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NOTE

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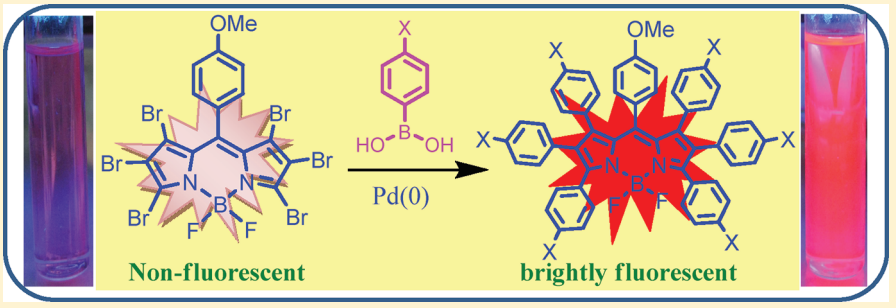
# Synthesis of Sterically Crowded Polyarylated Boron-Dipyrromethenes

Vellanki Lakshmi and Mangalampalli Ravikanth*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

Supporting Information

**ABSTRACT:**




A rapid synthetic route for polyarylated boron-dipyrromethenes using hexabromo boron-dipyrromethene as the key synthon is described. The X-ray structure revealed that the polyarylated BODIPY adopts a propeller-like conformation. These compounds exhibit red-shifted absorption and fluorescence bands with decent quantum yields and reversible oxidation and reduction waves when compared to unsubstituted boron-dipyrromethenes.

Boron-dipyrromethene dyes (BODIPY) are highly fluorescent dyes and have diverse applications as biolabels, artificial light harvesters, sensitizers for solar cells, fluorescent sensors, molecular photonic wires, and laser dyes.[1] This popularity of BODIPY dyes is presumably because of their advantageous spectroscopic properties such as high molar absorption coefficients, narrow band shapes with tunable wavelengths, high fluorescence quantum yields, and considerably high photostability. Furthermore, the BODIPY dyes can be easily functionalized, and the functionalized dyes can be used to introduce substituents at all positions of the BODIPY core, including the two fluorines of the boron atom.[2] Thus, the electronic properties of BODIPY dye can be fine-tuned by suitable substitution on the boron-dipyrromethene core. The extensive literature available on BODIPY dyes suggests that the introduction of substituents at the *meso* position does not alter the electronic properties of the dye significantly because the *meso* group is perpendicularly oriented and electronically decoupled.[3] On the other hand, the introduction of substituents at the 3,5-positions and 1,7-positions significantly alters the electronic properties of the dye.[4] For example, the introduction of two phenyl groups at the 3,5-positions shifts the absorption band to approximately 50 nm toward red, and introduction of two styryl groups at the same positions shifts the absorption band toward 100 nm red.[4a] Thus, various synthetic strategies were developed to obtain BODIPYs exhibiting absorption and emission bands in the visible or near-infrared (NIR) region of the spectrum. Few of the approaches reported in the literature to obtain BODIPYs with absorption/emission in the visible and NIR region with appreciable quantum yields are by introducing bulky aryl substituents on the BODIPY core or by fusing aryl groups to the pyrroles of the BODIPY core.[5] These kinds of systems are also found to be brightly fluorescent in the solid state. These properties are very important for their potential use in the field of optoelectronics, such as high-performance electroluminescent devices, light-emitting field-effect transistors, and lasers.[6] Although the literature on BODIPYs with alkyl substituents at the pyrrole carbons is exhaustive, the BODIPYs with aryl substituents at the pyrrole carbons are limited due to a lack of proper precursors and synthetic routes. It is shown in the literature that the aryl-substituted BODIPYs can be synthesized by using aryl-substituted pyrroles as key precursors, which are synthetically not easily accessible.[7] Dehaen and co-workers[8] developed a simple synthetic strategy to introduce a range of substituents at 3,5-positions by nucleophilic substitution using 3,5-dichloro-BODIPY as the precursor. However, this methodology has not been explored for the synthesis of other polyarylated BODIPYs containing more than two aryl groups at the pyrroles of the boron-dipyrromethene core. Recently, Wakamiya et al.[9] reported the synthesis of polyphenylated BODIPY **I** using triphenyl-substituted pyrrole as the key precursor, as shown in Scheme 1. However, this method requires several steps involving protection/deprotection reactions and extensive chromatographic purifications. Furthermore, to synthesize various polyarylated BODIPYs by using this method, one needs to prepare the corresponding triaryl pyrroles whose synthesis is difficult. In this note, we report the facile synthesis of polyarylated BODIPYs **1**−**4** using a hexabromo derivative of BODIPY **5** as a key

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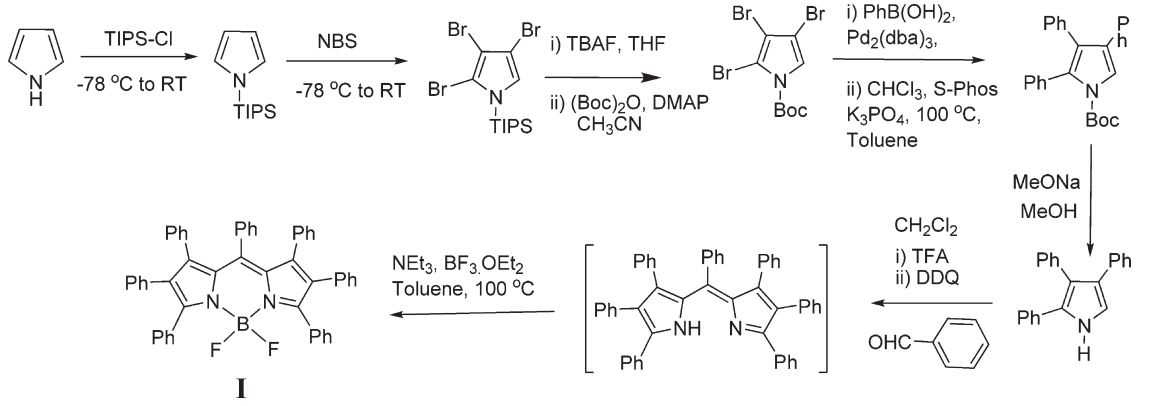
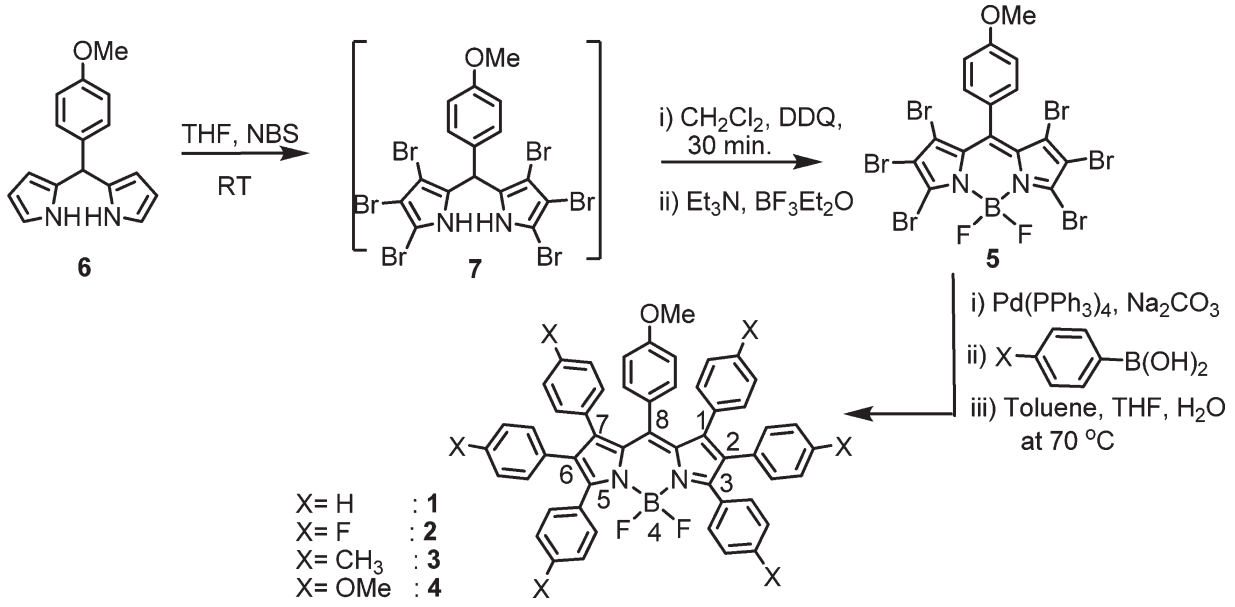
**Scheme 1. Reported Synthesis of Polyphenylated BODIPY I**




**Scheme 2. Synthesis of Polyarylated BODIPY Compounds (1−4)**




synthon. The unknown hexabromo derivative of BODIPY **5** can be synthesized in a 500 mg batch easily in a two-step one-pot reaction under mild reaction conditions. The advantages of our method over the reported method are the use of readily available precursors, mild reaction conditions, and simple column chromatographic purifications to afford polyarylated BODIPYs in decent yields. Furthermore, the method is applicable to synthesize a set of substituted polyarylated BODIPYs using the single precursor, hexabromo BODIPY **5** (Scheme 2).

To synthesize the hexabromo BODIPY **5**, first we synthesized the required *meso*-anisyl dipyrromethane[10] **6** by condensing 1 equiv of *p*-anisaldehyde with 25 equiv of pyrrole under mild acid-catalyzed reaction conditions followed by flash column chromatographic purification. The hexabromo *meso*-anisyl dipyrromethane **7** was synthesized by treating **6** with 10 equiv of *N*-bromosuccinimide in THF overnight at room temperature. The progress of the reaction was monitored by TLC analysis, which clearly indicated the formation of **7** as a sole product. Without isolation, compound **7** was subjected to a two-step one-pot reaction by oxidizing it in the first step with DDQ and reacted in a second step with $BF_3 \cdot OEt_2$ at room temperature. The TLC and absorption spectral analysis of the crude reaction mixture indicated the formation of hexabromo derivative of BODIPY **5**. The crude product was subjected to silica gel column chromatographic purification and afforded pure **5** as nonfluorescent green powder in 24% yield. Compound **5** was confirmed by $(M - F)^+$ ion peak in both ES-MS and HR-MS mass spectra and by the absence of signals corresponding to pyrrole protons of the BODIPY core because of their substitution with bromo groups in the $^1H$ NMR spectrum. Furthermore, compound **5** showed a typical quartet in $^{19}F$ NMR at −145.7 ppm with no shift compared to unsubstituted *meso*-anisyl BODIPY[3] **8** (Table 1). However, in $^{11}B$ NMR, compound **5** showed a triplet at 0.12 ppm, which experienced a ∼0.2 ppm upfield shift compared to **8** (0.35 ppm), indicating the electron-deficient nature of compound **5**. The absorption spectrum of **5** showed one strong $S_0 \rightarrow S_1$ absorption band at ∼550 nm. Compound **5** showed one reversible reduction at −0.34 V ($\Delta E_p$ = 65 mv) and one irreversible reduction at −1.40 V, which appeared less negative by ∼450 mV (Table 1) compared to **8**. This supports the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electron-deficient nature of **5** due to the presence of six bromo groups. Compound **5** was also characterized by X-ray diffraction analysis. The single crystal of **5** was obtained on slow evaporation of compound **5** in a $CH_2Cl_2$/petroleum ether mixture over a period of 3 days. The structure of compound **5** (Figure 2) shows that the two pyrrole rings and the central six-membered ring containing the boron are in one plane like any other BODIPY[3] such as compound **8**. The interesting feature of compound **5** is the orientation of the *meso*-aryl group, which is nearly perpendicular with respect to the plane defining various dipyrrin atoms (88°) unlike *meso*-tolyl boron-dipyrromethene[3] in which the dihedral angle is 53°. This indicates that the bromine atoms provide steric hindrance resulting in perpendicular orientation of the *meso*-aryl group to the dipyrrin plane in compound **5** (CCDC No. 823749). The presence of six bromine atoms also causes slight variations in various bond lengths and bond angles in compound **5** compared to compound **8**.

The polyarylated BODIPYs **1**−**4** were synthesized by coupling of compound **5** with corresponding arylboronic acids such as phenylboronic acid, 4-fluorophenylboronic acid, 4-methylphenylboronic acid, and 4-methoxyphenylboronic acid in a THF/toluene/$H_2O$ (1:1:1) mixture in the presence of a catalytic amount of $Pd(PPh_3)_4/Na_2CO_3$ overnight at 80 °C. TLC analysis initially showed more numbers of spots corresponding to various arylated BODIPYs, but as the reaction progressed, the spots corresponding to the other arylated BODIPYs disappeared and one major highly fluorescent spot corresponding to the required polyarylated BODIPYs was observed. The progress of the reaction can also be judged from clear color change of the reaction mixture from pink to a brightly fluorescent red solution and also by following absorption spectroscopy. The crude compounds were purified by silica gel column chromatography and afforded pure fluorescent solids **1**−**4** in 50−55% yields. The longer reaction times are needed for maximum conversion of hexabromo derivatives to polyarylated BODIPYs. The polyarylated BODIPYs **1**−**4** are stable and freely soluble in common organic solvents. The compounds **1**−**4** were characterized by mass, NMR, absorption, electrochemical, and fluorescence techniques. The HR-MS mass spectra showed the corresponding expected molecular ion peak confirming the identity of compounds **1**−**4**. In $^1$H NMR, the signals corresponding to the expected aryl groups are present in the 6.00−8.00 ppm region. Compounds **1**−**4** showed a characteristic quartet at ∼−131.0 ppm in $^{19}$F NMR (Figure 1a) and triplet at ∼1.1 ppm in $^{11}$B NMR (Figure 1b), which are significantly downfield shifted compared to **5** and **8** (Table 1) due to the presence of aryl groups at the periphery of the BODIPY core.

**Table 1. Comparison of Important Spectral and Electrochemical Data of Compounds 1, 5, and 8**

| | 8 | 5 | 1 |
|---|---|---|---|
| $^{19}$F ($\delta$ in ppm) | −145.03 | −145.73 | −131.25 |
| $^{11}$B ($\delta$ in ppm) | 0.35 | 0.12 | 1.20 |
| $\lambda_{abs}$ (nm) | 500 | 552 | 574 |
| $\lambda_{emi}$ (nm) | 516 | 566 | 609 |
| Stokes shift ($cm^{-1}$) | 580 | 480 | 1020 |
| quantum yield ($\Phi$) | 0.03 | $<10^{-4}$ | 0.36 |
| reduction potential (V) | −0.80 | −0.34 | −0.86 |

We solved the X-ray crystal structure of polyarylated BODIPY **1** (CCDC No. 823750) to show the arrangement of the peripheral aryl groups on the central BODIPY core, and the structure is presented in Figure 2. The single crystal of compound **1** was obtained from $CHCl_3$ solution on slow evaporation at ambient temperature over a period of 1 week. The compound **1** crystallizes as triclinic with a $P\bar{1}$ space group. Unlike compounds **5** and **8**, which possess planar indacene planes, compound **1** displayed distorted, "propeller-like" conformation. In compound **1**, the indacene plane deviates from planarity with an average dihedral angle of 14.5° between the central six-membered ring and the two pyrrole rings of the dipyrrin unit. The torsion angle between the two pyrrole rings is 19.4°. The highly distorted structure of compound **1** can be ascribed to the steric hindrance caused by the six phenyl rings on the BODIPY core, leading to the propeller-like conformation. The dihedral angles between the aryl substituents and the plane defining various dipyrrin atoms in compound **1** are in the range of 50−61°, and the *meso*-aryl group is twisted at 57° relative to the BODIPY core.

The electron-rich behavior of compounds **1**−**4** is evident in their redox properties. The comparison of cyclic voltammograms of compound **1** with those of compounds **5** and **8** is presented in Figure 3b. Unlike compounds **5** and **8**, which do not show any oxidation, compounds **1**−**4** showed one reversible oxidation ($\Delta E_p$ = 60−70 mV) at 1.30 V. Interestingly, the first reversible reduction ($\Delta E_p$ = 60−70 mV) of compounds **1**−**4** falls in the

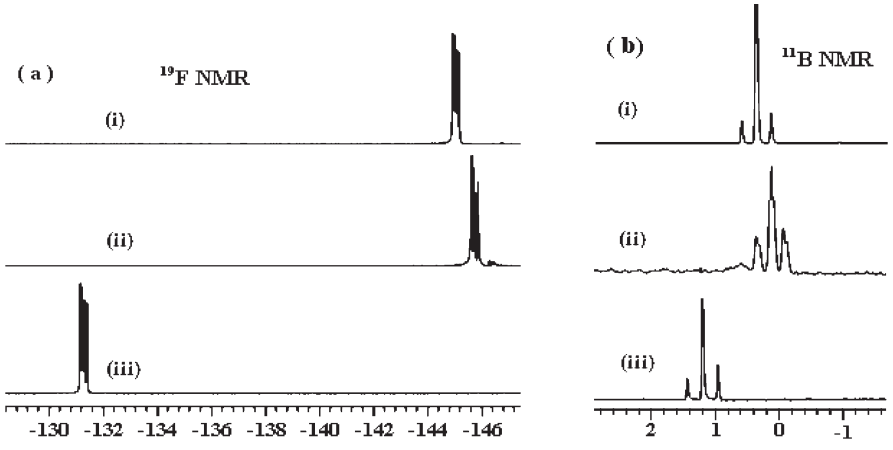


**Figure 1.** (a) Comparison of $^{19}$F NMR spectra of compounds (i) **8**, (ii) **5**, and (iii) **1**. (b) Comparison of $^{11}$B NMR spectra of compounds (i) **8**, (ii) **5**, and (iii) **1** recorded in $CDCl_3$ ($\delta$ in ppm).


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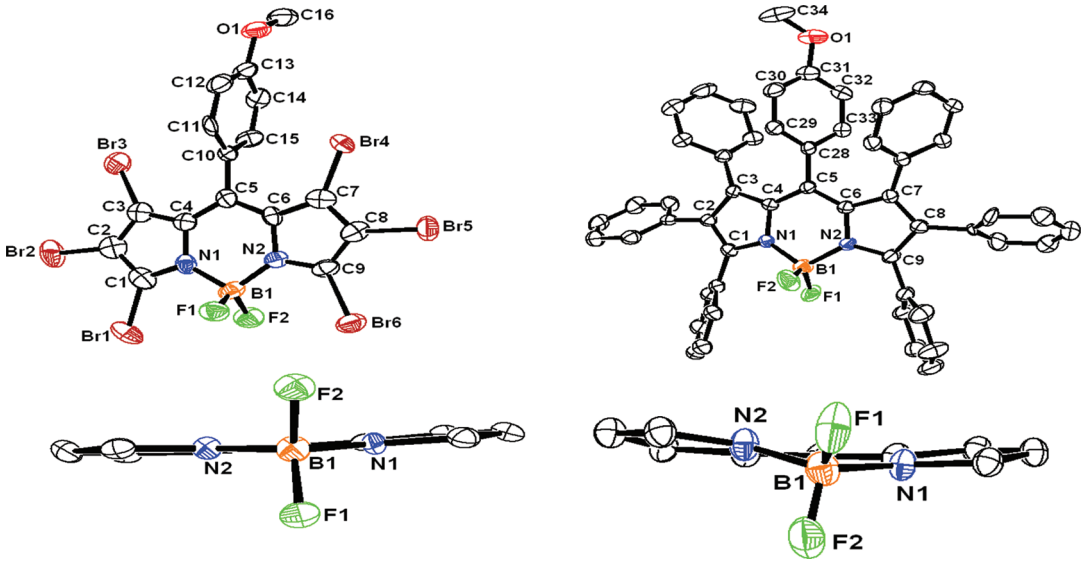


**Figure 2.** ORTEP diagrams of compounds **5** and **1**.

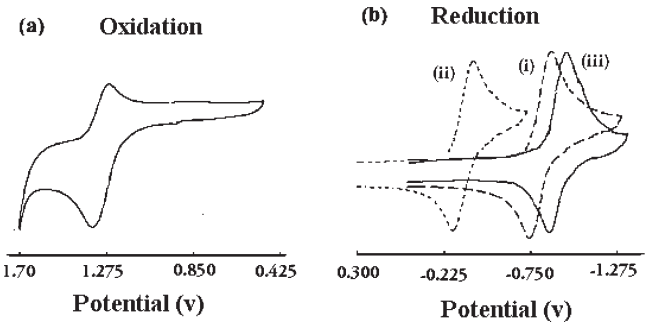


**Figure 3.** (a) Oxidation wave of compound **1** and (b) comparison of reduction waves of cyclic voltammograms of compounds (i) **8**, (ii) **5**, and (iii) **1** recorded in $CH_2Cl_2$ containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV $s^{-1}$ scan speed.

same range as that of compound **8** (Table 1), although we expected that these electron-rich compounds **1**−**4** are more difficult to reduce compared to **8**. We attribute this to the nonplanarity of the BODIPY core in compounds **1**−**4** induced by steric crowding of peripheral phenyl groups that reduce the effective electronic conjugation in compounds **1**−**4**. This is also reflected in their oxidation potential, which was observed at higher potential in spite of the presence of several electron-rich aryl groups at the periphery of the BODIPY core.

The absorption properties of compounds **1**−**4** along with those of compounds **5** and **8** were studied in five different solvents (Supporting Information). It is observed that introduction of six bromines at the pyrrole carbons of the BODIPY core in compound **5** results in ∼50 nm bathochromic shift of $S_0 \rightarrow S_1$ transition compared to that of unsubstituted BODIPY **8**. The polyarylated BODIPYs **1**−**4** showed broad $S_0 \rightarrow S_1$ transition which experienced a bathochromic shift of 70−100 nm (Table 1) compared to **8**. The fluorescence properties of compounds **1**−**4** are in line with the absorption properties (Supporting Information). Compound **5** is weakly fluorescent due to the presence of heavy bromine atoms, and the fluorescence band is red-shifted compared to **8**. The polyarylated BODIPYs **1**−**4** are strongly fluorescent and showed a relatively broad red-shifted fluorescence band with decent quantum yields of 0.2−0.5. Furthermore, compounds **1**−**4** exhibited relatively large Stoke's shift and showed similar photophysical behavior like any other BODIPY dye with a change of solvent polarity. The fluorescent decay profiles of compounds **1**−**4** in different solvents were collected and fitted to a single exponential. The fluorescence lifetime of compounds **1**−**4** in different solvents varies between 1.5 and 4 ns. These compounds also appear to be strongly fluorescent in the solid state, which will be investigated in due course of time.

In conclusion, we developed short and rapid route for the synthesis of polyarylated BODIPYs. This method avoids the use of aryl-substituted pyrroles whose synthesis is difficult. The hexabromo BODIPY which is the key synthon used in this method can be prepared in large quantities. Unlike the method in the literature which requires the synthesis of different aryl-substituted pyrroles, here we can use hexabromo BODIPY to prepare a set of aryl-substituted BODIPYs by coupling hexabromo BODIPY with appropriately substituted arylboronic acids under Pd(0) coupling conditions. The X-ray analysis showed that the structure is distorted, and electrochemical studies indicated that these compounds exhibit reversible oxidation and reduction waves. The photophysical studies revealed that both absorption and emission bands experienced large red shifts with decent quantum yields and an increase in lifetimes compared to unsubstituted BODIPYs; also these compounds are brightly fluorescent in the solid state (Supporting Information), which needs further investigation.

## EXPERIMENTAL SECTION

**General:** All NMR spectra ($\delta$ values, ppm) were recorded with 300 or 400 MHz spectrometers. Tetramethylsilane (TMS) was used as an external reference for recording $^1H$ (of residual proton; $\delta$ = 7.26 ppm) and $^{13}C$ ($\delta$ = 77.0 ppm) spectra in $CDCl_3$. 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


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(auxiliary) electrode, and a saturated calomel (reference) electrode. The experiments were performed in dry $CH_2Cl_2$ with 0.1 M TBAP as the supporting electrolyte. Half-wave potentials 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 $E_{1/2}$ ($F_c/F_c^+$) = 0.42 V vs SCE.[11] The quantum yields were calculated using Rhodamine 6G as reference ($\Phi$ = 0.88 in ethanol, $\lambda_{exc}$ = 488 nm).[8e] All $\Phi$ values are corrected for changes in refractive index.

**4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6,7-hexabromo-4-bora-3a,4a-diaza-*s*-indacene (5).** To a solution of 8-(4-methoxyphenyl)dipyrromethane **6** (0.5 g, 1.98 mmol) in dry THF was added an exccess of *N*-bromosuccinimide (3.53 g, 19.8 mmol) under $N_2$ atmosphere, and the reaction mixture was allowed to stir at room temperature overnight. TLC analysis indicated that the disappearance of spots corresponds to **6** and and appearance of a new spot corresponds to compound **7**. The solvent was removed on a rotary evaporator under vacuum, and the crude compound was passed through flash silica gel column chromatography using dichloromethane. The resultant compound was dissolved in freshly distilled dichloromethane and oxidized with DDQ (190 mg, 0.833 mmol) for 30 min at room temperature. The reaction mixture was then treated with a small amount of $Et_3N$ (3.9 mL, 27.9 mmol) followed by $BF_3 \cdot OEt_2$ (4.4 mL, 35.26 mmol), and the mixture was stirred for an additional 30 min at room temperature. The solvent was removed in a rotary evaporator, and the resultant crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (98:2) and afforded pure hexabromo BODIPY **5** as a green solid in 24% (0.35 g): $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.9 (s, 3H), 7.07 (d, 2H, $^3J$(H,H) = 9.0 Hz), 7.14 (d, 2H, $^3J$(H,H) = 8.7 Hz); $^{19}$F NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) −145.76 (q, $^3J$(B,F) = 57.8 Hz); $^{11}$B NMR (96.3 MHz, $CDCl_3$, $\delta$ in ppm) 0.88 (t, $^3J$(B,F) = 28.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ in ppm) 55.59, 115.26, 117.66, 121.56, 124.05, 130.27, 131.91, 135.00, 143.38, 161.79; HRMS calcd for $C_{16}H_7BBr_6F_2N_2O$ 746.5764 $(M - F)^+$, found 746.5736 $(M - F)^+$.

**General Method for the Synthesis of 4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6,7-hexaaryl-4-bora-3a,4a-diaza-*s*-indacenes (1−4).** Samples of **5** (100 mg, 0.13 mmol), appropriate arylboronic acid (387 mg, ∼2.6 mmol), and $Na_2CO_3$ (256 mg, 2.44 mmol) were taken in a 1:1:1 mixture of water/THF/toluene (15 mL) in a 100 mL round-bottomed flask fitted with a reflux condenser and 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 °C for 6−10 h. 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 and 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 polyarylated BODIPYs **1**−**4** in 50−55% yield.

**4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6,7-hexaphenyl-4-bora-3a,4a-diaza-*s*-indacene (1).** Compound **1** was obtained as a red solid in 51% yield (53 mg): $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.51 (s, 3H), 5.89 (d, 2H, $^3J$(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, $^3J$(H,H) = 5 Hz); $^{19}$F NMR (376.49 MHz, $CDCl_3$, $\delta$ in ppm) −131.30 (q, $^3J$(B,F) = 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.20 (t, $^3J$(B,F)= 30.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ 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 $(M - F)^+$.

**4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6,7-hexa(4-fluorophenyl)-4-bora-3a,4a-diaza-*s*-indacene (2).** Compound **2** was obtained as a red fluorescent solid in 53% yield (61 mg): $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.58 (s, 3 H), 6.02 (d, 2H, $^3J$(H,H) = 8.64 Hz), 6.47−6.50 (m, 8H), 6.55−6.58 (m, 4 H), 6.65−6.67 (m, 6H), 6.94 (t, 4H, $^3J$(H,H) = 8.76 Hz), 7.34−7.37 (m, 4H); $^{19}$F NMR (376.49 MHz, $CDCl_3$, $\delta$ in ppm) −131.30 (q, $^3J$(B,F) = 64.0 Hz), 111.33 (s), 114.98 (s), 115.74 (s); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.05 (t, $^3J$(B,F) = 30.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ in ppm) 55.40, 112.54, 114.4, 114.6, 114.9, 115.0, 115.1, 115.2, 123.4, 127.4, 128.7, 130.4, 131.8, 131.9, 132.3, 132.4, 132.8, 132.9, 133.4, 133.9, 143.2, 155.1, 159.8, 160.4, 160.65, 161.9, 162.9, 170.6; HRMS calcd for $(C_{52}H_{31}BF_8N_2O)$ 843.2418 $(M - F)^+$, found 843.2396 $(M - F)^+$.

**4,4-Difluoro-8-(4-methoxyphenyl)-1,2,3,5,6,7-hexa(4-methylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (3).** Compound **3** was obtained as a red solid in 51% yield (51 mg): $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 2.11 (s, 6H), 2.19 (s, 6H), 2.34 (s, 6H), 3.56 (s, 3H), 5.92 (d, 2H, $^3J$(H,H) = 8.4 Hz), 6.44 (d, 2H, $^3J$(H,H) = 8.4 Hz), 6.54 (d, 8H, $^3J$(H,H) = 8.54 Hz), 6.68 (d, 2H, $^3J$(H,H) = 8.76 Hz), 6.78 (d, 6H, $^3J$(H,H) = 8.9 Hz), 7.06 (d, 4H, $^3J$(H,H) = 8.2 Hz), 7.33 (d, 4H, $^3J$(H,H) = 8.9 Hz); $^{19}$F NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) −131.21 (q, $^3J$(B,F)= 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.18 (t, $^3J$(B,F) = 32.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ in ppm) 21.12, 21.30, 21.67, 55.15, 112.07, 124.17, 127.82, 128.27, 128.38, 129.24, 130.02, 130.56, 130.72, 130.81, 132.07, 132.54, 133.44, 134.26, 134.89, 135.58, 138.45, 144.02, 155.97, 160.00; HRMS calcd for $C_{58}H_{49}BF_2N_2O$ 819.3922 $(M - F)^+$, found 819.3945 $(M - F)^+$.

**4,4-Difluoro-8-(4-methoxyphenyl)1,2,3,5,6,7-hexa(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (4).** Compound **4** was obtained as a red solid in 49% yield (60 mg): $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.53 (s, 3H), 3.61 (s, 6H), 3.66 (s, 6H), 3.77 (s, 6H), 5.94 (d, 2H, $^3J$(H,H) = 8.6 Hz), 6.26 (d, 4H, $^3J$(H,H) = 8.7 Hz), 6.44 (d, 4H, $^3J$(H,H) = 8.9 Hz), 6.49 (d, 6H, $^3J$(H,H) = 8.76 Hz), 6.54 (d, 2H, $^3J$(H,H) = 8.92 Hz), 6.66 (d, 2H, $^3J$(H,H) = 8.7 Hz), 6.72 (d, 4H, $^3J$(H,H) = 8.9 Hz), 7.35 (d, 4H, $^3J$(H,H) = 8.9 Hz); $^{19}$F NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) −131.25 (q, $^3J$(B,F) = 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.20 (t, $^3J$(B,F) = 32.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ in ppm) 55.12, 55.22, 112.27, 112.94, 113.14, 113.20, 124.54, 125.99, 127.58, 131.56, 132.05, 132.51, 133.61, 155.56, 157.46, 157.87, 159.89; HRMS calcd for $C_{58}H_{49}BF_2N_2O_7$ 915.3617 $(M - F)^+$, found 915.3607 $(M - F)^+$.

**Characterization Data for Compounds 9, 10, and 11.** **9**: $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.63 (s, 3H), 6.15−6.17 (m, 4H), 6.45−6.47 (m, 2H), 6.55−6.56 (m, 2H), 6.79−6.81 (m, 2H), 6.90−6.94 (m, 4H), 7.04−7.07 (m, 2H), 7.16−7.17 (m, 2H), 7.43−7.44 (m, 2H), 7.63 (d, 2H, $^3J$(H,H) = 2.84 Hz); $^{19}$F NMR (376.49 MHz, $CDCl_3$, $\delta$ in ppm) −133.17 (q, $^3J$(B,F) = 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.14 (t, $^3J$(B,F) = 30.8 Hz); ES-MS calcd for $C_{40}H_{25}BF_2N_2OS_6$ $m/z$ 790.0352, observed 771.0901 $(M - F)^+$.

**10**: $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.18 (s, 3H), 5.89 (d, 2H, $^3J$(H,H) = 6.9 Hz), 6.59 (d, 2H, $^3J$(H,H) = 8.4 Hz), 6.66−6.70 (m, 4H), 6.83 (d, 2H, $^3J$(H,H) = 8.3 Hz), 6.91 (d, 2H, $^3J$(H,H) = 8.5 Hz), 7.07−7.12 (m, 8H), 7.14−7.20 (m, 8H), 7.24−7.30 (m, 8H), 7.32−7.39 (m, 8H), 7.44−7.53 (m, 8H), 7.57−7.63 (m, 4H), 7.75 (d, 2H, $^3J$(H,H) = 8.4 Hz); $^{19}$F NMR (376.49 MHz, $CDCl_3$, $\delta$ in ppm) −131.07 (q, $^3J$(B,F) = 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.19 (t, $^3J$(B,F) = 30.8 Hz); ES-MS calcd for $C_{88}H_{61}BF_2N_2O$ $m/z$ 1210.4, observed 1211.5 $(M + 1)^+$.

**11**: $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 2.98 (s, 3H), 6.72 (m, 4H), 6.79−6.83 (m, 2H), 7.13−7.19 (m, 12H), 7.24−7.29 (m, 10H), 7.32−7.40 (m, 6H), 7.46−7.54 (m, 6H), 7.59 (d, 2H, $^3J$(H,H) = 8.6 Hz), 7.66−7.69 (m, 4H); $^{19}$F NMR (376.49 MHz, $CDCl_3$, $\delta$ in ppm) −130.52 (q, $^3J$(B,F) = 64.0 Hz); $^{11}$B NMR (128.38 MHz, $CDCl_3$, $\delta$ in ppm) 1.43 (t, $^3J$(B,F) = 30.8 Hz); ES-MS calcd for $C_{76}H_{49}BF_2N_2O$ $m/z$ 1054.3, observed 1035.9 $(M - F)^+$.


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## ■ ASSOCIATED CONTENT

**Supporting Information.** Characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: ravikanth@chem.iitb.ac.in.

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