Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information

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

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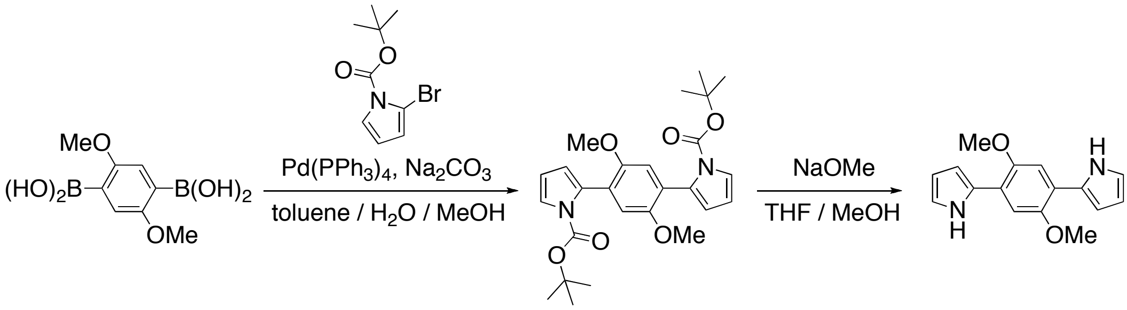
Contents

1. General

All chemicals were reagent grade, and used without further purification. 2,5-dimethylphenyl-1,4-diboronic acid,[1] *N*-*tert*-buthoxycarbonyl-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*-buthoxycarbonyl-*1H*-pyrrol-2-yl)-2,5-dimethoxybenzene

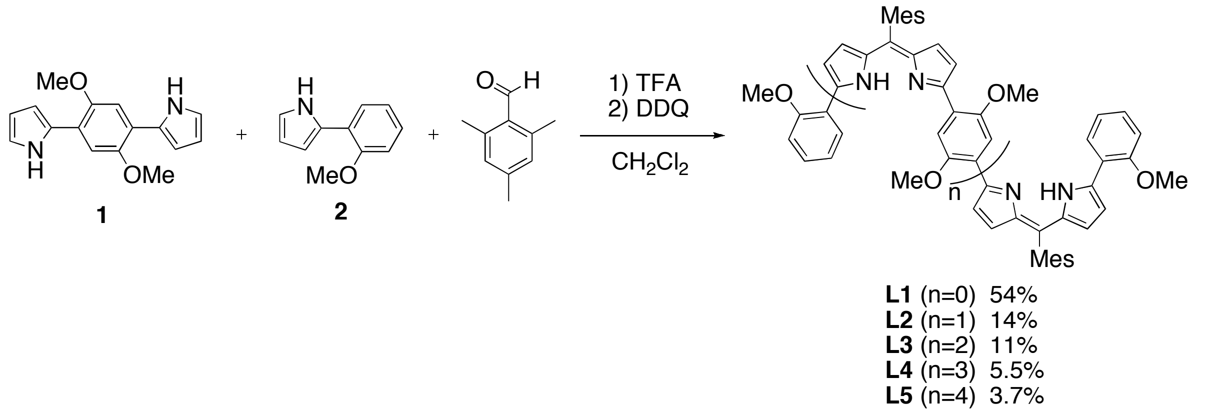
A 200 mL three-necked flask was charged with 2,5-dimethylphenyl-1,4-diboronic acid (1.35 g, 5.99 mmol), *N-tert*-buthoxycarbonyl-2-bromopyrrole (2.95 g, 12.0 mmol), Na_2CO_3 (2.54 g, 24.0 mmol), and tetrakis(triphenylphosphine)palladium (0.69 g, 0.60 mmol). The flask was evacuated then refilled with 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 Na_2SO_4, 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, ^{1}H NMR (300 MHz, $CDCl_3$) 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 $C_{26}H_{32}N_2O_6$: 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*-buthoxycarbonyl-*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 mixuture 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 Na_2SO_4 and concentrated in vacuo. From the resulted black oil the title compound (0.48 g, 77%) was obtained by recrystalization from ether-hexane.

Pale purple solid, ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 129.8, 119.1, 118.0, 110.0, 108.9, 105.7, 56.4. Anal. Calcd for $C_{16}H_{16}N_2O_2$•$0.25H_2O$: C, 70.44; H, 6.10; N, 10.27. C, 70.82; H, 5.96; N, 10.19. The ^{1}H and ^{13}C 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%).

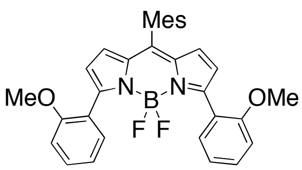
L1: red solid, mp 188-189 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.5 (s, 1H), 8.07 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.30 (td, *J* = 7.6, 1.6 Hz, 2H), 7.04 (td, *J* = 7.6, 1.6 Hz, 2H), 7.01 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.93 (s, 2H), 6.87 (d, *J* = 4.3 Hz, 2H), 6.41 (d, *J* = 4.3 Hz, 2H), 3.87 (s, 6H), 2.36 (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 $C_{32}H_{30}N_2O_2H$ *m/z* 475.2. Anal. Calcd for $C_{32}H_{30}N_2O_2$•$0.25H_2O$: 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, 6H), 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 $C_{58}H_{54}N_4O_4H_2$ *m/z* 436.2. Anal. Calcd for $C_{58}H_{54}N_4O_4$•$2H_2O$: 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), 7.71 (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, $CDCl_3$) δ 157.3, 152.6, 151.9, 151.8, 150.8, 141.5, 141.3, 141.1, 137.8, 137.7, 137.3, 137.2, 137.1, 137.1, 134.0, 133.9, 129.9, 128.8, 127.8, 127.7, 127.4, 127.2, 127.0, 123.4, 123.3, 122.6, 121.1, 119.0, 118.7, 118.6, 112.2, 112.1, 56.8, 56.7, 55.9, 21.2, 21.2, 20.2, 20.2. ESI-MS observed *m/z* 423.2 ($[M+3H]^{3+}$), calcd for $C_{84}H_{78}N_6O_6H_3$ *m/z* 423.2. Anal. Calcd for $C_{84}H_{78}N_6O_6$•$3H_2O$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.22; H, 6.09; N, 6.26.

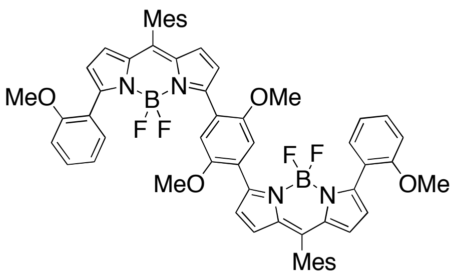
L4: purple solid, mp 245-246 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.6 (br, 4H), 8.04 (dd, J = 8.0, 1.7 Hz, 2H), 7.76 (s, 2H) , 7.68 (s, 2H), 7.67 (s, 2H), 7.19 (td, J = 8.0, 1.7 Hz, 2H), 6.98-6.85 (m, 20H), 6.47 (d, J = 4.2 Hz, 2H), 6.44-6.37 (m, 6H), 3.90 (s, 6H), 3.89 (s, 6H), 3.84 (s, 6H), 3.81 (s, 6H), 2.38 (s, 6H), 2.37 (s, 6H), 2.18 (s, 12H), 2.16 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, 127.3, 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* 417.0 ($[M+4H]^{4+}$), calcd for $C_{110}H_{102}N_8O_8H_4$ *m/z* 417.0. Anal. Calcd for $C_{110}H_{102}N_8O_8$•$0.5H_2O$: C, 78.97; H, 6.21; N, 6.70. Found: C, 78.99; H, 6.25; N, 6.47.

L5: purple solid, mp 258-259 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 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), 7.63 (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), 3.87 (s, 6H), 3.86 (s, 6H), 3.85 (s, 6H), 3.81 (s, 6H), 2.40-2.35 (m, 15H), 2.22-2.13 (m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 154.0, 152.0, 144.2, 138.4, 137.8, 137.3, 137.2, 137.1, 137.1, 134.0, 133.9, 129.8, 128.8, 127.8, 127.7, 127.2, 127.1, 123.6, 122.6, 121.0, 118.8, 118.7, 112.5, 112.3, 112.0, 56.9, 56.8, 56.7, 55.9, 21.1, 20.2, 20.2. ESI-MS observed *m/z* 413.0 ($[M+5H]^{5+}$), calcd for $C_{136}H_{126}N_{10}O_{10}H_5$ *m/z* 413.0. Anal. Calcd for $C_{136}H_{126}N_{10}O_{10}$•$H_2O$: C, 78.59; H, 6.21; N, 6.74. Found: C, 78.45; H, 6.22; N, 6.54.



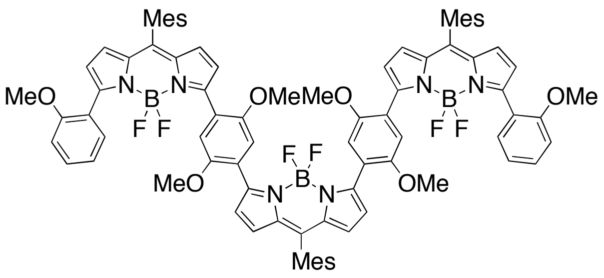
To a solution containing **L1** (108 mg, 0.23 mmol) and *N*-ethyldiisopropylamine (0.5 mL, 2.9 mmol) in toluene (50 mL) was added boron trifluoride-diethyletherate (0.5 mL, 4.0 mmol). After stirred for 17 h at 80 °C, chloroform (50 mL) was added and washed with water (3 × 50 mL). The organic phase was dried over Na_2SO_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 $C_{32}H_{29}BF_2N_2O_2$ *m/z* 522.2. Anal. Calcd for $C_{32}H_{29}BF_2N_2O_2$: C, 73.57; H, 5.60; N, 5.36. Found: C, 73.42; H, 5.72; N, 5.27.



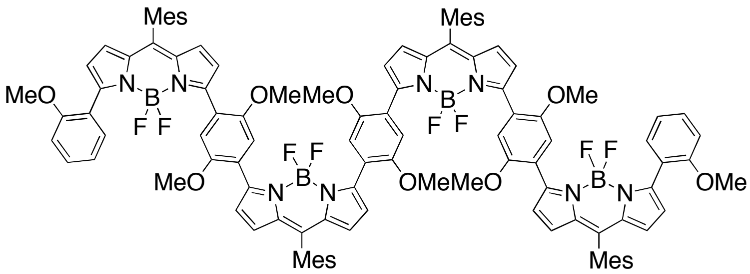
To a solution containing **L2** (49 mg, 0.06 mmol) and *N*-ethyldiisopropylamine (1.0 mL, 5.8 mmol) in toluene (20 mL) was added boron trifluoride-diethyletherate (1.0 mL, 8.0 mmol). After stirred for 7 h at 80 °C, chloroform (50 mL) was added and washed with water (3 × 50 mL). The organic phase was dried over Na_2SO_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 $C_{58}H_{52}B_2F_4N_4O_4$ *m/z* 966.4. Anal. Calcd for $C_{58}H_{52}B_2F_4N_4O_4$: C, 72.06; H, 5.42; N, 5.80. Found: C, 71.89; H, 5.55; N, 5.76.



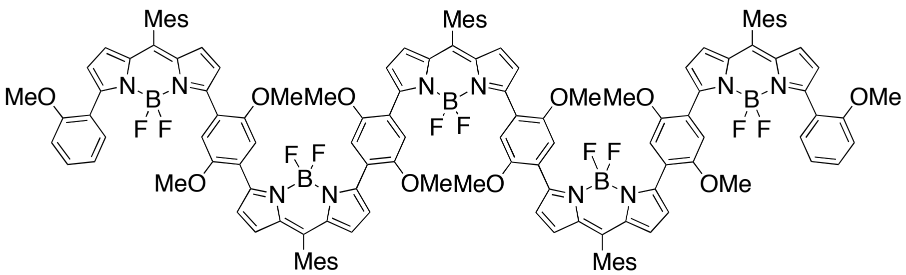
To a solution containing **L3** (85 mg, 0.07 mmol) and *N*-ethyldiisopropylamine (0.5 mL, 2.9 mmol) in toluene (30 mL) was added boron trifluoride-diethyletherate (0.2 mL, 1.6 mmol). After stirred for 2 h at 80 °C, ethyl acetate (50 mL) was added and washed with water (3 × 100 mL). The organic phase was dried over Na_2SO_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 **B3** (57 mg, 60%).

B3: blue solid, mp > 300 °C, ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 154.9, 154.6, 154.4, 151.3, 151.2, 142.6, 142.3, 138.3, 137.0, 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. ^{11}B NMR (128 MHz, $CDCl_3$) δ 1.48 (t, J_{BF} = 32 Hz), 1.38 (t, J_{BF} = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –133.3 (q, J_{FB} = 32 Hz, 2F), –134.4 (q, J_{FB} = 32 Hz, 4F). MALDI TOF-MS observed *m/z* 1410.4 ($[M]^+$), calcd for $C_{84}H_{75}B_3F_6N_6O_6$ *m/z* 1410.6. Anal. Calcd for $C_{84}H_{75}B_3F_6N_6O_6$: 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*-ethyldiisopropylamine (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, $CDCl_3$) δ 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, 6H), 3.76 (s, 6H), 3.75 (s, 6H), 3.74 (s, 6H), 2.38 (s, 6H), 2.38 (s, 6H), 2.22 (s, 12H), 2.22 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 1.48 (t, J_{BF} = 32 Hz), 1.38 (t, J_{BF} = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –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 $C_{110}H_{98}B_4F_8N_8O_8$ *m/z* 1854.8. Anal. Calcd for $C_{110}H_{98}B_4F_8N_8O_8 \bullet CH_2Cl_2 \bullet 3C_6H_{14}$: 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*-ethyldiisopropylamine (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, $CDCl_3$) δ 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, 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), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 1.8-1.0 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ –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 $C_{136}H_{121}B_5F_{10}N_{10}O_{10}$•$CH_2Cl_2$•$2C_6H_{14}$: C, 69.99; H, 5.95; N, 5.48. Found: C, 69.95; H, 5.71; N, 5.50.

3. NMR spectra

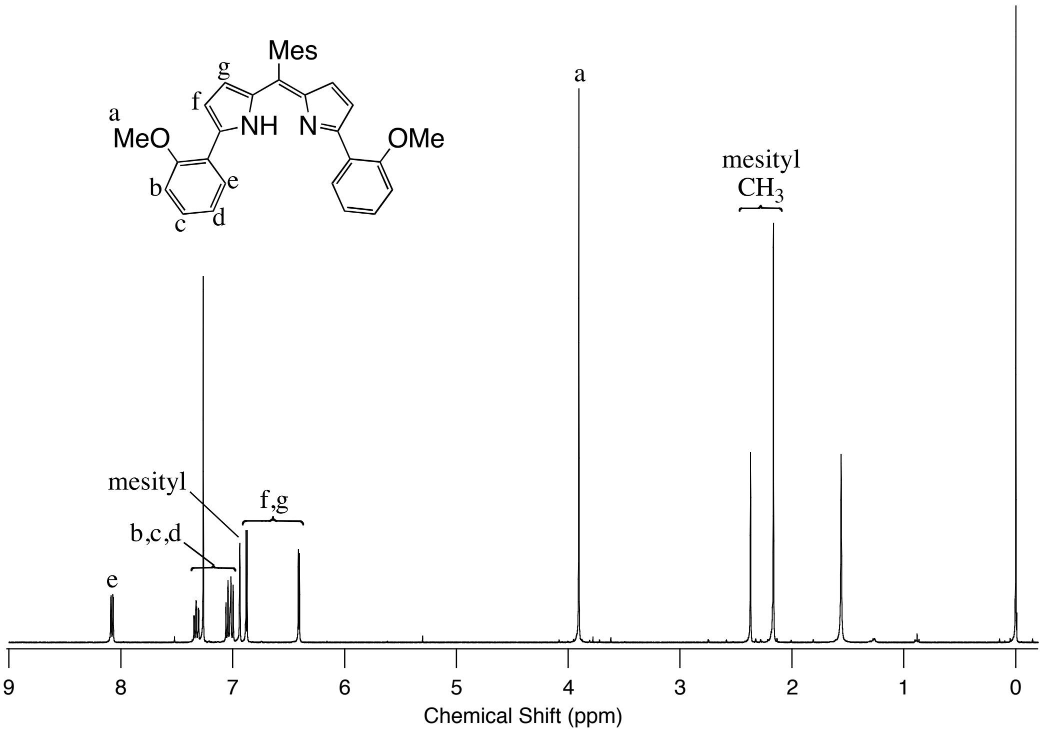


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L1**.

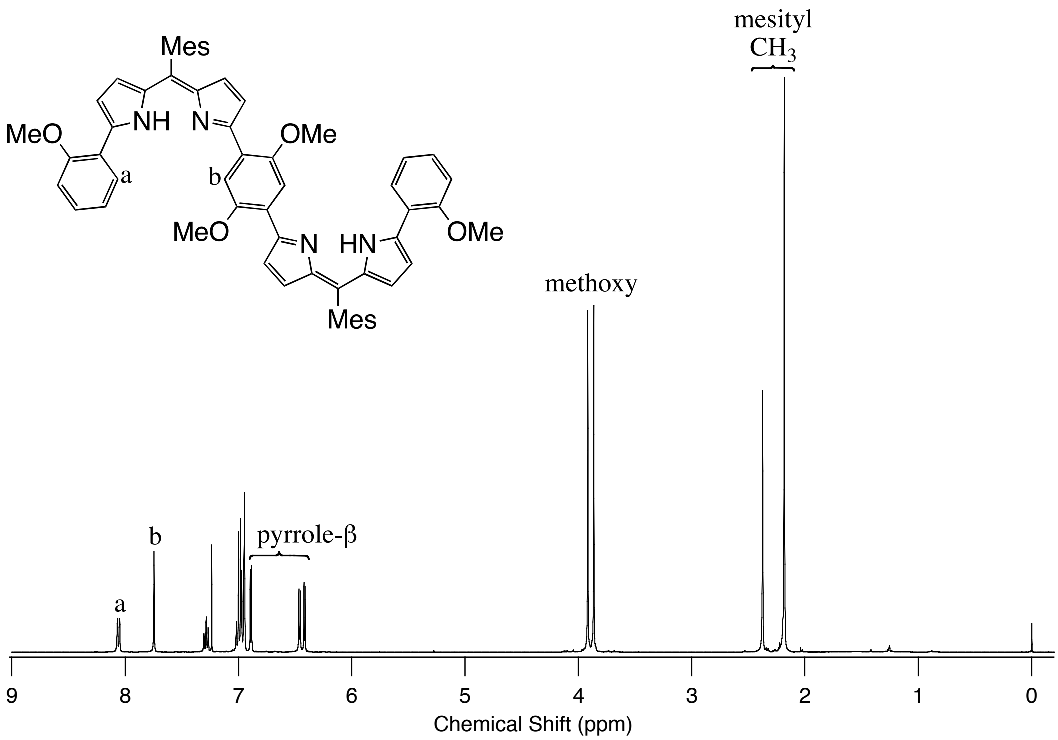


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L2**.

Electronic Supplementary Material (ESI) for Chemical Communications

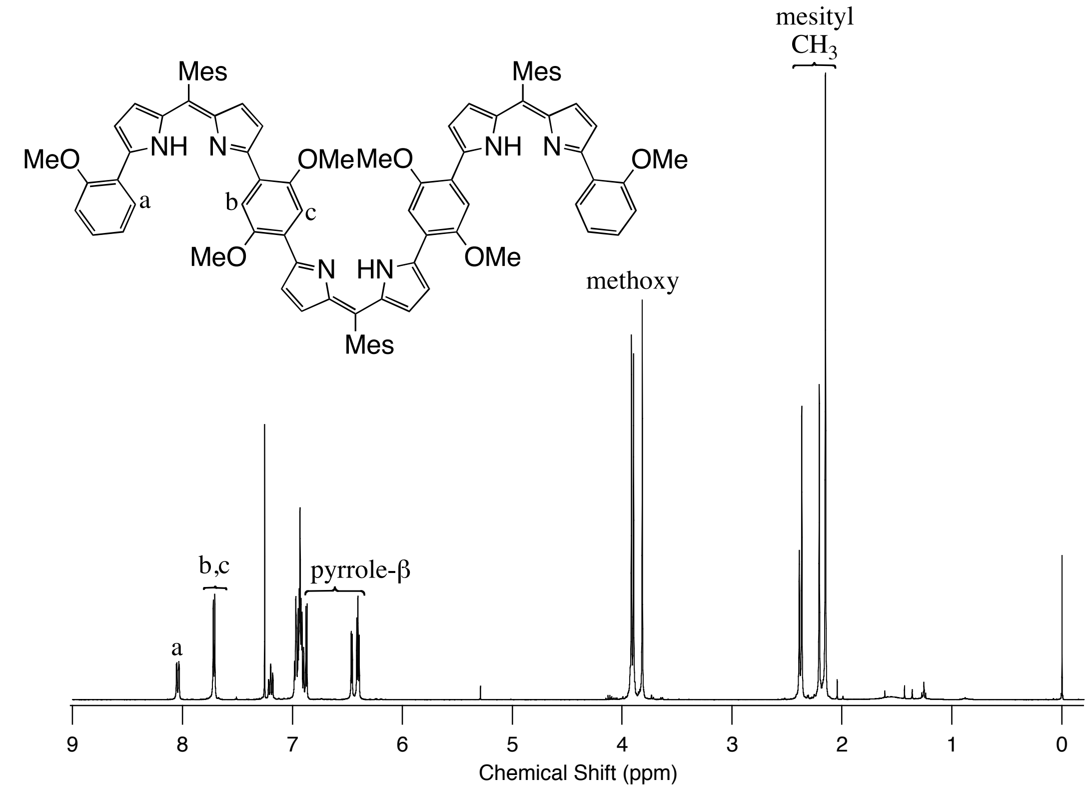


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L3**.

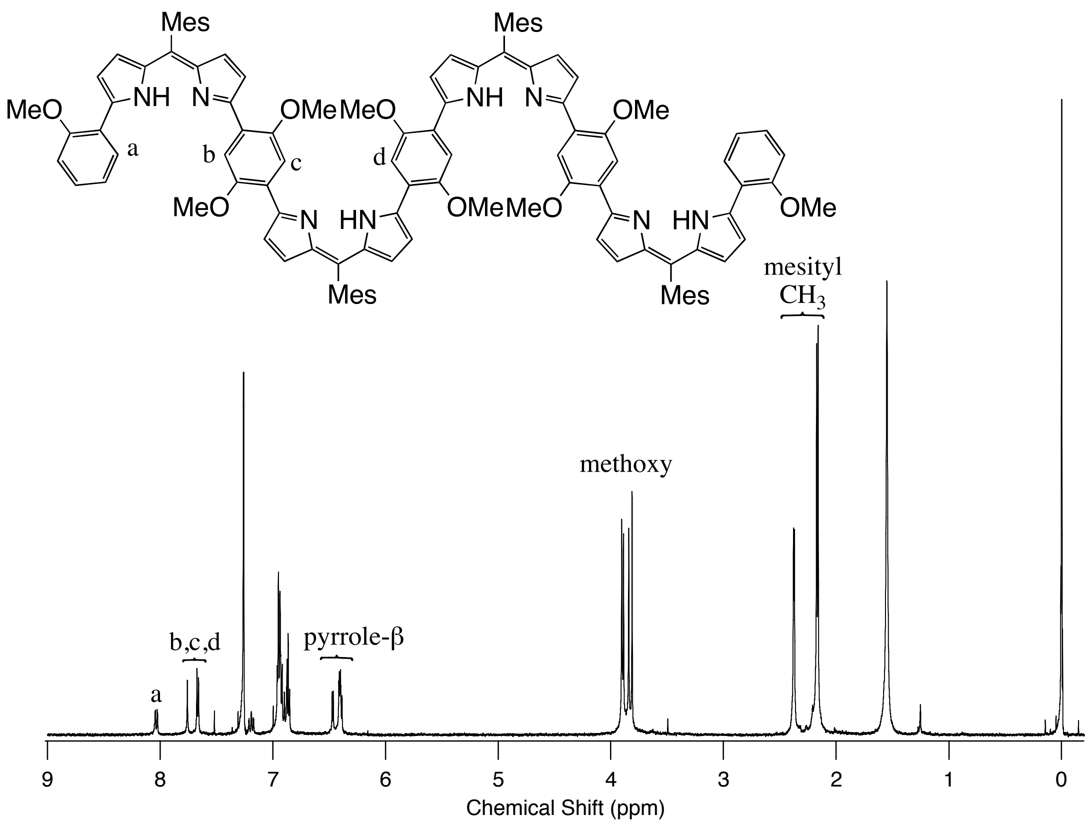


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L4**.

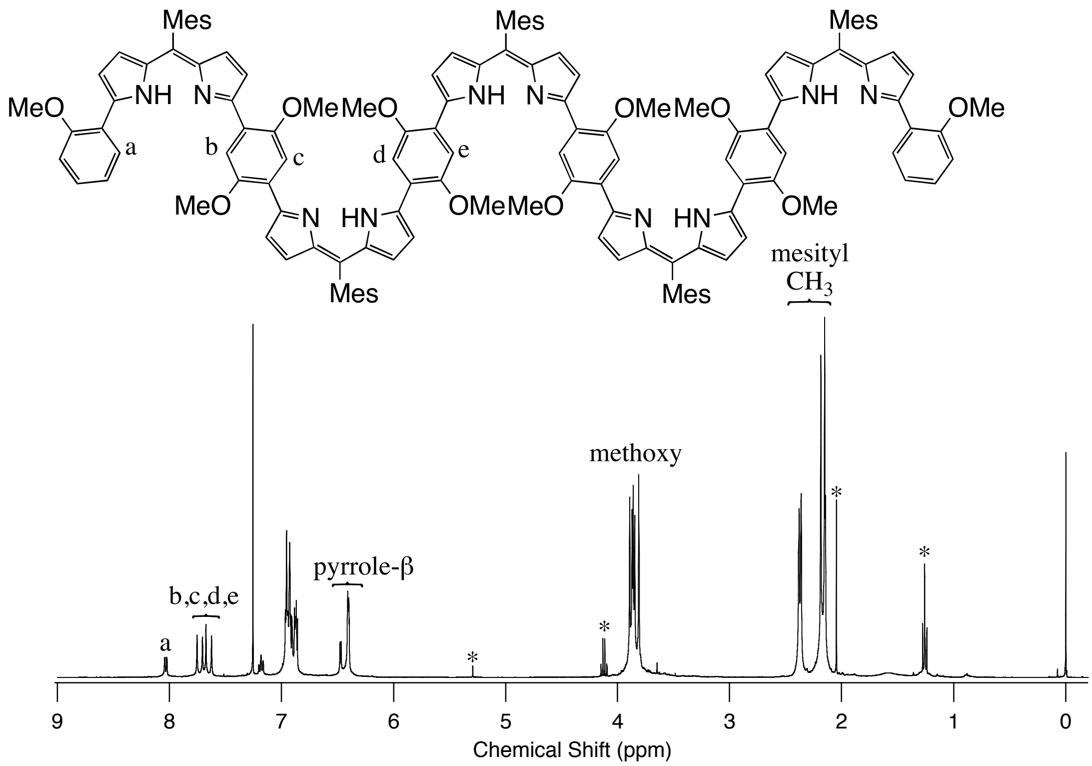


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L5**. Asterisks denote residual solvents.

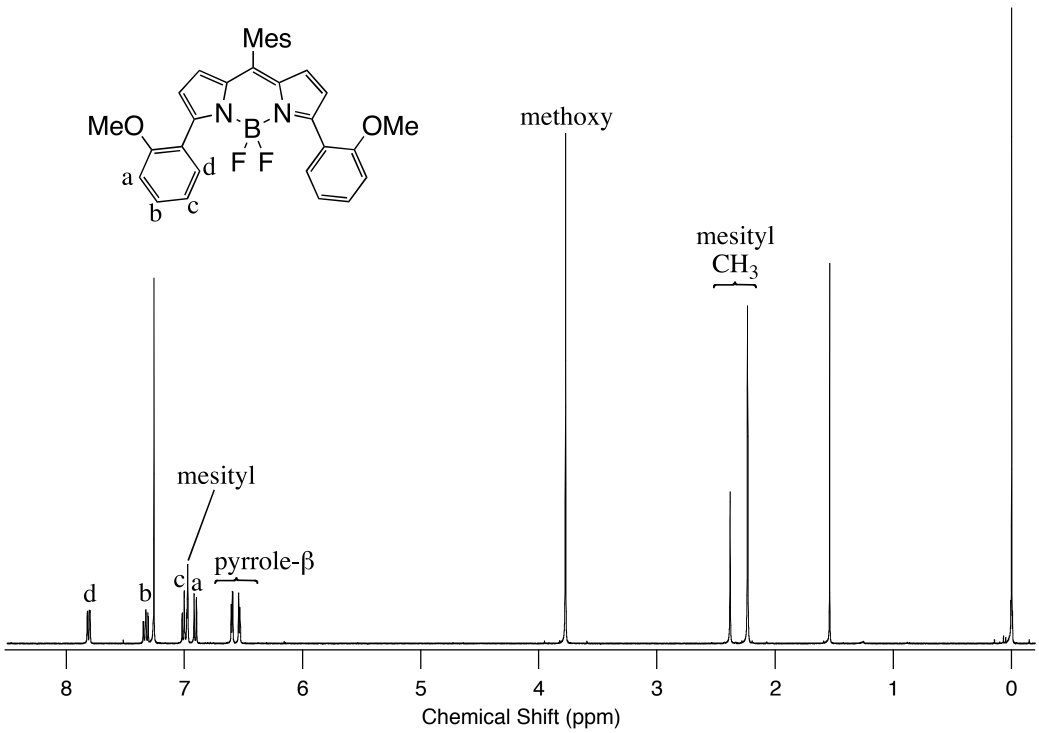


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **B1**.

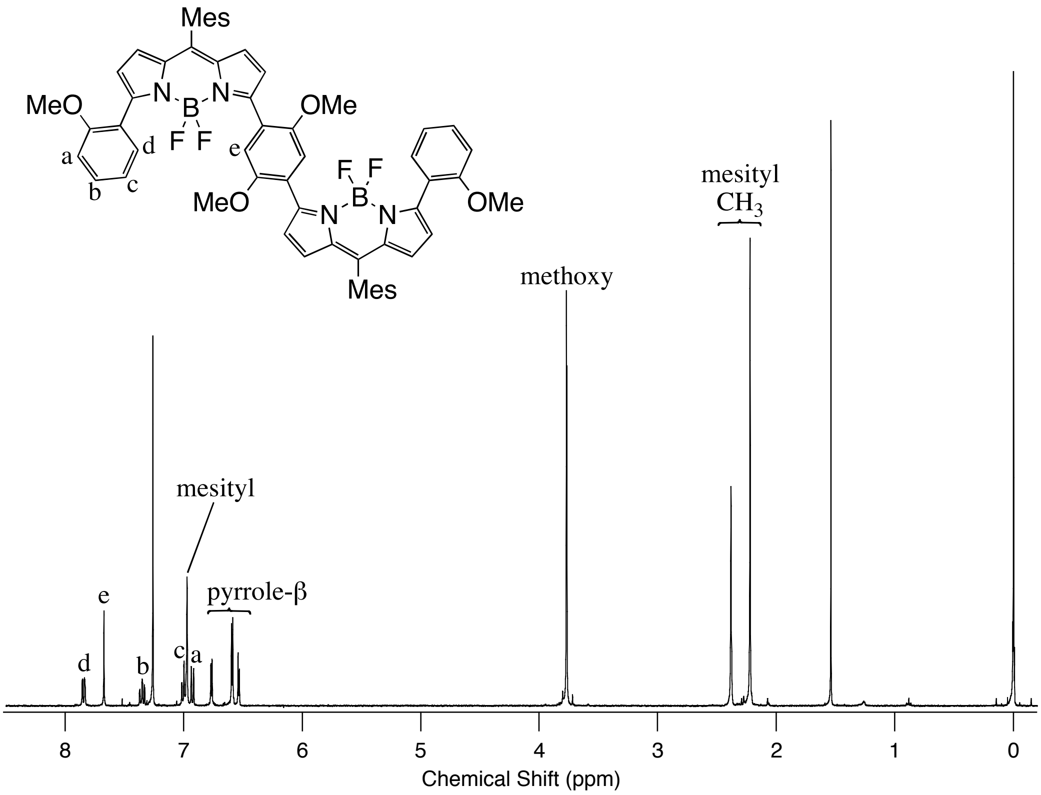


Figure S7. ^1H NMR (400 MHz, $CDCl_3$) spectrum of **B2**.

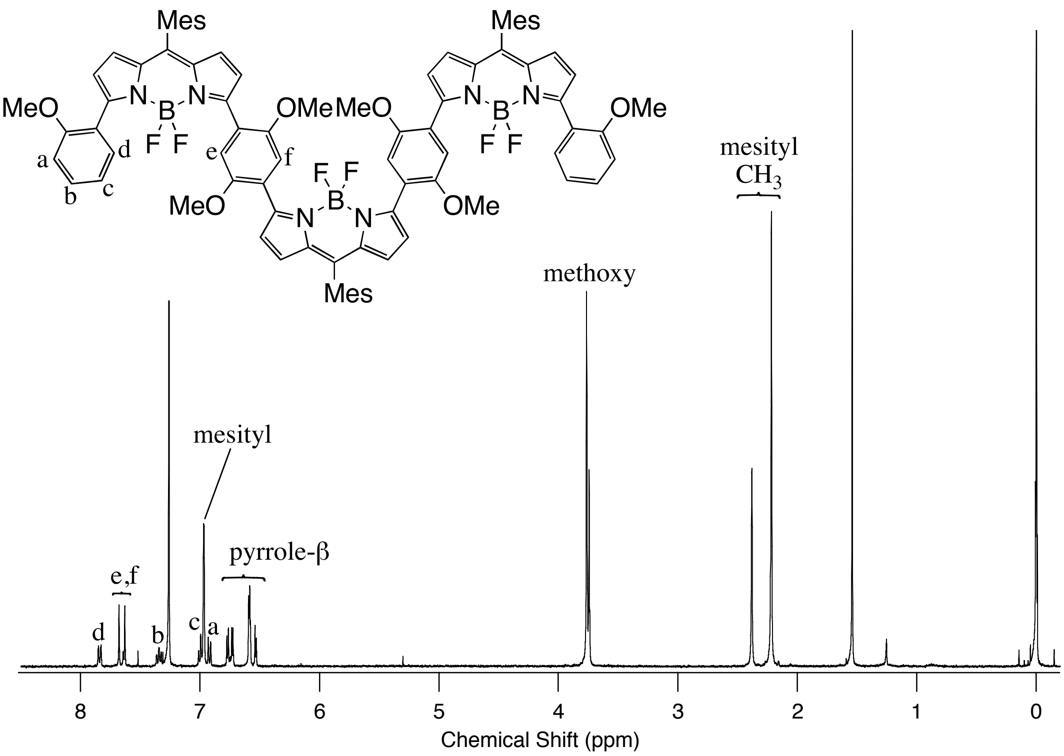


Figure S8. ^1H NMR (400 MHz, $CDCl_3$) spectrum of **B3**.

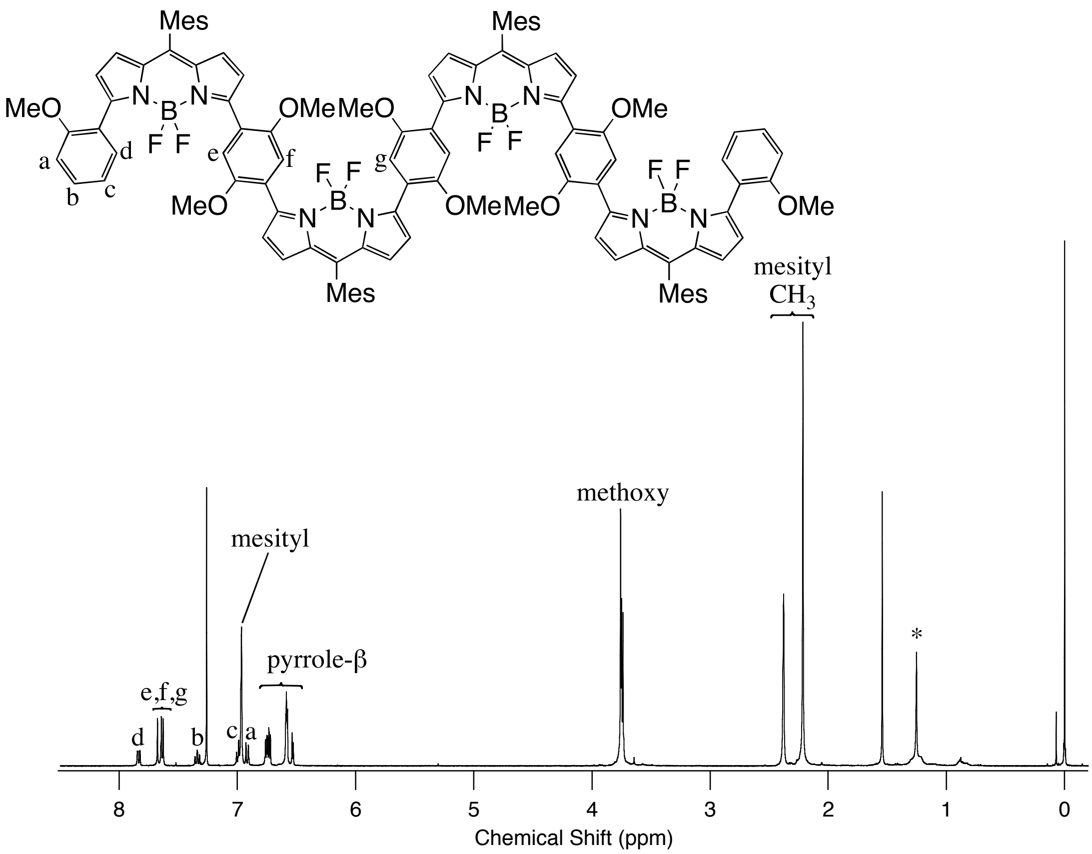


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **B4**. Asterisk denotes impurity.

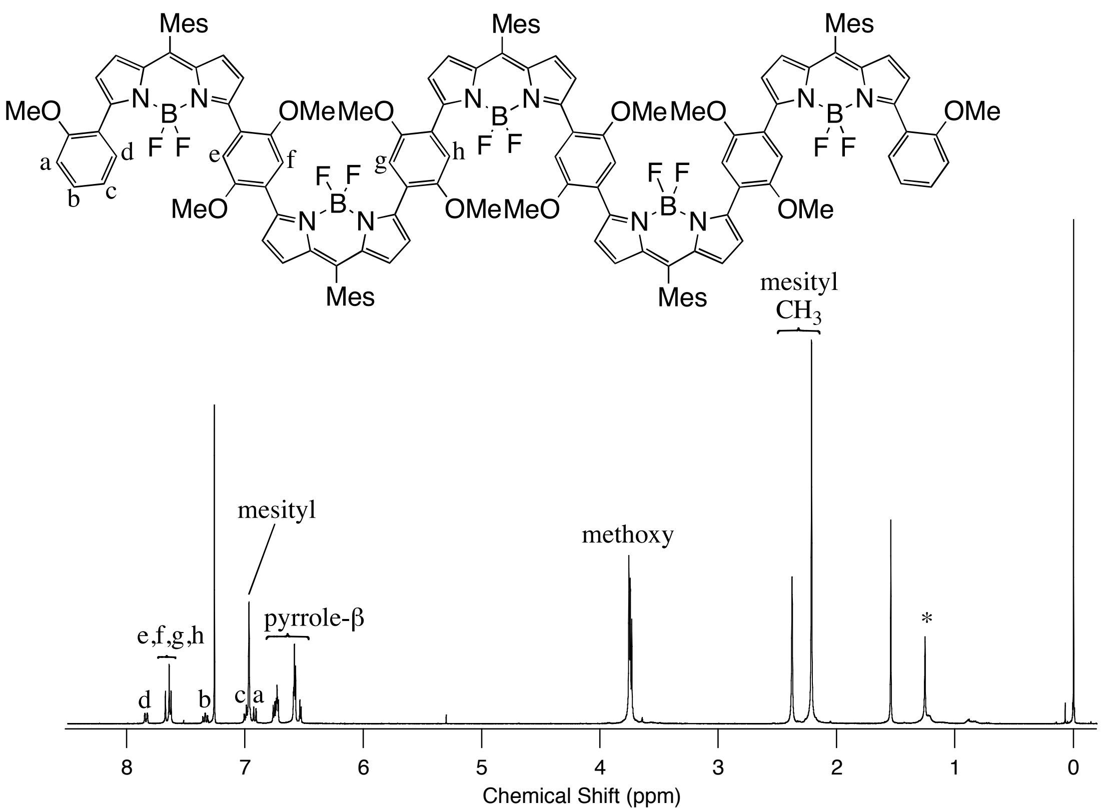


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **B5**. Asterisk denotes impurity.

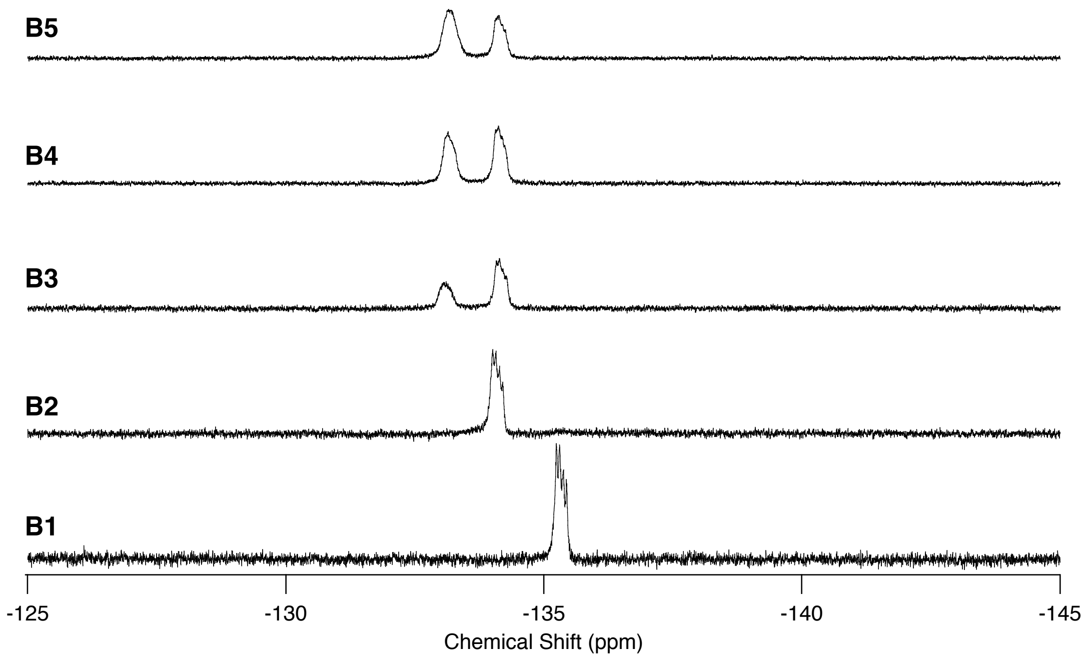


Figure S11. ^{19}F NMR (376 MHz, $CDCl_3$) spectra of BODIPY oligomers.

4. DFT calculation of B2[5]

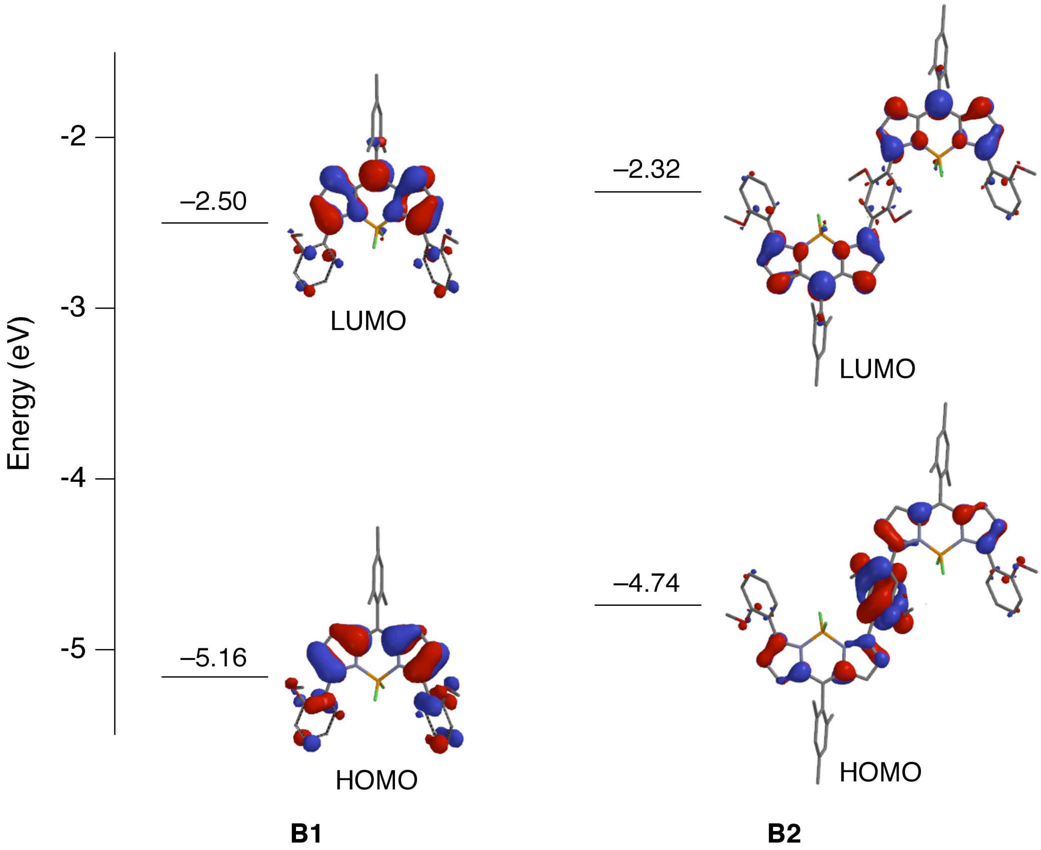


Figure S12. Diagram of calculated orbital energy level for **B1** and **B2** calculated at B3LYP/6-31G* level.

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

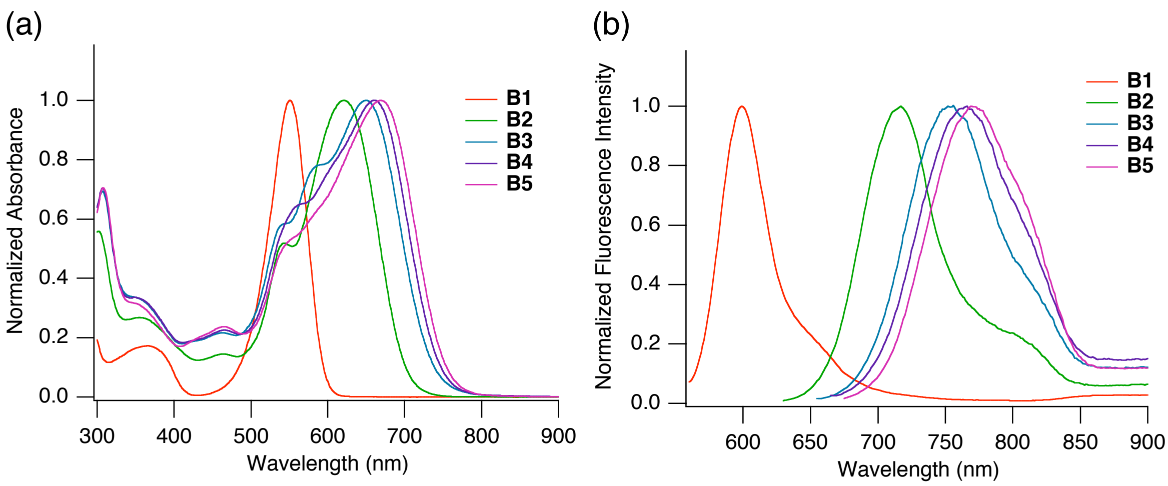


Figure S13. (a) Normalized UV-vis spectra and (b) fluorescence spectra of **B1-B5** recorded in $CHCl_3$. $\lambda_{ex} = \lambda_{abs}$.

6. Plot of transition energy (*E*) against reciprocal number of BODIPY units (1/*n*)[6]

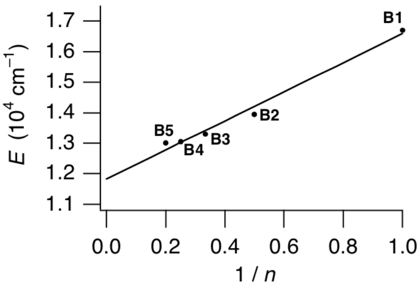


Figure S14. Plot of transition energy (*E*) obtained fluorescence spectra against reciprocal number of BODIPY units (1/*n*).

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

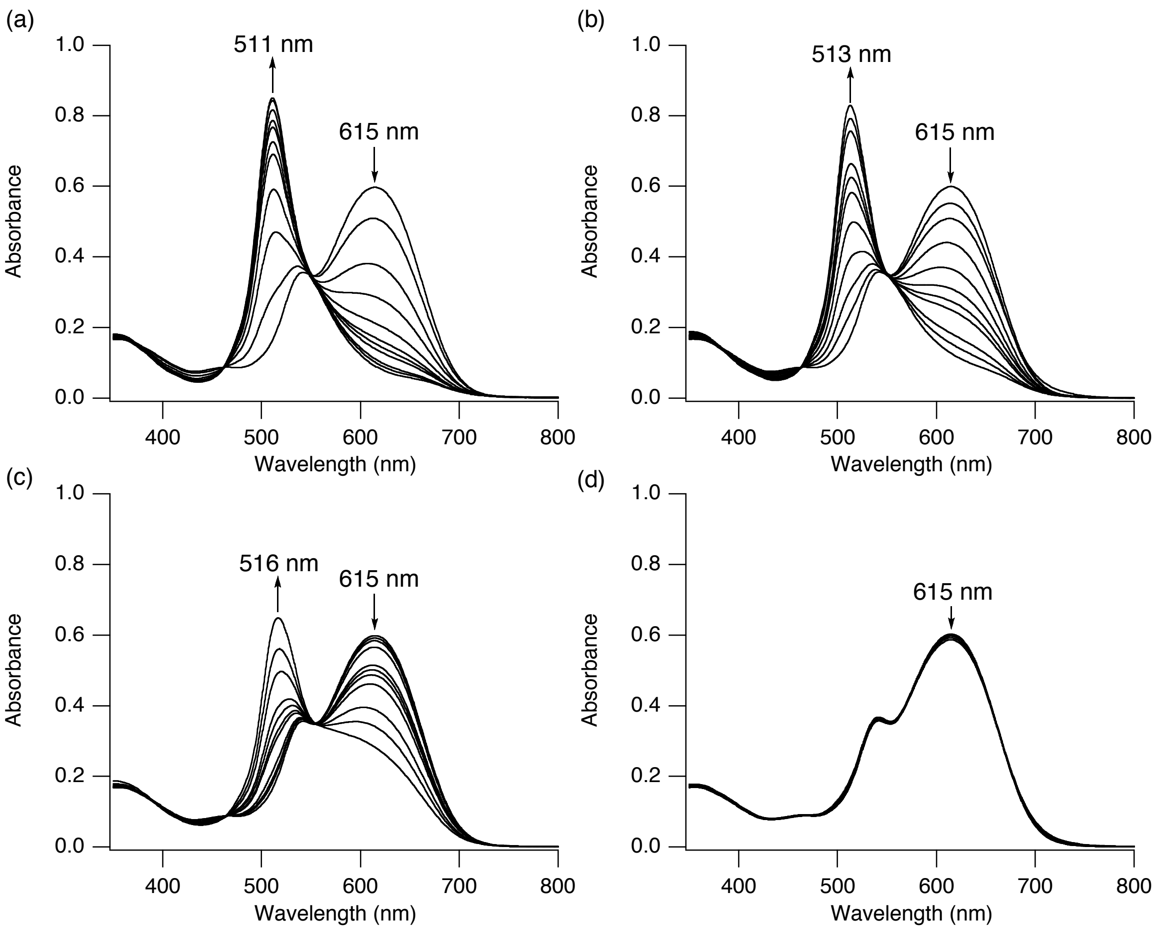


Figure S15. UV-vis spectral changes of **B2** upon addition of (a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB: [**B2**] = 10 μM, 0 < $[M^+]$/[**B2**] < 500, $CHCl_3/CH_3OH$ (10:1).

8. Fluorescence titration of B2 and M^+TFPB^- (M = K, Rb, and Cs)

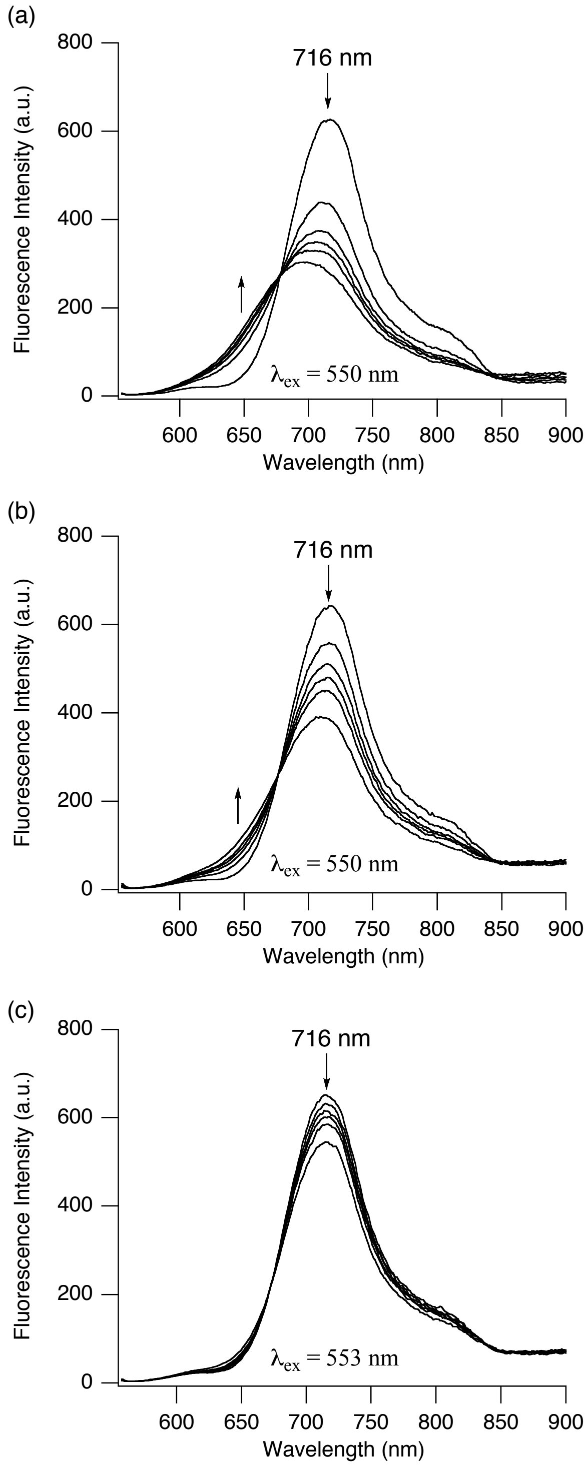


Figure S16. Fluorescence spectral changes of **B2** upon addition of (a) CsTFPB, (b) RbTFPB, or (c) KTFPB: [**B2**] = 1.0 μM, 0 < $[M^+]$/[**B2**] < 1000, $CHCl_3/CH_3OH$ (10:1), λ_{ex} = 550 nm.

9. UV-vis titration of B3 and M^+TFPB^- (M = Na, K, and Rb)

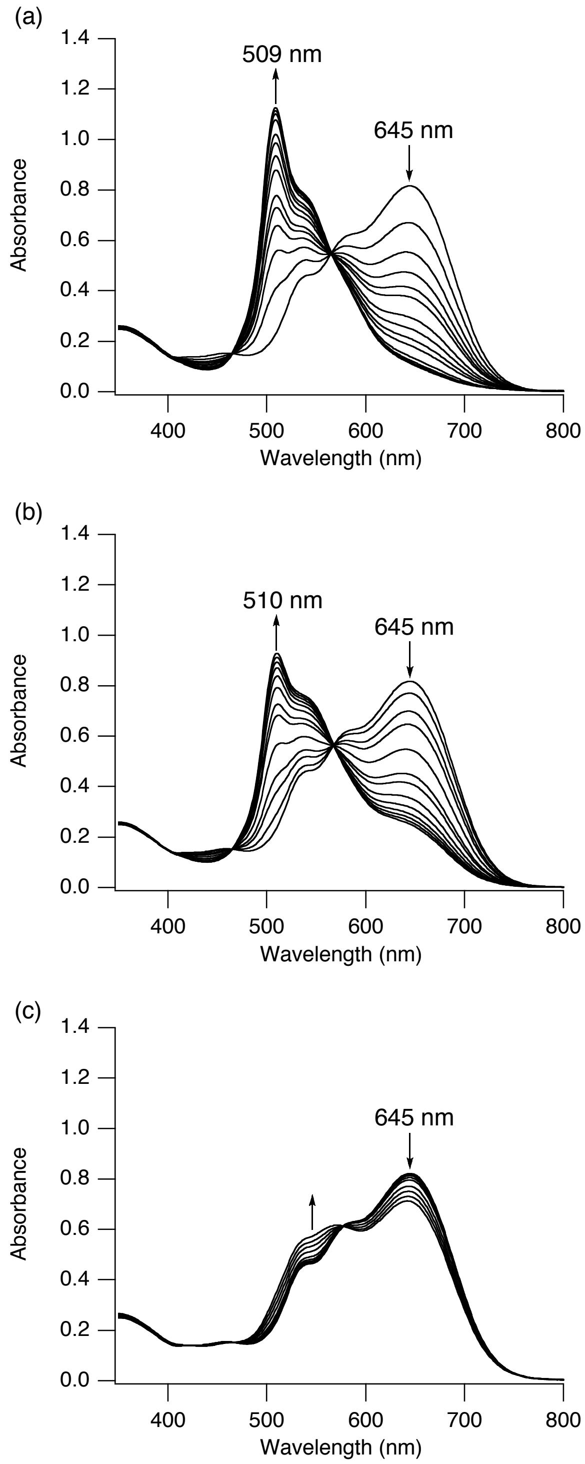


Figure S17. UV-vis spectral changes of **B3** upon addition of (a) RbTFPB, (b) KTFPB, or (c) NaTFPB: [**B3**] = 10 μM, 0 < [Rb^+]/[**B3**] < 50, 0 < [K^+]/[**B3**] < 100, 0 < [Na^+]/[**B3**] < 200, $CHCl_3/CH_3OH$ (10:1).

10. Fluorescence titration of B3 and M^+TFPB^- (M = Na, K, Rb, and Cs)

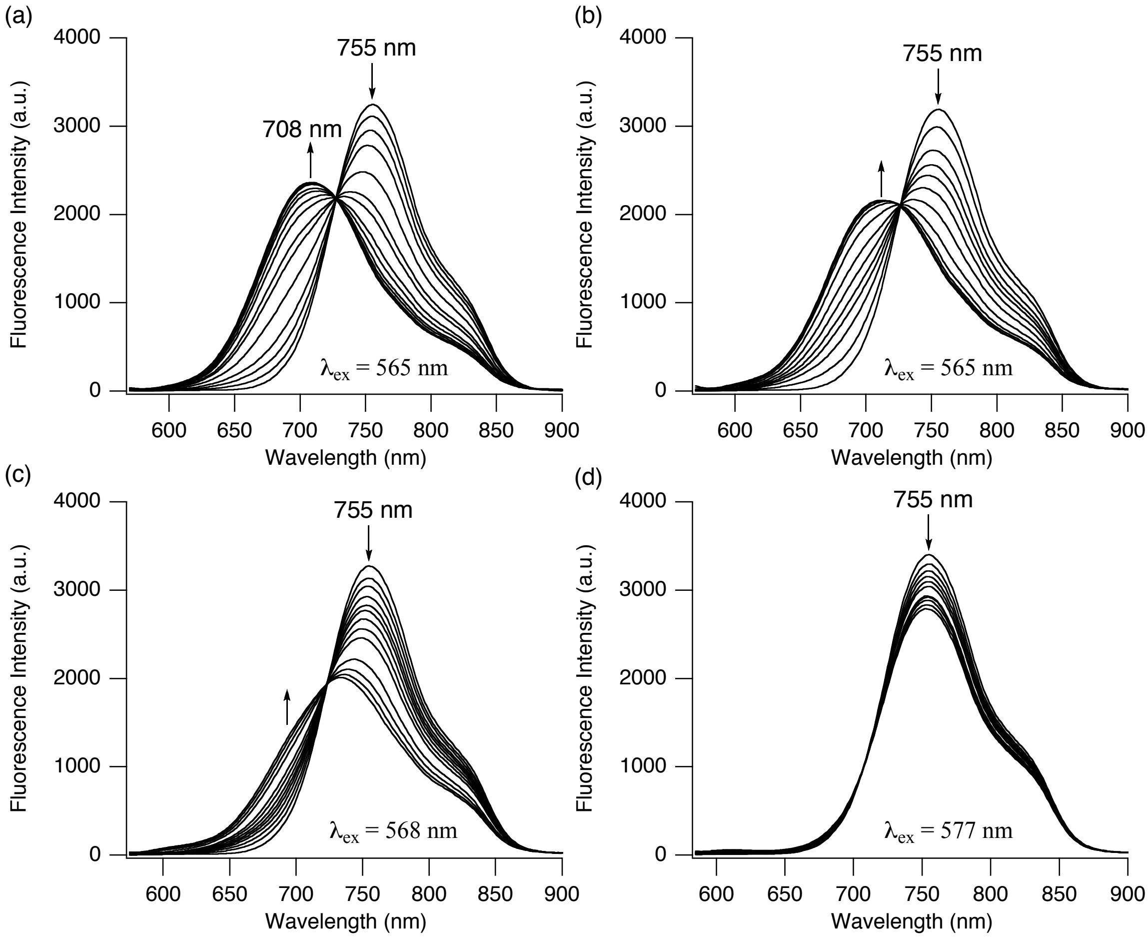
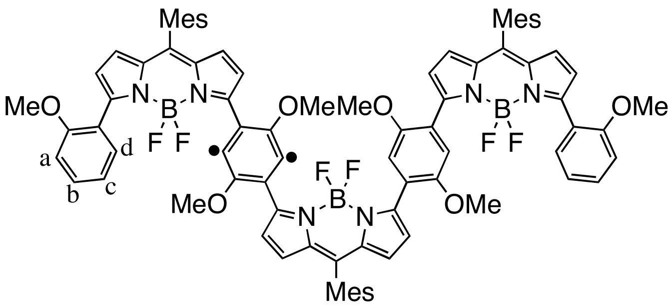


Figure S18. Fluorescence spectral changes of **B3** upon addition of (a) CsTFPB, (b) RbTFPB, (c) KTFPB, or (d) NaTFPB: [**B3**] = 1.0 μM, 0 < [Cs^+]/[**B3**] < 100, 0 < [Rb^+]/[**B3**] < 500, 0 < [K^+]/[**B3**] < 1000, 0 < [Na^+]/[**B3**] < 10000, $CHCl_3/CH_3OH$ (10:1).

11. NMR titration of B3 and $Cs^{+}TFPB^{-}$



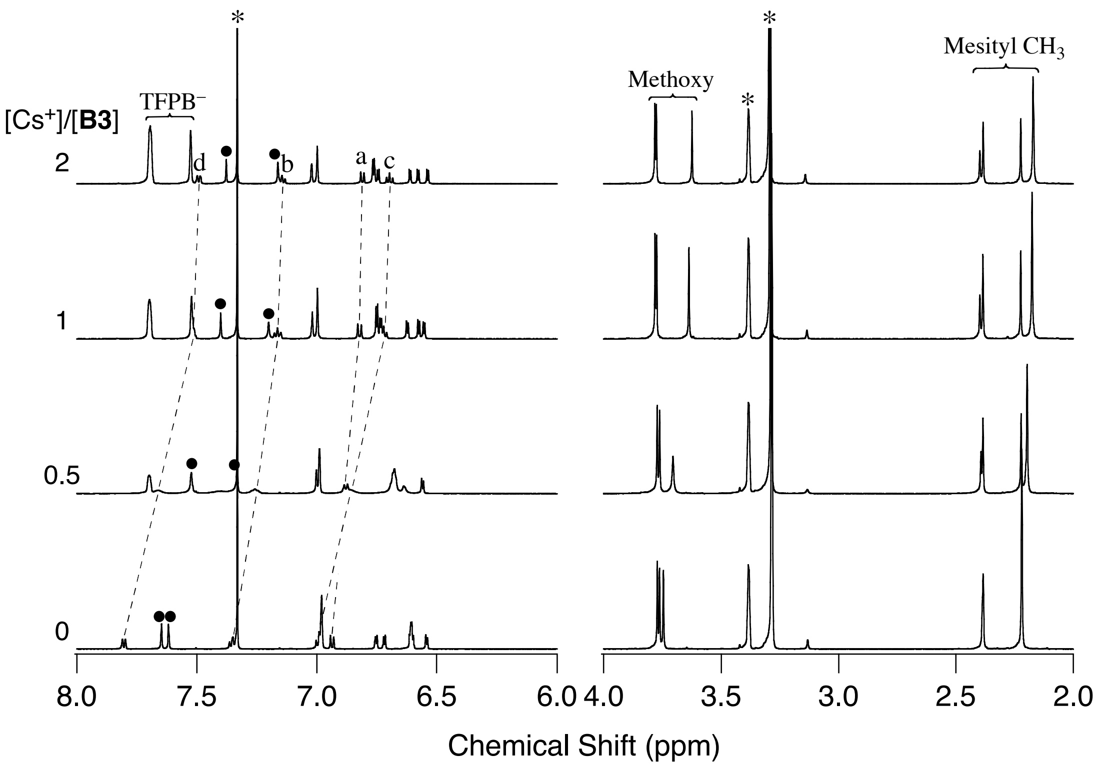


Figure S19 ^{1}H NMR (600 MHz, $CDCl_3$-CD_3OD(10:1)) spectral changes of **B3** upon addition of CsTFPB. Asterisks denote residual solvents.

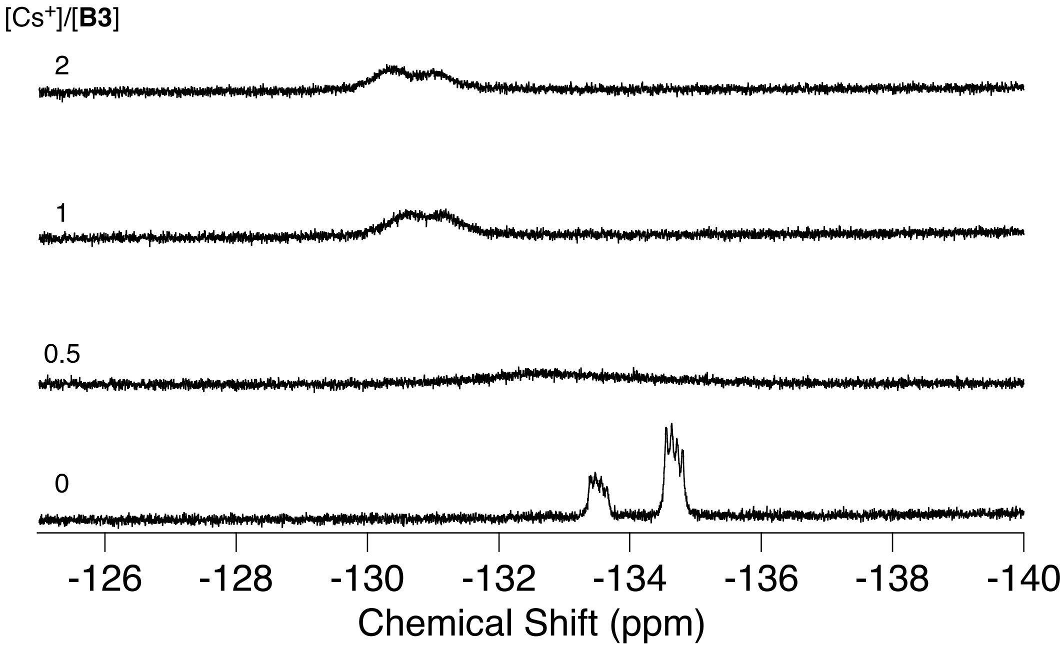


Figure S20. [19]F NMR (376 MHz, $CDCl_3$-CD_3OD(10:1)) spectral changes of **B3** upon addition of CsTFPB.

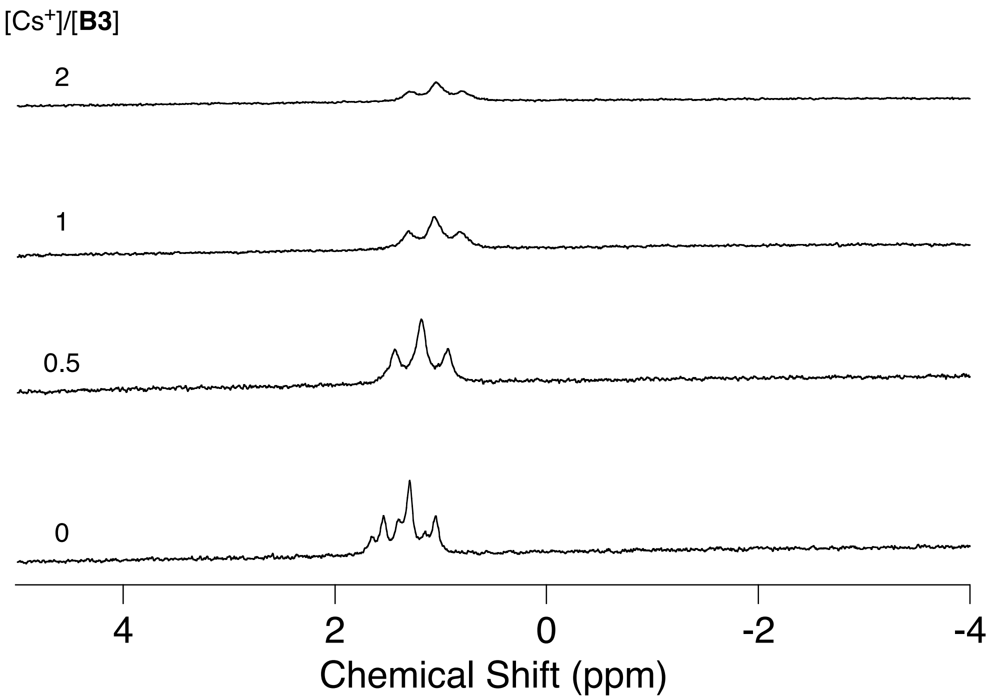
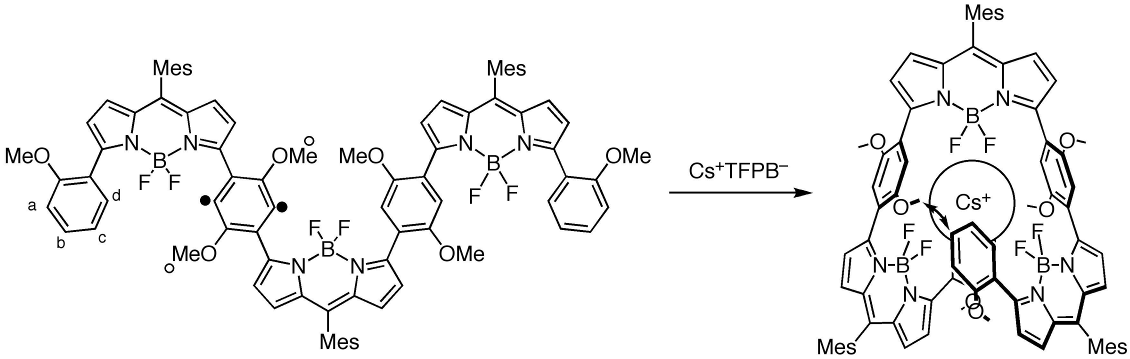


Figure S21. [11]B NMR (128 MHz, $CDCl_3$-CD_3OD(10:1)) spectral changes of **B3** upon addition of CsTFPB.

12. ROESY spectrum of B3•Cs$^+$



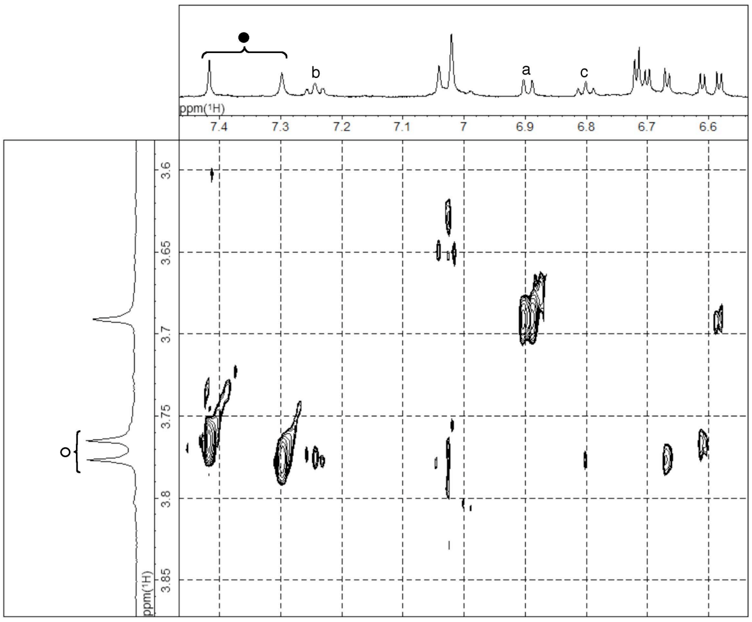


Figure S22. ROESY (600 MHz, CD_2Cl_2-CD_3OD(10:1)) spectrum of **B3**•Cs$^+$.

13. X-ray crystallographic analysis of B2[7]

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**·$2CH_2Cl_2$: $C_{60}H_{56}B_2Cl_4F_4N_4O_4$, monoclinic, $P2_1/c$, a = 15.0748(14), b = 9.8130(9), c = 20.2660(18) Å, β = 110.9900(10)°, V = 2799.0(4) Å^3, MW = 1136.51, Z = 2, D_{calc} = 1.348 g/cm^3, 31126 measured, 6427 independent, GOF = 1.050, $R_1[I > 2\sigma(I)]$ = 0.0571, wR_2(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)

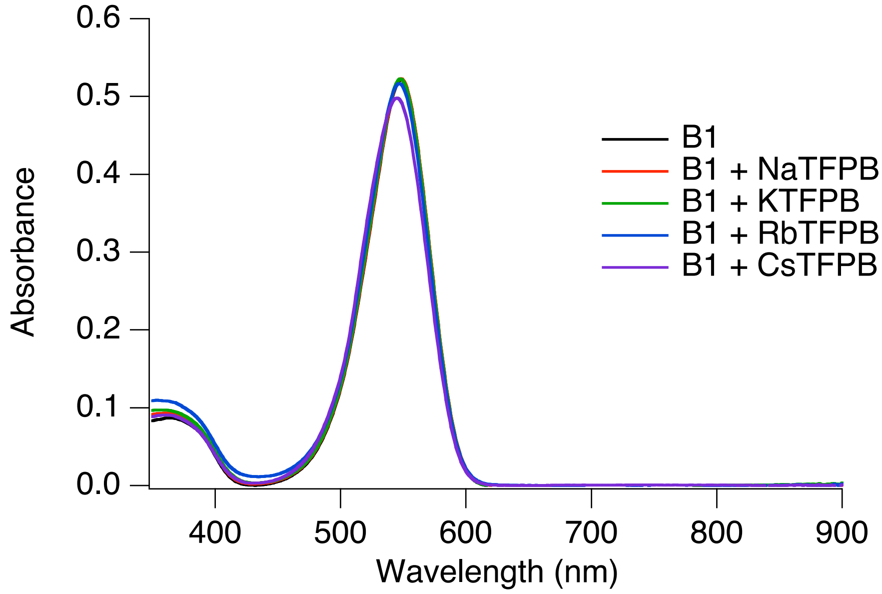


Figure S23. UV-vis spectra of **B1** in the presence of M^+TFPB^- (500 eq.).

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

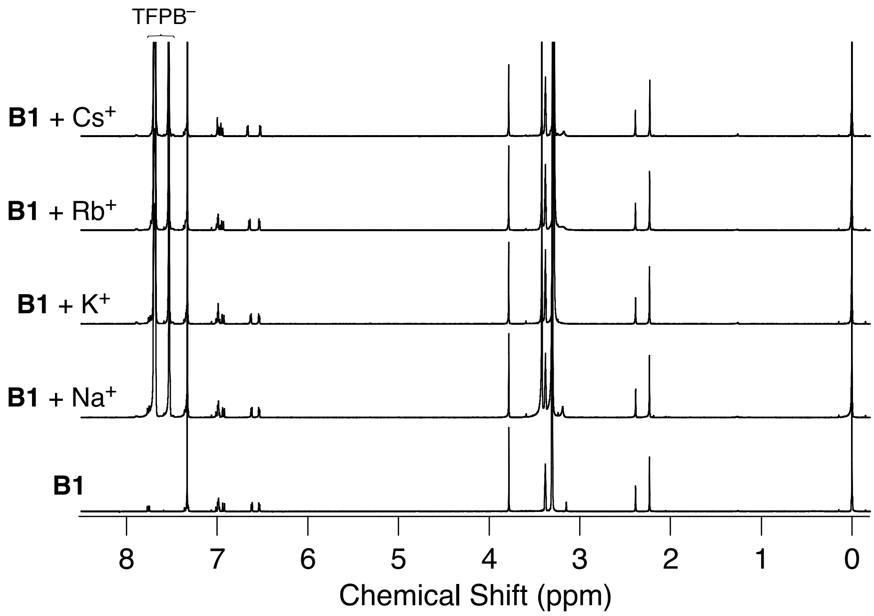


Figure S24. ^{1}H NMR spectra of **B1** in the presence of M^+TFPB^- (10 eq.).

16. Calculated structure of B3•Cs⁺

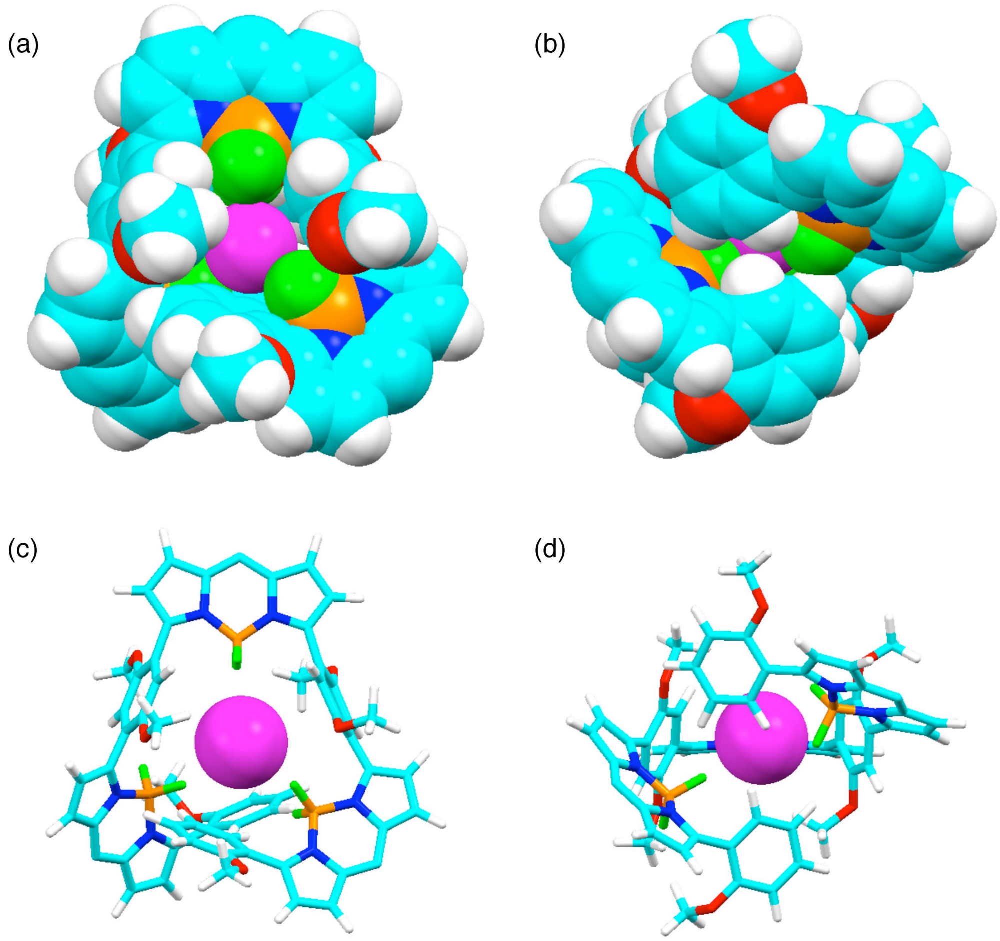


Figure S25. Calculated structure of **B3**•Cs^+ at the 3-21G level: (a,c) top view; (b,d) side view; (c,d) **B3** was displayed as stick model. Mesityl groups are omitted for clarity. Color: C, sky blue; H, white; B, orange; F, green; N, blue; O, red; Cs, purple.

References

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(3) A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, *J. Org. Chem.* 1999, **64**, 7813.

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(7) G. M. Sheldrick, *Acta. Cryst.,* 2008, **A64**, 112.