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Distyryl-boradiazaindacenes: facile synthesis of novel near IR emitting fluorophores

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Abstract—Boradiazaindacenes with methyl substituents at 3 and 5 positions were for the first time shown to undergo efficient double condensation reactions with an aromatic aldehyde yielding a series of extended conjugation dyes. These new fluorophores have absorption maxima in the range of 650–660 nm. The dyes reported here have large quantum yields with 20 nm Stokes' shifted emission peaks. The straightforward synthesis of such red shifted BODIPY derivatives is important in relation to the synthesis of novel and useful fluorescent chemosensors. In addition, this facile transformation may make these new fluorophores' building blocks in the construction of large functional supramolecular systems.

1. Introduction

Boradiazaindacenes (a.k.a., BODIPY dyes, BDPs, difluorobora-dipyrromethenes, etc.) are well known[1] fluorescent dyes with many applications, such as fluorescent labeling of biomolecules,[2] ion sensing, and signaling,[3] energy transfer cassettes,[4] light harvesting systems,[5] and fluorescent stains.[6] The parent dye absorbs near 480 nm and emits around 490 nm. While this is satisfactory for many applications, longer wavelength excitability and emission would be highly valuable considering Rayleigh scattering and pigmentation problems in many biological samples.[7] Thus, there have been many attempts[4b,8] to move the peak absorption wavelength to the red end of the visible spectrum, with varying degrees of success. The use of benzo- or naphthopyrroles leading to fused BODIPY's may hamper the solubility to a significant extent. In recent years we and others have shown[3g,9] that the absorption and emission characteristics of boradiazaindacenes can be altered to a great extent by simple condensation reactions of 3,5-dimethylboradiazaindacenes with *p*-dialkylamino substituted aromatic aldehydes. However, only one of the slightly acidic methyl groups was reported to condense to yield monostyryl derivatives. The dyes obtained showed strong charge transfer characteristics with reduced emission quantum yields in polar solvents. Here, we are reporting the first synthesis of doubly styryl substituted boradiazaindacenes (DS-BODIPY's), starting from 3,5-dimethylboradiazaindacene derivatives. The condensation reactions seem not to be limited to dialkylamino substituted aromatic aldehydes, which is an important finding for the broader applicability of the derivatization reaction. The novel alkoxystyryl derivatives have large quantum yields in polar solvents, thus partly demonstrating their potential as fluorescent labels.

2. Results and discussion

The synthesis of the dyes **11**, **13**, and **15** starts with the preparation of the standard BODIPY dyes **5**, **8**, and **9** (Scheme 1). 8-Phenyl- and 8-*tert*-butyloxycarbonylmethoxyphenyl derivatives were synthesized using appropriate aldehydes and purified by a standard work-up. These dyes were then treated with aldehyde **2** under reflux with azeotropic removal of water. In the other compounds, additional bromine substituents were placed as auxochromic groups. The reaction with the aldehyde produced both single and double condensation products, which can be separated by silica gel column chromatography. The presence of *tert*-butyl groups improved organic solubility to a great extent as expected. The absorption spectra of the dyes **10**–**15** were obtained in a polar protic solvent, isopropanol. The spectra are shown in Figure 1. The second styryl group causes a bathochromic shift of about 100 nm. The bromine substitution at the pyrrolic positions results in an additional 11 nm of shift toward the red end of the visible spectrum. These dyes show remarkable red fluorescence even under ambient light. The fluorescence spectra were also obtained in isopropanol. The novel fluorophores had relatively small Stokes' shifts of 15 nm, with

Keywords: DS-BODIPY; BODIPY derivatives; Near IR emitting dyes; Fluorophores; Chromophores.
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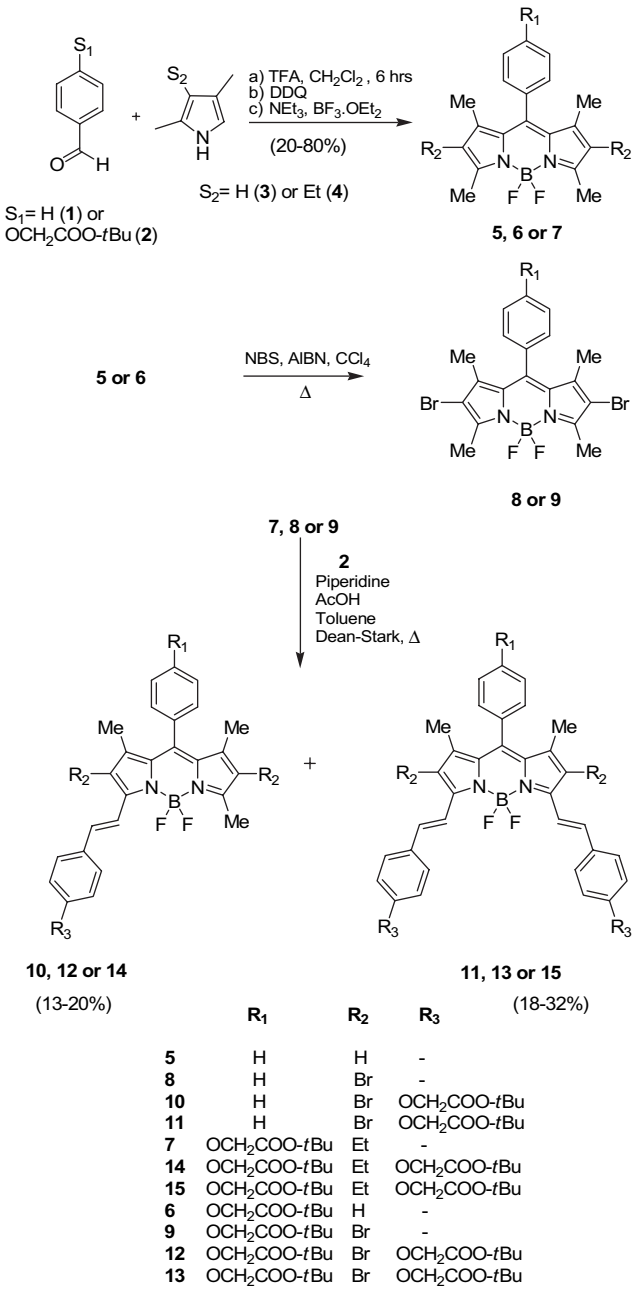

	R_1	R_2	R_3
5	H	H	-
8	H	Br	-
10	H	Br	OCH_2COO-*t*Bu
11	H	Br	OCH_2COO-*t*Bu
7	OCH_2COO-*t*Bu	Et	-
14	OCH_2COO-*t*Bu	Et	OCH_2COO-*t*Bu
15	OCH_2COO-*t*Bu	Et	OCH_2COO-*t*Bu
6	OCH_2COO-*t*Bu	H	-
9	OCH_2COO-*t*Bu	Br	-
12	OCH_2COO-*t*Bu	Br	OCH_2COO-*t*Bu
13	OCH_2COO-*t*Bu	Br	OCH_2COO-*t*Bu

Scheme 1. Synthesis of monostyryl- and distyryl-boradiazaindacene dyes.

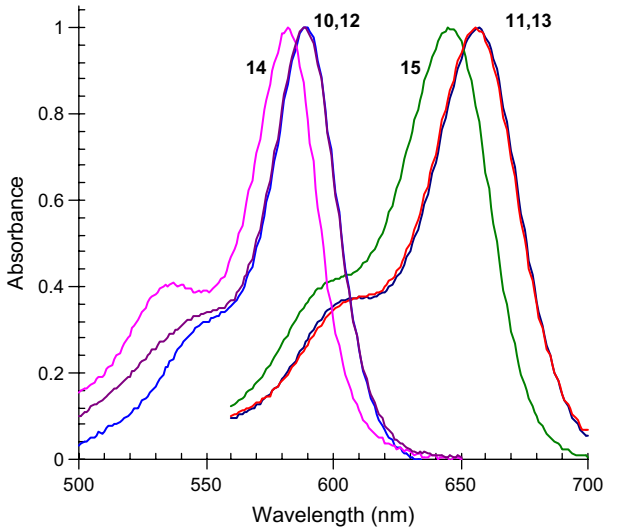

Figure 1. Normalized absorption spectra of extended conjugation BODIPY dyes in isopropanol. Compounds **10**, **12**, and **14** are monostyryl derivatives, whereas, **11**, **13**, and **15** are distyryl compounds.

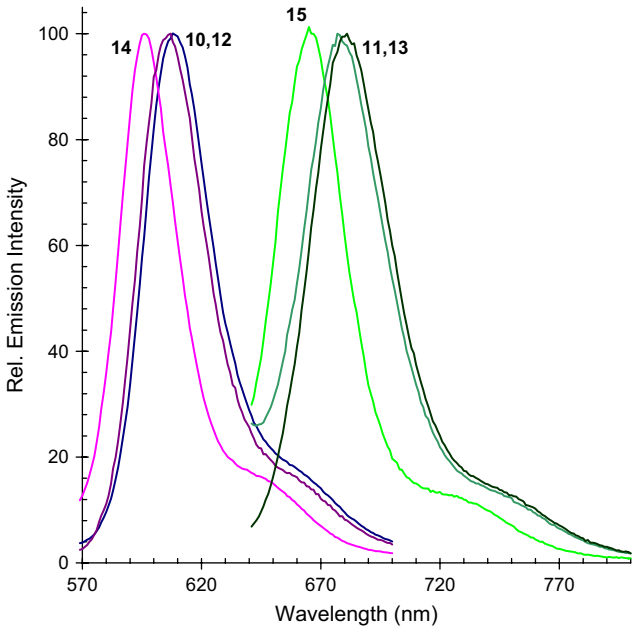

Figure 2. Normalized emission spectra of extended conjugation BODIPY dyes in isopropanol. Compounds **10**, **12**, and **14** are monostyryl derivatives, whereas, **11**, **13**, and **15** are distyryl compounds. The excitation wavelength was 530 nm for the monostyryl dyes and 610 nm for the distyryl dyes. Slit widths were 5 nm.

sharp emission peaks (Fig. 2). Compound **11** had the most red shifted emission peak at 679 nm. More importantly however, the fluorophores had only very little internal charge transfer characteristics; the emission peak position was only slightly moved bathochromically on changing the solvent from toluene to DMSO (Fig. 3). The quantum yield of emission for the dyes **11**, **13**, and **15** was determined using bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine as a reference[10] (Table 1). The extinction coefficients were also very large ($\log \varepsilon$ 4.94–5.00), thus the brightness factor ($\Phi_f \times \varepsilon$) for these novel fluorophores is in fact larger than fluorescein. This straightforward derivatization of parent boradiazaindacene structures to yield near IR emitting dyes is not only important for the development of new biologically relevant fluorescent labels, but also may very well transform these dyes into building blocks in functional supramolecular systems. We are at present investigating such paths for further development.

3. Conclusion

We have synthesized and characterized near IR emitting boradiazaindacene dyes in a very straightforward reaction. This is the first report of the double condensation reaction with 3,5-dimethylboradiazaindacenes. The use of Dean–Stark apparatus seems to be critical in removing any water

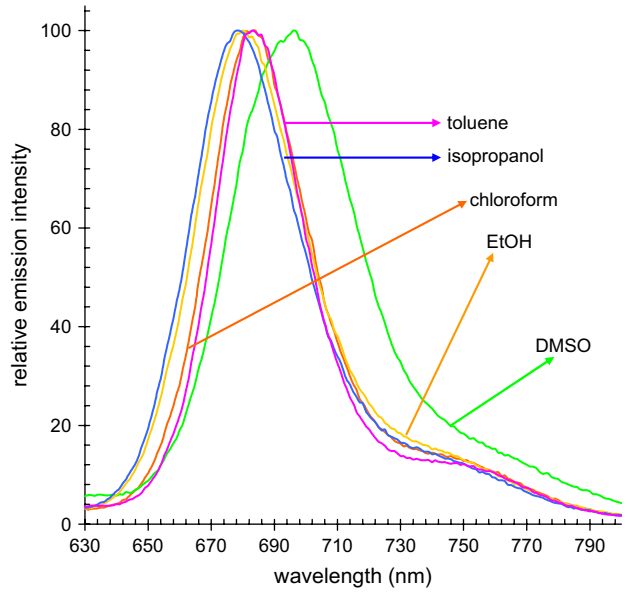

Figure 3. Normalized emission spectra of distyryl-BODIPY dye **13** in solvents of varying polarities. Excitation was at 610 nm with 5 nm slit widths.

Table 1. Selected spectral data of distyryl-BODIPY compounds **11**, **13**, and **15**

Distyryl-BODIPY	**11**	**13**	**15**
λ_{max} (abs, nm)	657	646	656
λ_{max} (em, nm)	679	668	678
fwhm (nm)	41	36	43
ε (M^{-1} cm^{-1})	1.01×10^5	8.85×10^4	8.79×10^4
Φ_{em}	0.42	0.44	0.40

formed in the reaction and thus shifting the equilibrium to the double condensation products, which are the distyrl-BODIPY dyes. The simplicity of the modification would allow facile synthesis of many other BODIPY dyes with desired functional groups. The synthesis has a modular character. The dyes display only a small degree of solvatochromism, this is most likely due to alkoxy group being a weakly electron donor substituent compared to dialkylamino group found in many strong ICT-character chromophores. With the well known advantages of working with red or near IR emitting fluorophores, we have no doubt that this series of boradiazaindacenes will be attractive candidates for practical applications.

4. Experimental

4.1. General

The compounds were characterized and analyzed by Nuclear Magnetic Resonance spectroscopy (NMR), UV–vis spectroscopy, and fluorescence spectroscopy. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra of all compounds were recorded in $CDCl_3$ with Bruker Gmbh DPX-400, 400 MHz High Performance Digital FTNMR Spectrometer. UV–vis spectra were recorded by Varian Bio 100 UV–vis Spectrophotometer. Fluorescence spectra were recorded using Varian Cary Eclipse Fluorescence Spectrophotometer. All solvents were distilled over $CaCl_2$ before use. *tert*-Butyl 2-(4-formylphenoxy)acetate was synthesized according to literature.[11] All chemicals were obtained from Aldrich, unless noted otherwise. Merck Silica Gel 60 F_{254} TLC Aluminum Sheets were used in monitoring reactions by thin layer chromatography. Merck Silica Gel 60 (particle size 0.040–0.0963 mm, 230–400 mesh ASTM) was used in column chromatography.

4.2. Synthesis

4.2.1. 2,6-Dibromo-1,3,5,7-tetramethyl-8-phenyl-4,4′-difluoroboradiazaindacene (8). 8-Phenyl-BODIPY (**5**, 0.33 g, 1.02 mmol), AIBN (0.335 g, 2.04 mmol), and NBS (0.363 g, 2.04 mmol) were refluxed for 30 min in CCl_4 (15 mL). Crude product was then concentrated under vacuum, and purified by silica gel column chromatography (hexane–EtOAc, 3:1). The red colored fraction was collected and the solvent was removed under reduced pressure to yield the desired compound (**5**) (393.3 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): 1.37 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 7.15–7.2 (m, 2H, Ar–H), 7.42–7.48 (m, 3H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$): 153.9, 142.1, 140.6, 134.4, 130.5, 129.5, 129.4, 129.2, 127.8, 28.0, 13.6. Elemental analysis: Found: C, 47.45; H, 3.62; N, 5.99. $C_{19}H_{17}BBr_2F_2N_2$ requires: C, 47.35; H, 3.56; N, 5.81. ESI-MS (*m*/*z*): 482 [M^+].

4.2.2. Monostyryl- and distyryl-BODIPY dyes (10 and 11). Compound **8** (500 mg, 1.037 mmol) and *tert*-butyl 2-(4-formylphenoxy)acetate (**2**, 0.245 g, 1.037 mmol) were refluxed in a mixture of toluene (50 mL), glacial acetic acid (0.77 mL), and piperidine (0.94 mL). Any water formed during the reaction was removed azeotropically by heating overnight in a Dean–Stark apparatus. Crude product was then concentrated under vacuum, and purified by silica gel column chromatography (EtOAc–hexane, 1:4). The blue colored fraction was collected and the solvent was removed under reduced pressure to yield the bright red fluorescent compound **10** (145 mg, 20%).

R_f 0.65. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.29 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 2.56 (s, 3H, CH_3), 4.5 (s, 2H, OCH_2), 6.84 (d, J=8.7 Hz, 2H, C═CH), 7.16–7.22 (m, 2H, Ar–H), 7.42–7.54 (m, 6H, Ar–H), 8.00 (d, J=16.6 Hz, 1H, C═CH).

^{13}C NMR (100 MHz, $CDCl_3$): 167.1, 159.0, 154.0, 148.5, 141.5, 140.6, 140.1, 138.5, 134.6, 131.3, 131.0, 130.5, 129.5, 129.4, 129.1, 128.0, 118.2, 116.3, 115.0, 110.1, 109.7, 82.5, 65.7, 28.0, 13.8, 13.6, 10.6. Elemental analysis: Found: C, 54.71; H, 4.58; N, 3.93. $C_{32}H_{31}BBr_2F_2N_2O_3$ requires: C, 54.89; H, 4.46; N, 4.00. ESI-MS (*m*/*z*): 707 [M^+].

The green colored fraction was collected and the solvent was removed under reduced pressure to yield the distyryl dye **11** (300 mg, 32%).

R_f 0.47. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.37 (s, 6H, CH_3), 1.42 (s, 18H, $C(CH_3)_3$), 4.5 (s, 4H, OCH_2), 6.88

(d, J=8.8 Hz, 4H, C=CH), 7.23 (dd, J=2.1 Hz, J=5.8 Hz, 2H, Ar–H), 7.42–7.47 (m, 3H, Ar–H), 7.51–7.58 (m, 6H, Ar–H), 8.01 (d, J=16.6 Hz, 2H, C=CH).

^{13}C NMR (100 MHz, $CDCl_3$): 168.6, 159.8, 149.3, 141.9, 139.9, 139.5, 135.7, 132.9, 131.4, 130.4, 130.3, 130.2, 129.9, 129.2, 117.3, 115.8, 83.5, 66.5, 29.0, 14.6. Elemental analysis: Found: C, 58.82; H, 5.01; N, 2.98. $C_{45}H_{45}BBr_2F_2N_2O_6$ requires: C, 58.85; H, 4.94; N, 3.05. ESI-MS (m/z): 918 [M^+].

4.2.3. 2,6-Diethyl-1,3,5,7-tetramethyl-8-(4-*tert*-butoxycarbonyl-methyloxyphenyl)-4,4′-difluoroboradiazaindacene (7). 2,4-Dimethyl-3-ethylpyrrole (**4**, 0.81 g, 6.55 mmol) and *tert*-butyl 2-(4-formylphenoxy)acetate (**2**, 0.75 g, 3.18 mmol) were dissolved in absolute CH_2Cl_2 (200 mL) under N_2 atmosphere, one drop of TFA was added and the solution was stirred at rt until TLC analysis showed complete consumption of the aldehyde. At this point, a solution of tetrachlorobenzoquinone (0.81 g, 3.18 mmol) in CH_2Cl_2 (150 mL) was added, stirring was continued for 15 min. Then, Et_3N (10.0 mL) and $BF_3\cdot OEt_2$ (10.0 mL) were added. After stirring for another 12 h, crude product was washed three times with water, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel ($CHCl_3$–MeOH, 96:4) to afford 324 mg (yield: 20%) of **7** in the form of orange needles.

^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (t, J=7.5 Hz, 6H, CH_3), 1.25 (s, 6H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 2.13–2.26 (q, J=7.5 Hz, 4H, CH_2), 4.50 (s, 2H, OCH_2), 6.94 (d, J=8.5 Hz, 2H, Ar–H), 7.1 (d, J=8.5 Hz, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.9, 156.6, 151.8, 138.2, 136.6, 130.9, 129.3, 127.87, 127.0, 113.4, 80.7, 64.1, 26.2, 15.2, 12.8, 10.7, 10.0. Elemental analysis: Found: C, 68.35; H, 7.39; N, 5.40. $C_{29}H_{37}BF_2N_2O_3$ requires: C, 68.24; H, 7.31; N, 5.49. ESI-MS (m/z): 510 [M^+].

4.2.4. Monostyryl- and distyryl-BODIPY dyes (14 and 15). A similar procedure was followed in the synthesis of these monostyryl and distyryl dyes; thus, the BODIPY dye **7** (0.2662 g, 0.5215 mmol) and the aldehyde **2** (0.246 g, 1.043 mmol), piperidine (0.47 mL) and acetic acid (0.39 mL) were used in this reaction. The desired compounds were purified by silica gel column chromatography ($CHCl_3$–hexane, 5:1). The blue colored fraction was collected and the solvent was removed under reduced pressure to yield the monostyryl compound **14** (50 mg, 13%).

R_f 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): 0.92 (t, J=7.3 Hz, 3H, CH_3), 1.04–1.09 (t, J=7.3 Hz, 3H, CH_3), 2.26 (q, 7.5 Hz, 2H, CH_3), 2.50 (s+q, 5H, CH_3+CH_2), 4.46 (s, 2H, OCH_2), 4.52 (s, 2H, OCH_2), 6.84 (d, J=8.5 Hz, 1H, C=CH), 6.94 (d, J=9.6 Hz, 2H, Ar–H), 7.03–7.22 (m, 3H, Ar–H), 7.34 (d, J=6.7 Hz, 1H, Ar–H), 7.48 (d, J=9.6 Hz, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.8, 167.7, 158.5, 158.3, 155.0, 149.2, 139.1, 138.7, 138.5, 134.5, 133.5, 132.8, 132.1, 131.2, 129.7, 128.9, 128.5, 118.4, 115.2, 114.9, 82.5, 82.4, 65.9, 65.8, 28.1, 28.0, 18.3, 17.1, 14.5, 14.1, 12.7, 11.9, 11.5. Elemental analysis: Found: C, 69.34; H, 7.01; N, 3.95. $C_{42}H_{51}BF_2N_2O_6$ requires: C, 69.23; H, 7.05; N, 3.84. ESI-MS (m/z): 728 [M^+].

The green colored fraction was collected and then the solvent was removed under reduced pressure to yield the distyryl compound **15** (90 mg, 18%).

R_f 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): 1.08 (t, J=7.3 Hz, 6H, CH_3), 1.30 (s, 6H), 1.42 (s, 27H, $C(CH_3)_3$), 2.48–2.58 (q, J=7.3 Hz, 4H, CH_2), 4.49 (s, 4H, OCH_2), 4.52 (s, 2H, OCH_2), 6.86 (d, J=8.6 Hz, 2H, Ar–H), 6.95 (d, J=8.5 Hz, 2H, Ar–H), 7.09–7.2 (m, 4H, Ar–H), 7.49 (d, J=8.6 Hz, 4H, Ar–H), 7.59 (d, J=16.7 Hz, 2H, C=CH).

^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 166.7, 157.5, 157.4, 149.4, 137.8, 134.1, 132.6, 132.3, 130.1, 128.9, 128.1, 127.7, 117.6, 114.3, 113.9, 111.3, 81.6, 81.5, 64.9, 64.8, 27.1, 27.0, 17.4, 13.1, 10.7. Elemental analysis: Found: C, 69.88; H, 6.98; N, 2.99. $C_{55}H_{65}BF_2N_2O_9$ requires: C, 69.76; H, 6.92; N, 2.96. ESI-MS (m/z): 946 [M^+].

4.2.5. 1,3,5,7-Tetramethyl-8-(4-*tert*-butoxycarbonyl-methyloxyphenyl)-4,4′-difluoroboradiazaindacene (6). A procedure very similar to the synthesis of compound **7** was applied in the synthesis of this BODIPY dye. Thus, *tert*-butyl 2-(4-formylphenoxy)acetate (**2**, 1.5 g, 6.35 mmol), 2,4-dimethylpyrrole (**3**, 1.25 g, 13.1 mmol), Et_3N (10.0 mL), $BF_3\cdot OEt_2$ (10.0 mL), and 1.62 g of DDQ were used in this reaction. The residue was chromatographed on silica gel ($CHCl_3$–MeOH, 95:5) to afford 0.784 g of compound **6** in the form of orange needles. Yield: 27%.

^{1}H NMR (400 MHz, $CDCl_3$): 1.35 (s, 6H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 2.48 (s, 6H, CH_3), 4.55 (s, 2H, OCH_2), 5.88 (s, 2H, Pyr–H), 6.94 (d, J=8.5 Hz, 2H, Ar–H), 7.10 (d, J=8.5 Hz, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 158.5, 155.3, 143.1, 141.5, 131.8, 129.3, 127.9, 121.2, 115.3, 82.6, 65.8, 61.7, 28.0, 14.5. Elemental analysis: Found: C, 66.17; H, 6.55; N, 6.11. $C_{25}H_{29}BF_2N_2O_3$ requires: C, 66.09; H, 6.43; N, 6.17. FABMS (m/z): 454 [M^+].

4.2.6. 2,6-Dibromo-1,3,5,7-tetramethyl-8-(4-*tert*-butoxycarbonyl-methyloxyphenyl)-4,4′-difluoroboradiazaindacene (9). Compound **6** (0.784 g, 1.73 mmol), AIBN (0.57 g, 3.46 mmol), and NBS (0.616 g, 3.46 mmol) were refluxed for 40 min in CCl_4 (40 mL). Crude product was concentrated under reduced pressure and purified by silica gel column chromatography ($CHCl_3$). The red colored fraction was collected and the solvent was removed under reduced pressure to yield the desired compound (**9**) (761 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (s, 6H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 2.52 (s, 6H, CH_3), 4.52 (s, 2H, OCH_2), 6.96 (d, J=8.5 Hz, 2H, Ar–H), 7.08 (d, J=8.5 Hz, 2H, Ar–H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.5, 158.9, 153.9, 143.0, 140.6, 130.7, 129.2, 127.2, 115.6, 111.7, 82.7, 82.7, 82.6, 68.0, 65.8, 28.0, 13.8. Elemental analysis: Found: C, 49.02; H, 4.49; N, 4.49. $C_{25}H_{27}BBr_2F_2N_2O_3$ requires: C, 49.05; H, 4.45; N, 4.58; O, 7.84. FABMS (m/z): 612 [M^+].

4.2.7. Monostyryl- and distyryl-BODIPY dyes (12 and 13). The applied procedure was very similar to the synthesis of other styryl dyes in this study. The dibromo compound **9** (0.761 g, 1.24 mmol), **2** (0.587 g, 2.49 mmol), piperidine (11.2 mL), and acetic acid (0.93 mL) were used in this reaction. Following the usual work-up, the reaction mixture was purified by silica gel column chromatography ($CHCl_3$–hexane, 5:1). The blue colored fraction was collected and the solvent was removed under reduced pressure to yield the desired compound **12** (0.154 g, 15%).

R_f 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): 1.35 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.47 (s, 18H, $C(CH_3)_3$), 2.58 (s, 3H, CH_3), 4.47 (s, 2H, OCH_2), 4.53 (s, 2H, OCH_2), 6.83 (d, J=8.7 Hz, 2H, Ar–H), 6.98 (d, J=8.5 Hz, 2H, Ar–H), 7.12 (d, J=8.5 Hz, 2H, Ar–H), 7.54–7.45 (m, 3H), 8.1 (d, J=15.5 Hz, 1H, C═CH).

^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 166.5, 159.1, 158.3, 156.2, 148.6, 143.0, 141.5, 138.3, 132.9, 129.5, 128.3, 126.9, 121.0, 115.5, 114.9, 82.7, 80.3, 65.8, 61.5, 39.3, 28.0, 23.2, 13.3. Elemental analysis: Found: C, 54.86; H, 4.88; N, 3.43. $C_{38}H_{41}BBr_2F_2N_2O_6$ requires: C, 54.97; H, 4.98; N, 3.37. ESI-MS (m/z): 830 [M^+].

The green colored fraction was collected and then the solvent was removed under reduced pressure to yield the desired compound **13** (0.248 g, 20%).

R_f 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): 1.39 (s, 6H, CH_3), 1.43 (s, 18H, $OC(CH_3)_3$), 1.50 (s, 9H, $OC(CH_3)_3$), 4.49 (s, 4H, OCH_2), 4.54 (s, 2H, OCH_2), 6.85 (d, J=8.6 Hz, 4H, Ar–H), 6.96 (d, J=8.5 Hz, 2H, Ar–H), 7.11 (d, J=8.6 Hz, 2H, Ar–H), 7.5 (m, 6H), 8.0 (d, J=16.6 Hz, 2H, C═CH).

^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 166.5, 157.9, 157.8, 147.3, 139.9, 137.6, 131.3, 129.5, 128.6, 128.3, 126.7, 115.4, 115.4, 114.5, 113.9, 109.1, 81.7, 81.6, 64.7, 64.6, 27.0, 27.0, 12.9. Elemental analysis: Found: C, 58.46; H, 5.35; N, 2.68. $C_{51}H_{55}BBr_2F_2N_2O_9$ requires: C, 58.42; H, 5.29; N, 2.67. ESI-MS (m/z): 1048 [M^+].

Acknowledgements

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