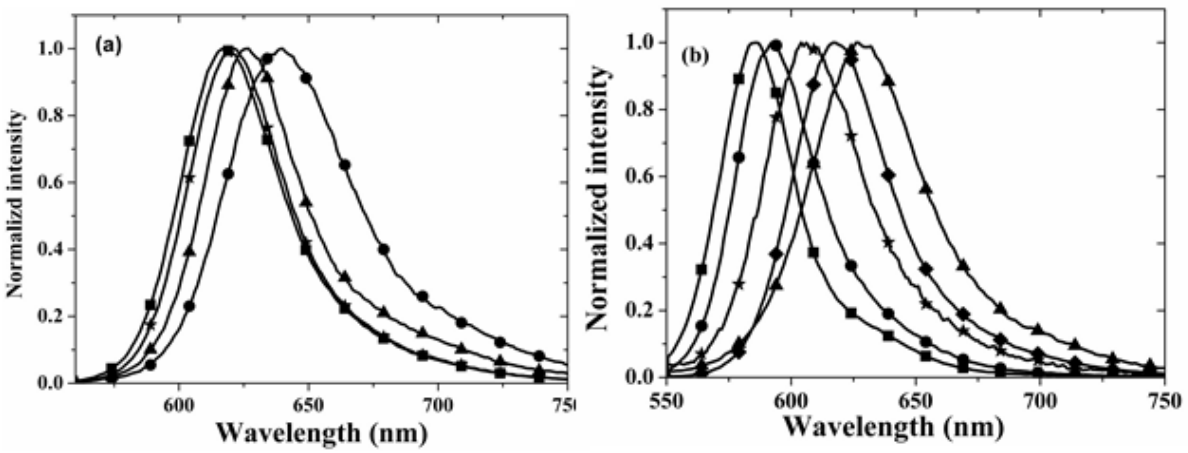

Figure 4

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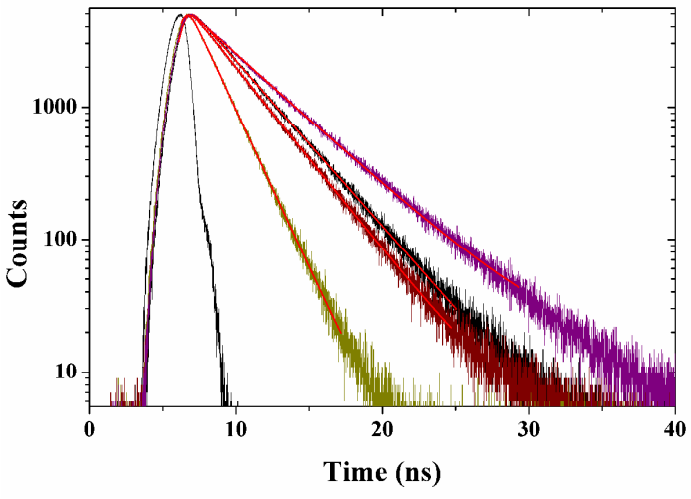

Figure 5

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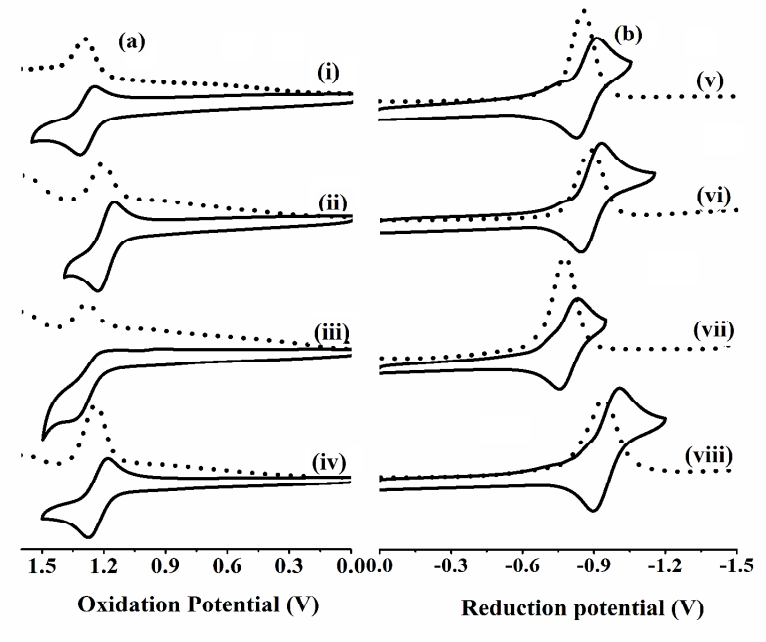

Figure 6

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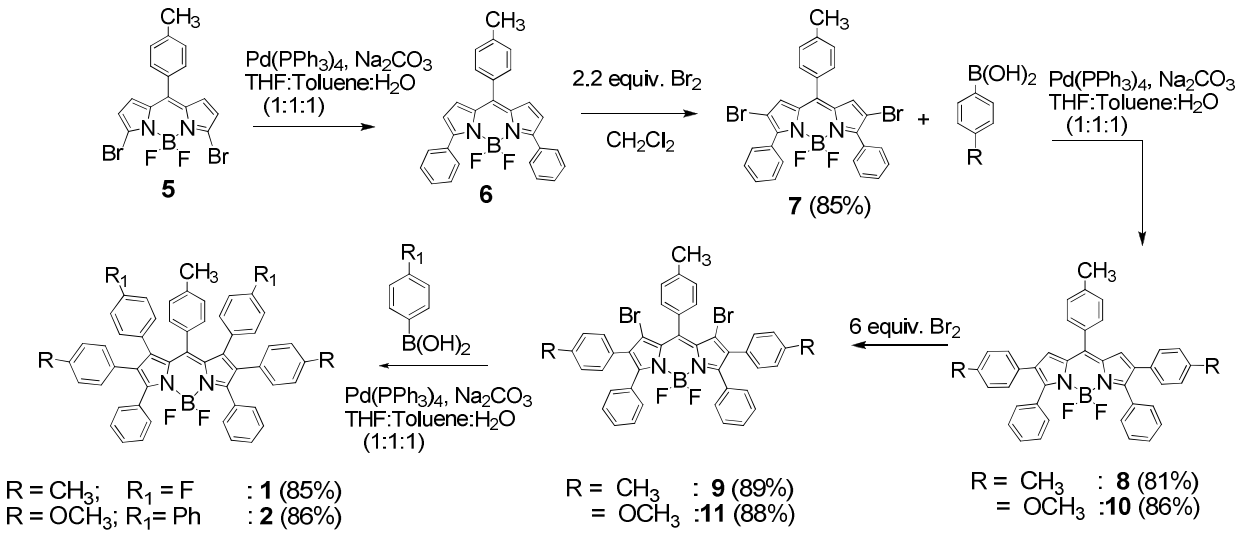
Scheme 1



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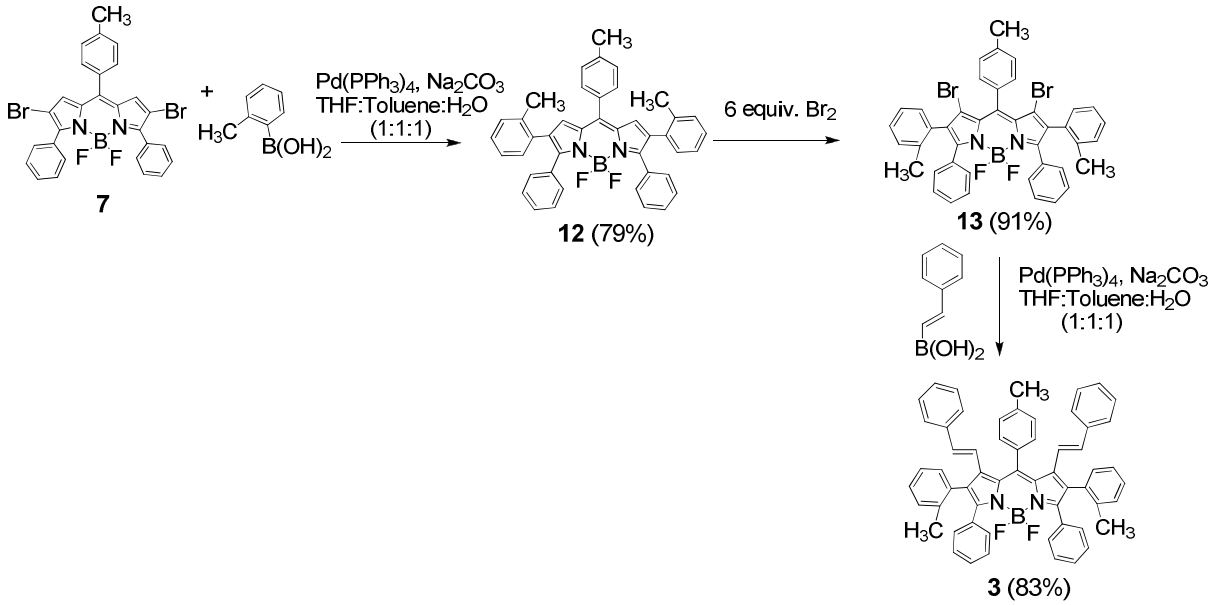
Scheme 2



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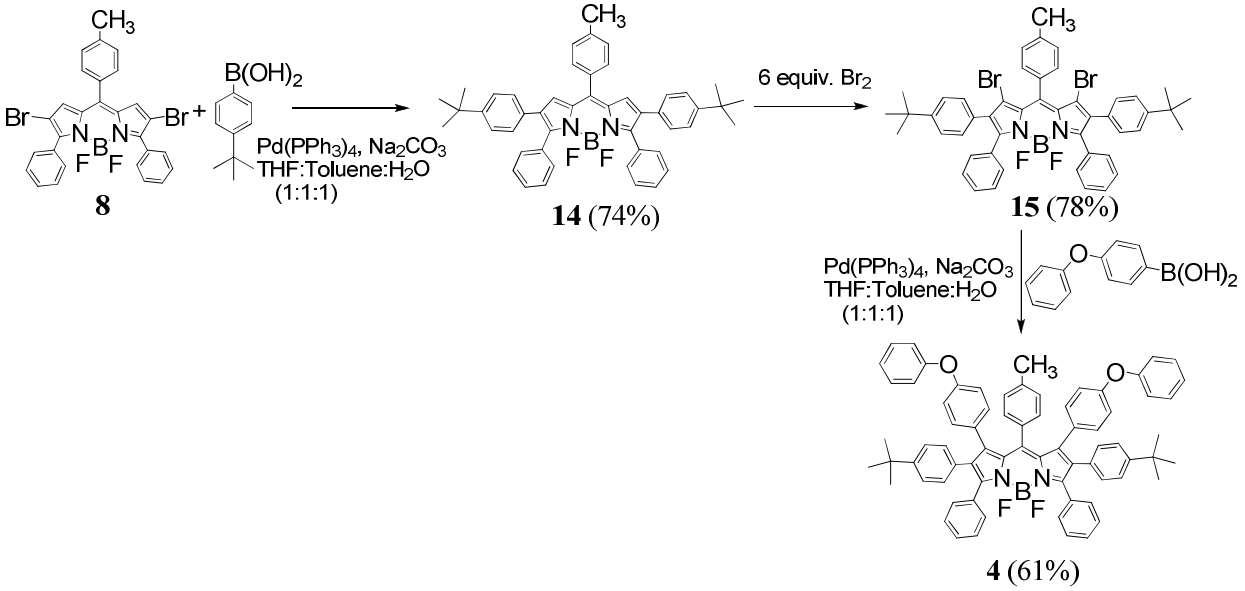
Scheme 3



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Graphical Abstract