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Synthesis of Hexasubstituted Boron-Dipyrromethenes Having a Different Combination of Substituents

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A series of sterically crowded, mixed hexasubstituted BODIPYs containing two different types of substituents on the pyrrole carbons have been synthesized in high yields by a stepwise approach. The mixed BODIPYs were synthesized by bromination of BODIPYs followed by coupling with appropriate boronic acids under Suzuki coupling conditions. This approach has allowed the introduction of two different types of methyl/aryl substituents at the designated positions of the BODIPY core. All the hexasubstituted BODIPYs are readily soluble in common organic solvents and have been characterized by various spectral and electrochemical techniques. The spectral studies indicated that the presence of mixed methyl/aryl substituents on the BODIPY core significantly alters the electronic properties, and the electrochemical studies revealed that the BODIPYs are stable under redox conditions.

Introduction

Dipyrrins or dipyrromethenes have been explored in metal complexation chemistry but the majority of research involving dipyrrins has focused on boron difluoride dipyrrin complexes (BODIPY), which are efficient fluorophores with a wide range of applications in biological labelling[1–3] and cell imaging, as logic gates and ion sensors,[4–6] and in dye-sensitized solar cells[7–10] and solution-processed bulk hyperconjunction solar cells.[11–15] BODIPYs exhibit excellent properties, including sharp absorption and fluorescence bands in the visible-to-NIR region, reasonably high fluorescence quantum yields, large molar absorption coefficients and are highly stable towards light and chemicals.[16–18] The properties of BODIPYs can be fine-tuned by introducing substituents on to the pyrrole carbon atoms, the *meso*-C as well as by replacing F at the boron atom.[16–18] Although BODIPYs have attracted tremendous attention because of their wide range of applications, their synthesis needs to be further improved to obtain high yields of certain desired BODIPYs that are currently not accessible due to constraints in their synthetic protocols. In particular, sterically crowded polyarylated BODIPYs are brightly fluorescent in the solid state[19] and have potential use in the field of optoelectronics, for example, in high-performance electroluminescent devices, light-emitting field-effect transistors and lasers.[20–22] Sterically crowded polyarylated BODIPYs can be prepared by using either substituted pyrroles[19,23–28] or functionalized BODIPYs as key precursors.[29] Substituted pyrroles are not easily accessible and their synthesis involves several synthetic steps.[19,30] In recent years, functionalized BODIPYs have been used as building blocks for the synthesis of a variety of substituted BODIPYs.[31–39] However, the functionalization of all six pyrrole carbons of BODIPY is not an easy task[19,29,40,41] and a perusal of the literature revealed that there are very few reports on the synthesis of sterically crowded BODIPYs starting from functionalized BODIPYs.[19,29] Recently we developed a rapid synthetic route to sterically crowded polyarylated symmetrical BODIPYs by coupling hexabromo-BODIPY[42] with arylboronic acids under Pd^0 coupling conditions.[29] Polyarylated BODIPYs exhibit very interesting photophysical and electrochemical properties[43] and exhibit good fluorescence in the solid state. Although we succeeded in synthesizing polyarylated BODIPYs[29] with one type of aryl group in high yields by using hexabromo-BODIPY[42] as the key precursor, it is a challenging task to prepare multiply polyarylated BODIPYs with different aryl groups. We considered whether we could adopt a step-wise approach to the synthesis of such novel sterically crowded multiply polyarylated BODIPYs by extending the synthetic strategy that we used for the synthesis of sterically crowded symmetrical BODIPYs. In this paper, we report the synthesis of a series of polyarylated BODIPYs containing two different types of aryl/methyl groups in different combinations on the pyrrole carbons of BODIPY. The synthesis involves bromination followed by coupling with arylboronic acid under Suzuki coupling conditions, and this strategy has allowed us to prepare a number of polyarylated BODIPYs.

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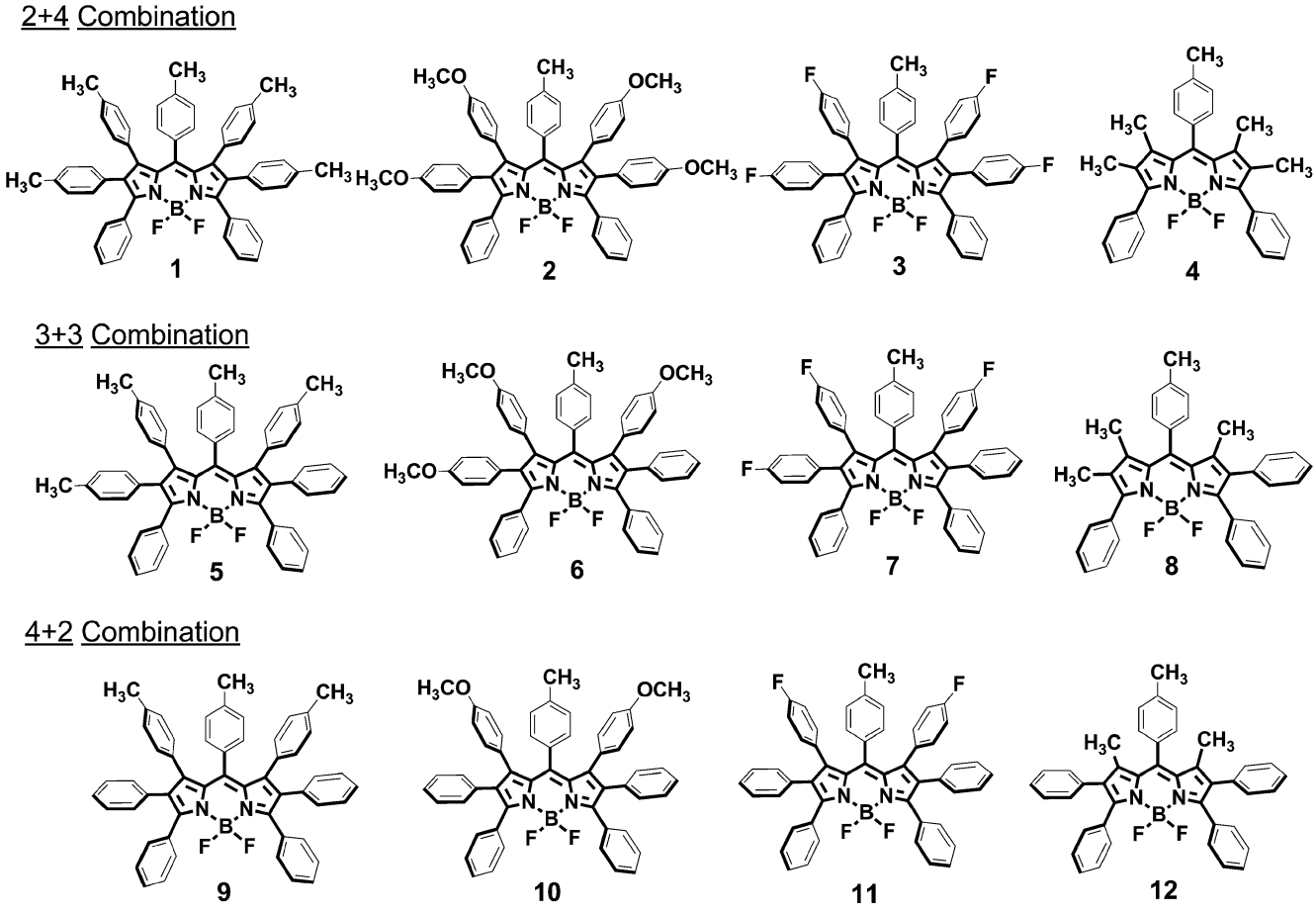
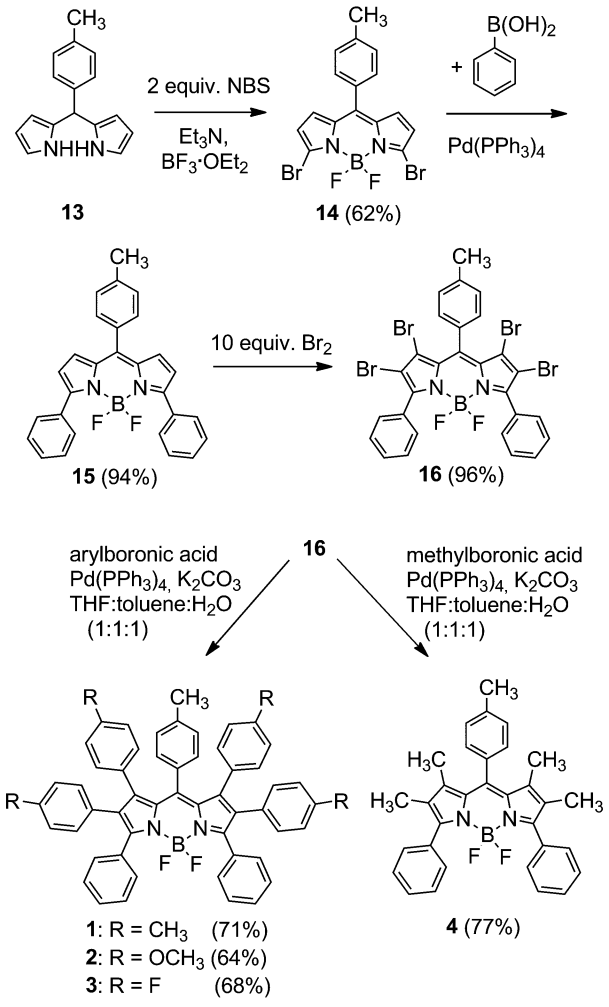
Results and Discussion

3,5-Diphenyl-1,2,6,7-tetraaryl/methyl-BODIPYs 1–4 (2+4 Combination)

The BODIPYs containing two phenyl groups at the 3- and 5-positions and four aryl/methyl groups at the 1-, 2-, 6- and 7-positions were prepared by the sequence of steps shown in Scheme 1. *meso*-Tolyldipyrromethane **13** was treated with 2 equiv. of *N*-bromosuccinimide (NBS) followed by complexation with $BF_3{\cdot}OEt_2$ to afford 3,5-dibromo-BODIPY **14** in 62% yield, as reported earlier.[44] In the next step, 3,5-dibromo-BODIPY **14** was treated with phenylboronic acid in the presence of $[Pd(PPh_3)_4]/K_2CO_3$ in THF/toluene/water (1:1:1) at 80 °C for 1 h followed by column chromatographic purification to afford 3,5-diphenyl-BODIPY **15** in 94% yield.[45] In the subsequent step, compound **15** was brominated with 10 equiv. of Br_2 in CH_2Cl_2 at room temperature for 1.5 h. TLC analysis of the reaction mixture showed the disappearance of compound **15** with the appearance of a less polar spot corresponding to the required tetrabrominated BODIPY **16**. The crude reaction mixture was subjected to column chromatographic purification to afford pure BODIPY **16** in 96% yield. In the ^{1}H NMR spectrum of **16**, the protons at the 1,7- and 2,6-positions observed at δ = 6.62 and 6.84 ppm, respectively, in the ^{1}H NMR spectrum of **15** had disappeared as a result of bromine substitution. In the last step, compound **16** was treated with 6 equiv. of the corresponding aryl/methylboronic acid under the same Suzuki coupling conditions as described above. The crude compounds were purified by silica gel column chromatography to afford hexasubstituted BODIPYs **1**–**4** in yields of 64–77%.

BODIPYs **1**–**4** are readily soluble in common organic solvents and their compositions were confirmed by HRMS analysis. Furthermore, BODIPYs **1**–**4** were characterized by 1D, 2D, ^{19}F and ^{11}B NMR spectroscopy. The 1D and 2D NMR spectra allowed all of the signals to be identified and the molecular structures of the compounds to be deduced, as described here for compound **1**. The ^{1}H and ^{1}H-^{1}H COSY NMR spectra of BODIPY **1** are shown in Figure 1. In the ^{1}H NMR spectrum, the methyl protons of three different types of tolyl groups appear as three singlets at δ = 1.97, 2.09 and 2.13 ppm, corresponding to three, six and six protons, respectively. The singlet at δ = 1.97 ppm was assigned to type I methyl protons of the *meso*-tolyl group, the singlet at δ = 2.13 ppm was assigned to type II methyl protons of the tolyl groups present at the 1- and 7-positions, and the singlet at δ = 2.09 ppm was assigned to type III methyl protons at the 2- and 6-positions. The type I methyl protons show a cross-peak correlation with the doublet at





Scheme 1. Synthesis of compounds **1**–**4**.

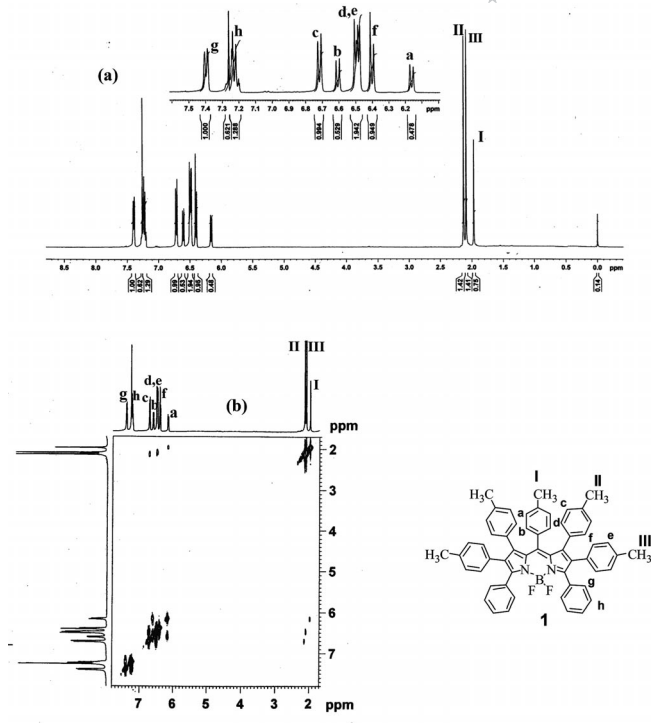


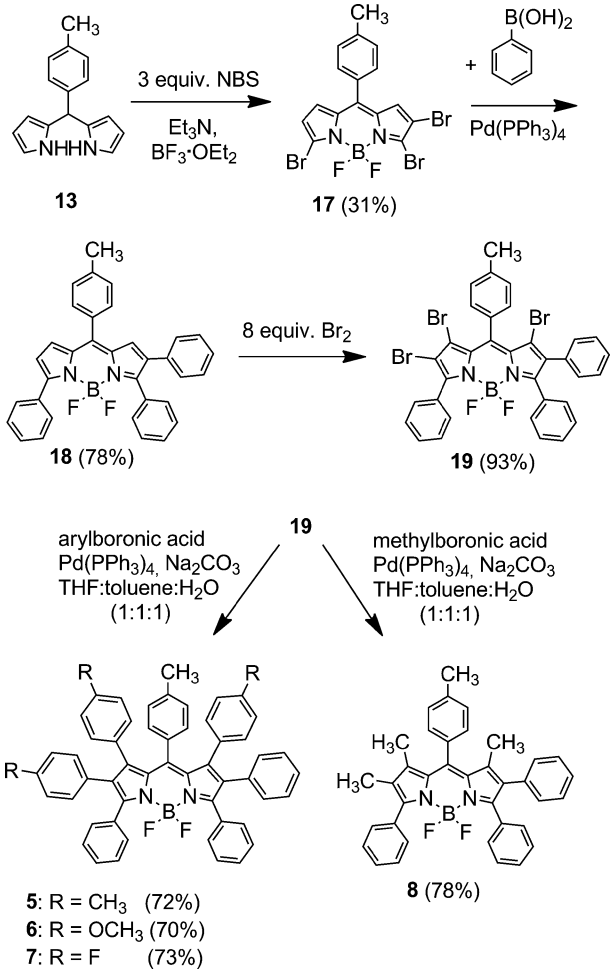
Figure 1. (a) ^{1}H NMR spectrum of compound **1**. (b) ^{1}H-^{1}H COSY spectrum of compound **1** recorded in $CDCl_3$.

δ = 6.16 ppm in the ^{1}H-^{1}H COSY spectrum, which we identified as type a aryl protons of the *meso*-tolyl group. The doublet at δ = 6.61 ppm was assigned to type b protons as this signal shows a cross-peak correlation with type a protons in the COSY spectrum. Similarly, the type c protons, which appear as a doublet at δ = 6.72 ppm, were identified as this signal shows a cross-peak correlation with the type II methyl protons at δ = 2.13 ppm. The type c protons show a cross-peak correlation with type d protons, which show a signal at δ = 6.50 ppm. The type e protons, which merge with the type d protons and appear at δ = 6.50 ppm, were identified as this signal shows a cross-peak correlation with type III methyl protons at δ = 2.09 ppm. The type e protons at δ = 6.50 ppm show a cross-peak correlation with the doublet at δ = 6.40 ppm, which we identified as type f protons. The phenyl protons of type g and type h protons appear at δ = 7.40 and 7.23 ppm, respectively. In this way, 1D and 2D NMR spectroscopy were used to deduce the molecular structures of BODIPYs **1**–**4**. Compounds **1**–**4** show a typical quartet at around –131 ppm in the ^{19}F NMR spectrum and a triplet at around 1.10 ppm in the ^{11}B NMR spectrum due to coupling with each other.

2,3,5-Triphenyl-1,6,7-triaryl/methyl-BODIPYs 5–8 (3+3 Combination)

BODIPYs **5**–**8** containing three phenyl groups at the 2-, 3- and 5-positions and three aryl/methyl groups at the 1-, 6- and 7-positions were prepared as presented in Scheme 2. 2,3,5-Tribromo-BODIPY was prepared by treating *meso*-tolyldipyrromethane **13** with 3 equiv. of NBS at –78 °C followed by complexation with BF_3·OEt_2 to afford compound **17** in 31% yield. Compound **17** was treated with 5 equiv. of phenylboronic acid under Pd^0 coupling conditions to afford 2,3,5-triphenyl-BODIPY **18** in 78% yield. Compound **18** was confirmed by HRMS and NMR analyses.

In the next step, compound **18** was brominated by treating it with 8 equiv. of Br_2 in CH_2Cl_2, and the crude compound was purified by column chromatography to afford pure triphenyl-tribromo-BODIPY **19** in 93% yield. The composition of BODIPY **19** was confirmed by HRMS. Furthermore, in the ^{1}H NMR spectrum of **19**, the signals observed in the ^{1}H NMR spectrum of **18** at δ = 6.64–7.00 ppm, corresponding to the three pyrrole protons in compound **18**, had disappeared due to bromine substitution. In the final step, BODIPY **19** was treated with the appropriate aryl/methylboronic acids under Suzuki coupling conditions to afford the corresponding sterically crowded hexasubstituted BODIPYs **5**–**8**. Compounds **5**–**8** were unambiguously confirmed by HRMS mass analysis and also characterized in detail by 1D, 2D, ^{19}F and ^{11}B NMR spectroscopy; here we describe in detail the NMR analysis of compound **5** as an example. The ^{1}H-^{1}H COSY NMR spectrum of BODIPY **5** is shown in Figure 2. The



Scheme 2. Synthesis of compounds **5**–**8**.

^{1}H NMR spectrum of BODIPY **5** shows four singlets at δ = 1.97, 2.08, 2.09 and 2.14 ppm for the CH_3 protons of the four tolyl groups placed at different positions on the BODIPY core, which we identified as type I, II, III and IV, respectively. The type I methyl protons of the *meso*-tolyl group at δ = 1.97 ppm show a cross-peak correlation with the doublet at δ = 6.17 ppm, which we identified as arising from type a protons of the *meso*-tolyl group. The type a signal shows a cross-peak correlation in the COSY spectrum with the multiplet signal at δ = 6.62 ppm, which was assigned to type b protons. The type II and type III methyl protons, which have very similar chemical shifts, show a cross-peak correlation with the multiplet signal at δ = 6.49 ppm, which we assigned to type c protons. The type c protons in turn show a cross-peak correlation with the multiplet at δ = 6.41 ppm, which we assigned to type d protons. The type IV methyl signal at δ = 2.14 ppm shows a cross-peak correlation with the doublet at δ = 6.72 ppm, which we identified as type e protons. The type e protons also show a cross-peak correlation with the multiplet at δ = 6.49 ppm. This multiplet was identified as arising from type f protons in addition to type c protons. The phenyl group present at the 2-position shows a multiplet at δ = 6.93 ppm, which corresponds to three protons of type g, and the remaining two protons of type h merge with the type b protons that appear as a multiplet at δ = 6.62 ppm. The two phenyl groups present at the 3- and 5-positions show two sets of signals; a doublet at δ = 7.40 ppm (i type) and a multiplet at δ = 7.23 ppm (j type). Thus, it is possible to identify and assign all signals from the correlations observed in the COSY spectrum.

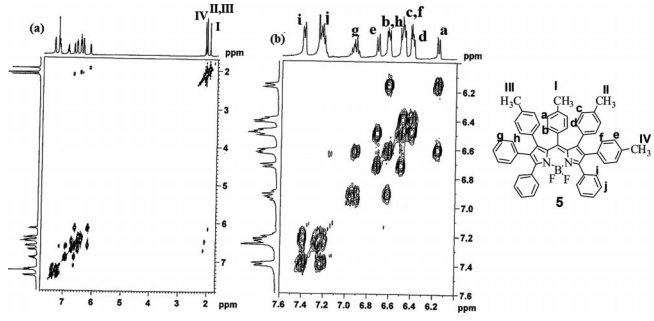
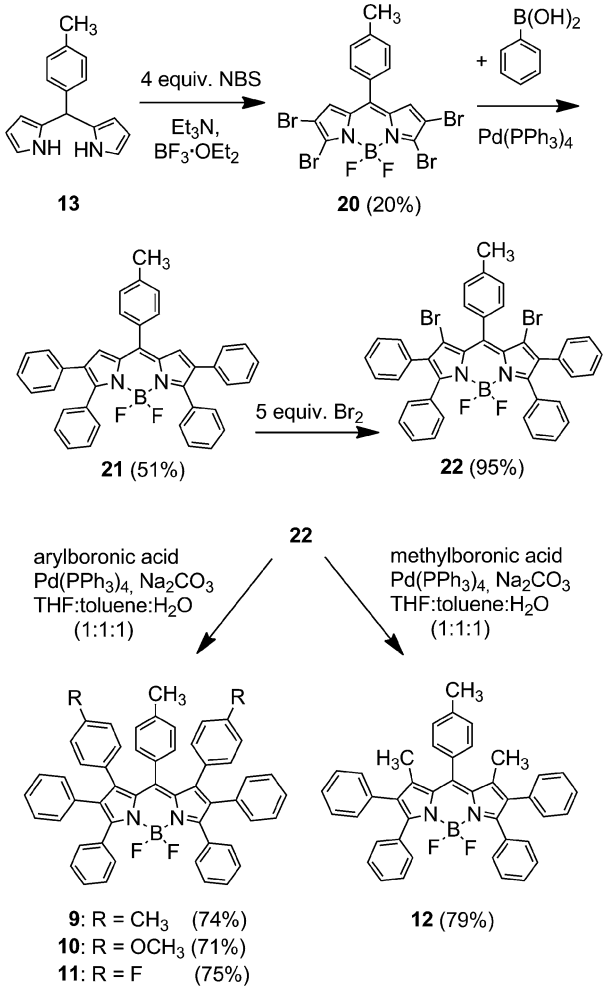


Figure 2. (a) ^{1}H-^{1}H COSY spectrum of compound **5** and (b) selected area of ^{1}H-^{1}H COSY spectrum of compound **5** recorded in $CDCl_3$.

2,3,5,6-Tetraphenyl-1,7-diaryl/methyl-BODIPYs 9–12 (4+2 Combination)

The hexasubstituted BODIPYs **9**–**12** containing four phenyl groups at the 2- ,3-, 5- and 6-positions and two aryl/methyl groups at the 1- and 7-positions were synthesized as shown in Scheme 3. 2,3,5,6-Tetrabromo-BODIPY **20** was synthesized by treating *meso*-tolyldipyrromethane **13** with 4 equiv. of NBS at –78 °C followed by complexation with BF_3·OEt_2. BODIPY **20** was treated with 6 equiv. of phenylboronic acid under Pd^0 coupling conditions to afford 2,3,5,6-tetraphenyl-BODIPY **21** in 51% yield. The BODIPY **21** was subjected to bromination with 5 equiv. of Br_2 followed by column chromatographic purification to afford 2,3,5,6-tetraphenyl-1,7-dibromo-BODIPY **22** in 95% yield. BODIPYs **20**–**22** were characterized by HRMS and a variety of spectroscopic techniques. In the last step, BODIPY **22** was treated with 4 equiv. of aryl/methylboronic acids under Suzuki coupling conditions to afford hexasubstituted BODIPYs **9**–**12** in yields of 71–79%.

BODIPYs **9**–**12** are readily soluble in common organic solvents and their identities were confirmed by HRMS analysis. The formation of BODIPYs **9**–**12** was further confirmed by detailed NMR studies. The COSY NMR spectrum presented in Figure 3 for BODIPY **9** shows two singlets at δ = 1.97 and 2.08 ppm corresponding to three and six protons, respectively. The singlet at δ = 1.97 ppm was identified as arising from type I methyl protons of the *meso*-tolyl group and the singlet at δ = 2.09 ppm was assigned to type II methyl protons of the tolyl groups present at the 1- and 7-positions. The type I methyl protons show a cross-peak correlation with the doublet at δ = 6.17 ppm, which we recognized as type a protons. The type a protons in turn



Scheme 3. Synthesis of compounds **9**–**12**.

show a cross-peak correlation with the signal at δ = 6.63 ppm, which we identified as type b protons of the *meso*-tolyl group. The type II methyl protons show a cross-peak correlation with the doublet at δ = 6.48 ppm, which we identified as type c protons of the tolyl groups present at the 1- and 7-positions. The doublet at δ = 6.41 ppm was identified as type d protons as it shows a cross-peak correlation with type c protons. The phenyl groups present at the 2- and 6-positions show one multiplet at δ = 6.93 ppm for six protons, which we assigned to type e protons. The multiplet signal at δ = 6.63 ppm was assigned to type f as well as type b protons as this multiplet shows a cross-peak correlation with type e protons. The type e protons show a cross-peak correlation with the multiplet assigned to type b protons at δ = 6.63 ppm. Similarly, the phenyl groups present at the 3- and 5-positions also show a doublet at δ = 7.40 ppm and a multiplet at δ = 7.24 ppm, which were assigned to type g and type h protons, respectively. Similarly, it was possible to identify all the signals in the ^{1}H NMR spectra of BODIPYs **10**–**12** by using 1D and 2D NMR spectroscopic techniques.

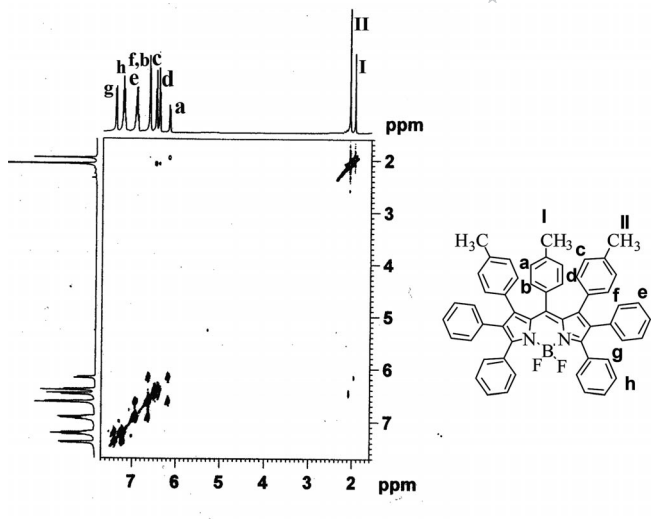
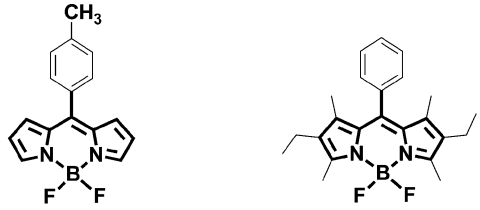


Figure 3. ^{1}H-^{1}H COSY spectrum of compound **9** recorded in $CDCl_3$.

Absorption, Fluorescence and Electrochemical Properties

The absorption spectra of hexasubstituted BODIPYs **1**–**12** were recorded in CH_2Cl_2 and the data for all these BODIPYs along with those for unsubstituted BODIPY[46] **23** are presented in Table 1. The absorption spectra of BODIPYs **1**–**4**, as examples, and **23** are shown in Figure 4 (a). The hexasubstituted BODIPYs **1**–**12** show a characteristic strong $S_0 \rightarrow S_1$ transition like unsubstituted BODIPY[46] **23**. However, the absorption bands of BODIPYs **1**–**12** are broader and experience a significant bathochromic shift compared with that of BODIPY **23**. Furthermore, the magnitude of the redshift depends on the nature of the aryl/methyl substituents present on the BODIPY core. For example, the BODIPYs containing a combination of methyl and aryl substituents experience a smaller bathochromic shift than BODIPYs containing two types of aryl substituents.



23 **24**

The fluorescence properties of BODIPYs **1**–**12** were also investigated by both steady-state and time-resolved fluorescence studies. The emission spectra of BODIPYs **1**–**4** and **23** are shown in Figure 4b and the relevant data for all BODIPYs are included in Table 1. The fluorescence bands of BODIPYs **1**–**12** are broader and experience a significant redshift compared with that of **23**. The magnitude of the redshift of the fluorescence band depends on the nature of aryl/methyl substituents on the BODIPY core. BODIPYs **1**–**12** show moderate fluorescence with quantum yields (Φ_f) in the range of 0.1–0.4, unlike **23** which is weakly fluores-

Table 1. Photophysical and electrochemical data for compounds **1**–**12**, **23** and **24** recorded in CH_2Cl_2.

	λ_{max} [nm] ($\log[\varepsilon_{max}$ ($M^{-1}cm^{-1}$)])	λ_{em} [nm]	$\Delta\nu_{st}$ [cm^{-1}]	Φ_f	τ_f [ns]	E [V] vs. SCE E_{ox}	E_{red}
1	570 (4.83)	613	1230	0.22	2.8	1.24	–0.95
2	579 (4.80)	637	1572	0.11	2.7	1.18	–0.97
3	569 (4.86)	608	1127	0.34	3.2	1.35	–0.83
4	541 (4.76)	570	940	0.35	2.6	1.19	–1.05
5	569 (4.84)	610	1181	0.22	2.6	1.27	–0.93
6	572 (4.81)	626	1508	0.094	2.2	1.32	–0.83
7	570 (4.82)	608	1096	0.36	3.2	1.42	–0.76
8	543 (4.78)	576	1055	0.39	3.2	1.30	–0.94
9	567 (4.87)	604	1080	0.22	2.4	1.29	–0.92
10	569 (4.82)	604	1018	0.22	2.7	1.29	–0.91
11	569 (4.85)	607	1100	0.32	3.0	1.34	–0.86
12	548 (4.84)	584	1125	0.43	3.5	1.24	–1.02
23[a]	501 (4.74)	517	618	0.03	0.5	–	–0.80
24[b]	527 (3.85)	542	525	0.75	4.9	0.98	–1.40

[a] See ref.[46] [b] See ref.[47]

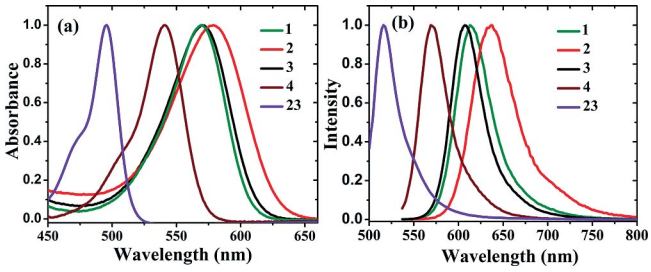


Figure 4. Normalized absorption spectra (a) and emission spectra (b) of compounds **1**–**4** and **23**.

cent[46] (Φ_f = 0.03). All the BODIPYs exhibit large Stokes shifts compared with **23**, and compounds containing aryl substituents on the pyrrole carbons exhibit larger Stokes shifts than compounds containing methyl substituents (Table 1). BODIPYs **1**–**12** show a single exponential decay and their singlet-state lifetimes (τ_f) are in the range of 2.2–3.5 ns (Table 1). Thus, the absorption and fluorescence studies on BODIPYs **1**–**12** indicate that the presence of methyl/aryl substituents on the BODIPY core significantly alter the electronic properties compared with unsubstituted BODIPY[46] **23**. Furthermore, in comparison with hexa-alkylated BODIPYs such as 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-3a,4a-diaza-*s*-indacene[47] (**24**), BODIPYs **1**–**12** show significant bathochromic shifts of the absorption and emission bands (Table 1), but have lower fluorescence yields and singlet-state lifetimes, which indicates that the aryl groups in BODIPYs **1**–**12** undergo free rotation thereby enhancing the non-radiative decay channels.

The electrochemical properties of BODIPYs **1**–**12** were studied by cyclic voltammetry in CH_2Cl_2 using tetrabutylammonium perchlorate as the supporting electrolyte. The oxidation and reduction waves of BODIPYs **1**–**4** are presented in Figure 5 and the redox data is included in Table 1. In general, unsubstituted BODIPY **23** shows one reversible reduction but no oxidation because of its electron-deficient nature. However, BODIPYs **1**–**12** exhibit one reversible oxidation and one reversible reduction, which indicate the electron-rich nature of BODIPYs **1**–**12**. Furthermore, the reduction potentials of BODIPYs **1**–**12** experience a cathodic shift compared with **23**, which indicates their electron-rich nature. However, compared with alkylated BODIPY[47] **24**, BODIPYs **1**–**12** are difficult to oxidize and easier to reduce. Thus, the potential shifts of BODIPYs **1**–**12** depend on the electron-donating and -withdrawing nature of the substituents present on the BODIPY core. Thus, electrochemical studies indicate that the hexasubstituted BODIPYs are stable under redox conditions.

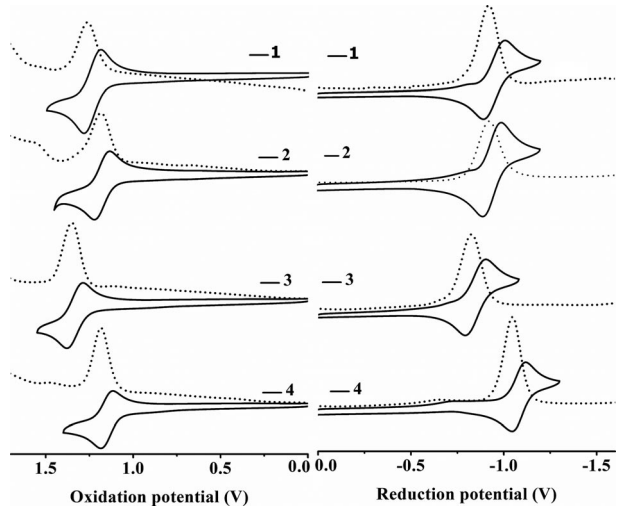


Figure 5. Cyclic (solid line) and differential pulse (dotted line) voltammograms of compounds **1**–**4** recorded in CH_2Cl_2.

Conclusions

We adopted a step-wise strategy for the synthesis of a series of hexasubstituted BODIPYs containing mixed methyl/aryl substituents on the BODIPY core under simple Pd^0 coupling conditions. All the compounds were prepared by bromination of the BODIPY precursors followed by coupling with aryl/methylboronic acids under Pd^0 coupling conditions. Our synthetic strategy has allowed us to prepare hexasubstituted BODIPYs containing two different types of substituents on the pyrrole carbon atoms. These BODIPYs exhibit interesting absorption, fluorescence and electrochemical properties that are significantly different to those of unsubstituted BODIPY. The hexasubstituted BODIPYs are strongly fluorescent in the solid state and we are currently investigating the solid-state fluorescence properties of hexasubstituted BODIPYs in our laboratory.

Experimental Section

General: All NMR spectra (δ values, ppm) were recorded with a 400 MHz spectrometer. Tetramethylsilane (TMS) was used as external reference for ^1H (residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.2 ppm) NMR spectra in $CDCl_3$. Multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. HRMS spectra were recorded by using the electron spray ionization method with a TOF analyser. Cyclic voltammetric (CV) and

differential pulse voltammetric (DPV) studies were carried out by using an electrochemical system with 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 tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Half-wave potentials were measured by DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated against the saturated calomel electrode as reference by the addition of ferrocene as an internal standard and with $E_{1/2}(Fc/Fc^+)$ = 0.45 V versus SCE. The quantum yields were calculated in CH_2Cl_2 (5×10^{-6} M) with Sulforhodamine B as reference (= 0.69 in ethanol, λ_{exc} = 530 nm).[48] All values of are corrected for changes in refractive index of solvent.

1,2,6,7-Tetrabromo-4,4-difluoro-3,5-diphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (16): A solution of liquid bromine (0.12 mL, 2.3 mmol) and $NaHCO_3$ (101 mg, 1.20 mmol) in CH_2Cl_2 (3 mL) was added to a solution of compound **15** (100 mg, 0.23 mmol) in dry CH_2Cl_2 and the mixture was stirred for 2 h at room temperature under N_2. The progress of the reaction was followed by TLC and absorption spectroscopy. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with an aqueous solution of sodium thiosulfate (3 × 50 mL). The organic layers were combined, dried with Na_2SO_4, and the solvents evaporated to dryness under rotary evaporation. The crude compound was subjected to silica gel column chromatography using petroleum ether/ethyl acetate (95:5) as eluent to afford the desired compound **16** as a red solid in 96% yield (163 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.51 (s, 3 H), 7.24 (d, J = 7.93 Hz, 2 H), 7.39 (d, J = 8.24 Hz, 2 H), 7.41–7.45 (m, 6 H), 7.51–7.57 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9, 115.7, 124.0, 128.0, 128.2, 128.9, 130.0, 130.2, 130.3, 1130.6, 140.4, 145.4, 156.1 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.43 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.42 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{27}H_{17}BBr_4F_2KN_2O$ 788.7772 $[M + K]^+$; found 788.7784.

General Procedure for the Synthesis of Compounds 1–4: In a two-necked 50 mL round-bottomed flask fitted with a reflux condenser, gas inlet and gas outlet tubes for nitrogen purging, compound **16** (50 mg), the appropriate boronic acid (5 equiv.) and Na_2CO_3 (5 equiv.) were dissolved in water/THF/toluene (1:1:1, 15 mL) and purged with N_2 for 10 min. The reaction flask was then placed in an oil bath, [$Pd(PPh_3)_4$] (6 mol-%), was added and the reaction mixture was stirred at 80 °C for 7 h. TLC analysis of the reaction mixture showed the complete disappearance of the spot corresponding to precursor compound **16** with the appearance of a new spot corresponding to the desired product. The reaction mixture was diluted with water and extracted with diethyl ether (50 mL). The organic layer was washed with water and brine, and dried with $NaSO_4$. The solvent was evaporated on a rotary evaporator under vacuo and the resulting crude product was purified on a silica gel column by using petroleum ether/ethyl acetate (95:5) as eluent to afford the desired product as a red solid.

4,4-Difluoro-3,5-diphenyl-1,2,6,7,8-penta(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (1): Yield 38 mg, 71%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 3 H), 2.09 (s, 6 H), 2.13 (s, 6 H), 6.16 (d, J = 8.07 Hz, 2 H), 6.38–6.43 (d, J = 7.70 Hz, 4 H), 6.49–6.51 (m, 8 H), 6.61 (d, J = 8.07 Hz, 2 H), 6.72 (d, J = 7.70 Hz, 4 H), 7.21–7.25 (m, 6 H), 7.40 (d, J = 6.60 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0, 21.2, 21.3, 126.9, 127.5, 127.7, 128.2, 128.5, 128.6, 130.2, 130.3, 130.7, 130.8, 131.8, 131.9, 132.2, 132.5, 134.3, 135.1, 135.7, 138.3, 144.3, 147.6, 155.9 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.32 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.14 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{56}H_{45}BF_2N_2Na$ 817.3545 $[M + Na]^+$; found 817.3538.

1,2,6,7-Tetra(*p*-anisyl)-4,4-difluoro-3,5-diphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (2): Yield 37 mg, 64%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 4 H), 3.61 (s, 6 H), 3.63 (s, 6 H), 6.21–6.27 (m, 6 H), 6.41–6.49 (m, 8 H), 6.50–6.55 (m, 4 H), 6.65 (d, J = 8.03 Hz, 2 H), 7.21–7.25 (m, 6 H), 7.38–7.42 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.9, 55.1, 55.2, 112.8, 113.1, 125.7, 127.1, 127.3, 127.6, 128.7, 130.9, 131.4, 131.9, 132.1, 132.2, 132.5, 134.0, 137.9, 143.8, 147.2, 155.9, 157.7, 157.9 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.37 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.12 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{56}H_{45}BF_2N_2O_4K$ 897.3081 $[M + K]^+$; found 897.3082.

4,4-Difluoro-1,2,6,7-tetrakis(4-fluorophenyl)-3,5-diphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (3): Yield 37 mg, 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.03 (s, 3 H), 6.30 (d, J = 7.78 Hz, 2 H), 6.39–6.45 (m, 4 H), 6.47–6.52 (m, 4 H), 6.54–6.59 (m, 4 H), 6.62–6.68 (m, 6 H), 7.23–7.30 (m, 6 H), 7.38 (d, J = 6.78 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.9, 114.2, 114.4, 114.7, 114.9, 127.4, 128.3, 128.8, 129.9, 129.1, 130.4, 130.5, 130.7, 131.5, 131.7, 131.8, 131.9, 132.3, 132.4, 133.9, 139.3, 143.2, 147.5, 156.2, 160.0, 160.3, 162.5, 162.8 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.41 (q, $J_{F\text{-}B}$ = 60 Hz), –116.18, –115.38 ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.09 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{52}H_{33}BF_6KN_2$ 849.2281 $[M + K]^+$; found 849.2285.

4,4-Difluoro-1,2,6,7-tetramethyl-3,5-diphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4): Yield 26 mg, 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (s, 6 H), 1.75 (s, 6 H), 2.49 (s, 3 H), 7.33–7.37 (m, 6 H), 7.47 (d, J = 6.54 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.1, 12.7, 21.7, 127.9, 128.3, 128.7, 129.9, 130.1, 132.2, 132.7, 133.0, 139.1, 140.1, 143.3, 155.8 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –132.68 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.81 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{32}H_{29}BF_2N_2Na$ 513.2290 $[M + Na]^+$; found 513.2285.

2,3,5-Tribromo-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (17): A solution of *meso*-(*p*-tolyl)dipyrromethane (**13**; 530 mg, 2.24 mmol) in dry THF (20 mL) was cooled to –78 °C under nitrogen for 10 min. *N*-Bromosuccinimide (1.2 g, 6.73 mmol) was added to this solution in three or four portions over a period of 1 h. The reaction mixture was warmed to room temperature and the solvent was evaporated on a rotary evaporator under vacuum. The crude compound was subjected to flash column chromatography using CH_2Cl_2 as eluent. The resultant compound was dissolved in CH_2Cl_2 and DDQ (483 mg, 2.12 mmol) was added to oxidize the compound. The reaction mixture was stirred for 1 h at room temperature. Triethylamine (75.4 mmol) followed by $BF_3{\cdot}Et_2O$ (89.97 mmol) were added and stirring was continued at room temperature for an additional 1 h. TLC analysis of the crude compound showed three spots corresponding to dibromo, tribromo and tetrabromo derivatives; the desired tribromo derivative was the major, which was eluted as the second spot. The crude product was subjected to silica gel column chromatography and the second band was collected by using petroleum ether/dichloromethane (75:25) as eluent. The solvent was removed on a rotary evaporator under vacuo to afford **17** as a purple powder (360 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 6.53 (d, J = 4.28 Hz, 1 H), 6.82 (d, J = 4.28 Hz, 2 H), 7.32 (d, J = 7.90 Hz, 2 H), 7.38 (d, J = 7.90 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 110.8, 123.7, 129.4, 129.7, 130.6, 132.4, 133.1, 134.7, 134.8, 135.9, 142.2, 143.6 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –147.46 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.48 (t,

J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{16}H_{10}BBr_3F_2N_2Na$ 538.8350 $[M + Na]^+$; found 538.8346.

4,4-Difluoro-2,3,5-triphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (18): Following the procedure used for the synthesis of compound **1**, compound **17** (100 mg, 0.19 mmol), phenylboronic acid (117 mg, 0.96 mmol) and Na_2CO_3 (102 mg, 0.96 mmol) in water/THF/toluene (1:1:1, 15 mL) were allowed to react in the presence of $[Pd(PPh_3)_4]$ (6 mol-%) at 80 °C for 3 h. The solvent was evaporated and the crude product was purified on a silica gel column by using petroleum ether/ethyl acetate (95:5) as eluent to afford triphenylated BODIPY **18** as red solid in 78% yield (77 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.50 (s, 3 H), 6.64 (d, J = 4.02 Hz, 1 H), 6.95 (d, J = 4.02 Hz, 1 H), 6.99–7.05 (m, 3 H), 7.12–7.18 (m, 3 H), 7.32–7.43 (m, 8 H), 7.50 (d, J = 7.28 Hz, 2 H), 7.55 (d, J = 8.03 Hz, 2 H), 7.85 (dd, J = 7.15, 1.88 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 21.6, 121.1, 127.0, 128.0, 128.3, 129.2, 129.3, 129.6, 129.7, 130.6, 130.9, 131.4, 131.7, 132.1, 132.7, 134.1, 134.5, 136.8, 140.9, 144.6, 159.3 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –132.72 (q, J_{F-B} = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.29 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{34}H_{25}BF_2N_2K$ 549.1716 $[M + K]^+$; found 549.1723.

1,6,7-Tribromo-4,4-difluoro-2,3,5-triphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (19): $NaHCO_3$ (99 mg, 1.18 mmol, 8 equiv.) followed by bromine (0.06 mL, 1.18 mmol, 8 equiv.) were added to a solution of BODIPY **18** (0.075 g, 0.15 mmol) in 25 mL of CH_2Cl_2 and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by addition of an aqueous solution of $Na_2S_2O_3$. The crude reaction mixture was washed with water (3× 50 mL), dried with $NaSO_4$, filtered and the solvents evaporated to dryness under rotary evaporation. The crude compound was subjected to silica column chromatography using petroleum ether/ethyl acetate (95:5) as eluent to give the desired product **19** was obtained as a red solid (103 mg) in 93% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.49 (s, 3 H), 6.96–7.00 (m, 2 H), 7.16–7.22 (m, 3 H), 7.24–7.28 (m, 4 H), 7.28–7.33 (m, 4 H), 7.37 (d, J = 7.93 Hz, 2 H), 7.39–7.44 (m, 2 H), 7.56 (dd, J = 6.41, 2.75 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9, 114.6, 122.2, 122.7, 127.8, 127.9, 128.0, 128.1, 128.6, 129.2, 129.7, 129.9, 130.1, 130.3, 130.5, 130.7, 132.1, 137.2, 140.1, 145.4, 154.2, 158.5 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.10 (q, J_{F-B} = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.63 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{33}H_{22}BBr_3F_2N_2OK$ 786.8981 $[M + K]^+$; found 786.8996.

General Procedure for the Synthesis of Compounds 5–8: Compound **19** (40 mg), the appropriate boronic acid (5 equiv.) and Na_2CO_3 (5 equiv.) were dissolved in water/THF/toluene (1:1:1, 15 mL) in a two-necked round-bottomed flask fitted with a reflux condenser, gas inlet and gas outlet tubes and stirred under N_2 for 10 min. $[Pd(PPh_3)_4]$ (6 mol-%) was added to this solution and the reaction mixture was heated at reflux at 80 °C for 5 h. After completion of the reaction as judged by TLC analysis, the reaction mixture was diluted with water and extracted with diethyl ether (1× 50 mL). The combined organic layers were washed with water and brine, and dried with $NaSO_4$. The solvent was evaporated and the crude product was purified on a silica gel column by using petroleum ether/ethyl acetate (97:3) as eluent to afford the desired product as a red solid.

4,4-Difluoro-2,3,5-triphenyl-1,6,7,8-tetra(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5): Yield 38 mg, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 3 H), 2.09 (d, J = 3.87 Hz, 6 H), 2.14 (s, 3 H), 6.17 (d, J = 7.74 Hz, 2 H), 6.37–6.43 (m, 4 H), 6.45–6.53 (m, 6 H), 6.59–6.65 (m, 4 H), 6.72 (d, J = 8.17 Hz, 2 H), 6.88–6.97 (m, 3 H), 7.20–7.25 (m, 6 H), 7.40 (d, J = 6.45 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0, 21.1, 21.3, 126.2, 126.9, 127.5, 127.6, 127.7, 127.8, 128.3, 128.5, 128.7, 130.2, 130.3, 130.6, 130.9, 131.7, 131.8, 131.9, 132.0, 132.1, 132.4, 132.6, 133.5, 134.3, 134.4, 135.2, 135.7, 138.4, 144.3, 144.5, 147.8, 155.6, 156.2 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.33 (q, J_{F-B} = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.15 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{55}H_{43}BF_2N_2Na$ 803.3389 $[M + Na]^+$; found 803.3405.

1,6,7-Tri(*p*-anisyl)-4,4-difluoro-2,3,5-triphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (6): Yield 39 mg, 70%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (s, 3 H), 3.61–3.63 (m, 6 H), 3.64 (s, 3 H), 6.21–6.27 (m, 6 H), 6.41–6.55 (m, 8 H), 6.60–6.68 (m, 4 H), 6.90–6.98 (m, 3 H), 7.20–7.26 (m, 6 H), 7.40 (d, J = 6.24 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.9, 55.1, 55.2, 112.7, 112.8, 113.1, 125.6, 126.2, 127.1, 127.2, 127.5, 127.6, 128.6, 128.7, 130.8, 130.9, 131.4, 131.9, 132.1, 133.5, 138.0, 157.7, 157.9 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.33 (q, J_{F-B} = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.05 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{55}H_{43}BF_2N_2O_3Na$ 851.3236 $[M + Na]^+$; found 851.3227.

4,4-Difluoro-1,6,7-tris(4-fluorophenyl)-2,3,5-triphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (7): Yield 39 mg, 73%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.03 (s, 3 H), 6.30 (d, J = 7.78 Hz, 2 H), 6.37–6.45 (m, 4 H), 6.46–6.53 (m, 4 H), 6.53–6.68 (m, 8 H), 6.90–7.00 (m, 3 H), 7.20–7.31 (m, 6 H), 7.36–7.42 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.9, 114.0, 114.1, 114.3, 114.4, 114.7, 114.9, 126.6, 127.4, 127.7, 128.4, 129.0, 130.5, 130.5, 130.6, 130.8, 131.5, 131.6, 131.8, 131.9, 132.0, 132.3, 132.4, 132.5, 132.9, 139.3, 142.9, 143.4, 147.4, 155.8, 156.7, 160.0, 160.3, 162.5, 162.8 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.35 (q, J_{F-B} = 60 Hz), –116.43 (s), 116.29 (s), –115.49 (s) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.12 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{52}H_{34}BF_5N_2Na$ 815.2636 $[M + Na]^+$; found 815.2646.

4,4-Difluoro-1,6,7-trimethyl-2,3,5-triphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (8): Yield 29 mg, 78%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.42 (m, 6 H), 1.78 (s, 3 H), 2.47 (s, 3 H), 6.88 (d, J = 7.53 Hz, 2 H), 7.11–7.21 (m, 5 H), 7.29–7.42 (m, 10 H), 7.50 (d, J = 6.78 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.1, 12.7, 13.4, 21.7, 126.6, 127.5, 127.9, 128.0, 128.1, 128.5, 128.8, 129.8, 130.1, 130.5, 130.7, 132.2, 132.3, 132.5, 132.9, 134.0, 134.1, 139.2, 140.9, 144.1, 154.3, 157.1 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.99 (q, J_{F-B} = 61 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.96 (t, J_{B-F} = 32 Hz) ppm. HRMS: calcd. for $C_{37}H_{31}BF_2N_2Na$ 575.2447 $[M + Na]^+$; found 575.2459.

2,3,5,6-Tetrabromo-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (20): *meso*-(*p*-Tolyl)dipyrromethane (**13**; 500 mg, 2.12 mmol) was dissolved in dry THF (20 mL) and cooled to –78 °C under nitrogen. *N*-Bromosuccinimide (1.51 g, 8.46 mmol) was added in three or four portions over a period of 1 h. The reaction mixture was warmed to room temperature and the solvent was evaporated on a rotary evaporator under vacuum. The crude compound was subjected to flash column chromatography using CH_2Cl_2 as eluent. The resultant compound was dissolved in CH_2Cl_2 and DDQ (483 mg, 2.12 mmol) was added to oxidize the compound. The reaction mixture was stirred for 1 h at room temperature. Triethylamine (75.4 mmol) followed by $BF_3{\cdot}Et_2O$ (89.97 mmol) were added and stirring was continued at room temperature for an additional 1 h. TLC analysis of the crude compound showed three spots corresponding to the tri-, tetra- and pentabromo derivatives; the desired tetrabromo derivative was the second spot. The crude product was subjected to silica gel column

chromatography and the second band was collected by using petroleum ether/dichloromethane (75:25) as eluent. The solvent was removed on a rotary evaporator under vacuo to afford **20** as a purple powder (260 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 6.82 (d, J = 4.28 Hz, 2 H), 7.32–7.38 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.7, 112.0, 129.1, 129.8 (d), 130.6, 130.7, 131.7, 134.8, 134.9, 142.6 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –148.24 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.30 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{16}H_9BBr_4F_2N_2Na$ 616.7455 [M + Na]$^+$; found 616.7458.

4,4-Difluoro-2,3,5,6-tetraphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (21): Following the procedure used for the synthesis of compound **1**, a mixture of compound **20** (100 mg, 0.167 mmol), phenylboronic acid (122 mg, 1 mmol) and Na_2CO_3 (107 mg, 1 mmol) in water/THF/toluene (1:1:1, 15 mL) was subjected to Pd^0 Suzuki coupling conditions. The crude product was purified on a silica gel column by using petroleum ether/ethyl acetate (95:5) to afford phenylated BODIPY **21** as red solid in 51% yield (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 3 H), 6.98–7.02 (m, 4 H), 7.04 (s, 2 H), 7.13–7.17 (m, 6 H), 7.29–7.35 (m, 4 H), 7.38 (d, J = 7.93 Hz, 2 H), 7.45–7.49 (m, 4 H), 7.59 (d, J = 7.93 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.6, 127.0, 128.0, 128.3, 128.4, 128.8, 129.2, 129.3, 130.5, 130.9, 131.7, 131.9, 134.0, 134.6, 134.8, 141.0, 144.5, 156.4 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –132.65 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.05 (t, $J_{B\text{-}F}$ = 32 Hz) ppm.

1,7-Dibromo-4,4-difluoro-2,3,5,6-tetraphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (22): $NaHCO_3$ (0.85 mmol) followed by bromine (0.044 mL, 0.85 mmol) were added to a solution of BODIPY **21** (0.100 g, 0.17 mmol) in 25 mL of CH_2Cl_2 and the reaction mixture was stirred at room temperature for 2 h. After quenching the reaction with an aqueous solution of $Na_2S_2O_3$, the crude reaction mixture was washed with water (3× 50 mL), dried with $NaSO_4$, filtered and the solvents evaporated to dryness. The crude compound was purified by silica column chromatography using petroleum ether/ethyl acetate (95:5) as eluent to afford the desired product **22** as a purple solid in 95% yield (120 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 6.99–7.03 (m, 4 H), 7.17–7.21 (m, 8 H), 7.21–7.25 (m, 4 H), 7.32–7.37 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.9, 121.1, 127.7, 128.0, 129.0, 129.4, 129.9, 130.4, 131.1, 132.4, 136.3, 139.8, 145.6, 156.6 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –130.65 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 0.85 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{40}H_{27}BBr_2F_2N_2Na$ 768.0430 [M + Na]$^+$; found 767.0430.

General Procedure for the Synthesis of Compounds 9–12: A mixture of compound **22** (30 mg), the appropriate boronic acid (4 equiv.) and Na_2CO_3 (4 equiv.) in water/THF/toluene (1:1:1, 15 mL) was stirred under N_2 for 10 min. [$Pd(PPh_3)_4$] (6 mol-%) was added to this solution and the reaction mixture was heated at reflux at 80 °C for 2 h. TLC analysis of the reaction mixture showed the complete conversion of the starting material into the desired product. The reaction mixture was diluted with water and extracted with diethyl ether (50 mL). The organic layer was washed with water and brine, and dried with $NaSO_4$ The solvent was evaporated and the crude compound purified on a silica gel column by using petroleum ether/ethyl acetate (97:3) as eluent to afford the desired product as red crystals in good yield.

4,4-Difluoro-2,3,5,6-tetraphenyl-1,7,8-tri(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (9): Yield 39 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 2.09 (s, 6 H), 6.17 (d, J = 7.63 Hz, 2 H), 6.39 (d, J = 8.04 Hz, 4 H), 6.48 (d, J = 7.92 Hz, 4 H), 6.63 (d, J = 7.92 Hz, 6 H), 6.89–6.99 (m, 6 H), 7.20–7.25 (m, 6 H), 7.40 (d, J = 7.04 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.1, 21.2, 126.2, 127.0, 127.5, 127.6, 127.8, 128.4, 128.7, 130.2, 130.9, 131.7, 131.9, 132.0, 132.5, 133.4, 133.4, 134.4, 135.2, 138.4, 144.5, 155.9 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.31 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.18 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{54}H_{41}BF_2N_2K$ 805.2971 [M + K]$^+$; found 805.2970.

1,7-Di(*p*-anisyl)-4,4-difluoro-2,3,5,6-tetraphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (10): Yield 38 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 3.61 (s, 6 H), 6.21–6.27 (m, 6 H), 6.44 (d, J = 8.78 Hz, 4 H), 6.63 (d, J = 6.78 Hz, 4 H), 6.67 (d, J = 8.03 Hz, 2 H), 6.90–6.98 (m, 6 H), 7.21–7.25 (m, 6 H), 7.40 (d, J = 6.53 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.1, 55.2, 112.8, 126.2, 127.1, 127.2, 127.5, 127.6, 128.6, 128.8, 130.8, 130.9, 131.4, 132.0, 132.1, 133.4, 138.0, 144.2, 156.0, 157.7 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.32 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.16 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{54}H_{41}BF_2N_2NaO_2$ 821.3130 [M + K]$^+$; found 821.3130.

4,4-Difluoro-1,7-bis(4-fluorophenyl)-2,3,5,6-tetraphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (11): Yield 39 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 6.29 (d, J = 7.34 Hz, 2 H), 6.36–6.43 (m, 4 H), 6.47–6.53 (m, 4 H), 6.61 (d, J = 7.04 Hz, 4 H), 6.65 (d, J = 7.63 Hz, 2 H), 6.92–7.00 (m, 6 H), 7.18–7.29 (m, 6 H), 7.40 (d, J = 7.04 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0, 114.0, 114.2, 126.5, 127.3, 127.7, 128.4, 129.0, 130.7, 130.8, 131.7, 131.8, 131.9, 132.0, 132.4, 133.0, 134.9, 139.2, 143.1, 147.4, 156.3, 160.0, 162.4 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.33 (q, $J_{F\text{-}B}$ = 60 Hz), –116.55 (s) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.12 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{52}H_{35}BF_4N_2Na$ 797.2730 [M + Na]$^+$; found 797.2728.

4,4-Difluoro-1,7-dimethyl-2,3,5,6-tetraphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (12): Yield 33 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6 H), 2.47 (s, 3 H), 6.90 (dd, J = 7.40, 2.13 Hz, 4 H), 7.14–7.22 (m, 12 H), 7.33–7.38 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.5, 21.7, 126.8, 127.5, 128.0, 128.7, 129.4, 130.3, 130.5, 130.7, 132.2, 132.8, 133.8, 134.7, 139.3, 140.1, 144.9, 155.5 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –131.36 (q, $J_{F\text{-}B}$ = 60 Hz) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 1.05 (t, $J_{B\text{-}F}$ = 32 Hz) ppm. HRMS: calcd. for $C_{42}H_{33}BF_2N_2K$ 653.2344 [M + K]$^+$; found 653.2346.

Supporting Information (see footnote on the first page of this article): Characterization data for all new compounds.

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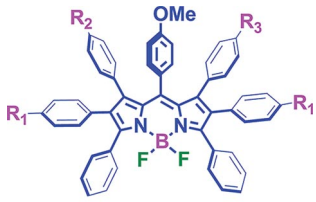
Boron-Dipyrromethenes

We have synthesized and studied the properties of hexasubstituted BODIPYs containing two different types of aryl/alkyl substituents on their pyrrole carbon atoms.



R_1, R_2, R_3 = CH_3/OCH_3/F

R_1 = Ph; R_2, R_3 = CH_3/OCH_3/F

R_1, R_2 = Ph; R_3 = CH_3/OCH_3/F

Keywords: Nitrogen heterocycles / Fluorescence / UV/Vis spectroscopy / Voltammetry / Substituent effects

