Supplementary information

α-Bridged BODIPY Oligomers with Switchable Near-IR Photoproperties by External-Stimuli-Induced Foldamer Formation and Disruption

Naoya Sakamoto, Chusaku Ikeda, Masaki Yamamura, Tatsuya Nabeshima*

Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Tsukuba Research Center for Interdisciplinary Material Science (TIMS), University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Contents
1. General
2. Synthesis
3. NMR spectra
4. DFT calculation of B2
5. UV-vis and fluorescence spectra of B1-B5
6. Plot of transition energy (E) against reciprocal number of BODIPY units (1/n)
7. UV-vis titration of B2 and M\(^{+}\)TFPB\(^{-}\) (M = Na, K, Rb, and Cs)
8. Fluorescence titration of B2 and M\(^{+}\)TFPB\(^{-}\) (M = Na, K, Rb, and Cs)
9. UV-vis titration of B3 and M\(^{+}\)TFPB\(^{-}\) (M = Na, K, and Rb)
10. Fluorescence titration of B3 and M\(^{+}\)TFPB\(^{-}\) (M = Na, K, and Cs)
11. NMR titration of B3 and Cs\(^{+}\)TFPB\(^{-}\)
12. ROESY spectrum of B3•Cs\(^{+}\)
13. X-ray crystallographic analysis of B2
14. UV-vis spectra of B1 in the presence of M\(^{+}\)TFPB\(^{-}\) (M = Na, K, Rb, and Cs)
15. \(^1\)H NMR spectra of B1 in the presence of M\(^{+}\)TFPB\(^{-}\) (M = Na, K, Rb, and Cs)
16. Caluculated structure of B3•Cs\(^{+}\)
1. General

All chemicals were reagent grade, and used without further purification. 2,5-dimethylphenyl-1,4-diboronic acid,\(^1\) \textit{N-tert}-butoxycarbonyl-2-bromopyrrole,\(^2\) and 2-(2-methoxyphenyl)pyrrole\(^3\) were prepared as previously reported. All reactions were performed under nitrogen atmosphere. Column chromatography was performed with Kanto Chemical silica gel 60 N (spherical, neutral). Melting points were determined on a Yanaco melting point apparatus and not corrected. \(^1\)H NMR spectra were recorded on a Bruker AC300 spectrometer at 300 MHz, Bruker AV400 spectrometer at 400 MHz, or a Bruker AV600 spectrometer at 600 MHz. \(^13\)C NMR spectra were recorded on a Bruker AV400 spectrometer at 100 MHz. In \(^1\)H and \(^13\)C NMR measurements, tetramethylsilane was used as an internal standard. \(^19\)F NMR spectra were recorded on a Bruker Avance400 spectrometer at 376 MHz. Hexafluorobenzene was used as an external standard (–162 ppm). \(^11\)B NMR spectra were recorded on a Bruker Avance400 spectrometer at 128 MHz. BF\(_3\)•OEt\(_2\) was used as an external standard (0 ppm). UV-Vis spectra were recorded on JASCO V-660 spectrophotometer. Fluorescence spectra and absolute quantum yields were measured on a Hitachi F-4500 spectrometer and a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02, respectively. ESI-TOF mass spectra were recorded on an Applied Biosystems QStar Pulsar \(i\) spectrometer. MALDI-TOF mass spectra were recorded on an AB SCIEX TOF/TOF5800 at Chemical Analysis Center, University of Tsukuba. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba. X-ray crystallographic analysis were performed by Rigaku Mercury CCD diffractometer at Chemical Analysis Center, University of Tsukuba.
2. Synthesis

1,4-bis(N-tert-butoxycarbonyl-1H-pyrrol-2-yl)-2,5-dimethoxybenzene

A 200 mL three-necked flask was charged with 2,5-dimethylphenyl-1,4-diboronic acid (1.35 g, 5.99 mmol), N-tert-butoxycarbonyl-2-bromopyrrole (2.95 g, 12.0 mmol), Na₂CO₃ (2.54 g, 24.0 mmol), and tetrakis(triphenylphosphine)palladium (0.69 g, 0.60 mmol). The flask was evacuated then refilled with nitrogen three times. Degassed toluene (32 mL), degassed methanol (4 mL), and degassed water (6 mL) were added in one portion. The mixture was stirred under nitrogen at 80 °C for 20 h. After cooling, water (50 mL) and ethyl acetate (25 mL) were added and the organic layer was separated. The combined organic layer was washed with water (50 mL), dried over Na₂SO₄, and evaporated. The resulted oil was purified by column chromatography on silica gel using ethyl acetate-hexane (5:95 → 30:70) as eluent to give the title compound (1.04 g, 37%).

White solid, ¹H NMR (300 MHz, CDCl₃) δ 7.35 (dd, J = 3.3, 1.8 Hz, 2H), 6.81 (s, 2H), 6.25 (t, J = 3.3 Hz, 2H), 6.18 (dd, J = 3.3, 1.8 Hz, 2H), 3.71 (s, 6H), 1.39 (s, 18H). Anal. Calcd for C₂₆H₃₂N₂O₆: C, 66.65; H, 6.88; N, 5.98. Found C, 66.43; H, 6.99; N, 5.84.

1,4-bis(1H-pyrrol-2-yl)-2,5-dimethoxybenzene

To a stirred solution of 1,4-bis(N-tert-butoxycarbonyl-1H-pyrrol-2-yl)-2,5-dimethoxybenzene (1.09 g, 2.33 mmol) in THF (30 mL) was added 28% sodium methoxide methanol solution (4.93 g, 25.6 mmol). The reaction mixture was stirred at room temperature for 2 h, diluted with ether (100 mL), and then washed with water (2 × 100 mL) and brine (100 mL). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. From the resulted black oil the title compound (0.48 g, 77%) was obtained by recrystallization from ether-hexane.

Pale purple solid, ¹H NMR (400 MHz, CDCl₃) δ 9.88 (br s, 2H), 7.23 (s, 2H), 6.88-6.86 (m, 2H), 6.61-6.58 (m, 2H), 6.31-6.28 (m, 2H), 3.98 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 129.8, 119.1, 118.0, 110.0, 108.9, 105.7, 56.4. Anal. Calcd for C₁₆H₁₆N₂O₂•0.25H₂O: C, 70.44; H, 6.10; N, 10.27. C, 70.82; H, 5.96; N, 10.19. The ¹H and ¹³C NMR spectra were shown to be identical with reported data.⁴
To a solution containing 2,5-dimethoxy-1,4-bis(pyrrol-2-yl)benzene (0.19 g, 0.70 mmol), 2-(2-methoxyphenyl)pyrrole (0.247 g, 1.43 mmol), and 2,4,6-trimethylbenzaldehyde (0.211 g, 1.42 mmol) in dichloromethane (150 mL) was added a solution of trifluoroacetic acid (100 µL, 1.34 mmol) in dichloromethane (50 mL). The reaction mixture was stirred in dark condition for 18 h and DDQ (0.318 g, 1.46 mmol) was added. After stirred for 1 h, triethylamine (0.2 mL, 1.4 mmol) was added and the reaction mixture was loaded into a short alumina column and eluted with dichloromethane. Eluting bands were collected and evaporated to dryness that was purified by using GPC to give L1 (183 mg, 0.39 mmol, 54%), L2 (85 mg, 0.01 mmol, 14%), L3 (49 mg, 0.04 mmol, 11%), L4 (21 mg, 0.01 mmol, 6%), and L5 (13 mg, 0.007 mmol, 4%).

**L1**: red solid, mp 188-189 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 13.5 (s, 1H), 8.07 (dd, $J$ = 7.6, 1.6 Hz, 2H), 7.30 (td, $J$ = 7.6, 1.6 Hz, 2H), 7.04 (td, $J$ = 7.6, 1.6 Hz, 2H), 7.01 (dd, $J$ = 7.6, 1.6 Hz, 2H), 6.93 (s, 2H), 6.87 (d, $J$ = 4.3 Hz, 2H), 6.41 (d, $J$ = 4.3 Hz, 2H), 3.87 (s, 6H), 2.36 (s, 3H), 2.16 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.3, 151.9, 140.8, 137.9, 137.1, 134.1, 129.6, 129.0, 127.7, 127.1, 122.6, 120.9, 118.3, 111.6, 55.9, 21.1, 20.1. ESI-MS observed m/z 475.3 ([M+H]+), calcd for C$_{32}$H$_{30}$N$_2$O$_2$H m/z 475.2. Anal. Calcd for C$_{32}$H$_{30}$N$_2$O$_2$•0.25H$_2$O: C, 80.22; H, 6.42; N, 5.85. Found: C, 80.34; H, 6.58; N, 5.86.

**L2**: purple solid, mp 203-204 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 13.6 (s, 2H), 8.06 (dd, $J$ = 7.8, 1.6 Hz, 2H), 7.75 (s, 2H), 7.29 (td, $J$ = 7.8, 1.6 Hz, 2H), 7.04-6.90 (m, 10H), 6.89 (d, $J$ = 4.3 Hz, 2H), 6.46 (d, $J$ = 4.2 Hz, 2H), 6.42 (d, $J$ = 4.3 Hz, 2H), 3.92 (s, 6H), 3.86 (s, 6H), 2.38 (s, 3H), 2.18 (s, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.3, 152.3, 151.9, 151.2, 141.8, 140.5, 137.9, 137.2, 137.1, 134.0, 129.7, 128.8, 127.7, 127.6, 126.8, 123.5, 122.5, 121.1, 119.2, 118.1, 112.1, 112.0, 56.7, 56.0, 21.2, 20.2. ESI-MS observed m/z 436.2 ([M+2H]$_2$), calcd for C$_{58}$H$_{54}$N$_4$O$_4$•2H$_2$O: C, 76.80; H, 6.44; N, 6.18. Found: C, 77.09; H, 6.21; N, 6.08.

**L3**: purple solid, mp 226-227 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 13.6 (s, 3H), 8.04 (dd, $J$ = 7.7, 1.5 Hz, 2H), 7.72 (s, 2H), 7.19 (td, $J$ = 7.7, 1.5 Hz, 2H), 7.00-6.85 (m, 16H),...
6.46 (d, \( J = 4.2 \) Hz, 2H), 6.44-6.37 (m, 4H), 3.92 (s, 6H), 3.90 (s, 6H), 3.81 (s, 6H), 2.39 (s, 3H), 2.36 (s, 6H), 2.21 (s, 6H), 2.15 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 157.3, 152.6, 151.9, 151.8, 150.8, 141.1, 141.0, 137.8, 137.7, 137.3, 137.2, 137.1, 134.0, 133.9, 129.9, 128.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.3, 122.5, 121.1, 118.8, 112.4, 112.3, 112.1, 112.0, 56.9, 56.8, 56.7, 55.9, 21.2, 21.2, 20.4, 20.2. ESI-MS observed \( m/z \) 423.2 ([M+3H]\(^3+\)), calcd for C\(_{84}\)H\(_{78}\)N\(_6\)O\(_6\)H\(_3\) \( m/z \) 423.2. Anal. Calcd for C\(_{84}\)H\(_{78}\)N\(_6\)O\(_6\)•3H\(_2\)O: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.22; H, 6.09; N, 6.26.

**L4**: purple solid, mp 245-246 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 13.6 (br, 4H), 8.04 (dd, \( J = 8.0, 1.7 \) Hz, 2H), 7.76 (s, 2H), 7.68 (s, 2H), 7.67 (s, 2H), 7.19 (td, \( J = 8.0, 1.7 \) Hz, 2H), 6.98-6.85 (m, 20H), 6.47 (d, \( J = 4.2 \) Hz, 2H), 6.44-6.37 (m, 6H), 3.90 (s, 6H), 3.89 (s, 6H), 3.84 (s, 6H), 3.81 (s, 6H), 2.38 (s, 6H), 2.37 (s, 6H), 2.18 (s, 12H), 2.16 (s, 12H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 157.3, 152.2, 152.0, 151.8, 142.4, 141.2, 141.1, 137.8, 137.8, 137.3, 137.2, 137.1, 134.0, 133.9, 129.9, 128.8, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 127.2, 126.5, 123.6, 122.5, 121.1, 118.8, 112.4, 112.3, 112.1, 56.9, 56.8, 56.7, 55.9, 21.2, 21.2, 20.4, 20.2. ESI-MS observed \( m/z \) 417.0 ([M+4H]\(^4+\)), calcd for C\(_{110}\)H\(_{102}\)N\(_8\)O\(_8\)H\(_4\) \( m/z \) 417.0. Anal. Calcd for C\(_{110}\)H\(_{102}\)N\(_8\)O\(_8\)•0.5H\(_2\)O: C, 78.97; H, 6.21; N, 6.70. Found: C, 78.99; H, 6.25; N, 6.47.

**L5**: purple solid, mp 258-26 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 13.7 (br, 5H), 8.03 (dd, \( J = 7.8, 1.3 \) Hz, 2H), 7.75 (s, 2H), 7.71 (s, 2H), 7.67 (s, 2H), 7.19 (td, \( J = 7.8, 1.3 \) Hz, 2H), 7.00-6.85 (m, 24H), 6.47 (d, \( J = 4.1 \) Hz, 2H), 6.44-6.38 (m, 8H), 3.89 (s, 6H), 3.86 (s, 6H), 3.85 (s, 6H), 3.81 (s, 6H), 3.80 (s, 6H), 2.40-2.35 (m, 15H), 2.22-2.13 (m, 30H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 157.3, 154.0, 152.0, 151.8, 142.4, 141.2, 141.1, 137.8, 137.8, 137.3, 137.2, 137.1, 134.0, 133.9, 129.9, 128.8, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 127.2, 126.5, 123.6, 122.5, 121.1, 118.8, 112.4, 112.3, 112.1, 56.9, 56.8, 56.7, 55.9, 21.2, 20.2, 20.2. ESI-MS observed \( m/z \) 413.0 ([M+5H]\(^5+\)), calcd for C\(_{136}\)H\(_{126}\)N\(_{10}\)O\(_{10}\) \( m/z \) 413.0. Anal. Calcd for C\(_{136}\)H\(_{126}\)N\(_{10}\)O\(_{10}\)•H\(_2\)O: C, 78.59; H, 6.21; N, 6.74. Found: C, 78.45; H, 6.22; N, 6.54.

To a solution containing **L1** (108 mg, 0.23 mmol) and \( N \)-ethyldiisopropylamine (0.5 mL, 2.9 mmol) in toluene (50 mL) was added boron trifluoride-diethyletherate (0.5 mL, 4.0 mmol). After stirred for 17 h at 80 °C, chloroform (50 mL) was added and washed with water (3 × 50 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered, evaporated to dryness. The obtained residue was purified by column chromatography on silica gel using chloroform as
the eluent to give **B1** (127 mg, >99%).

**B1**: red solid, mp 229-230 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.81 (dd, $J$ = 7.5, 1.7 Hz, 2H), 7.33 (td, $J$ = 7.5, 1.7 Hz, 2H), 7.00 (td, $J$ = 7.5, 1.7 Hz, 2H), 6.97 (s, 2H), 6.91 (dd, $J$ = 7.5, 1.7 Hz, 2H), 6.60 (d, $J$ = 4.2 Hz, 2H), 6.54 (d, $J$ = 4.2 Hz, 2H), 3.77 (s, 6H), 2.38 (s, 3H), 2.23 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.6, 155.2, 143.0, 138.3, 136.9, 135.6, 132.0, 130.6, 130.5, 128.1, 128.0, 122.2, 122.0, 120.3, 110.9, 55.7, 21.2, 20.3.

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 1.23 (t, $J_{BF}$ = 31 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ –135.6 (q, $J_{FB}$ = 31 Hz, 2F).

MALDI TOF-MS observed $m/z$ 522.6 ([M]$^+$), calcd for C$_{32}$H$_{29}$BF$_2$N$_2$O$_2$ $m/z$ 522.2. Anal. Calcd for C$_{32}$H$_{29}$BF$_2$N$_2$O$_2$: C, 73.35; H, 5.60; N, 5.36. Found: C, 73.42; H, 5.72; N, 5.27.

To a solution containing L2 (49 mg, 0.06 mmol) and N-ethyldiisopropylamine (1.0 mL, 5.8 mmol) in toluene (20 mL) was added boron trifluoride-diethyletherate (1.0 mL, 8.0 mmol). After stirred for 7 h at 80 °C, chloroform (50 mL) was added and washed with water (3 × 50 mL). The organic phase was dried over Na$_2$SO$_4$, filtered, evaporated to dryness. The obtained residue was purified by column chromatography on silica gel using ethyl acetate/n-hexane (3:7) as the eluent to give **B2** (35 mg, 63%).

**B2**: blue solid, mp > 300 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, $J$ = 7.5, 1.6 Hz, 2H), 7.67 (s, 2H), 7.35 (td, $J$ = 7.5, 1.6 Hz, 2H), 7.00 (td, $J$ = 7.5, 1.6 Hz, 2H), 6.97 (s, 4H), 6.93 (dd, $J$ = 7.5, 1.6 Hz, 2H), 6.77 (d, $J$ = 4.4 Hz, 2H), 6.61-6.58 (m, 4H), 6.54 (d, $J$ = 4.2 Hz, 2H), 3.77 (s, 6H), 3.76 (s, 6H), 2.38 (s, 6H), 2.22 (s, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.6, 154.8, 154.6, 151.3, 142.6, 138.3, 136.9, 136.1, 135.5, 131.9, 130.6, 130.6, 128.3, 128.0, 127.9, 123.2, 122.8, 122.2, 122.0, 120.0, 115.0, 111.0, 56.1, 55.8, 21.2, 20.3. $^{11}$B NMR (128 MHz, CDCl$_3$) δ 1.39 (t, $J_{BF}$ = 32 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ –134.4 (q, $J_{FB}$ = 32 Hz, 4F). MALDI TOF-MS observed $m/z$ 966.3 ([M]$^+$), calcd for C$_{58}$H$_{52}$B$_2$F$_4$N$_4$O$_4$ $m/z$ 966.4. Anal. Calcd for C$_{58}$H$_{52}$B$_2$F$_4$N$_4$O$_4$: C, 72.06; H, 5.42; N, 5.80. Found: C, 71.89; H, 5.55; N, 5.76.
To a solution containing L3 (85 mg, 0.07 mmol) and N-ethyl-diisopropylamine (0.5 mL, 2.9 mmol) in toluene (30 mL) was added boron trifluoride-diethyletherate (0.2 mL, 1.6 mmol). After stirred for 2 h at 80 °C, ethyl acetate (50 mL) was added and washed with water (3 × 100 mL). The organic phase was dried over Na₂SO₄, filtered, evaporated to dryness. The obtained residue was purified by column chromatography on silica gel using ethyl acetate/n-hexane (3:7) as the eluent to give B₃ (57 mg, 60%).

B₃: blue solid, mp > 300 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 7.9, 1.8 Hz, 2H), 7.68 (s, 2H), 7.63 (s, 2H), 7.34 (td, J = 7.9, 1.8 Hz, 2H), 6.99 (td, J = 7.9, 1.8 Hz, 2H), 6.97 (s, 2H), 6.97 (s, 4H), 6.92 (dd, J = 7.9, 1.8 Hz, 2H), 6.78 (d, J = 4.4 Hz, 2H), 6.73 (d, J = 4.2 Hz, 2H), 6.61-6.57 (m, 6H), 6.53 (d, J = 4.2 Hz, 2H), 3.76 (s, 6H), 3.76 (s, 6H), 3.74 (s, 6H), 2.38 (s, 3H), 2.38 (s, 6H), 2.22 (s, 6H), 2.22 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 154.9, 154.6, 154.4, 151.3, 151.2, 142.6, 142.3, 138.3, 138.0, 136.0, 136.0, 131.9, 130.6, 130.6, 128.3, 128.1, 128.0, 127.9, 123.2, 123.2, 123.1, 122.9, 122.1, 120.0, 115.1, 114.8, 111.0, 56.2, 56.0, 55.7, 21.2, 20.2. ¹¹B NMR (128 MHz, CDCl₃)  δ 1.48 (t, JBF = 32 Hz), 1.38 (t, JBF = 32 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ –133.3 (q, JFB = 32 Hz, 2F), –134.4 (q, JFB = 32 Hz, 4F). MALDI TOF-MS observed m/z 1410.4 ([M⁺]), calcd for C₈₄H₇₅B₃F₆N₆O₆ m/z 1410.6. Anal. Calcd for C₈₄H₇₅B₃F₆N₆O₆: C, 71.50; H, 5.36; N, 5.96. Found: C, 71.36; H, 5.56; N, 5.75.

To a solution containing L4 (5 mg, 0.003 mmol) and N-ethyl-diisopropylamine (0.5 mL, 2.9 mmol) in toluene (10 mL) was added boron trifluoride-diethyletherate (0.1 mL, 0.8 mmol). After stirred for 2 h at 80 °C, the solvent was evaporated. The obtained residue was purified by column chromatography on silica gel using chloroform as the eluent to give B₄ (2.6 mg,
46%).

**B4**: blue solid, mp > 300 °C, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 8.4$, 1.7 Hz, 2H), 7.68 (s, 2H), 7.65 (s, 2H), 7.63 (s, 2H), 7.34 (td, $J = 8.4$, 1.7 Hz, 2H), 6.99 (td, $J = 8.4$, 1.7 Hz, 2H), 6.97 (s, 4H), 6.97 (s, 4H), 6.92 (dd, $J = 8.4$, 1.7 Hz, 2H), 6.76 (d, $J = 4.3$ Hz, 2H), 6.74 (d, $J = 4.4$ Hz, 2H), 6.73 ($J = 4.4$ Hz, 2H), 6.60-6.57 (m, 8H), 6.53 (d, $J = 4.2$ Hz, 2H), 3.76 (s, 2H), 3.76 (s, 2H), 3.75 (s, 2H), 3.74 (s, 2H), 2.38 (s, 6H), 2.38 (s, 6H), 2.22 (s, 12H), 2.22 (s, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6, 154.9, 154.6, 151.3, 151.2, 151.2, 142.6, 138.3, 136.9, 136.0, 135.5, 131.9, 130.6, 128.3, 128.0, 127.9, 123.1, 123.0, 122.9, 122.1, 120.0, 114.8, 111.0, 56.2, 56.1, 56.0, 55.7, 21.2, 20.2. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 1.48 (t, $J_{BF} = 32$ Hz), 1.38 (t, $J_{BF} = 32$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -133.2 - -133.6 (m, 4F), -134.4 (q, $J_{FB} = 32$ Hz, 4F). MALDI TOF-MS observed m/z 1854.6 ([M$^+$]), calcd for C$_{110}$H$_{98}$B$_4$F$_8$N$_8$O$_8$ m/z 1854.8. Anal. Calcd for C$_{110}$H$_{98}$B$_4$F$_8$N$_8$O$_8$·CH$_2$Cl$_2$·3C$_6$H$_{14}$: C, 70.47; H, 6.51; N, 5.10. Found: C, 70.66; H, 6.28; N, 4.99.

To a solution containing L5 (9 mg, 0.004 mmol) and $N$-ethylisopropylamine (0.5 mL, 2.9 mmol) in toluene (10 mL) was added boron trifluoride-diethyletherate (0.1 mL, 0.8 mmol). After stirred for 2 h at 80 °C, the solvent was evaporated. The obtained residue was purified by column chromatography on silica gel using chloroform as the eluent to give **B5** (3.1 mg, 31%).

**B5**: blue solid, mp > 300 °C, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (dd, $J = 7.5$, 1.6 Hz, 2H), 7.67 (s, 2H), 7.64 (s, 2H), 7.64 (s, 2H), 7.63 (s, 2H), 7.34 (td, $J = 7.5$, 1.6 Hz, 2H), 6.99 (td, $J = 7.5$, 1.6 Hz, 2H), 6.97 (s, 2H), 6.97 (s, 2H), 6.97 (s, 4H), 6.97 (s, 4H), 6.91 (dd, $J = 7.5$, 1.6 Hz, 2H), 6.77-6.71 (m, 8H), 6.60-6.56 (m, 10H), 6.53 d, $J = 4.2$ Hz, 2H), 3.76 (s, 6H), 3.76 (s, 6H), 3.75 (s, 6H), 3.74 (s, 6H), 3.73 (s, 6H), 2.38 (s, 3H), 2.38 (s, 6H), 2.38 (s, 6H), 2.21 (s, 6H), 2.21 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6, 154.9, 154.5, 151.3, 151.2, 151.2, 142.3, 138.3, 136.9, 136.0, 135.6, 130.6, 128.3, 128.1, 128.1, 128.0, 123.1, 123.1, 123.0, 122.9, 122.1, 120.0, 111.0, 56.2, 56.1, 56.1, 56.0, 55.7, 21.2, 20.2. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 1.8-1.0 (m). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -133.2 - -133.7 (m, 6F), -134.4 (q, $J_{FB} = 32$ Hz, 4F). MALDI TOF-MS observed m/z 2298.7 ([M$^+$]), calcd for
$C_{136}H_{121}B_5F_{10}N_{10}O_{10}$ m/z 2299.0. Anal. Calcd for $C_{136}H_{121}B_5F_{10}N_{10}O_{10} \cdot CH_2Cl_2 \cdot 2C_6H_{14}$: C, 69.99; H, 5.95; N, 5.48. Found: C, 69.95; H, 5.71; N, 5.50.
3. NMR spectra

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of L1.

Figure S2. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of L2.
**Figure S3.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of L3.

**Figure S4.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of L4.
**Figure S5.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of L5. Asterisks denote residual solvents.

**Figure S6.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of B1.
Figure S7. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of B2.

Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of B3.
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of B4. Asterisk denotes impurity.

Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of B5. Asterisk denotes impurity.
Figure S11. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of BODIPY oligomers.
4. DFT calculation of B2

Figure S12. Diagram of calculated orbital energy level for B1 and B2 calculated at B3LYP/6-31G* level.

5. UV-vis and fluorescence spectra of B1-B5

Figure S13. (a) Normalized UV-vis spectra and (b) fluorescence spectra of B1-B5 recorded in CHCl₃. λ_ex = λ_abs.
6. Plot of transition energy ($E$) against reciprocal number of BODIPY units ($1/n$)

![Plot of transition energy ($E$) against reciprocal number of BODIPY units ($1/n$).](image)

Figure S14. Plot of transition energy ($E$) obtained fluorescence spectra against reciprocal number of BODIPY units ($1/n$).

7. UV-vis titration of B2 and $M^+\text{TFPB}^-$ ($M = \text{Na, K, Rb, and Cs}$)

(a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB: $[\text{B2}] = 10 \mu\text{M}, 0 < [M^+]/[\text{B2}] < 500$, CHCl$_3$/CH$_3$OH (10:1).

![UV-vis spectral changes of B2 upon addition of (a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB.](image)

Figure S15. UV-vis spectral changes of B2 upon addition of (a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB: $[\text{B2}] = 10 \mu\text{M}, 0 < [M^+]/[\text{B2}] < 500$, CHCl$_3$/CH$_3$OH (10:1).
8. Fluorescence titration of B2 and M⁺TFPB⁻ (M = K, Rb, and Cs)

Figure S16. Fluorescence spectral changes of B2 upon addition of (a) CsTFPB, (b) RbTFPB, or (c) KTFPB: [B2] = 1.0 μM, 0 < [M⁺]/[B2] < 1000, CHCl₃/CH₃OH (10:1), λₑₓ = 550 nm.
9. UV-vis titration of B3 and M⁺TFPB⁻ (M = Na, K, and Rb)

![Graph](image)

**Figure S17.** UV-vis spectral changes of B3 upon addition of (a) RbTFPB, (b) KTFPB, or (c) NaTFPB: [B3] = 10 µM, 0 < [Rb⁺]/[B3] < 50, 0 < [K⁺]/[B3] < 100, 0 < [Na⁺]/[B3] < 200, CHCl₃/CH₃OH (10:1).
Fluorescence titration of B3 and M\(^+\)TFPB \((M = \text{Na, K, Rb, and Cs})\)

**Figure S18.** Fluorescence spectral changes of B3 upon addition of (a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB: \([\text{B3}] = 1.0 \mu\text{M}, 0 < [\text{Cs}^+] / [\text{B3}] < 100, 0 < [\text{Rb}^+] / [\text{B3}] < 500, 0 < [\text{K}^+] / [\text{B3}] < 1000, 0 < [\text{Na}^+] / [\text{B3}] < 10000, \text{CHCl}_3/\text{CH}_3\text{OH} (10:1).\)
11. NMR titration of B3 and Cs⁺TFPB⁻

**Figure S19** ¹H NMR (600 MHz, CDCl₃-CD₃OD(10:1)) spectral changes of B3 upon addition of CsTFPB. Asterisks denote residual solvents.
Figure S20. $^{19}$F NMR (376 MHz, CDCl$_3$-CD$_3$OD(10:1)) spectral changes of B3 upon addition of CsTFPB.

Figure S21. $^{11}$B NMR (128 MHz, CDCl$_3$-CD$_3$OD(10:1)) spectral changes of B3 upon addition of CsTFPB.
12. ROESY spectrum of B3•Cs⁺

Figure S22. ROESY (600 MHz, CD₂Cl₂-CD₃OD(10:1)) spectrum of B3•Cs⁺.
13. X-ray crystallographic analysis of B2

The single crystals of B2 were obtained by recrystallization of B2 from dichloromethane/n-hexane. X-ray diffraction data for single crystal of B2 were collected on a CCD area-detector diffractometer at 100 K with monochromatic MoKα radiation (λ = 0.71073 Å), and yielded reflections was merged after multi-scan absorption correction (Sheldrick, G. M. SADABS. University of Göttingen: Göttingen, Germany, 1997). The structure was solved by dual methods using SHELX-97 (Sheldrick, G. M. SHELX-97: Program for the Solution and Refinement of Crystal Structures; Universität Göttingen: Göttingen, Germany, 1997) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically with reflection weights using SHELX-97.

Crystal data for B2·2CH2Cl2: C60H56B2Cl4F4N4O4, monoclinic, P21/c, a = 15.0748(14), b = 9.8130(9), c = 20.2660(18) Å, β = 110.9900(10)°, V = 2799.0(4) Å³, MW = 1136.51, Z = 2, Dcalc = 1.348 g/cm³, 31126 measured, 6427 independent, GOF = 1.050, R1[I > 2σ(I)] = 0.0571, wR2(all data) = 0.1405.

CCDC 841547 contains the supplementary crystallographic data for this paper, which can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
14. UV-vis spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (M = Na, K, Rb, and Cs)

![UV-vis spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (M = Na, K, Rb, and Cs)](image)

**Figure S23.** UV-vis spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (500 eq.).

15. \(^1\)H NMR spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (M = Na, K, Rb, and Cs)

![\(^1\)H NMR spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (M = Na, K, Rb, and Cs)](image)

**Figure S24.** \(^1\)H NMR spectra of B1 in the presence of M\(^+\)TFPB\(^-\) (10 eq.).
16. Calculated structure of B3•Cs⁺

![Calculated structure of B3•Cs⁺ at the 3-21G level: (a,c) top view; (b,d) side view; (c,d) B3 was displayed as stick model. Mesityl groups are omitted for clarity. Color: C, sky blue; H, white; B, orange; F, green; N, blue; O, red; Cs, purple.](image)

**Figure S25.** Calculated structure of B3•Cs⁺ at the 3-21G level: (a,c) top view; (b,d) side view; (c,d) B3 was displayed as stick model. Mesityl groups are omitted for clarity. Color: C, sky blue; H, white; B, orange; F, green; N, blue; O, red; Cs, purple.

**References**

(5) Spartan08 for Windows; Wavefunction, Inc.: Irvine, CA.