**Electronic Supplementary Information**

**Tuning the Nonlinear Optical Properties of BODIPYs by Functionalization with Dimethylaminostyryl Substituents**

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**Synthesis**

*(E)-4,4-difluoro-5-(4-(dimethyl)amino)styryl)-1,3,7-trimethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (B1).*

4,4-Difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (650 mg, 2 mmol) and 4-dimethylamino­benzal­­­dehyde (350 mg, 2.3 mmol) were refluxed for 24 h in a mixture of toluene (50 mL), glacial acetic acid (1.5 mL) and piperidine (1.8 mL). Any water formed during the reaction was removed azeotropically by heating in a Dean-Stark apparatus. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography with AcOEt/Hexane (2:1). The blue fraction was collected and recrystallized from CHCl3/cyclohexane to give B1 as deep blue needles (230 mg, 0.50 mmol, 25 %). 1H NMR (300 MHz, CDCl3) *δ* 1.36 (s, 3 H), 1.40 (s, 3 H), 1.45 (s, 3 H), 3.05 (s, 6 H), 5.99 (s, 1 H), 6.62 (s, 1 H), 6.71 (m, 2 H), 7.22 (d, 1 H, *J*=16.3 Hz), 7.30–7.34 (m, 2 H), 7.48–7.54 (m, 6 H); 13C NMR (126 MHz, CDCl3) 157.3, 151.1, 142.4, 138.8, 136.2, 135.7, 131.6, 129.4, 129.2, 129.1, 128.9, 128.2, 125.2, 121.2, 117.5, 116.9, 115.8, 112.6, 40.3, 14.7, 14.6, 14.3. HR-MS (EI, 70 eV): m/z found 456.2452, calcd for [M+H]+ C28H28N3BF2 456.2423. UV-Vis (CH2Cl2) λmax 598 nm.

*(E)-4,4-difluoro-3,5-di-(4-(dimethyl)amino)styryl)-1,7-dimethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (B2).*

The same conditions were applied to 4,4-Difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a, 4a-diaza-*s*-indacene (650 mg, 2 mmol) and 4-dimethylaminobenzaldehyde (760 mg, 5.0 mmol). After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography with AcOEt/Hexane (2:1). The green fraction was collected and recrystallized from CHCl3/cyclohexane to give B2 as black needles (235 mg, 0.4 mmol, 20 %). 1H NMR (300 MHz, CDCl3) *δ* 1.44 (s, 6 H), 3.05 (s, 12 H), 6.62 (s, 2 H), 6.70 (m, 4 H), 7.21 (d, 2 H, *J*=16.3 Hz), 7.28–7.33 (m, 5 H), 7.45–7.55 (m, 6 H); 13C NMR (126 MHz, CDCl3) *δ* 152.7, 150.8, 141.5, 136.8, 135.7, 135.6, 131.9, 129.2, 128.6, 128.4, 125.6, 125.2, 117.8, 115.1, 112.1, 40.3, 14.5. HR-MS (EI, 70 eV): m/z found 587.3152, calcd for [M+H]+ C37H38N4BF2 587.3158. UV-Vis (CH2Cl2) λmax 692 nm.