Supporting Information

Synthesis of Directly Connected BODIPY Oligomers through Suzuki–Miyaura Coupling

Yosuke Hayashi, Shigeru Yamaguchi, Won Young Cha, Dongho Kim,* and Hiroshi Shinokubo*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.
Department of Chemistry, Yonsei University, Seoul 120-749, Korea

E-mail: hshino@apchem.nagoya-u.ac.jp; dongho@yonsei.ac.kr

Table of Contents

Instrumentation and Materials ................................................................. S2
General Procedures and Compound Data .................................................. S2
Spectra of Compounds .......................................................... S11
X-ray Structure of 7 and 8 ......................................................... S21
UV/vis Absorption Spectra of 2, 3, 5, 9 and 10 .................................... S22
Excitation Spectra of 4, 6, and 7 ..................................................... S23
Photophysical Measurements on 1, 4, and 6 .......................................... S24
**Instrumentation and Materials**

$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra were recorded on a Varian INOVA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl$_3$ ($\delta = 7.260$ ppm) for $^1$H NMR and CDCl$_3$ ($\delta = 77.0$ ppm) for $^{13}$C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on JASCO FP-6500 spectrometer. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions. X-ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**Synthesis of 2 with NBS**

To a solution of 1 (310 mg, 1.00 mmol) in DMF/CH$_2$Cl$_2$ (25 mL/25 mL) was added dropwise a solution of NBS (214 mg, 1.20 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The mixture was stirred at room temperature for 30 min. The reaction was monitored by TLC analysis, which finally indicated the presence of 2 as a major product. The resulting mixture was poured into brine and extracted with CH$_2$Cl$_2$. The organic layer was dried with Na$_2$SO$_4$. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$/hexane as an eluent) to afford 2 (321 mg, 824 $\mu$mol) and 3 (56.5 mg, 121 $\mu$mol) in 82% and 12% yield, respectively.

**Synthesis of 3 with NBS**

To a solution of 1 (310 mg, 1.00 mmol) in DMF/CH$_2$Cl$_2$ (25 mL/25 mL) was added dropwise a solution of NBS (427 mg, 2.40 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature. The mixture was stirred at room temperature for 2 h. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$/hexane as an eluent) to provide 2 (321 mg, 824 $\mu$mol) and 3 (433 mg, 925 $\mu$mol) in 6% and 93% yield, respectively.
Synthesis of 2 with PIFA–Me3SiBr

To a stirred solution of 1 (310 mg, 1.00 mmol) in CH2Cl2 (15 mL), phenyliodine bis(trifluoroacetate) (PIFA, 430 mg, 1.00 mmol) and Me3SiBr (158 µL, 1.20 mmol) were quickly added at –78 °C. The reaction mixture was then stirred for 1 h. The reaction temperature was maintained below –40 °C. After completion of the reaction, saturated aqueous NaHCO3 was added to the mixture, which was then stirred for 10 min at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH2Cl2. The combined extract was dried with Na2SO4. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH2Cl2/hexane as an eluent) to provide 2 (340 mg, 873 µmol) and 3 (21.7 mg, 46.4 µmol) in 87% and 5% yield, respectively.

Synthesis of 4

A Schlenk tube was charged with 2 (195 mg, 0.50 mmol), Pd2(dba)•CHCl3 (5.2 mg, 5.0 µmol), X-Phos (19.0 mg, 40 µmol), bis(pinacolato)diboron (63.5 mg, 0.25 mmol), Cs2CO3 (326 mg, 1.0 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with N2 (this sequence was carried out two times). 1,4-Dioxane (3 mL) and H2O (0.05 mL) were added via syringe through the septum, and the Schlenk tube was sealed. The reaction mixture was stirred at room temperature during 48 h. The reaction mixture was then filtered through a thin pad of Celite and eluted with CH2Cl2. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH2Cl2 as an eluent). Recrystallization from CH2Cl2/hexane afforded 4 (125 mg, 0.201 mmol) in 81% yield as blue crystals.

Synthesis of 5

A Schlenk tube was charged with 2 (195 mg, 0.500 mmol), Pd2(dba)•CHCl3 (5.2 mg, 5.0 µmol), X-Phos (9.6 mg, 20 µmol), bis(pinacolato)diboron (380 mg, 1.50 mmol), KOAc (147 mg, 1.50 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with N2 (this sequence was carried out two times). 1,4-Dioxane (3 mL) was added via syringe through the septum,
and the Schlenk tube was sealed. The reaction mixture was heated to 110 °C until 2 had been completely consumed by TLC analysis. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of Celite and eluted with CH$_2$Cl$_2$. After removal of solvents in vacuo, the mixture was purified by silica-gel short column chromatography (CH$_2$Cl$_2$ as an eluent) and eluent was removed in vacuo. The residue was washed with hexane and recrystallization from CH$_2$Cl$_2$/hexane afforded 5 (226.9 mg, 0.520 mmol) in 69% yield as green crystals.

**Synthesis of 6**

A round-bottom flask was charged with 3 (58.3 mg, 0.125 mmol), 5 (131 mg 0.300 mmol), Pd$_2$(dba)$_3$•CHCl$_3$ (13.0 mg, 12.5 µmol), t-Bu$_3$P•HBF$_4$ (14.5 mg, 50.0 µmol), Cs$_2$CO$_3$ (163 mg, 0.500 mmol). The round-bottom flask was capped with a rubber septum and then evacuated and backfilled with N$_2$ (this sequence was carried out two times). THF (30 mL) and H$_2$O (0.20 mL) were added via syringe through the septum, and the round-bottom flask was sealed. The reaction mixture was stirred at room temperature for 96 h. The reaction solution was then filtered through a thin pad of Celite and eluted with CH$_2$Cl$_2$. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$ as an eluent). Recrystallization from CH$_2$Cl$_2$/hexane afforded 6 (81.7 mg, 88.2 µmol) in 71% yield as black crystals.

**Synthesis of 7**

A round-bottom flask was charged with 3 (58.3 mg, 0.125 mmol), 4-nitrophenylboronic acid (50.0 mg 0.300 mmol), Pd$_2$(dba)$_3$•CHCl$_3$ (13.0 mg, 12.5 µmol), t-Bu$_3$P•HBF$_4$ (14.5 mg, 50.0 µmol), Cs$_2$CO$_3$ (163 mg, 0.500 mmol). The round-bottom flask was capped with a rubber septum and then evacuated and backfilled with N$_2$ (this sequence was carried out two times). THF (30 mL) and H$_2$O (0.20 mL) were added via syringe through the septum, and the round-bottom flask was sealed. The reaction mixture was stirred at room temperature for 24 h. The reaction solution was then filtered through a thin
pad of Celite and eluted with CH$_2$Cl$_2$. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$ as an eluent). Recrystallization from CH$_2$Cl$_2$/hexane afforded 7 (47.4 mg, 90.7 µmol) in 73% yield as brown crystals.

**Synthesis of 8**

A round-bottom flask was charged with 3 (58.3 mg, 0.125 mmol), N,N-4-dimethylaminophenylboronic acid (49.5 mg 0.300 mmol), Pd$_2$(dba)$_3$•CHCl$_3$ (13.0 mg, 12.5 µmol), t-Bu$_3$P•HBF$_4$ (14.5 mg, 50.0 µmol), Cs$_2$CO$_3$ (163 mg, 0.500 mmol). The round-bottom flask was capped with a rubber septum and then evacuated and backfilled with N$_2$ (this sequence was carried out two times). THF (30 mL) and H$_2$O (0.20 mL) were added via syringe through the septum, and the round-bottom flask was sealed. The reaction mixture was allowed to stand at room temperature during 24 h. The reaction solution was then filtered through a thin pad of Celite and eluted with CH$_2$Cl$_2$. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH$_2$Cl$_2$ as an eluent). Recrystallization from CH$_2$Cl$_2$/hexane afforded 8 (42.2 mg, 77.0 µmol) in 62% yield as blue crystals.

**Synthesis of 9**

A Schlenk tube was charged with 2 (97.3 mg, 0.250 mmol), 4-nitrophenylboronic acid (41.8 mg, 0.250 mmol), Pd$_2$(dba)$_3$•CHCl$_3$ (2.6 mg, 2.50 µmol), X-Phos (9.6 mg, 20.0 µmol), Cs$_2$CO$_3$ (163 mg, 0.500 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with N$_2$ (this sequence was carried out two times). 1,4-Dioxane (3 mL) and H$_2$O (0.05 mL) were added via syringe, through the septum, and the Schlenk tube was sealed. The reaction mixture was allowed to stand at room temperature during 48 h. The reaction solution was then filtered through a thin pad of Celite and eluted with CH$_2$Cl$_2$. After removal of solvents in vacuo, the mixture was purified by silica-gel short column chromatography (CH$_2$Cl$_2$/hexane as an eluent) to give 9 (91.7 mg, 0.213 mmol) in 85% yield as an orange solid.
Synthesis of 10

To a solution of 9 (43.1 mg, 0.100 mmol) in DMF/CH₂Cl₂ (3 mL/3 mL) was added dropwise a solution of NBS (21.4 mg, 0.120 mmol) in CH₂Cl₂ (2 mL). The mixture was stirred at room temperature for 1.5 h, until TLC analysis indicated almost full consumption of 9. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH₂Cl₂/hexane as an eluent) to give 10 (42.1 mg, 82.5 µmol) in 83% yield as a red solid.

Synthesis of 11

A round-bottom flask was charged with 10 (128 mg, 0.250 mmol), N,N-4-dimethylaminophenylboronic acid (49.5 mg 0.300 mmol), Pd₂(dba)₃•CHCl₃ (13.0 mg, 12.5 µmol), t-Bu₃P•HBF₄ (14.5 mg, 50.0 µmol), Cs₂CO₃ (163 mg, 0.500 mmol). The round-bottom flask was capped with a rubber septum and then evacuated and backfilled with N₂ (this sequence was carried out two times). THF (30 mL) and H₂O (0.20 mL) were added via syringe through the septum, and the round-bottom flask was sealed. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then filtered through a thin pad of Celite and eluted with CH₂Cl₂. After removal of solvents in vacuo, the mixture was purified by silica-gel column chromatography (CH₂Cl₂ as an eluent). Recrystallization from CH₂Cl₂/hexane afforded 11 (69.0 mg, 0.125 mmol) in 50% yield as black crystals.

Compound Data

BODIPY 2

¹H NMR (CDCl₃): δ 7.98 (s, 1H, α), 7.76 (s, 1H, α), 6.96 (s, 2H, mesityl), 6.76 (d, J = 4.0 Hz, 1H, β), 6.62 (s, 1H, β), 6.52 (d, J = 4.0 Hz, 1H, β), 2.36 (s, 3H, mesityl), and 2.10 (s, 6H, mesityl) ppm; ¹³C NMR (CDCl₃): δ 147.8, 146.6, 142.4, 139.4, 136.4, 136.1, 134.8, 131.9, 129.2, 128.9, 128.5, 119.8, 106.2, 21.3, 20.1 ppm; UV/vis (CH₂Cl₂): λ_max (ε [M⁻¹ cm⁻¹]) = 366 (9100), and 518 (58000) nm;
Fluorescence (CH$_2$Cl$_2$): $\lambda_{em} = 537$ nm ($\lambda_{ex} = 480$ nm) $\Phi_i = 0.16$; HR-MS (ESI-MS): $m/z = 388.058$, calcd for (C$_{18}$H$_{16}$BBrF$_2$N$_2$)$^-$ = 388.0567 [(M$^-$)].

**BODIPY 3**

$^1$H NMR (CDCl$_3$): $\delta$ 7.82 (s, 2H, $\alpha$), 6.96 (s, 2H, mesityl), 6.70 (s, 2H, $\beta$), 2.36 (s, 3H, mesityl), and 2.10 (s, 6H, mesityl) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 147.7, 144.5, 139.6, 136.1, 135.2, 130.2, 128.6, 128.4, 107.3, 21.1, and 20.0 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 374 (10000), and 538 (58000) nm; Fluorescence (CH$_2$Cl$_2$): $\lambda_{em} = 577$ nm ($\lambda_{ex} = 500$ nm) $\Phi_i = 0.14$; HR-MS (ESI-MS): $m/z = 465.9671$, calcd for (C$_{18}$H$_{15}$BBr$_2$F$_2$N$_2$)$^-$ = 465.9672 [(M$^-$)].

**BODIPY 4**

$^1$H NMR (CDCl$_3$): $\delta$ 8.05 (s, 2H, $\alpha$), 7.91 (s, 2H, $\alpha$), 6.97 (s, 4H, mesityl), 6.69 (d, $J = 4.0$ Hz, 2H, $\beta$), 6.60 (s, 2H, $\beta$), 6.48 (dd, $J = 1.5$ Hz, 4.0 Hz, 2H, $\beta$), 2.38 (s, 6H, mesityl), and 2.10 (s, 12H, mesityl) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 147.1, 144.8, 141.6, 139.0, 136.3, 135.8, 130.3, 129.5, 128.3, 126.4, 123.0, 118.8, 21.1, and 20.0 ppm. One peak was not observed probably because of overlap; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 397 (16000), 421 (17000), and 609 (60000) nm; Fluorescence (CH$_2$Cl$_2$): $\lambda_{em} = 655$ nm ($\lambda_{ex} = 580$ nm) $\Phi_i = 0.15$; HR-MS (ESI-MS): $m/z = 641.2672$, calcd for (C$_{36}$H$_{32}$B$_2$F$_4$N$_4$)$^+$ = 641.2653 [(M + Na)$^+$]. Single crystals were obtained by vapor diffusion of MeOH into a chloroform solution. C$_{36}$H$_{32}$B$_2$F$_4$N$_4$, $M_w = 618.28$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.4027(13)$ Å, $b = 13.081(2)$ Å, $c = 13.958(2)$ Å, $\beta = 99.794(3)^\circ$, $V = 1511.8(4)$ Å$^3$, $Z = 2$, $D_{calc} = 1.358$ g/cm$^3$, $T = 153(2)$ K, $R_1 = 0.0573$ ($I > 2.0 \sigma(I)$), $R_w = 0.1710$ (all data), GOF = 1.051 ($I > 2.0 \sigma(I)$).

**BODIPY 5**

$^1$H NMR (CDCl$_3$): $\delta$ 8.20 (s, 1H, $\alpha$), 7.94 (s, 1H, $\alpha$), 7.04 (s, 1H, $\beta$), 6.93 (s, 2H, mesityl), 6.73 (d, $J = 4.5$ Hz, 1H, $\beta$), 6.49 (d, $J = 3.0$ Hz, 1H, $\beta$), 2.35 (s, 3H, mesityl), 2.08 (s, 6H, mesityl), and 1.29 (s, 12H, pinacol-H) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 150.2, 148.2, 145.0, 138.8, 137.2, 136.4, 136.3, 135.8,
130.6, 129.6, 128.1, 119.1, 83.7, 24.7, 21.1, and 19.9 ppm. One peak was not observed probably because of overlap; UV/vis \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{max}}\) \((\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 303\) (3800), 361 (7100), and 502 (80000) nm; Fluorescence \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{em}} = 515\) nm \((\lambda_{\text{ex}} = 450\) nm) \(\Phi_t = 0.89\); HR-MS (ESI-MS): \(m/z = 459.2196\), calcd for \((\text{C}_{24}\text{H}_{28}\text{B}_{2}\text{F}_{2}\text{N}_{2}\text{O}_{2})^+ = 459.2206 [(M + Na)^+]\).

**BODIPY 6**

\(^1\text{H} \text{NMR} \quad \text{(CDCl}_3)\): \(\delta\) 8.07 (s, 4H, \(\alpha\)), 7.92 (d, \(J = 0.5\) Hz, 2H, \(\alpha\)), 6.98 (s, 2H, mesityl), 6.97 (s, 4H, mesityl), 6.68 (d, \(J = 3.5\) Hz, 2H, \(\beta\)), 6.58 (s, 4H, \(\beta\)), 6.48 (dd, \(J = 2.0\) Hz, 3.5 Hz, 2H, \(\beta\)), 2.39 (s, 3H, mesityl), 2.37 (s, 6H, mesityl), 2.10 (s, 6H, mesityl), and 2.10 (s, 12H, mesityl) ppm; \(^{13}\text{C} \text{NMR} \quad \text{(CDCl}_3)\): \(\delta\) 147.1, 146.3, 145.0, 142.3, 141.6, 139.2, 139.0, 136.4, 136.3, 136.2, 135.8, 130.4, 129.5, 129.4, 128.3, 126.7, 126.2, 123.0, 122.9, 118.9, 21.1 and 20.0 ppm. Four peaks were not observed probably because of overlap; UV/vis \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{max}}\) \((\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 401\) (15000), 516 (12000), and 678 (49000) nm; Fluorescence \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{em}} = 731\) nm \((\lambda_{\text{ex}} = 620\) nm) \(\Phi_t = 0.25\); HR-MS (ESI-MS): \(m/z = 949.3985\), calcd for \((\text{C}_{54}\text{H}_{47}\text{B}_{3}\text{F}_{6}\text{N}_{6})^- = 949.3962 [(M + Na)^-\].

**BODIPY 7**

\(^1\text{H} \text{NMR} \quad \text{(CDCl}_3)\): \(\delta\) 8.37 (s, 2H, \(\alpha\)), 8.23 (dt, \(J = 9.0\) Hz, 2.0 Hz, 4H, Ph), 7.65 (dt, \(J = 9.0\) Hz, 2.0 Hz, 4H, Ph), 7.06 (s, 2H, \(\beta\)), 7.00 (s, 2H, mesityl), 2.43 (s, 3H, mesityl), and 2.19 (s, 6H, mesityl) ppm; \(^{13}\text{C} \text{NMR} \quad \text{(CDCl}_3)\): \(\delta\) 149.1, 146.9, 142.9, 139.8, 138.7, 136.8, 136.3, 132.3, 128.9, 128.6, 125.9, 125.7, 124.5, 21.2 and 20.1 ppm; UV/vis/NIR \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{max}}\) \((\varepsilon [\text{M}^{-1}\text{cm}^{-1}]) = 380\) (21000), and 577 (67000) nm; Fluorescence \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{em}} = 606\) nm \((\lambda_{\text{ex}} = 520\) nm) \(\Phi_t = 0.78\); HR-MS (ESI-MS): \(m/z = 552.1781\), calcd for \((\text{C}_{30}\text{H}_{23}\text{BF}_{2}\text{N}_{4}\text{O}_{4})^- = 552.1791 [(M)^-\]. Single crystals were obtained by vapor diffusion of \(i\)-PrOH into a 1,2-dichloroethane solution. \(\text{C}_{30}\text{H}_{23}\text{BF}_{2}\text{N}_{4}\text{O}_{4}\), \(M_w = 522.33\), monoclinic, space group \(P2_1/c\) (No. 14), \(a = 7.602(2)\) Å, \(b = 24.077(6)\) Å, \(c = 14.334(4)\) Å, \(\beta = 102.602(5)^\circ\), \(V = 2560.5(11)\) Å\(^3\), \(Z = 4\), \(D_{\text{calc}} = 1.433\) g/cm\(^3\), \(T = 153(2)\) K, \(R_1 = 0.0605\) \((I > 2.0\ \alpha(I))\), \(R_w = 0.1484\) (all data), GOF = 1.038 \((I > 2.0\ \alpha(I))\).
BODIPY 8

$^1$H NMR (CDCl$_3$): $\delta$ 8.18 (s, 2H, $\alpha$), 7.37 (dt, $J = 9.5$ Hz, 2.5 Hz, 4H, Ph), 7.00 (s, 2H, mesityl), 6.69 (dt, $J = 9.5$ Hz, 2.5 Hz, 4H, Ph), 6.65 (s, 2H, $\beta$), 2.97 (s, 12H, -NCH$_3$), 2.41 (s, 3H, mesityl), and 2.18 (s, 6H, mesityl) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 149.9, 144.4, 141.5, 138.6, 136.6, 136.2, 134.5, 130.2, 128.2, 126.3, 121.3, 120.9, 112.6, 40.5, 21.2, and 20.1 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e [M$^{-1}$ cm$^{-1}$]) = 303 (31000), 428 (22000), and 686 (27000) nm; HR-MS (ESI-MS): m/z = 548.2928, calcd for (C$_{34}$H$_{35}$BF$_2$N$_4$)$^+$ = 548.2934 [(M$^+$)]. Single crystals were obtained by vapor diffusion of hexane into a chloroform solution. C$_{138}$H$_{140}$B$_4$Cl$_6$F$_8$N$_{16}$, $M_w$ = 2430.60, monoclinic, space group $C2/c$ (No. 15), $a = 57.842(5)$ Å, $b = 7.955(5)$ Å, $c = 29.332(5)$ Å, $\beta = 113.676(5)^\circ$, $V = 12361(8)$ Å$^3$, $Z = 4$, $D_{calc} = 1.306$ g/cm$^3$, $T = 153(2)$ K, $R_1 = 0.0545$ ($I > 2.0 \alpha(I)$), $R_w = 0.1536$ (all data), GOF = 0.812 ($I > 2.0 \alpha(I)$).

BODIPY 9

$^1$H NMR (CDCl$_3$): $\delta$ 8.26 (s, 1H, $\alpha$), 8.21 (dt, $J = 9.0$ Hz, 2.0 Hz, 2H, Ph), 8.04 (s, 1H, $\alpha$), 7.01 (s, 2H, mesityl), 6.90 (s, 1H, $\beta$), 6.80 (d, $J = 4.0$ Hz, 1H, $\beta$), 6.57 (d, $J = 4.5$ Hz, 1H, $\beta$), 2.40 (s, 3H, mesityl), and 2.14 (s, 6H, mesityl) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 148.3, 146.8, 146.6, 140.4, 139.4, 139.3, 136.5, 136.3, 135.8, 131.8, 131.0, 129.2, 128.4, 125.6, 124.4, 124.3, 120.0, 21.2, and 20.0 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e [M$^{-1}$ cm$^{-1}$]) = 307 (9000), 374 (18000), and 537 (62000) nm; Fluorescence (CH$_2$Cl$_2$): $\lambda_{em} = 565$ nm ($\lambda_{ex} = 500$ nm) $\Phi_f = 0.81$; HR-MS (ESI-MS): m/z = 431.1644, calcd for (C$_{24}$H$_{20}$BF$_2$N$_3$O$_2$)$^-$ = 431.1626 [(M$^-$)].

BODIPY 10

$^1$H NMR (CDCl$_3$): $\delta$ 8.31 (s, 1H, $\alpha$), 8.22 (dt, $J = 9.0$ Hz, 2.0 Hz, 2H, Ph), 7.87 (s, 1H, $\alpha$), 7.63 (dt, $J = 9.5$ Hz, 2.0 Hz, 2H, Ph), 7.01 (s, 2H, mesityl), 6.96 (s, 1H, $\beta$), 6.74 (s, 1H, $\beta$), 2.39 (s, 3H, mesityl), and 2.14 (s, 6H, mesityl) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 148.4, 146.8, 144.9, 142.6, 139.7, 138.7, 136.3, 136.2, 135.7, 132.0, 130.2, 128.7, 128.5, 125.8, 125.7, 124.4, 107.7, 21.2, and 20.0 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e [M$^{-1}$ cm$^{-1}$]) = 372 (20000), and 558 (68000) nm; Fluorescence (CH$_2$Cl$_2$): $\lambda_{em} = 583$ nm
(λ<sub>ex</sub> = 500 nm) Φ<sub>i</sub> = 0.35; HR-MS (ESI-MS): m/z = 509.0718, calcd for (C<sub>24</sub>H<sub>19</sub>BBF<sub>2</sub>N<sub>3</sub>O<sub>2</sub>)<sup>−</sup> = 509.0732 [(M)−].

**BODIPY 11**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.40 (s, 1H, α), 8.20 (dt, J = 9.0 Hz, 2.0 Hz, 2H, Ph), 8.18 (s, 1H, α), 7.61 (dt, J = 9.0 Hz, 2.0 Hz, 2H, Ph), 7.40 (dt, J = 9.0 Hz, 2.5 Hz, 2H, Ph), 7.03 (s, 2H, mesityl), 6.80 (s, 1H, β), 6.76 (s, 1H, β), 6.69 (dt, J = 9.0 Hz, 2.5 Hz, 2H, Ph), 3.00 (s, 6H, -NCH<sub>3</sub>), 2.42 (s, 3H, mesityl), and 2.18 (s, 6H, mesityl) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 150.4, 146.5, 146.3, 145.7, 139.9, 139.1, 138.5, 137.7, 136.8, 136.5, 135.6, 130.1, 129.5, 128.4, 126.5, 125.4, 124.4, 122.7, 122.4, 119.5, 112.4, 40.3, 21.2 and 20.1 ppm; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε [M<sup>−1</sup> cm<sup>−1</sup>]) = 381 (19000), 477 (21000), and 644 (27000) nm; HR-MS (ESI-MS): m/z = 550.2371, calcd for (C<sub>32</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>4</sub>O<sub>2</sub>)<sup>−</sup> = 550.2363 [(M)−]. Single crystals were obtained by vapor diffusion of i-PrOH into a chloroform solution. C<sub>32</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>4</sub>O<sub>2</sub>, M<sub>w</sub> = 550.40, monoclinic, space group P2<sub>1</sub>/c (No. 14), a = 7.676(5) Å, b = 24.661(5) Å, c = 14.676(5) Å, β = 100.684(5)°, V = 2730(2) Å<sup>3</sup>, Z = 4, D<sub>calc</sub> = 1.339 g/cm<sup>3</sup>, T = 153(2) K, R<sub>i</sub> = 0.0794 (I > 2.0 σ(I)), R<sub>w</sub> = 0.1739 (all data), GOF = 1.065 (I > 2.0 σ(I)).
\* = solvents and impurities

**Figure S1.** \(^1\)H NMR spectrum of 2 in CDCl\(_3\).

**Figure S2.** \(^{13}\)C NMR spectrum of 2 in CDCl\(_3\).
**Figure S3.** $^1$H NMR spectrum of 3 in CDCl$_3$.

**Figure S4.** $^{13}$C NMR spectrum of 3 in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 4 in CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum of 4 in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of 5 in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum of 5 in CDCl$_3$. 
Figure S9. $^1$H NMR spectrum of 6 in CDCl$_3$.

Figure S10. $^{13}$C NMR spectrum of 6 in CDCl$_3$. 
**Figure S11.** $^1$H NMR spectrum of 7 in CDCl$_3$.

**Figure S12.** $^{13}$C NMR spectrum of 7 in CDCl$_3$. 
Figure S13. $^1$H NMR spectrum of 8 in CDCl$_3$.

Figure S14. $^{13}$C NMR spectrum of 8 in CDCl$_3$. 
Figure S15. $^1$H NMR spectrum of 9 in CDCl$_3$.

Figure S16. $^{13}$C NMR spectrum of 9 in CDCl$_3$. 
Figure S17. $^1$H NMR spectrum of 10 in CDCl$_3$.

Figure S18. $^{13}$C NMR spectrum of 10 in CDCl$_3$. 
Figure S19. $^1$H NMR spectrum of 11 in CDCl$_3$.

Figure S20. $^{13}$C NMR spectrum of 11 in CDCl$_3$. 
Figure S21. X-ray crystal structure of 7. The thermal ellipsoids are scaled to the 50% probability level.

Figure S22. X-ray crystal structure of 8. The thermal ellipsoids are scaled to the 50% probability level.
Figure S23. UV/vis absorption spectra of 1 (black), 2 (red), and 3 (blue) in CH$_2$Cl$_2$.

Figure S24. UV/vis absorption spectra of 5 (green), 9 (orange), and 10 (purple) in CH$_2$Cl$_2$. 
Figure S25. (a) Excitation spectrum of 4 monitored at 665 nm in CH$_2$Cl$_2$. (b) excitation spectrum of 6 monitored at 731 nm in CH$_2$Cl$_2$. (c) Excitation spectrum of 7 monitored at 606 nm in CH$_2$Cl$_2$. 
Figure S26. Fluorescence lifetime measured by time correlated single-photon counting (TCSPC) measurement.

Table S1. Summary of photophysical data.

<table>
<thead>
<tr>
<th></th>
<th>$\Phi_r$</th>
<th>$\tau_n$ (ns)</th>
<th>$k_r$ ($\times 10^3$)</th>
<th>$k_{nr}$ ($\times 10^3$)</th>
<th>$\Phi'$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>0.98</td>
<td>6.7</td>
<td>1.46</td>
<td>0.0325</td>
<td>40</td>
</tr>
<tr>
<td>Dimer</td>
<td>0.15</td>
<td>1.8</td>
<td>0.833</td>
<td>4.72</td>
<td>124</td>
</tr>
<tr>
<td>Trimer</td>
<td>0.25</td>
<td>1.8</td>
<td>1.39</td>
<td>4.17</td>
<td>303</td>
</tr>
</tbody>
</table>

$\Phi_r$: quantum yield  
$\tau_n$: lifetime  
$k_{nr}$: non-radiative constant  
$k_r$: radiative constant  
$\Phi'$: rotational diffusion time

Figure S27. (a) Steady-state excitation fluorescence anisotropy spectra and (b) time-resolved fluorescence anisotropy spectra.