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PAPER

# Brominated boron dipyrrins: synthesis, structure, spectral and electrochemical properties†

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*meso*-Anisyl boron dipyrrins (BODIPYs) **1–6** containing one to six bromines at the pyrrole carbons have been synthesized by treating *meso*-anisyl dipyrromethane with '*n*' equivalents of *N*-bromosuccinimide in THF at room temperature followed by oxidation with DDQ, neutralization with triethylamine and further complexation with $BF_3{\cdot}OEt_2$. The brominated compounds were characterized by HR-MS mass, detailed $^1H$, $^{19}F$ and $^{11}B$ NMR and X-ray diffraction studies. The crystal structures solved for compounds **2–6** indicate that the boron dipyrrinato framework comprised two pyrrole rings and one six membered boron containing ring in one plane like other reported BODIPYs. However, the dihedral angle between the BODIPY core and the *meso*-anisyl group varied from 48° to 88° and the *meso*-anisyl ring has an almost perpendicular orientation in penta **5** and hexabrominated **6** BODIPYs. The absorption and emission studies showed a bathochromic shift and reached a maximum for tetrabrominated derivative **4**, after which there was no change in the peak maxima for penta **5** and hexabrominated **6** derivatives. However, the quantum yields were reduced with the increasing number of bromines. The electrochemical studies revealed that brominated BODIPY compounds **1–6** are easier to reduce compared to unsubstituted *meso*-anisyl BODIPY **8** and the reduction potential is linearly related to the number of Br groups.

## Introduction

Among the fluorophores available, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives have become preferred fluorophores which have applications in many different areas because of their excellent properties.[1] The valuable qualities of BODIPY fluorophores are their high absorption coefficients, high fluorescence quantum yields, narrow emission bandwidths with high peak intensities, elevated photostability and chemical stability, excitation/emission wavelengths above 500 nm. From the synthetic viewpoint, it is relatively straightforward to synthesize many different BODIPY analogues with their emission maxima ranging from 500 to over 700 nm.[2] Specifically, the pyrrole substituted and pyrrole fused BODIPY systems possess excellent photophysical properties and most of these systems were prepared using the substituted pyrroles as key synthons.[3] However, the synthesis of substituted pyrrole precursors is not straightforward and has limited synthetic accessibility. Alternately, the functionalized BODIPY dyes such as halogenated BODIPYs can be used to synthesize substituted BODIPYs. Recently Dehaen, Boens and co-workers used 3,5-dihalo BODIPYs[4,5a] to carry out nucleophilic substitution with O-, N-, S- and C-nucleophiles to synthesize a variety of 3,5-disubstituted BODIPYs.[5] We recently reported the synthesis of sterically crowded highly fluorescent polyarylated BODIPYs using 1,2,3,5,6,7-hexabromo *meso*-anisyl BODIPY as a key synthon.[6] Thus, the halogenated BODIPYs are important precursors to synthesize a variety of substituted BODIPYs. However, the effect of halogen substitution at the pyrrole carbons of boron dipyrrin core on spectral, structure, photophysical and electrochemical properties remained largely unexplored. It has been shown with other chromophoric systems such as porphyrins, how the systematic alteration of the electronic properties of the porphyrins can be achieved as a function of the number of halogens at the β-pyrrole carbons.[7] Incidentally, while we were preparing this manuscript, Jiao *et al.*[8] reported regioselective stepwise bromination of BODIPY by treating BODIPY with "*n*" equivalents of $Br_2$ in $CHCl_3$. In this paper, we report the synthesis, structure, spectral and electrochemical properties of pyrrole brominated BODIPYs where the number of Br groups on the BODIPY core has been varied from 0 to 6. However, our approach for the synthesis of pyrrole brominated BODIPYs is completely different from Jiao *et al.* We used *meso*-anisyl dipyrromethane **7**[9] as key precursor and brominated it by treating with "*n*" equivalents of *N*-bromosuccinimide in THF at room temperature followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and complexation with $BF_3{\cdot}OEt_2$. The monobromo and dibrominated BODIPYs prepared by this approach are different from Jiao *et al.* method.[8] Furthermore, Jiao *et al.*[8] failed to isolate the tribromo BODIPY which we were successfully isolated and characterized. We also carried out

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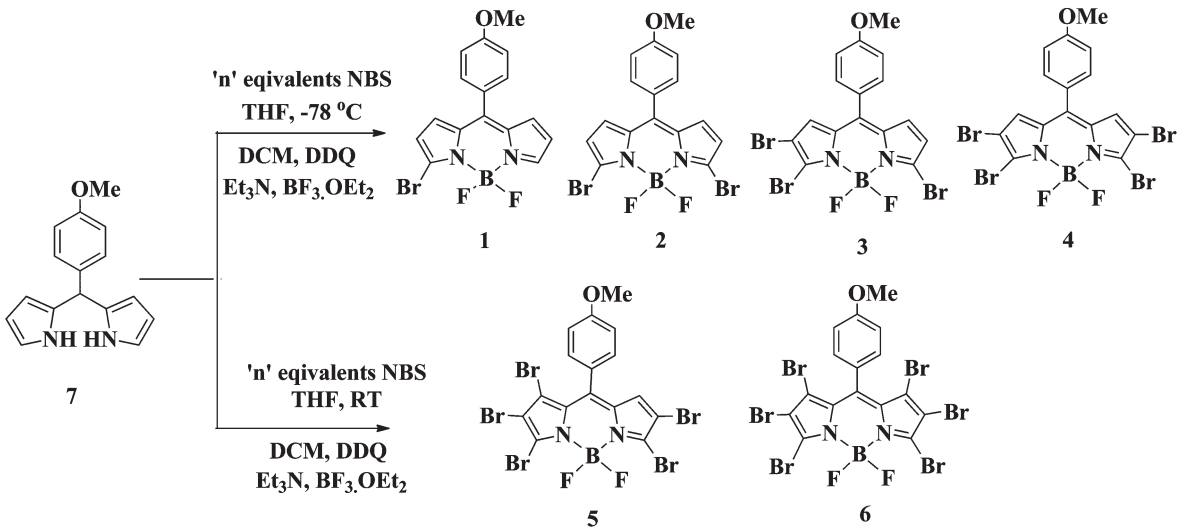
† Electronic supplementary information (ESI) available: Characterization data for all new compounds. CCDC **2** (849331), **3** (849334), **4** (849332), **5** (849333) and **6** (823749). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt00019a




**Scheme 1** Synthesis of brominated compounds **1–6**.



systematic studies to increase the number of bromines at the pyrrole carbons of BODIPY on the spectral as well as electrochemical properties. Thus, both these approaches are very useful in synthesis of pyrrole brominated BODIPYs which can be used as precursors for the synthesis of various new substituted BODIPY derivatives.

## Results and discussion

### Synthesis and characterization

The mono and dibromination at the 3-, 3,5-, 2- and 2,6-positions of BODIPY has been reported previously by adopting different synthetic routes. The bromination at 2- and 2,6-positions were carried out by treating the corresponding *meso*-substituted BODIPY with one and two equivalents of NBS respectively in DMF at room temperature[10] whereas the 3-bromo BODIPY **1** and 3,5-dibromo BODIPY **2** were prepared by treating the corresponding *meso*-substituted dipyrromethane with one and two equivalents of NBS in THF at −78 °C followed by oxidation with DDQ and complexation with $BF_3{\cdot}OEt_2$.[4] Recently, the 1,7-dibrominated BODIPY was prepared by treating the substituted BODIPY with vacant 1,7-positions with two equivalents of $Br_2$ in $CH_2Cl_2$ at 0 °C.[11] We synthesized brominated BODIPYs **1–6** where the number of Br groups on the BODIPY core increased from 0 to 6 using *meso*-anisyl dipyrromethane **7**[9] as the key precursor (Scheme 1). The 3-bromo *meso*-anisyl BODIPY **1** and 3,5-dibromo *meso*-anisyl BODIPY **2** were synthesized by adopting the literature procedures.[12] The other brominated BODIPYs such as 2,3,5-tribromo BODIPY **3**, 2,3,5,6-tetrabromo *meso*-anisyl BODIPY **4**, 1,2,3,5,6-pentabromo *meso*-anisyl BODIPY **5** and 1,2,3,5,6,7-hexabromo *meso*-anisyl BODIPY[6] **6** were prepared by slightly modifying the reaction conditions. The tribromo **3** and tetrabromo **4** BODIPYs were synthesized in two steps. In the first step, the dipyrromethane **7** was treated with three and four equivalents of NBS in THF at −78 °C for 30 min. In the second step, the resulted brominated dipyrromethanes without characterization were oxidized with DDQ for 1 h followed by complexation with $BF_3{\cdot}OEt_2$ at room temperature for an additional 1 h. The progress of the reaction was followed by TLC analysis and absorption spectroscopy. TLC analysis of crude reaction mixture showed the major spot corresponding to the desired brominated BODIPY along with two minor spots corresponding to the unsubstituted BODIPY **8** and one higher analogue of brominated BODIPY. The crude compounds were subjected to silica gel column chromatographic purification using petroleum ether–$CH_2Cl_2$ and isolated pure compounds **3** and **4** in ~20% yield.

The compounds **5** and **6** were prepared by treating **7** with five and ten equivalents respectively with NBS in THF at room temperature for 5–6 h. The resulting crude brominated dipyrromethanes were flash chromatographed on silica and then subjected to oxidation with DDQ for 1 h followed by complexation with $BF_3{\cdot}OEt_2$ for an additional 1 h at room temperature. The crude reaction mixtures were subjected to silica gel column chromatographic purification and afforded pure compounds **5** and **6** in ~25% yield. All bromination reactions worked smoothly and the $R_f$ values of brominated BODIPYs are sufficiently distinct from each other to isolate the pure compounds by column chromatography. The compounds **1–6** are freely soluble in common organic solvents and characterized by mass, NMR, absorption, electrochemistry and fluorescence techniques.

The compounds **1–6** showed characteristic $M^+$ and $(M - F)^+$ ions in ES-MS mass spectra confirming the identity of the compounds. The compounds **1–6** were characterized by $^1H$, $^{19}F$ and $^{11}B$ NMR studies. The comparison of $^1H$, $^{19}F$ and $^{11}B$ NMR spectra of compounds **1–6** along with **8** is shown in Fig. 1 and the relevant NMR data are presented in Table 1. As is clear from Fig. 1 on introduction of bromines at the pyrrole carbons, the corresponding pyrrole proton signals disappear and in the case of compound **6**, the pyrrole signals are completely absent confirming the substitution of bromines at the pyrrole carbons of the BODIPY core. In general, the pyrrole signals did not show significant changes in their chemical shifts on increasing the number of bromine groups from 0 to 4 but on introduction of the 5th bromine group, the type 'c' proton adjacent to the

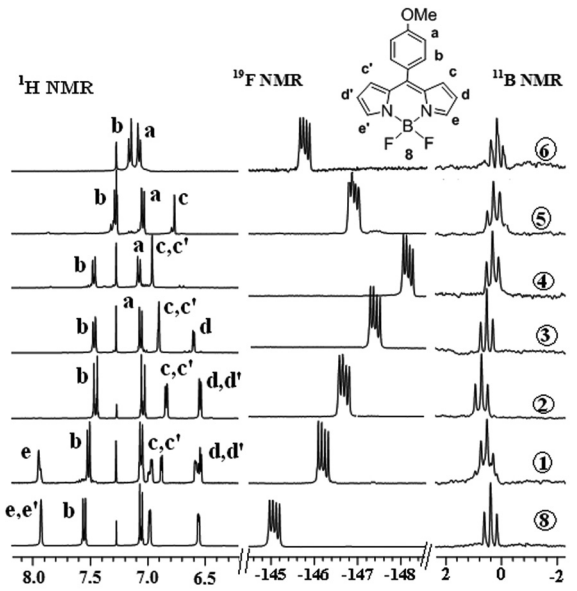



**Fig. 1** Comparison of $^{1}$H, $^{19}$F and $^{11}$B NMR spectra ($\delta$ in ppm) of compounds **1–6** in a selected region.

*meso*-anisyl group experienced an ~0.2 ppm upfield shift in compound **5** compared to **8** (Fig. 1). This is attributed to the near orthogonal orientation of the *meso*-anisyl group in compound **5** because of steric hindrance between the bulky bromine atom at the 7-position and the *meso*-anisyl ring which reduces the π-conjugation in the BODIPY core. This is also clearly evident in the chemical shift of *meso*-anisyl protons of type 'a' which experienced an upfield shift in compounds **5** and **6** compared to other brominated BODIPYs. The compounds **1–6** showed a typical triplet in $^{11}$B and quartet in $^{19}$F NMR due to B–F coupling. The $^{11}$B and $^{19}$F NMR also showed slight changes in chemical shifts as the number of bromine groups increased. For example, in $^{19}$F NMR, the signal shifts towards upfield upto compounds **1–4** and then shifts towards downfield in compounds **5** and **6** indicating that the π-delocalization is altered in the boron-dipyrrin core upon introducing bromines at the pyrrole carbons of BODIPY.

## Crystallographic studies

The brominated BODIPYs **2–6** were characterized by X-ray diffraction analysis. The single crystals of compounds **2–6** were obtained on slow evaporation of $CH_2Cl_2$–hexane mixture over a period of one week. The compounds **2**, **3** and **4** were crystallized in triclinic with a $P\bar{1}$ space group whereas compounds **5** and **6** were crystallized in monoclinic with a $P2_1/n$ space group. We recently reported[6] the crystal structure of compound **6** but it is included here for comparison purposes. The crystal structures for compounds **2–6** are shown in Fig. 2 and the selected bond lengths, bond angles and dihedral angle are summarized in Table 2. The crystallographic data for compounds **2–6** are listed in Table 3. The common feature of all these structures is that the two pyrrole rings and the central six-membered ring containing boron atom are in one plane like any other reported BODIPY

**Table 1** $^{1}$H, $^{19}$F and $^{11}$B NMR data ($\delta$ in ppm) of compounds **1–6**

| Compound | $^{1}$H NMR ($\delta$ in ppm) | | | $^{19}$F NMR ($\delta$ in ppm) | $^{11}$B NMR ($\delta$ in ppm) |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | | |
| **8** | 7.05 | 7.47 | 6.95 | −145.03 | 0.35 |
| **1** | 7.05 | 7.50 | 6.84 | −146.35 | 0.48 |
| **2** | 7.01 | 7.42 | 6.84 | −146.64 | 0.68 |
| **3** | 7.05 | 7.46 | 6.90 | −147.35 | 0.49 |
| **4** | 7.07 | 7.46 | 6.95 | −148.11 | 0.28 |
| **5** | 7.03 | **7.25** | 6.76 | −146.86 | 0.25 |
| **6** | 7.07 | **7.14** | — | −145.73 | 0.12 |

dyes.[13c] The two fluoride atoms from boron are equidistant and present above and below the plane of the pyrrole moieties. The various bond lengths and bond angles observed in these compounds are similar with the reported BODIPYs.[13c] The most interesting feature of these structures is the variation of dihedral angle between the *meso*-anisyl group and boron dipyrrin ring (C4C5C10C15). This angle is in the range of 50°–60° in compounds **2–4** which is commonly noted for other BODIPYs. However, the dihedral angle increases to 83° in compound **5** and to 88° in compound **6**. This is due to steric hindrance caused by bromines present at 1 and 7-positions of BODIPY core which restricts the rotation of *meso*-anisyl group resulting in a nearly perpendicular orientation of the *meso*-anisyl group with the BODIPY core. This kind of nearly perpendicular orientation of the *meso*-aryl group was observed previously in other sterically restricted BODIPY dyes such as *meso*-(*o*-tolyl) boron dipyrrin in which the dihedral angle is 85°.[13c] Thus, X-ray studies of compounds **2–6** indicate that only the bromine group(s) present at the 1 and 7-positions causes steric strain and restricts the rotation of the *meso*-aryl group.

## Photooptical and electrochemical studies

The absorption spectra of brominated BODIPYs **1–6** were recorded in five different solvents of varying polarizability and the data are presented in Table 4. The comparison of absorption spectra of brominated BODIPYs **1–6** along with **8** recorded in toluene using the same concentration is shown in Fig. 3. For all brominated BODIPYs **1–6**, the absorption spectra showed typical BODIPY absorption features with a strong band in 500–550 nm region corresponding to the $S_0 \rightarrow S_1$ transition with a vibronic transition on the higher energy side as a shoulder and an ill-defined, weak band corresponding to the $S_0 \rightarrow S_2$ transition at ~420 nm. However, each stepwise increase in the number of bromine groups at the pyrrole carbons of BODIPY core resulted in a bathochromic shift compared to **8** and the magnitude of the red shift of the absorption band depends on the number of bromines substituted at the BODIPY core.[7,14] It is noted that each bromine substitution at the pyrrole carbon contributes an additional 10 nm red shift with respect to the absorption band observed for **8**. However, this systematic red shift was observed only up to the introduction of four bromines and compounds **5** and **6** did not show any further red shift. This is also evident in the non-linear nature of the plot of magnitude of red shift *versus* the number of bromines substituted which indicates

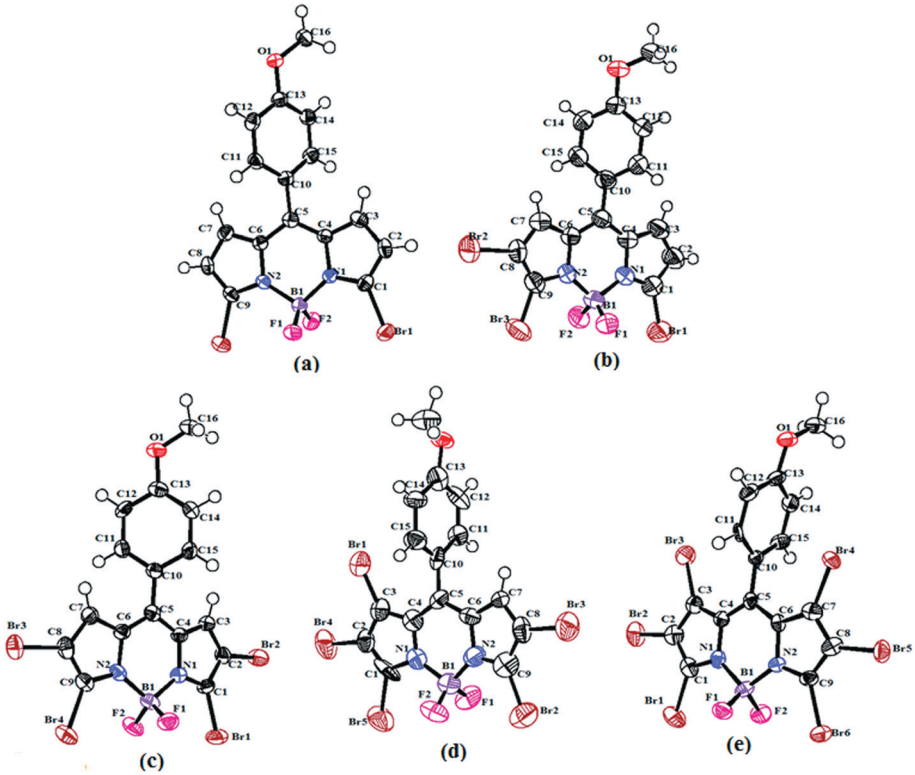



**Fig. 2** The X-ray crystal structures of compounds **2–6**: (a) **2**, (b) **3**, (c) **4**, (d) **5** and (e) **6**.

**Table 2** Comparison of some selected bond lengths [Å], bond angles [°] and dihedral angles [°] obtained from X-ray crystal structure

| | BODIPY | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| C4C5C10C15 | 60(1) | 53(3) | 48(5) | 52(5) | 83(1) | 88(1) |
| C5C6C7 | 130.4(1) | 130.1(2) | 130.0(3) | 130.1(3) | 130.1(7) | 132.3(5) |
| C2C3C4 | 107.3(1) | 108.3(2) | 108.0(3) | 107.0(3) | 106.7(7) | 107.9(5) |
| C6C5C10 | 120.2(1) | 119.8(2) | 119.8(3) | 120.4(3) | 115.1(7) | 116.1(5) |
| F1BF2 | 110.3(1) | 110.9(2) | 110.8(3) | 111.4(3) | 113.7(8) | 110.8(5) |
| B–N1 | 1.547(2) | 1.569(4) | 1.559(6) | 1.559(4) | 1.58(1) | 1.572(8) |
| B–N2 | 1.547(2) | 1.557(3) | 1.545(6) | 1.568(6) | 1.58(1) | 1.538(9) |
| C5–C10 | 1.481(1) | 1.479(4) | 1.477(4) | 1.470(4) | 1.47(1) | 1.491(8) |
| C5–C6 | 1.396(2) | 1.405(4) | 1.412(5) | 1.401(5) | 1.39(1) | 1.416(8) |
| B–F1 | 1.381(1) | 1.370(4) | 1.383(5) | 1.364(3) | 1.36(1) | 1.377(7) |
| B–F2 | 1.381(1) | 1.389(4) | 1.376(4) | 1.377(4) | 1.37(1) | 1.383(7) |

BODIPY = 4,4-difluoro-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene.[13c]

that the magnitude of red shift with each bromine substitution is non-additive (inset in Fig. 3). The bathochromic shift of absorption band and non-linear nature of plot of absorption band shift *versus* the number of bromines in brominated BODIPYs has been ascribed to an antagonistic inductive effect by bromines present at the pyrrole carbons of the BODIPY core. The electronic absorption spectra of brominated BODIPYs **1–6** in different solvents show a blue shift of the $S_0 \rightarrow S_1$ absorption band with increasing solvent polarizability as was observed for apolar BODIPY derivatives without an amine donor.[13] Furthermore, the absorption bandwidths and the full-width at half maximum (FWHM) is independent of solvent polarizability for compounds **1–6**.

The fluorescence properties of compounds **1–6** were studied in five different solvents by steady state and time-resolved fluorescence techniques and the data are tabulated in Table 4. A comparison of steady state fluorescence spectra of compounds **1–6** along with **8** recorded using the same concentration is shown in Fig. 4. The steady state fluorescence studies on compounds **1–6** reveal the following: (1) The compounds **1–6** showed one single broad emission band which shifts gradually to higher wavelength with the increase of number of bromine groups (Fig. 4). (2) The maximum red shifts were observed for compounds **5** and **6**. (3) The quantum yields were decent for compounds **1–4** but significantly low for compounds **5** and **6**. The presence of bromines on fluorophores generally decreases the quantum yield due to the heavy halogen effect. However, it is pronounced only in compounds **5** and **6**. (4) The emission maxima are slightly blue shifted and the fluorescence quantum yield decreases significantly with increasing solvent

**Table 3** Crystal data and structure refinement parameters for compounds **2**, **3**, **4**, **5** and **6**

| Parameters | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|
| Mol. formula | $C_{16}H_{11}BBr_2F_2N_2O$ | $C_{16}H_{10}BBr_3F_2N_2O$ | $C_{16}H_9BBr_4F_2N_2O$ | $C_{16}H_8BBr_5F_2N_2O$ | $C_{16}H_7BBr_6F_2N_2O$ |
| For. weight | 455.90 | 534.80 | 613.70 | 692.60 | 771.51 |
| Temp/K | 150(2) | 293(2) | 150(2) | 150(2) K | 150(2) K |
| Cryst sym | Triclinic | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ |
| $\lambda$/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $a$/Å | 8.0532(4) | 8.2231(10) | 7.8922(4) | 8.9535(17) | 11.7228(3) |
| $b$/Å | 9.4760(4) | 10.6391(10) | 11.1893(6) | 19.7020(4) | 8.8692(2) |
| $c$/Å | 11.2338(5) | 10.7273(6) | 11.3508(5) | 11.1720(3) | 19.6265(5) |
| $\alpha$ (°) | 78.222(4) | 105.580(7) | 73.442(4) | 90 | 90 |
| $\beta$ (°) | 83.573(4) | 92.262(7) | 74.044(4) | 90.84(2) | 92.39(2) |
| $\gamma$ (°) | 67.746(4) | 106.758(9) | 84.062(4) | 90 | 90 |
| Volume/Å$^3$ | 776.15(6) | 858.63(14) | 923.44(8) | 1970.60(7) | 2038.83(9) |
| $Z$ | 2 | 2 | 2 | 4 | 4 |
| $\mu$/mm$^{-1}$ | 5.250 | 7.074 | 8.744 | 10.224 | 11.844 |
| $D_{calcd}$/Mg m$^{-3}$ | 1.951 | 2.069 | 2.207 | 2.335 | 2.513 |
| $F$(000) | 444 | 512 | 580 | 1296 | 1432 |
| $\theta$ range (°) | 3.14–25.00 | 3.47–25.00 | 3.69–32.80 | 3.56–30.51 | 3.48–25.00 |
| $e$ data/unique | 5582/2727 | 6019/3015 | 10 011/6014 | 21 069/5993 | 13 921/3595 |
| $R_{int}$ | 0.0154 | 0.0279 | 0.0255 | 0.1355 | 0.0509 |
| Data/restraints/parameters | 2727/0/218 | 3015/0/227 | 6014/0/236 | 5993/0/245 | 3595/0/254 |
| GOF on $F^2$ | 1.075 | 0.953 | 1.058 | 0.863 | 1.082 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0216, 0.0584 | 0.0298, 0.0751 | 0.0391, 0.0795 | 0.0686, 0.1528 | 0.0379, 0.0954 |
| $R_1$, w$R_2$ (all data) | 0.0269, 0.0593 | 0.0436, 0.0777 | 0.0593, 0.0893 | 0.1842, 0.1679 | 0.0483, 0.0968 |
| Largest diff. peak/hole, e Å$^{-3}$ | 0.593/−0.334 | 0.844/−0.631 | 1.497/−1.225 | 2.201/−1.301 | 1.430/−1.105 |

**Table 4** Photophysical data of BODIPYs **1–6** in different solvents

| Compd | Solvent | $\lambda_{abs}$ [nm] | $\lambda_{emi}$ [nm] | FWHM (abs.) [cm$^{-1}$] | $\Delta\nu_{st}$ [cm$^{-1}$] | log $\varepsilon_{max}$ | $\Phi_f$ | $\tau$ [ns] | $k_f$ ($10^9$ s$^{-1}$) | $k_{nr}$ ($10^9$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **8** | Toluene | 501 | 517 | 1079 | 617 | 4.76 | 0.11 | 0.72 | 0.16 | 1.23 |
| | $CHCl_3$ | 499 | 515 | 1173 | 620 | 4.76 | 0.097 | 0.72 | 0.14 | 1.25 |
| | THF | 497 | 515 | 1180 | 701 | 4.74 | 0.052 | 0.41 | 0.13 | 2.3 |
| | EtOAc | 495 | 511 | 1184 | 632 | 4.75 | 0.035 | 0.32 | 0.18 | 1.93 |
| | MeCN | 494 | 511 | 1317 | 673 | 4.71 | 0.0013 | 0.24 | 0.13 | 4.04 |
| **1** | Toluene | 510 | 526 | 1145 | 597 | 4.77 | 0.255 | 1.58 | 0.16 | 0.47 |
| | $CHCl_3$ | 509 | 523 | 1100 | 526 | 4.75 | 0.194 | 1.21 | 0.16 | 0.66 |
| | THF | 506 | 521 | 1199 | 573 | 4.74 | 0.120 | 0.69 | 0.165 | 1.28 |
| | EtOAc | 504 | 519 | 1390 | 571 | 4.76 | 0.064 | 0.64 | 0.17 | 1.38 |
| | MeCN | 502 | 518 | 1209 | 610 | 4.70 | 0.043 | 0.36 | 0.17 | 2.6 |
| **2** | Toluene | 522 | 535 | 975 | 467 | 4.86 | 0.29 | 2.23 | 0.20 | 0.25 |
| | $CHCl_3$ | 521 | 532 | 1070 | 394 | 4.91 | 0.25 | 1.30 | 0.23 | 0.54 |
| | THF | 517 | 530 | 881 | 472 | 4.81 | 0.11 | 0.74 | 0.21 | 1.14 |
| | EtOAc | 515 | 528 | 982 | 477 | 4.87 | 0.14 | 0.73 | 0.24 | 1.12 |
| | MeCN | 514 | 526 | 982 | 444 | 4.83 | 0.048 | 0.30 | 0.23 | 3.1 |
| **3** | Toluene | 537 | 551 | 960 | 472 | 4.76 | 0.26 | 2.51 | 0.11 | 0.28 |
| | $CHCl_3$ | 536 | 550 | 968 | 477 | 4.81 | 0.33 | 1.83 | 0.19 | 0.35 |
| | THF | 530 | 545 | 1117 | 518 | 4.53 | 0.12 | 1.03 | 0.12 | 0.84 |
| | EtOAc | 529 | 544 | 959 | 524 | 4.82 | 0.14 | 1.02 | 0.17 | 0.81 |
| | MeCN | 526 | 544 | 955 | 631 | 4.70 | 0.08 | 0.43 | 0.21 | 2.12 |
| **4** | Toluene | 554 | 569 | 1043 | 481 | 4.77 | 0.30 | 2.38 | 0.13 | 0.37 |
| | $CHCl_3$ | 553 | 568 | 953 | 457 | 4.88 | 0.22 | 2.14 | 0.15 | 0.54 |
| | THF | 546 | 563 | 1283 | 555 | 4.67 | 0.097 | 1.24 | 0.09 | 0.71 |
| | EtOAc | 545 | 562 | 960 | 559 | 4.79 | 0.14 | 1.19 | 0.13 | 0.70 |
| | MeCN | 541 | 559 | 1172 | 594 | 4.69 | 0.009 | 0.53 | 0.17 | 1.71 |
| **5** | Toluene | 554 | 569 | 1232 | 579 | 4.93 | 0.027 | nd | nd | nd |
| | $CHCl_3$ | 552 | 565 | 1107 | 515 | 4.99 | 0.033 | nd | nd | nd |
| | THF | 547 | 562 | 1361 | 694 | 4.93 | 0.008 | nd | nd | nd |
| | EtOAc | 545 | 560 | 1173 | 624 | 5.00 | 0.007 | nd | nd | nd |
| | MeCN | 543 | 558 | 1216 | 496 | 4.94 | 0.001 | nd | nd | nd |
| **6** | Toluene | 554 | 564 | 1035 | 508 | 5.00 | 0.016 | nd | nd | nd |
| | $CHCl_3$ | 551 | 565 | 852 | 574 | 5.08 | 0.009 | nd | nd | nd |
| | THF | 547 | 560 | 995 | 681 | 4.99 | 0.008 | nd | nd | nd |
| | EtOAc | 545 | 559 | 966 | 709 | 5.05 | 0.004 | nd | nd | nd |
| | MeCN | 543 | 558 | 1341 | 686 | 4.99 | 0.003 | nd | nd | nd |

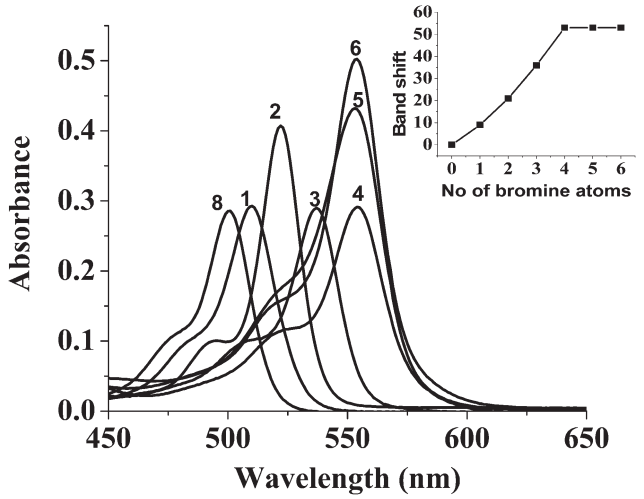



**Fig. 3** Comparison of absorption spectra of compounds **1–6** recorded in toluene. The concentration used was $1 \times 10^{-6}$ M. The inset shows the plot of magnitude of red shift in absorption band *versus* the number of bromines.

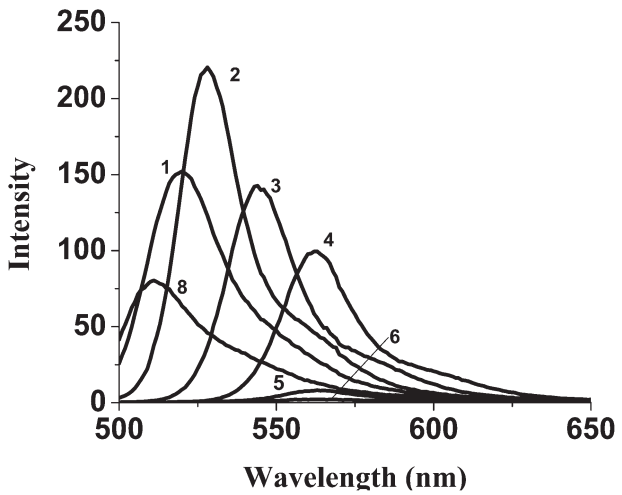



**Fig. 4** Comparison of the fluorescence spectra of brominated compounds **1–6** along with **8** recorded in toluene using the same concentration ($1 \times 10^{-6}$ M).

polarizability. (5) The Stokes shift was small and independent of solvent polarizability indicating that the excited state is not very distorted from the ground state.

The redox properties of brominated BODIPYs **1–6** were probed through cyclic voltammetric and differential pulse voltammetric studies using tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) in dichloromethane as solvent. A comparison of first reduction waves of compounds **1–6** along with **8** is shown in Fig. 5 and the data are presented in Table 5. In general, the compounds **1–6** showed one reversible reduction ($\Delta E$ = 60–80 mV) and one irreversible reduction. No oxidation was noted between 0 to 2.0 V due to the electron deficient nature of BODIPY dyes **1–6**. It is clear from Fig. 5 and the data in Table 5 that addition of each bromine resulted in a successive anodic shift of reduction potential compared to **8** indicating that the boron dipyrrin dye becomes easier to reduce with the

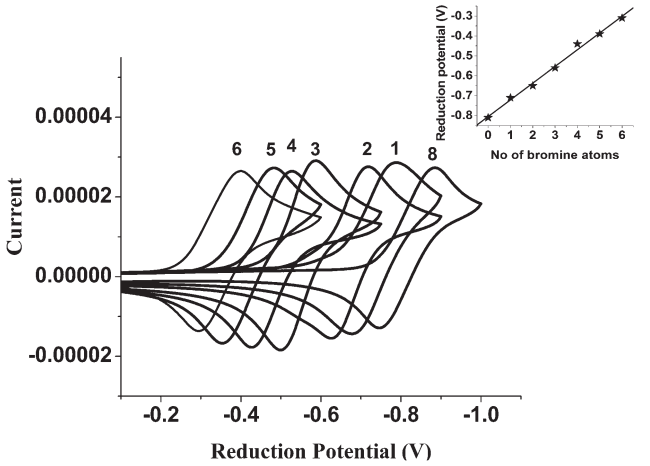



**Fig. 5** Comparison of first reduction waves of compounds **1–6** along with **8** in $CH_2Cl_2$, measured using n-$Bu_4N^+P(ClO_4)_6^-$ (0.1 M) as supporting electrolyte at a scan rate of 50 mV $s^{-1}$. The inset shows the plot between the no. of bromine atoms *versus* reduction potential.

**Table 5** Electrochemical redox data of compounds **1–6** along with compound **8** in $CH_2Cl_2$

| | Reduction potential (V) | |
|---|---|---|
| Compound | I | II |
| **8** | −0.81 | −1.91 |
| **1** | −0.71 | −1.76 |
| **2** | −0.66 | −1.70 |
| **3** | −0.56 | −1.60 |
| **4** | −0.44 | −1.43 |
| **5** | −0.39 | −1.37 |
| **6** | −0.31 | −1.29 |

increasing number of Br groups. Thus, the difference between the first reduction potential $\Delta E_{1/2}$ of unbrominated BODIPY **8** and hexabrominated BODIPY **6** is 500 mV. The relationship between $E_{1/2}$ for the first reduction and the number of Br groups on the BODIPY core is shown as an inset in Fig. 5. The positive shift in $E_{1/2}$ with increase in the number of Br groups is additive and the slope of the straight-line plot is 80 mV/Br group. This kind of linear relationship between reduction potential shift and the number of bromine groups were observed earlier for β-brominated porphyrins, metalloporphyrins and halogenated metallacarboranes.[7]

Time-resolved fluorescence studies were carried out for compounds **1–6** in different solvents and the representative fluorescence decay profile for compound **4** in $CHCl_3$ collected at the corresponding emission wavelength is shown in Fig. 6. We failed to measure the singlet state lifetime $\tau$ for compounds **5** and **6** which are very weakly fluorescent. The fluorescence decay profiles of compounds **1–4** were fitted to a single exponential and the lifetimes are parallel to the fluorescence quantum yields of the compounds. The fluorescence lifetimes of compounds **1–4** increase with increasing solvent polarizability which is in line with the fluorescence quantum yields. Using the experimental $\Phi_f$ and $\tau$ values, we calculated the radiative $k_f$ and nonradiative $k_{nr}$ rate constants which are consistent with the quantum yield and singlet state life time data. Thus, the steady state and

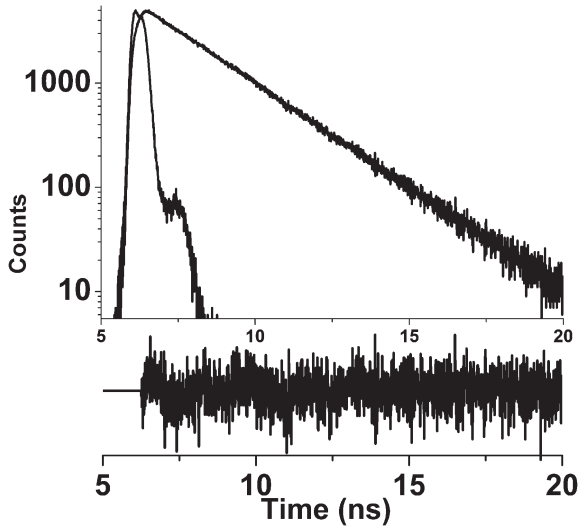



**Fig. 6** A representative fluorescence decay profile and weighted residual distribution fit of **4** in $CHCl_3$. The excitation wavelength used was 440 nm and emission was detected at 570 nm.

time-resolved fluorescence studies indicates that compounds **1–4** are decently fluorescent and follow the same trend with the change of polarizability of solvents as noted earlier for several BODIPY dyes.[13]

## Conclusions

In summary, we systematically introduced one to six bromines on the boron dipyrrin core by treating dipyrromethane with different equivalents of *N*-bromosuccinimide in THF followed by oxidation with DDQ and complexation with $BF_2$ unit. The $R_f$ values of mono to hexabrominated BODIPYs are quite distinct and so can be separated by column chromatography and the compounds isolated in decent yields. $^1$H NMR spectroscopy was used in identifying the location of the bromine group on the BODIPY core. Absorption spectroscopy revealed that the absorption band shift towards higher wavelength on addition of each bromine group upto four bromines after which no further shift was observed with the addition of five and six bromines. The fluorescence band also experienced red shift on addition of bromines. However, the quantum yields reduced significantly for penta and hexabrominated BODIPYs. These low quantum yields are due to the heavy halogen effect which because of spin–orbit coupling enhances the non-radiative decay pathways. The first reduction potential exhibits anodic shifts with the addition of each bromine and follows a linear trend with increase in the number of bromine groups. Thus, the BODIPYs with **1–6** bromines can be easily prepared which can be used as synthons to prepare various BODIPY derivatives and such synthetic efforts are currently underway in our laboratory.

## Experimental section

### General

THF and toluene were dried over sodium benzophenone ketyl and chloroform, ethyl-acetate, methanol, acetonitrile dried over calcium hydride prior to use. $BF_3{\cdot}OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Spectrochem (India) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh and 100–120 mesh). $^1$H NMR spectra ($\delta$ in ppm) were recorded using Varian VXR 300, 400 MHz and Bruker 400 MHz spectrometer. $^{13}$C NMR spectra were recorded on the Bruker operating at 100.6 MHz. $^{19}$F NMR spectra were recorded on the Bruker operating at 376.4 MHz. $^{11}$B NMR spectra were recorded on the Bruker operating at 128.4 MHz. TMS was used as an internal reference for recording $^1$H (of residual proton; $\delta$ 7.26) and $^{13}$C ($\delta$ 77.0 signal) in $CDCl_3$. Absorption and steady-state fluorescence spectra were obtained with Perkin-Elmer Lambda-35 and PC1 Photon Counting Spectrofluorometer manufactured by ISS, USA instruments respectively. Fluorescence spectra were recorded at 25 °C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields ($\Phi_f$) were estimated from the emission and absorption spectra by a comparative method at the excitation wavelength of 488 nm in ethanol using Rhodamine 6G ($\Phi_f$ = 0.88)[15] as standard. The time-resolved fluorescence decay measurements were carried out at the magic angle using a picosecond-diode-laser-based, time-correlated, single-photon-counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to a single exponential.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated *versus* saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}$ ($Fc/Fc^+$) = 0.42 V, *vs.* SCE.[16] The ES-MS mass spectra were recorded with a Q-Tof micro mass spectrometer. A high-resolution mass spectrum was obtained from a Q-TOF instrument by the electron spray ionization (ESI) technique.

### X-ray diffraction studies

A single crystal X-ray structural study was performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instrument with a low-temperature attachment. Data were collected at 293(2) K (in the case of compound **3**) and 150 (2) K (in the case of **2**, **4** and **5**) using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda_\alpha$ = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques and were scaled and reduced using CrysAlisPro RED software. Structure solutions for the compounds **2–6** were obtained using direct methods (SHELXS-97)[17] and refined using full-matrix least-squares methods on $F^2$ using SHELXL-97.[18] The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The

hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 $U_{eq}$ of their parent atoms.

The single crystals of compounds **2–6** were obtained on slow evaporation of hexane–$CH_2Cl_2$ over a period of one week.

### General method for the synthesis of compounds 1–4

The compounds **1–4** were prepared by a sequence of steps in a one pot reaction. *meso*-(*p*-Methoxyphenyl)-dipyrromethane **7** (500 mg, 1.98 mmol) was treated with appropriate equivalents of *N*-bromosuccinimide in dry THF (50 mL) at −78 °C under nitrogen for 1 h. The reaction mixture was warmed to room temperature and the solvent was evaporated by a rotary evaporator. The crude compound was subjected to flash column chromatography using $CH_2Cl_2$. 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 continued at room temperature for an additional 1 h. The reaction mixture was washed successively with 0.1 M NaOH solution and water. The organic layers were combined, dried over $Na_2SO_4$, filtered, and evaporated. The TLC analysis of crude compound showed three spots; the major spot corresponding to the required bromo derivative of BODIPY and the two minor spots corresponding to the other substituted bromo BODIPY and unsubstituted BODIPY. The crude compound was subjected to silica gel column chromatography and the required bromo derivative of BODIPY was collected as a second band using petroleum ether–dichloromethane (90 : 10). The solvent was removed on a rotary evaporator under vacuum and afforded pure bromo BODIPY in 20–40% yield.

### 3-Bromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (1)

(250 mg, 40% yield). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.91 (s, 3H; $OCH_3$), 6.53 (m, 1H; py), 6.57 (m, 1H; py), 6.84 (d, $^3J$ = 4.28 Hz, 1H; py), 6.96 (d, $^3J$ = 3.70 Hz, 1H; py), 7.05 (d, $^3J$ = 7.95 Hz, 2H; Ar), 7.51 (d, $^3J$ = 7.95 Hz, 2H; Ar), 7.94 (s, 1H, py); $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 55.7, 114.2, 114.3, 118.4, 119.0, 122, 126.4, 132.4, 132.5, 132.6, 134.8, 143.5, 144.2, 145.6, 162.3; $^{19}$F NMR (282.2 MHz, $CDCl_3$, $\delta$ in ppm) −146.34 (q, $J_{B–F}$ = 56.5 Hz); $^{11}$B NMR (96.3 MHz, $CDCl_3$, $\delta$ in ppm) 0.48 (t, $J_{B,F}$ = 28.2 Hz); HRMS calcd for ($C_{16}H_{13}BBrF_2N_2$) 357.0205 $[M - F]^+$ found 357.0210 $[M - F]^+$.

### 3,5-Dibromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (2)

(208 mg, 25% yield); $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 3.9 (s, 3H; –$OCH_3$), 6.52 (d, $^3J$ = 4.28 Hz, 2H; py), 6.82 (d, $^3J$ = 4.28 Hz, 2H; py), 7.01 (d, $^3J$ = 7.9 Hz, 2H; Ar), 7.42 (d, $^3J$ = 7.9 Hz, 2H; Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ in ppm) 55.6, 114.2, 122.5, 124.8, 131.6, 131.8, 132.3, 135.4, 148.4, 162.2; $^{19}$F NMR (282.2 MHz, $CDCl_3$, $\delta$ in ppm)−146.64 (q, $J_{B,F}$ = 57.8 Hz); $^{11}$B NMR (96.3 MHz, $CDCl_3$, $\delta$ in ppm) 0.68 (t, $J_{B,F}$ = 28.2Hz); HRMS calcd for $C_{16}H_{11}BBr_2F_2N_2O$ 434.9315 $[M - 19]^+$ found 434.9309 $[M - 19]^+$.

### 2,3,5-Tribromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (3)

(202 mg, 19% yield). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.91 (s, 3H; $OCH_3$), 6.59 (d, $^3J$(H,H) = 4.28 Hz, 1H; Py), 6.90 (s, 2H; Py), 7.05 (d, $^3J$(H,H) = 4.28 Hz, 2H; Ar), 7.46 (d, $^3J$(H, H) = 4.28 Hz, 2H; Ar); $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 55.7, 110.6, 114.5, 123.5, 124.5, 130.4, 131.8, 132.4, 132.9, 134.3, 134.5, 135.8, 143.3, 162.5; $^{19}$F NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) −147.3; $^{11}$B NMR (96.3 MHz, $CDCl_3$, $\delta$ in ppm) 0.49 (t, $^3J$(B,F) = 28.2 Hz); HRMS calcd for ($C_{16}H_{10}BBr_3F_2N_2O$) 512.8435 $[M - F]^+$ found 512.8420 $[M - F]^+$.

### 2,3,5,6-Tetrabromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (4)

(244 mg, 20% yield). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 3.91 (s, 3H; $OCH_3$), 6.95 (s, 2H; py), 7.07 (d, $^3J$(H,H) = 7.9 Hz, 2H; Ar), 7.46 (d, $^3J$(H,H) = 7.9 Hz, 2H; Ar); $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$ in ppm) 55.8, 111.8, 114.7, 124.3, 131.5, 132.5, 134.3, 134.8, 143.1, 162.8; $^{19}$F NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) −148.1; $^{11}$B NMR (376.5 MHz, $CDCl_3$, $\delta$ in ppm) 0.28 (t, $^3J$(B,F) = 28.2 Hz); HRMS calcd for ($C_{16}H_9BBr4F_2N_2O$) 590.7525 $[M - F]^+$ found 590.7523 $[M - F]^+$.

### Synthesis of 1,2,3,5,6-pentabromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (5)

To a solution of 8-(4-methoxyphenyl)dipyrromethane **7** (0.5 g, 1.98 mmol) in dry THF, five equivalents of *N*-bromosuccinimide (1.76 g, 9.9 mmol) were added under $N_2$ atmosphere and the reaction mixture was allowed to stir at room temperature for 4 h. The TLC analysis indicated the disappearance of the spot corresponding to **7** and the appearance of two new spots corresponding to compound **5** along with a faint spot which is corresponding to compound **6**. The solvent was removed on a rotary evaporator under vacuum and the crude compound was passed through a flash silica gel column chromatograph using dichloromethane. The resultant compound was dissolved in freshly distilled dichloromethane and oxidized with DDQ (2.38 mmol) for 30 min at room temperature. Triethylamine (75.4 mmol) followed by $BF_3{\cdot}OEt_2$ (89.97 mmol) were added to the reaction mixture and stirring was continued at room temperature for an additional 30 min. The solvent was removed and the crude compounds were purified using silica gel column chromatography using petroleum ether–ethyl acetate (98 : 2) which afforded the desired pentabromo-BODIPYs **5** as green colour solid.

(0.25 g, 16% yield). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 3.91 (s, 3H; –$OCH_3$), 6.76 (s, 1H; py), 7.03 (d, 2H, $^3J$(H,H) = 9.0 Hz; Ar), 7.25 (d, 2H, $^3J$(H,H) = 8.7 Hz; Ar); $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 55.6, 114.3, 114.3, 122.4, 122.5, 123.2, 131.4, 132.3, 136.4, 136.6, 143.2, 144.8, 145.5, 162.0; $^{19}$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); HRMS calcd for $C_{16}H_7BBr_5F_2N_2O$ 688.6631 $(M - F)^+$ found 668.6657 $(M - F)^+$.

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