CHAPTER-3

MESO-FUNCTIONALIZATION OF BODIPY MOLECULES
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3.1. Preamble

The Bodipy-BF\textsubscript{2} compounds have not only gained recognition for their laser applications but are also valued for making opto-electronic devices.\textsuperscript{19,67} Functionalization of the Bodipy core is an important synthetic goal as it helps in tuning their property to light- and electron transfer-induced processes, improving hydrophilicity, and anchoring to various matrices. All these widen the scope of their applications. Most of the previous research, directed to this end were targeted to functionalize the pyrrole moieties of the Bodipy core by (i) halogenation followed by organometallic coupling to introduce alkene/alkyne/arene substitutions;\textsuperscript{39a,68a} ii) direct nucleophilic substitution;\textsuperscript{2b,28a,68b} and (iii) \textit{de novo} syntheses of the Bodipy core from modified pyrroles.\textsuperscript{4a,9b} However, substitution at the pyrrole moiety may bring about undesirable changes in the physical properties, affecting the targeted function adversely. For example, presence of electron-donating groups in the pyrrole ring would reduce the fluorescence quantum yields of the Bodipy molecules especially in polar solvents.\textsuperscript{69}

Instead, \textit{meso}-functionalization of the Bodipy moiety with alkyl/arylalkyl moiety would provide new Bodipy-based functional molecules without perturbing the photo-electronic properties. Presence of \textit{sp}/\textit{sp}\textsuperscript{2}-hybridized carbon at the \textit{meso}-position adversely affects the fluorescence and lasing efficiency of the Bodipy molecules.\textsuperscript{42b,56a} Earlier, Liebeskind-Srogl cross-coupling of 8-thiomethylbodipy with various boronic acids has been used for \textit{meso}-functionalization of the Bodipy moiety.\textsuperscript{70} However, this requires reagents that are expensive and/or have to be synthesized by multi-step routes. Direct synthesis of these types of Bodipy molecules \textit{via} the condensation of substituted pyrroles with aliphatic aldehydes/acid chlorides has inherent limitations due to the instability of the required acid chlorides, and non-reactivity of the aldehydes.\textsuperscript{1,19,67a}
3.2. Meso-Substituted Bodipy Dyes

The commercially available Bodipy dyes, PM567 (21) and PM597 (32) (Figure 3.2.1) contain CH₃ substitutions at the pyrrole rings and at the C-8 (meso-) position. Mulliken-charge analysis of the 1,3,5,7,8-pentamethyl Bodipy dye showed that the electron density on the core carbon atoms follows the order: C-8 > C-1/7 > C-3/5. Thus, the CH₃ groups at those positions can undergo the base-catalyzed Knoevenagel-type condensation with various aryl aldehydes according to their relative acidities C-3/C-5 > C-2/C-7 > C-8. This strategy provides a simpler avenue for functionalization of the Bodipy moiety, and has been exploited extensively to develop C-3/C-5 styryl Bodipy derivatives with red-shifted fluorescence. In all these studies, the chosen Bodipy substrates had an aryl substituent at the meso-position, ensuring the reaction to proceed regioselectively at the C-3 and C-5 methyl groups. More recently, syntheses of tri- and tetrastyryl Bodipys by this route are also reported under specific conditions. However, this strategy has never been used for meso-functionalization. In the present studies, a conceptually new strategy is developed to drive the reaction selectively at the meso-position. The rationale of the synthetic design and the efficacy of the protocol is described in this chapter.

(a)  

(b)  

Figure 3.2.1 (a) Meso-substitution, (b) Chemical structures of the Bodipy dyes
3.2.1. Synthesis

As mentioned previously, the acidity factor of the Me groups of the Bodipy compounds 21 and 32 predicts that their Knoevenagel-type condensation with aldehydes would take place at those Me groups, attached to the pyrrole rings. Our previous conformational analysis revealed that in the planer form of 21, the van der Waals radii of even the hydrogen atoms of the C-1/ C-7 and the meso-Me groups can overlap. This makes the meso-site spatially crowded to force the Me group out of the Bodipy plane. As a result, the highly twisted meso-substituents are largely decoupled from the Bodipy core.\(^{73}\) Consistent with this, Costela et al. showed that compound 33, the meso-H analogue of 21 is planner.\(^{74a,b}\) It was envisaged that a Knoevenagel-type condensation of the Bodipy molecules at the meso-Me groups of the dyes 21 and 33 would alleviate such an unfavourable steric interaction. Thus, the release of steric strain may drive the condensation selectively at the meso-position, overriding the least acidity of the meso-methyl protons. In this study, we proved the hypothesis by selective meso-functionalization of the Bodipy dyes 21 and 32 using readily available and inexpensive reagents (Scheme 3.2.1.1). To this end, the steric and acidity factors were separately addressed, and discussed below.

3.2.1.1. Steric factor

Initially, following a known procedure,\(^{33a}\) the condensation between 32 and 62a was carried out in the presence of piperidine and AcOH. The dye 32 is highly twisted due to a strong co-axial steric repulsion between the 2- (and 6-) tert-butyl and other methyl groups at the pyrrole moieties. The steric distortion in 32 is even more in the excited state, resulting in an uncharacteristically high stokes shift (~1350 cm\(^{-1}\)), compared to other Bodipy dyes.\(^{75}\) Hence, its condensation was expected to take place regio-selectively at the meso-position to reduce the steric strain. True to our expectation, the reaction proceeded uneventfully to furnish compound
63a, the meso-styryl analogue of 32 as the single product within 30 min. Due to its C2-symmetry, the 1H NMR spectrum of 63a was much simpler, and also showed disappearance of the singlet for the C-8 methyl protons of 32 along with the appearance of an one-proton olefinic doublets at δ 6.51 (J = 16.3 Hz) as well as resonances at δ 6.92-7.02 (3H) and δ 7.41 (3H) for the other olefinic and four aryl protons, confirming the formation of vinyl bond at the meso-site (Figure 3.2.1.2 a). Appearance of the triplet at δ 1.13 in the 11B NMR spectrum also confirmed that F-atoms were retained in the product (Figure 3.2.1.2 b). Earlier, condensation of 21 with benzaldehyde, under similar conditions furnished the 3-styryl derivative in a very low yield (<3%) along with a large number of unidentified products.76 Thus, the present result with 32 indicated steric factor as the major driving force for the regioslectivity of the reaction, which was also confirmed by analyzing the X-ray crystal structure of 63a (Figure 3.2.1.3). The degree of steric relaxation in forming 63a was evident from dihedral angle between the two pyrrole units (C4-C5-C6-C3) and the torsion angles of the pyrrole rings (C1-C2-C3-C4 and C6-C7-C8-C9) in 32 and 63a. The crystallographic data revealed that the torsion angles of the pyrrole rings and the C4-C5-C6-C3 dihedral angle of 63a was significantly less than those viz. 3.8° and 172.8° respectively of 32.75 These suggested that the Bodipy chromophore of 63a was comparatively more planner than that in 32. With these encouraging results, the synthetic strategy was extended for the condensation of 32 with 62b as well as 62c to obtain the meso-styryl Bodipy compounds 63b and 63c respectively. The results are shown in Table 3.2.1.1.
Table 3.2.1.1: Synthesis of compounds 63a-f.

<table>
<thead>
<tr>
<th>Bodipy</th>
<th>Aldehyde, R&lt;sup&gt;i&lt;/sup&gt;</th>
<th>Product, R&lt;sup&gt;i&lt;/sup&gt;, R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>% yield&lt;sup&gt;[a]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>62a, OMe</td>
<td>63a, OMe, t-Bu</td>
<td>65</td>
</tr>
<tr>
<td>32</td>
<td>62b, OH</td>
<td>63b, OH, t-Bu</td>
<td>50</td>
</tr>
<tr>
<td>32</td>
<td>62c, NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>63c, NO&lt;sub&gt;2&lt;/sub&gt;, t-Bu</td>
<td>67</td>
</tr>
<tr>
<td>21</td>
<td>62a, OMe</td>
<td>63d, OMe, Et</td>
<td>10&lt;sup&gt;[b]&lt;/sup&gt;</td>
</tr>
<tr>
<td>21</td>
<td>62c, NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>63e, NO&lt;sub&gt;2&lt;/sub&gt;, Et</td>
<td>55</td>
</tr>
<tr>
<td>21</td>
<td>62d, Br</td>
<td>63f, Br, Et</td>
<td>61</td>
</tr>
</tbody>
</table>

<sup>[a]</sup> based on isolation; <sup>[b]</sup> 3% 3-styryl analogue was also isolated.

Figure 3.2.1.1 X-ray crystal structure of 63a
Figure 3.2.1.2 The NMR spectrum of 63a (a) $^1$H NMR, (b) $^{11}$B NMR.
3.2.1.2. Acidity factor

To address the acidity issue, the condensation between the dye 21 and 62a, under the same conditions was attempted. Unlike the dye 32 that has two bulky tert-Bu groups at C-2/ C-6, the dye 21 contains the much smaller Me groups at those positions. Hence its meso-position is sterically less crowded, and the acidity factor was expected to contribute to the reaction course.

True to the hypothesis, the reaction afforded the meso-styryl (63d) and C-3 styryl (63d') analogues of 21 in 10% and 13% yields respectively as the major isolated compounds along with some unanalyzed products (possibly poly-styryl and degradation products) (Scheme 3.2.1.2). Nevertheless, the formation of the compound 63d supported the steric factor hypothesis. Formation of compound 63d was confirmed from the $^1$H NMR and $^{11}$B NMR spectra (Figures 3.2.1.3 a-b). The main diagnostic features of the $^1$H NMR spectrum (Figure 3.2.1.4) of 63d' were the appearances of two triplets and two quartets for the –CH$_3$ and –CH$_2$ protons of the ethyl groups, consistent with its lack of the C$_2$-symmetry unlike compound 63d. Based on the available X-ray crystallography data, the torsion angle (0.8°) of the pyrrole rings in 21 is known to be much less than that in 32. $^{75}$ Hence, the release of steric strain on condensation at the meso-position of the dye 21 will be less than that with 32, explaining the distribution of the products.

![Scheme 3.2.1.2 Synthesis of the compounds 63d and 63d']
Figure 3.2.1.3 The NMR spectrum of 63d (a) $^1$H NMR, (b) $^{11}$B NMR.
Figure 3.2.1.4 $^1$H NMR spectrum of compound 63d'

It was reasoned that use of more electrophilic aldehydes might negate the acidity factor of the *meso* and pyrrole Me protons to direct the condensation at the *meso*-position even with the less strained molecule 21. To confirm this, compound 21 was subjected to condensation with 62c. The reaction was slow and attained an equilibrium at 4 h to furnish the *meso*-styryl analogue 63e along with the recovered dye 21 (40%). Formation of the C-3 and/or C-5 styryl derivatives was not noticed, despite the higher acidities of the designated Me protons. This also established that relaxation of steric strain was the major determinant of the reaction. The reaction proceeded through the intermediacy of a pink colored stable product that could be isolated (30% yield at 2 h) and characterized as 64 by spectroscopy, CHN analysis and X-ray crystallography (Figure 3.2.1.5). To the best of our knowledge, this is the first report of isolation and characterization of the intermediate in a Knovenagel type condensation with the Bodipy dyes. The intermediacy of compound 64 in the reaction was confirmed by its conversion to 63e along with some amount of
21 on heating in the presence of piperidine and AcOH. The partial recovery of 21 also explained the sluggishness of the reaction and lesser yield due to the attainment of an equilibrium. The mechanism of the formation of 63e can be represented as shown in Scheme 3.2.1.3.

![Scheme 3.2.1.3 Mechanism of formation of 63e](image)

The $^1$H NMR showed three multiplates between $\delta$ 3.18-3.73 ppm related with the C-8 protons (–CH$_2$, –CH). The twelve protons multiplets at $\delta$ 2.37-2.48 in its $^1$H NMR spectrum (Figure 3.2.1.7) corresponded to the five –CH$_2$ groups of piperidine ring and two protons of –CH$_2$ group of pyrrole at C-2 position. Its LCMS molecular ion peak [M$^+$] at m/e 536.3 and the fragment peaks at m/z 452.2, 219.1 and 173.12 etc. further established the formation of compound 64. In a similar manner, the styryl derivative 63f could also be synthesized in 61% yield (Table 3.2.1.1) by condensing the dye 21 with 62d.

![Figure 3.2.1.5 X-ray crystal structures of 64](image)
Figure 3.2.1.6 The NMR spectrum of compound 63e (a) $^1$H NMR, (b) $^{13}$C NMR.
Figure 3.2.1.7 The NMR spectrum of compound 64 (a) $^1$H NMR, (b) $^{13}$C NMR.
(i) H₂/10% Pd-C/CH₂Cl₂-EtOH. ii) a. p-OMeC₆H₄(CH₂)₂CHO /TFA/CH₂Cl₂/25 °C/1 h; b. DDQ/4 h; c. Et₃N/1 h; d. BF₃·Et₂O /25°C/ 4 h. iii) 9a/piperidine/AcOH/Toluene/Δ.

Scheme 3.2.1.4 Synthesis of the compounds 65 and 66.

3.2.1.3. Applications

To illustrate the utility of the new meso-functionalization method, a few new Bodipy compounds were synthesized (Scheme 3.2.1.4) using some of the above meso-styryl Bodipy compounds. For example, the highly fluorescent dye 65 was synthesized by catalytic hydrogenation of 63d that showed a very weak fluorescence (vide infra). The ¹H NMR spectrum of 65 showed two new multiplets at δ 2.84-2.93 and 3.27-3.36, each accounting for two protons for the vinylic and benzylic CH₂ groups in place of the olefinic resonances, confirming its formation (Figure 3.2.1.8). It is worth mentioning that compound 65 could not be synthesized via the conventional route of condensing kryptopyrrole (58) with p-methoxydihydrocinnamaldehyde, due to low reactivity of the arylalkyl aldehydes.¹⁹

The polystyryl Bodipys are useful functional molecules. Previously, Akkaya et al. synthesized a tetrastyryl Bodipy (A₄ system),²⁵a while Ziessel et al. synthesized AB, A₂B₂ and ABCD types of polystyryl Bodipy dyes.⁷³ In the present work, the Bodipy compound 63e was condensed with the aldehyde 62a to furnish the 3,5,8-tristyril substituted Bodipy dye 66, belonging to a new AB₂ system of polystyryl Bodipy dye. The ¹H-NMR spectrum (Figure
3.2.1.9) of 66 exhibited all the characteristic signals of the tristyryl-Bodipy unit. For example, the eighteen-protons resonances between $\delta$ 6.74-8.29 corresponded to the three phenyl subunits and six vinyl protons on the tristyryl arms, while the six-protons singlet at $\delta$ 2.50 due to the 3,5-methyls disappeared.

Figure 3.2.1.8 $^1$H NMR spectrum of compound 65.
Figure 3.2.1.9 The NMR spectrum of compound 66 (a) $^1$H NMR, (b) $^{13}$C NMR.
3.2.2. Photophysical characteristics

The spectroscopic properties (Table 3.2.2.1) of all the compounds, recorded in CH$_2$Cl$_2$ revealed that the \textit{meso}-styryl Bodipys (63a-e) were significantly less fluorescent ($\Phi_{fl} < 0.01$) and showed reduced Stokes’ shifts, compared to the corresponding precursor Bodipys. The results were consistent with the previous report$^{75b}$ and provided direct evidence of the steric relaxation after \textit{meso}-styryl modification. Interestingly, saturation of the styryl double bond as in 63d augmented the fluorescence ($\Phi_{fl} = 0.76$) significantly, offering the possibility of constructing on/off chemical sensors. The rather large red shifts (8-13 nm) of the absorption $\lambda_{\text{max}}$ \textit{vis-à-vis} excitation $\lambda_{\text{ext}}$ of 63a-e indicated complex excited state transition.

**Table 3.2.2.1:** Photophysical parameters of the dyes in CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{\text{ext}}$ (nm)</th>
<th>$\lambda_{\text{fl}}$ (nm)</th>
<th>$\Phi_{fl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>525.0</td>
<td>81000</td>
<td>531.0</td>
<td>556.0</td>
<td>0.34$^a$</td>
</tr>
<tr>
<td>63a</td>
<td>533.0</td>
<td>59000</td>
<td>522.0</td>
<td>529.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>63b</td>
<td>533.0</td>
<td>60000</td>
<td>521.0</td>
<td>529.0</td>
<td>0.01</td>
</tr>
<tr>
<td>63c</td>
<td>536.2</td>
<td>54000</td>
<td>524.0</td>
<td>532.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>21</td>
<td>520.0</td>
<td>71000</td>
<td>525.0</td>
<td>534.0</td>
<td>0.79$^b$</td>
</tr>
<tr>
<td>63d</td>
<td>528.5</td>
<td>58000</td>
<td>520.0</td>
<td>542.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>63e</td>
<td>531.5</td>
<td>51000</td>
<td>518.0</td>
<td>532.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>63f</td>
<td>529.6</td>
<td>61000</td>
<td>520.0</td>
<td>537.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>63d'</td>
<td>577.5</td>
<td>84000</td>
<td>581.0</td>
<td>593.0</td>
<td>0.66</td>
</tr>
<tr>
<td>64</td>
<td>534.2</td>
<td>56000</td>
<td>536.0</td>
<td>559.0</td>
<td>0.02</td>
</tr>
<tr>
<td>65</td>
<td>523.2</td>
<td>75000</td>
<td>526.0</td>
<td>537.0</td>
<td>0.72</td>
</tr>
<tr>
<td>66</td>
<td>666.0</td>
<td>89000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Relative to that (0.43) in EtOH; $^b$Relative to that (0.84) in EtOH.
3.2.3. Electrochemical Studies

Functional fluorescent dyes are of central importance as active components for light and electron transfer induced processes, mainly in the field of materials science and analysis.\textsuperscript{77} A combination of reversible electron transfer and of efficient light absorption/emission is essential for constructing photovoltaic/photoelectrochemical devices.\textsuperscript{78} Due to their high absorption coefficients and quantum yields of emission, the Bodipy compounds have favorable photonic qualities.\textsuperscript{79} However, for photovoltaic applications, the radical cations and anions formed during electron transfer need to be fairly stable. The meso-position of the indacene framework is of crucial importance in stabilizing the radical anions. The cyclic voltammograms of some selected Bodipy compounds (21, 63d, 63d' and 66) are shown in Figures 3.2.3.1a-d. The CV results (Table 3.2.3.1) revealed reversible cathodic waves, assigned to the one-electron reduction of the Bodipy units.\textsuperscript{61} Compound 63d ($E_{\text{red}} = -1.36$ V) was easily reducible by $\sim 220$ mV than 21 ($E_{\text{red}} = -1.58$ V), while reduction of the tri-styryl compound 66 was even easier by $\sim 600$ mV than 21.
These suggested better stability of the radical anions due to meso-styryl modification. However, this alone did not alter the oxidation potential, as is reflected from the same $E_{\text{ox}}^0$ values (1.02 V) of 21 and 66. In case of 66, two anodic waves were observed, the first oxidation step ($E_{\text{ox}}^0 = 0.75$ V) was assigned to the removal of one electron from the Bodipy core, while the higher potential could be due to the oxidation of the styryl residue ($E_{\text{ox}}^0 = 1.23$ V).\textsuperscript{61} Similarly, two anodic waves were observed in case of 63d' showing the oxidation of Bodipy core ($E_{\text{ox}}^0 = 0.83$ V) and styryl residue ($E_{\text{ox}}^0 = 1.26$ V). Compound 63e ($E_{\text{red}}^0 = -1.02$ V) was easily reducible by ~560 mV than 21.

Table 3.2.3.1: Electrochemical data of various compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}^0$/V</th>
<th>(ΔE)</th>
<th>$E_{\text{red}}^0$/V</th>
<th>(ΔE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>1.02</td>
<td>0.437</td>
<td>-1.58</td>
<td>0.416</td>
</tr>
<tr>
<td>63d</td>
<td>1.02</td>
<td>0.332</td>
<td>-1.36</td>
<td>0.429</td>
</tr>
<tr>
<td>63d'</td>
<td>0.83, 1.26</td>
<td>0.428</td>
<td>-1.43</td>
<td>0.410</td>
</tr>
<tr>
<td>63e</td>
<td>1.06</td>
<td>0.344</td>
<td>-1.02</td>
<td>0.379</td>
</tr>
<tr>
<td>66</td>
<td>0.75, 1.23</td>
<td>0.253</td>
<td>-0.98</td>
<td>0.474</td>
</tr>
</tbody>
</table>
Figure 3.2.3.1 Cyclic voltammogram of the meso-methyl and meso-functionalized Bodipys. (a): 21; (b): 63d; (c): 63d'; (d): 66. The experiments were carried out in CH₂Cl₂ at 25 °C using 0.1 M Bu₄NClO₄ (TBAP) as the supporting electrolyte and ferrocene (Fc) as internal reference at +0.38V.

3.2.4. Theoretical interpretation

The excited state of the Bodipy core has inherent charge redistribution towards the meso-position.⁶⁷c Presence of the electron withdrawing meso-styryl group would facilitate it further and may alter the localization of the LUMO and HOMO. For example, our theoretical calculation revealed maximum electron densities of the LUMO and HOMO of 66 on the meso-styryl and Bodipy moieties respectively (Figure 3.2.4.1 and 3.2.4.2). Hence the emission process
with the meso-styryl Bodipys would be symmetry forbidden, explaining their low/ non-fluorescence. However, such a charge distribution may be important in using the meso-styryl compounds as potential sensitizers for rapid electron injection into the conduction band of TiO$_2$ in dye sensitized solar cells (DSSCs).\textsuperscript{67c}

3.3. Summary

In conclusion, we have tactically used the inherent steric strain of the Bodipy moieties to functionalize them at the meso-position. The styryl substitutions at the meso-position alleviate the steric strain of the parent Bodipys. Also, the steric strain release hypothesis was proved from the single crystal X-ray data that showed reduced torsional angle and increased dihedral angle on introduction of a meso-styryl moiety in the dyes 32 and 21. The strain release was more for 32, to furnish the products in higher yields compared to that with 21. For the less strained Bodipy 21, the meso-selectivity could be achieved by increasing the electrophilicity of the aldehyde. Identification of the isolated intermediate 64 of the Knoevenagel condensation also established the reaction mechanism. This method allows for the preparation of a rich variety of 8-substituted
Bodipys using readily available aromatic aldehydes. The new meso-styryl Bodipys could be useful for development of chemical sensors and DSSCs.

3.4. Experimental

3.4.1. General Methods

The general details of the synthetic methodologies and spectroscopic studies have already been discussed in Chapter-2.

3.4.2. Synthesis

Typical process for the Knoevenagel-type condensation. A mixture of 21/32 (1.0 mmol), 62a-d (1.1 mmol), glacial acetic acid (0.5 mL) and piperidine (3.5 mL) was refluxed in toluene (35 mL) with simultaneous azeotropic removal of water formed during the reaction. After the consumption of 21/32, H2O (100 mL) was added into the reaction mixture, which was extracted with CHCl3 (3 × 20 mL). The organic layer was dried and concentrated in vacuo to give a residue, which on column chromatography (silica gel, hexane-EtOAc) furnished the respective styryl derivatives.

2,6-Di-tert-butyl-4,4-difluoro-8-p-hydroxystyryl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indocene 63a. red needles (CH2Cl2/cyclohexane); mp: 249 °C; IR: 2948, 2835, 1632, 1603, 1439 cm⁻¹; ¹H NMR: δ 1.38 (s, 18H), 2.31 (s, 6H), 2.70 (s, 6H), 3.85 (s, 3H), 6.51 (d, J = 16.3 Hz, 1H), 6.92-7.02 (m, 3H), 7.41 (d, J = 8.6 Hz, 2H); ¹³C NMR (50 MHz): δ 16.7, 18.2, 31.9, 33.2, 55.3, 114.5, 122.3, 127.9, 129.3, 131.6, 136.6, 137.1, 138.1, 138.8, 153.1, 160.3; ¹¹B NMR (96 MHz): δ 1.13 (t, J = 34.0 Hz); EI-MS (m/z): 493 [M+1]⁺, 492 [M]⁺. Anal. Calcd. for C₃₀H₃₉BF₂N₂O: C, 73.17; H, 7.98; N, 5.69%; Found: C, 73.13; H, 7.67; N, 5.56%.

2,6-Di-tert-butyl-4,4-difluoro-8-p-methoxystyryl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indocene 63b. red solid; mp: >250 °C; IR: 3501, 2989, 1737, 1510 cm⁻¹; ¹H NMR (500 MHz): δ
1.38 (s, 18H), 2.31 (s, 6H), 2.70 (s, 6H), 6.52 (d, J = 16.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 16.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz): δ 16.8, 18.2, 31.9, 33.2, 115.9, 122.1, 128.1, 136.5, 137.1, 138.2, 153.0, 156.1; EI-MS (m/z): 478 [M]+, 477 [M-1]+.

Anal. Calcd. for C$_{29}$H$_{37}$BF$_2$N$_2$: C, 72.80; H, 7.80; N, 5.86%. Found: C, 72.99; H, 7.80; N, 5.56%.

2,6-Di-tert-butyl-4,4-difluoro-1,3,5,7-tetramethyl-8-p-nitrostyryl-4-bora-3a,4a-diaza-s-indene 63c. red needles (CH$_2$Cl$_2$/cyclohexane); mp: >250 °C; IR: 2965, 1745, 1513 cm$^{-1}$; $^1$H NMR (500 MHz): δ 1.38 (s, 18H), 2.27 (s, 6H), 2.72 (s, 6H), 6.67 (d, J = 16.5 Hz, 1H), 7.31 (d, J = 16.5 Hz, 1H), 7.62 (d, J = 8 Hz, 2H), 8.27 (d, J = 8 Hz, 2H); $^{13}$C NMR (125 MHz): δ 16.8, 18.2, 31.8, 33.2, 124.4, 127.0, 129.4, 131.3, 133.9, 136.0, 137.6, 142.3, 147.8, 154.3; EI-MS (m/z): 507 [M]+, 506 [M-1]+. Anal. Calcd. for C$_{29}$H$_{36}$BF$_2$N$_3$: C, 68.64; H, 7.15; N, 8.28%. Found: C, 68.78; H, 7.31; N, 8.66%.

2,6-Diethyldifluoro-3-p-methoxystyryl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indene 63d. red cuboidals (CH$_2$Cl$_2$/cyclohexane); mp: 185 °C; IR: 2963, 1637, 1604, 1477 cm$^{-1}$; $^1$H NMR: δ 1.02 (t, J = 7.6 Hz, 6H), 2.13 (s, 6H), 2.35 (q, J = 7.6 Hz, 4H), 2.51 (s, 6H), 3.84 (s, 3H), 6.61 (d, J = 16.3 Hz, 1H), 6.87-7.01 (m, 3H), 7.42 (d, J = 8.7 Hz, 2H); $^{13}$C NMR: δ 12.4, 14.3, 14.7, 17.1, 55.3, 114.5, 120.5, 128.0, 129.0, 130.8, 132.5, 137.3, 137.4, 139.1, 152.8, 160.3; $^{11}$B NMR (96 MHz): δ 1.04 (t, J = 33.4 Hz); EI-MS (m/z): 437 [M+1]+, 417 [M-19]+. Anal. Calcd. for C$_{26}$H$_{31}$BF$_2$N$_2$: C, 71.57; H, 7.16; N, 6.42%. Found: C, 71.17; H, 6.95; N, 6.32%.

2,6-Diethyl-4,4-difluoro-3-p-methoxystyryl-1,5,7,8-tetramethyl-4-bora-3a,4a-diaza-s-indene 63d'. pink cuboidals (CH$_2$Cl$_2$/cyclohexane); mp: 235 °C; IR: 2961, 1635, 1606, 1478 cm$^{-1}$; $^1$H NMR: δ 1.05 (t, J = 7.5 Hz, 3H), 1.20 (t, J = 7.5 Hz, 3H), 2.32-2.47 (m, 8H), 2.53 (s,
2.57-2.74 (m, 3H), 3.83 (s, 3H), 6.87 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 16.8 Hz, 1H), 7.48-7.62 (m, 3H); $^{13}$C NMR: δ 12.5, 14.0, 14.4, 14.7, 17.1, 18.3, 55.3, 114.2, 118.1, 128.4, 130.5, 132.4, 132.7, 133.1, 134.2, 136.5, 136.7, 138.8, 148.0, 153.2, 159.9. El-MS (m/z): 437 [M+1]$^+$, 417 [M-19]$^+$. Anal. Calcd. for C$_{26}$H$_{31}$BF$_2$N$_2$O: C, 71.57; H, 7.16; N, 6.42%; Found: C, 71.10; H, 7.21; N, 6.18%.

2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-p-nitrostyryl-4-bora-3a,4a-diaza-s-indecene

red needles (CH$_2$Cl$_2$/cyclohexane); mp: >250 °C; IR: 2930, 2868, 1634, 1597, 1478 cm$^{-1}$; $^1$H NMR: δ 1.02 (t, J = 7.5 Hz, 6H), 2.08 (s, 6H), 2.34 (q, J = 7.5 Hz, 4H), 2.51 (s, 6H), 6.73 (d, J = 16.4 Hz, 1H), 7.22 (d, J = 16.4 Hz, 1H), 7.61 (d, J = 8.6 Hz, 2H), 8.25 (d, J = 8.6 Hz, 2H); $^{13}$C NMR: δ 12.5, 14.2, 14.6, 17.1, 124.4, 127.1, 127.7, 130.3, 133.0, 135.1, 136.7, 137.1, 142.1, 147.8, 153.9; El-MS (m/z): 451 [M]$^+$, 432 [M-19]$^+$. Anal. Calcd. for C$_{25}$H$_{28}$BF$_2$N$_3$O$_2$: C, 66.53; H, 6.25; N, 9.31%; Found: C, 66.12; H, 6.02; N, 9.36%.

8-p-Bromostyryl-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indecene

red needles (CH$_2$Cl$_2$/cyclohexane); mp: 223 °C; IR: 2965, 1538, 1472 cm$^{-1}$; $^1$H NMR (500 MHz): δ 1.03 (t, J = 7.5 Hz, 6H), 2.11 (s, 6H), 2.36 (q, J = 7.5 Hz, 4H), 2.52 (s, 6H), 6.64 (d, J = 16.0 Hz, 1H), 7.08 (d, J = 16.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H); $^{13}$C NMR (125 MHz): δ 12.5, 14.3, 14.7, 17.1, 122.8, 123.6, 128.0, 130.5, 132.2, 132.7, 134.9, 136.2, 137.2, 137.9, 153.3; El-MS (m/z): 485 [M]$^+$, 483 [M-2]$^+$. Anal. Calcd. for C$_{25}$H$_{28}$BBrF$_2$N$_2$: C, 61.88; H, 5.82; N, 5.77%; Found: C, 61.86; H, 5.50; N, 6.04%.

Compound 64. A mixture of 21 (100 mg, 0.32 mmol), p-nitrobenzaldehyde (71 mg, 0.47 mmol), glacial acetic acid (0.2 mL) and piperidine (1 mL) was refluxed in toluene (10 mL) for 2 h. Water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus. After that, water (100 mL) was added into it and the reaction mixture was extracted
with CHCl₃ (3 × 50 mL). The organic layer was then dried over Na₂SO₄ and the solvent was removed under reduced pressure. Column chromatography of the residue (silica gel, hexane-EtOAc) furnished 64 as a red solid. Yield: 51 mg (30%); red needles (CH₂Cl₂/cyclohexane); mp: 162 °C; IR: 2932, 2864, 1478 cm⁻¹; ¹H NMR: δ 0.77 (t, J = 7.5 Hz, 3H), 1.07 (t, J = 7.5 Hz, 3H), 1.40-1.61 (m, 6H), 2.00 (s, 3H), 2.10 (q, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.35-2.49 (m, 12H), 3.14-2.24 (m, 1H), 3.52-3.62 (m, 1H), 3.72-3.85 (m, 1H), 7.30 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H); ¹³C NMR: δ 12.3, 13.8, 14.2, 14.8, 16.8, 17.2, 24.6, 26.4, 26.9, 32.4, 52.5, 72.5, 122.6, 128.5, 131.6, 132.6, 133.1, 134.2, 135.6, 141.6, 147.1, 148.5, 151.5, 153.0; EI-MS (m/z): 537 [M+1]⁺, 452, 219, 174. Anal. Calcd. for C₃₀H₃₉BF₂N₄O₂: C, 67.17; H, 7.33; N, 10.44%; Found: C, 66.82; H, 7.41; N, 10.07%.

**Compound 65.** To a stirred degassed solution of 63d (60 mg, 0.19 mmol) in CH₂Cl₂/EtOH (10 mL/10 mL) under Ar was added 10% Pd/C (6 mg, 10% mol.), and the mixture stirred at 25 °C under H₂ (atmospheric pressure). After complete consumption of the starting material (cf. TLC, 48 h), the mixture was filtered through celite, concentrated in vacuo and the crude product purified by flash column chromatography (silica gel, hexane/EtOAc, 80:20) to get 65. Yield: 36 mg (60%); red powder; mp: 157 °C; IR: 2963, 1477 cm⁻¹; ¹H NMR: δ 1.05 (t, J = 7.5 Hz, 6H), 2.33-2.47 (m, 10H), 2.51 (s, 6H), 2.84-2.93 (m, 2H), 3.27-3.36 (m, 2H), 3.80 (s, 3H), 6.85 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H); ¹³C NMR (75 MHz): δ 12.5, 13.7, 14.9, 17.2, 29.8, 36.5, 55.3, 114.1, 114.4, 128.1, 128.8, 130.9, 132.4, 132.7, 135.6, 143.6, 152.4, 158.3; EI-MS (m/z): 438 [M]⁺, 437 [M-1]⁺. Anal. Calcd. for C₂₆H₃₉BF₂N₂O₂: C, 71.24; H, 7.59; N, 6.39%; Found: C, 71.11; H, 7.95; N, 6.18%.

**Compound 66:** A mixture of 63e (120 mg, 0.267 mmol), 62a (72.6 mg, 0.534 mmol), glacial acetic acid (0.150 mL) and piperidine (1 mL) was refluxed in toluene (10 mL) for 4 h. Water
formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus. After the total consumption of the starting material, water (100 mL) was added into it and the reaction mixture was extracted with CHCl₃ (3 × 50 mL). The organic layer was dried and the solvent removed under reduced pressure. Column chromatography of the residue (silica gel, hexane-EtOAc) furnished 13. Yield: 125 mg (82%); green needles (CH₂Cl₂/cyclohexane); mp: > 250 °C; IR: 2929, 2871, 1630, 1479 cm⁻¹; ¹H NMR: δ 1.20 (t, J = 7.4 Hz, 6H), 2.16 (s, 6H), 2.67 (q, J = 7.47 Hz, 4H), 3.85 (s, 6H), 6.74 (d, J = 16.3 Hz, 1H), 6.92 (d, J = 8.7 Hz, 4H), 7.18-7.39 (m, 3H), 7.55-7.77 (m, 8H), 8.25 (d, J = 8.7 Hz, 2H); ¹³C NMR (75 MHz): δ 14.1, 14.2, 18.5, 29.7, 31.9, 55.4, 114.3, 118.0, 124.5, 127.2, 128.2, 128.8, 130.3, 133.9, 135.2, 135.7, 137.3, 150.6, 160.3; EI-MS (m/z): 688 [M+1]⁺, 668 [M-19]⁺. Anal. Calcd. for C₄₁H₄₀BF₅N₃O₄: C, 71.62; H, 5.86; N, 6.11%; Found: C, 71.23; H, 5.98; N, 6.32%.

3.4.3. Photophysical Studies

The absorption and emission spectra of the dyes (~10⁻⁶ M) in CH₂Cl₂ were recorded using a 1 cm quartz cuvette at ambient room temperature (298 ± 1 K). The fluorescence quantum yields (Φₘ) of the dyes 63a-f, 63d', 64 and 65 were measured relative to that of 32 and 21 respectively.

3.4.4. Electrochemical Studies

All the cyclic voltammetry experiments were done in deoxygenated CH₂Cl₂ containing TBAP (0.1 M), and a solute concentration of 1-5 × 10⁻³ M, at 25 °C. The redox potentials were standardized with ferrocene (Fc) as the internal reference and converted to SCE assuming that E₁/₂ (Fc/Fc⁺) = 0.38 V SCE. The error in half-wave potentials is ±10 mV. All waves were monoelectronic unless specified otherwise.