Supporting Information

Oxidation of 2-amino-substitued BODIPYs providing pyrazine-fused BODIPY trimers

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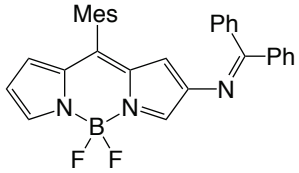
Instrumentation and Materials

^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{19}F NMR (470 MHz) spectra were recorded on a Varian INOVA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm) and CH_2Cl_2 (δ = 5.320 ppm) for ^{1}H NMR, $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR, and hexafluorobenzene (δ = –162.9 ppm) for ^{19}F NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Emission spectra were recorded on a JASCO FP-6500 spectrometer and absolute fluorescence quantum yields were measured by photon-counting method using an integration sphere. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF or APCI-TOF method for acetonitrile solutions. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

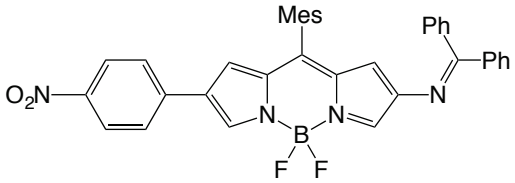
Experimental Section

Synthesis of 2a



A Schlenk tube containing compound **1a** (101 mg, 0.258 mmol), Cs_2CO_3 (167 mg, 0.512 mmol), Xantphos (15.4 mg, 26.6 μmol), and $Pd_2dba_3{\cdot}CHCl_3$ (13.7 mg, 13.2 μmol) was flushed with N_2 three times. To the Schlenk, dry 1,4-dioxane (3 mL) and benzophenone imine (64.6 μL, 0.385 mmol) were added. The mixture was stirred for 3 h at 100 °C. After the reaction, the resulting mixture was cooled down to room temperature, passed through a short pad of Celite, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/CH_2Cl_2) afforded compound **2a** (87.6 mg, 0.179 mmol) in 69% yield as a purple solid. ^{1}H NMR ($CDCl_3$): δ 7.80 (s, 1H), 7.71–7.74 (m, 2H), 7.52 (s, 1H), 7.42–7.45 (m, 1H), 7.35–7.38 (m, 5H), 7.13–7.14 (m, 2H), 6.86 (s, 2H), 6.57 (d, J = 4.5 Hz, 1H), 6.40 (dd, J = 3.8, 1.8 Hz, 1H), 5.60 (s, 1H), 2.34 (s, 3H), 1.96 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 168.4, 146.6, 143.6, 143.2, 142.2, 139.0, 138.5, 137.1, 136.1, 135.1, 134.2, 130.9, 129.4, 129.0, 128.9, 128.8, 128.2, 128.1, 127.9, 120.5, 117.8, 21.09, 19.86 ppm; APCI-MS: m/z = 490.2257, calcd for $(C_{31}H_{27}BF_2N_3)^+$ = 490.2266 [$(M+H)^+$].

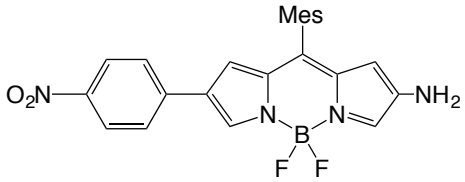
Synthesis of 2b



A Schlenk tube containing compound **1b** (50.7 mg, 99.4 μmol), Cs_2CO_3 (66.3 mg, 0.203 mmol), Xantphos (23.2 mg, 40.1 μmol), $Pd_2dba_3{\cdot}CHCl_3$ (20.7 mg, 20.0 μmol) was flushed with N_2 three times. To the Schlenk, dry 1,4-dioxane (3 mL) and benzophenone imine (24.7 μL, 0.147 mmol)

were added. The mixture was stirred for 2 h at 100 °C. After the reaction, the resulting mixture was cooled down to room temperature and passed through a short pad of Celite, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/CH_2Cl_2) afforded compound **2b** (33.0 mg, 54.1 μmol) in 54% yield as a purple solid. ^{1}H NMR ($CDCl_3$): δ 8.17–8.19 (m, 2H), 8.15 (s, 1H), 7.72–7.74 (m, 2H), 7.65 (s, 1H), 7.57–7.59 (m, 2H), 7.45–7.48 (m, 1H), 7.37–7.40 (m, 5H), 7.14–7.16 (m, 2H), 6.92 (s, 2H), 6.78 (s, 1H), 5.68 (s, 1H), 2.37 (s, 3H), 2.00 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 169.6, 146.6, 146.3, 145.2, 145.1, 144.9, 139.6, 139.2, 139.0, 138.7, 136.8, 136.1, 135.5, 135.5, 131.2, 130.2, 129.2, 129.1, 129.0, 128.9, 128.3, 128.1, 125.4, 124.3, 123.0, 120.9, 21.14, 19.92 ppm; APCI-MS: m/z = 611.2407, calcd for $(C_{37}H_{30}BF_2N_4O_2)^+$ = 611.2431 [$(M+H)^+$].

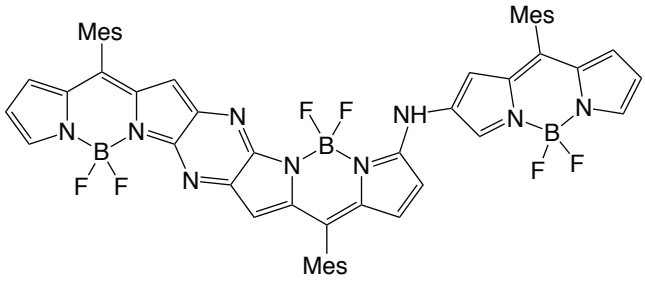
Synthesis of 3b



Compound **2b** (20.2 mg, 33.1 μmol) in THF (2.69 mL) was added 1 M HCl (0.587 mL) and the mixture was stirred for 1 h at 60 °C. After the reaction, the resulting mixture was cooled down to room temperature, and then aqueous $NaHCO_3$ was added into reaction mixture. The resulting solution was extracted with CH_2Cl_2 and the organic layer was washed with water, dried over with Na_2SO_4, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/CH_2Cl_2) afforded compound **3b** (13.5 mg, 30.2 μmol) in 91% yield as a dark blue solid. ^{1}H NMR ($CDCl_3$): δ 8.16–8.18 (m, 2H), 8.05 (s, 1H), 7.80 (s, 1H), 7.57–7.58 (m, 2H), 6.98 (s, 2H), 6.67 (s, 1H), 5.85 (s, 1H), 3.63 (s, 2H), 2.38 (s, 3H), 2.15 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 146.0, 143.0, 142.7, 141.9, 140.3, 138.9, 136.9, 136.4, 136.4, 135.0, 129.6, 128.9, 128.3, 125.2, 124.3,

121.0, 108.8, 21.16, 19.99 ppm; APCI-MS: m/z = 447.1788, calcd for $(C_{24}H_{22}BF_2N_4O_2)^+$ = 447.1803 [$(M+H)^+$].

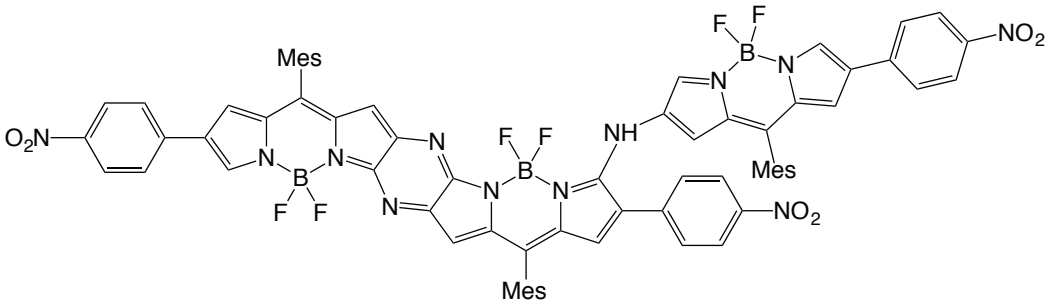
Synthesis of 4a



Compound **2a** (30.2 mg, 61.7 μmol), THF (5.0 mL), and 1M HCl (1.1 mL) were added into a 30 mL round-bottomed flask, and the mixture was stirred for 1 h at 60 °C. After the reaction, the resulting solution was cooled down to room temperature, and then aqueous $NaHCO_3$ was added. The resulting mixture was extracted with $CHCl_3$ and then the organic extract was washed with water, dried over with Na_2SO_4, and evaporated the solvent to ca. 40 mL of the total volume. The solution was diluted with $CHCl_3$ (40 mL) and degassed by bubbling with N_2 for 45 minutes. To the resulting solution was added DDQ (29.3 mg, 129 μmol). The reaction mixture was stirred for 30 min at room temperature. After the reaction, the resulting mixture was concentrated in vacuo. Purification by silica-gel column chromatography (hexane/EtOAc) afforded compound **4a** (6.69 mg, 6.92 μmol) in 34% yield (2 steps) as a blue solid. ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H), 8.08 (s, 1H), 7.85 (s, 1H), 7.04 (s, 1H), 6.98 (s, 2H), 6.97 (s, 2H), 6.97 (s, 2H), 6.89 (d, J = 4.5 Hz, 1H), 6.87 (d, J = 5.2 Hz, 1H), 6.83 (d, J = 4.1 Hz, 1H), 6.68 (dd, J = 0.8, 4.3 Hz, 1H), 6.57–6.59 (m, 3H), 6.52 (s, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.12 (s, 6H), 2.10 (s, 6H), 2.09 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 161.0, 151.6, 151.3, 149.4, 148.6, 147.7, 145.5, 143.8, 140.4, 139.8, 139.6, 139.3, 139.0, 138.5, 137.3, 137.0, 136.6, 136.3, 136.1, 135.4, 133.3, 132.9, 132.8, 131.1, 129.1, 128.7, 128.5, 128.4, 128.2, 123.0, 120.7, 119.9, 119.2, 118.0, 109.5, 21.17, 21.13, 20.13, 20.06, 20.05 ppm;

UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 359 (14000), 507 (21000), 700 (120000) nm; APCI-MS: *m/z* = 968.4118, calcd for $(C_{54}H_{47}B_3F_6N_9)^+$ = 968.4156 [$(M+H)^+$].

Synthesis of 4b



A Schlenk tube containing compound **3b** (4.93 mg, 11.0 μmol) and DDQ (5.15 mg, 22.7 μmol) was flushed with N_2 three times. To the Schlenk, dry $CHCl_3$ (3.66 mL) was added. The mixture was stirred for 4 h at room temperature. After the reaction, the resulting mixture was passed through short pad of Celite, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/CH_2Cl_2) afforded compound **4b** (2.91 mg, 2.19 μmol) in 59% yield as a black solid. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1H), 8.54 (s, 1H), 8.28 (s, 1H), 8.23 (d, *J* = 9.0 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H) 7.73 (d, *J* = 9.0 Hz, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.32 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.16 (s, 1H), 7.06 (s, 3H), 7.04 (s, 2H), 6.96 (s, 3H), 6.93 (s, 1H), 6.58 (s, 1H), 6.43 (s, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.17 (s, 6H), 2.17 (s, 6H), 2.02 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 157.9, 152.4, 150.0, 149.0, 148.6, 148.4, 147.8, 147.4, 147.0, 146.2, 144.8, 144.3, 140.8, 140.5, 139.9, 139.8, 139.5, 139.0, 138.8, 138.1, 137.7, 137.2, 137.0, 136.9, 136.6, 135.8, 135.6, 135.4, 133.5, 133.0, 133.0, 132.1, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 126.5, 126.4, 126.3, 126.0, 124.5, 124.4, 123.5, 121.3, 120.2, 110.6, 21.18, 21.15, 20.23, 19.88 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 587 (34000), 762 (170000) nm; APCI-MS: *m/z* = 1353.4495, calcd for $(C_{72}H_{55}B_3F_6N_{12}O_6Na)^+$ = 1353.4473 [$(M+Na)^+$].

^{1}H and ^{13}C NMR Spectra

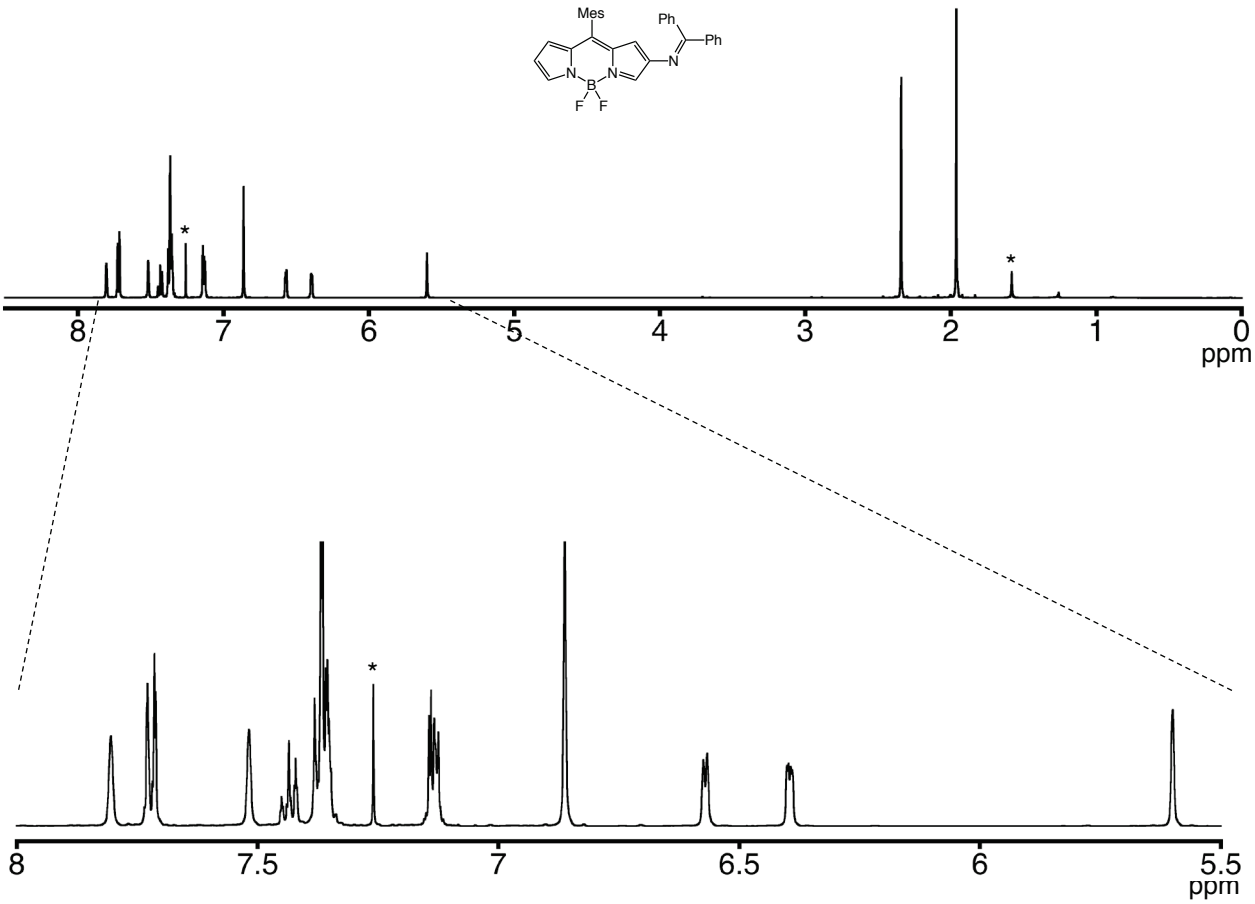


Fig. S1 ^{1}H NMR spectrum of **2a** in $CDCl_3$.

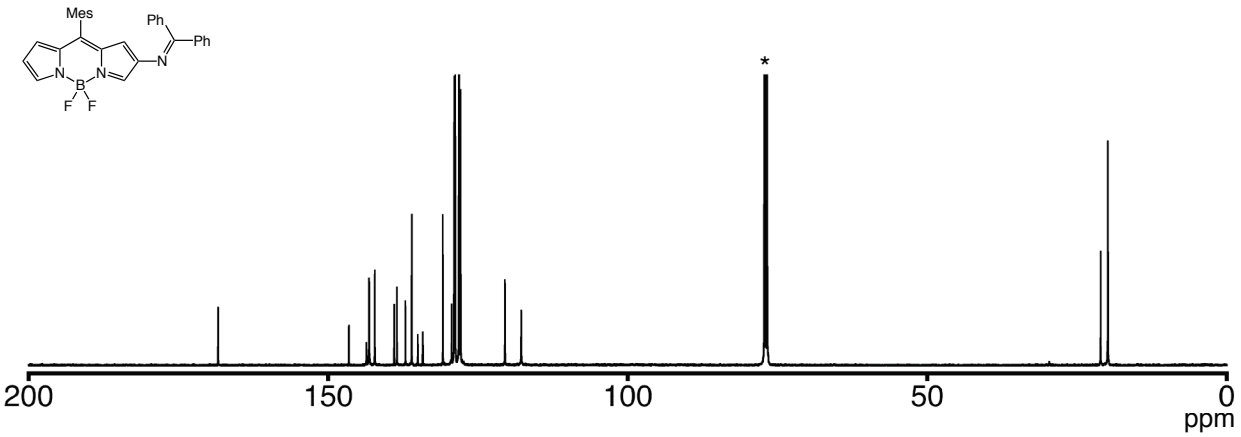


Fig. S2 ^{13}C NMR spectrum of **2a** in $CDCl_3$.

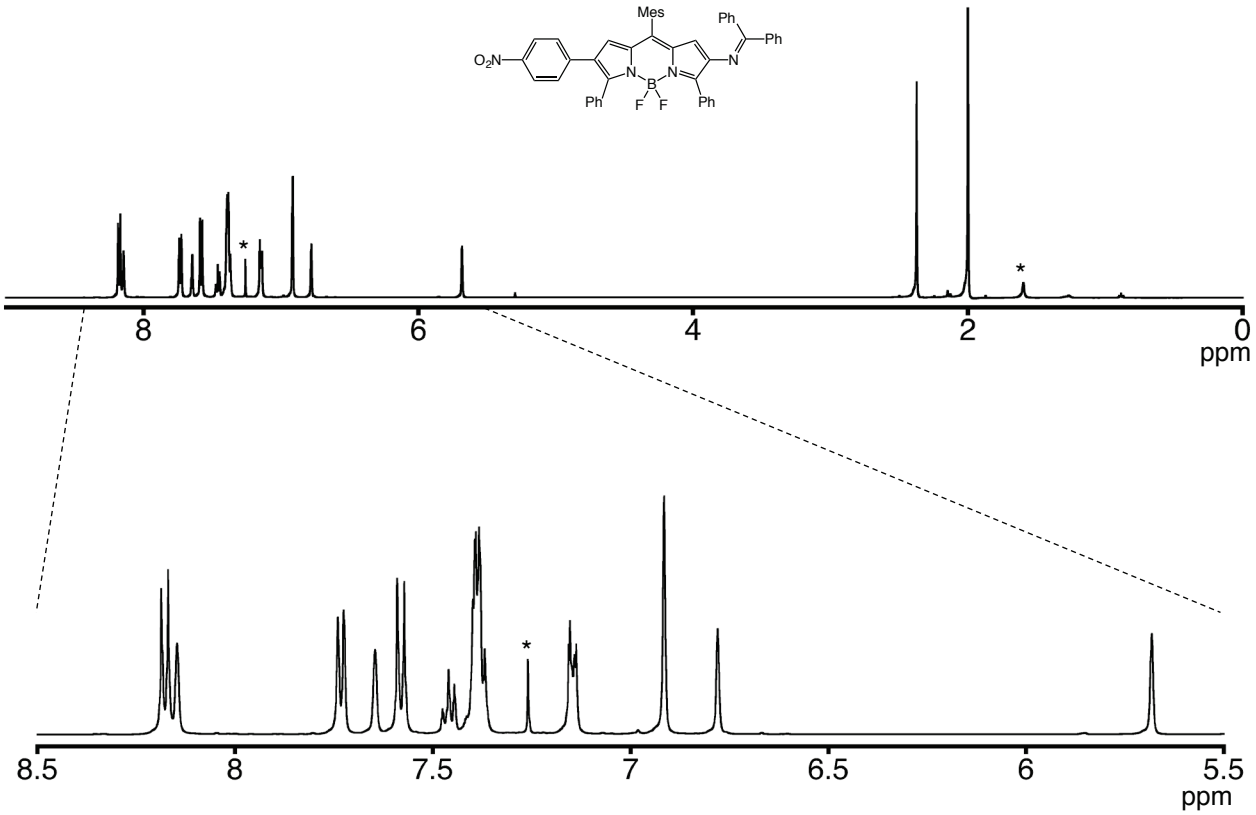


Fig. S3 ^{1}H NMR spectrum of **2b** in $CDCl_3$.

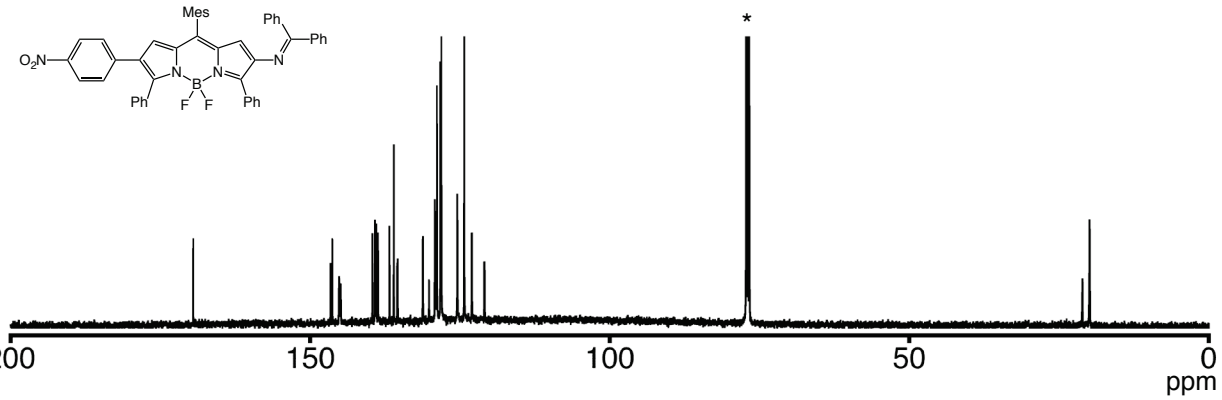


Fig. S4 ^{13}C NMR spectrum of **2b** in $CDCl_3$.

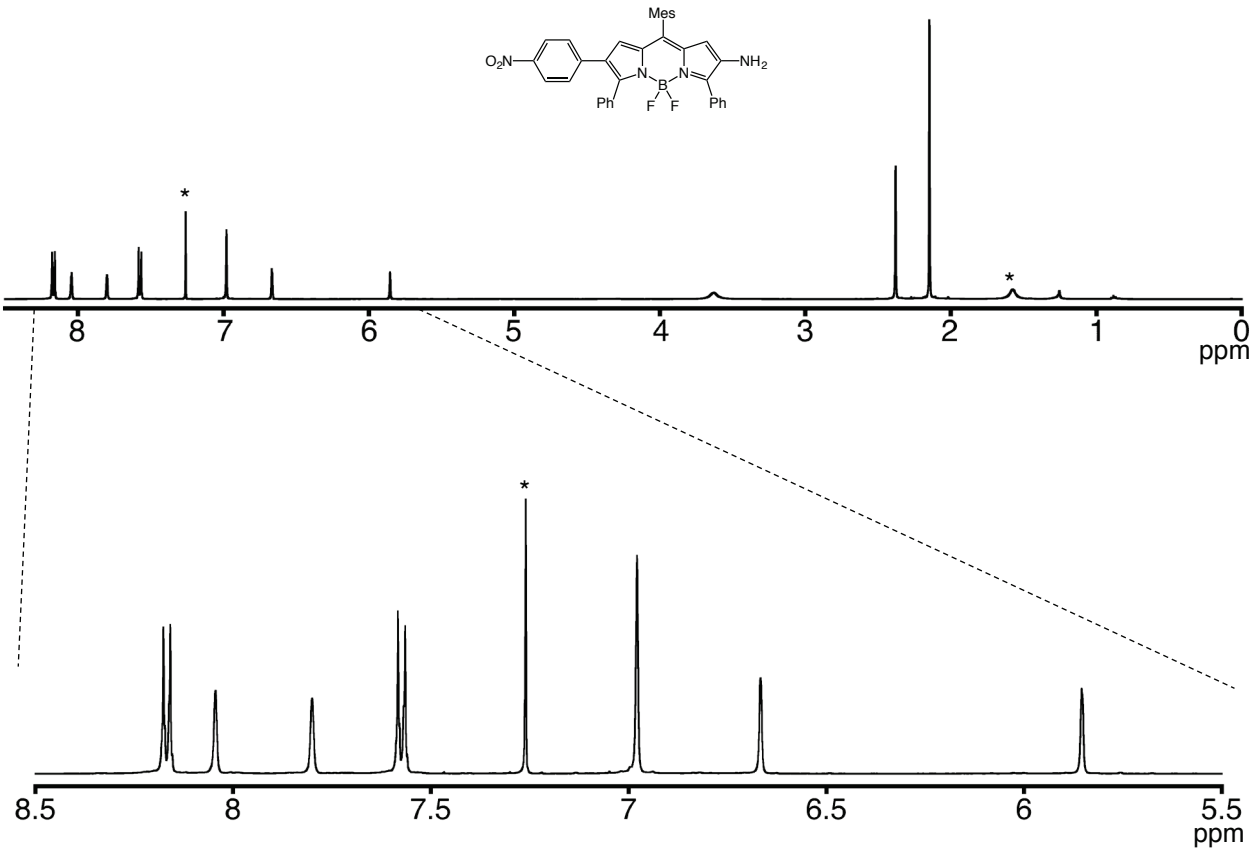


Fig. S5 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

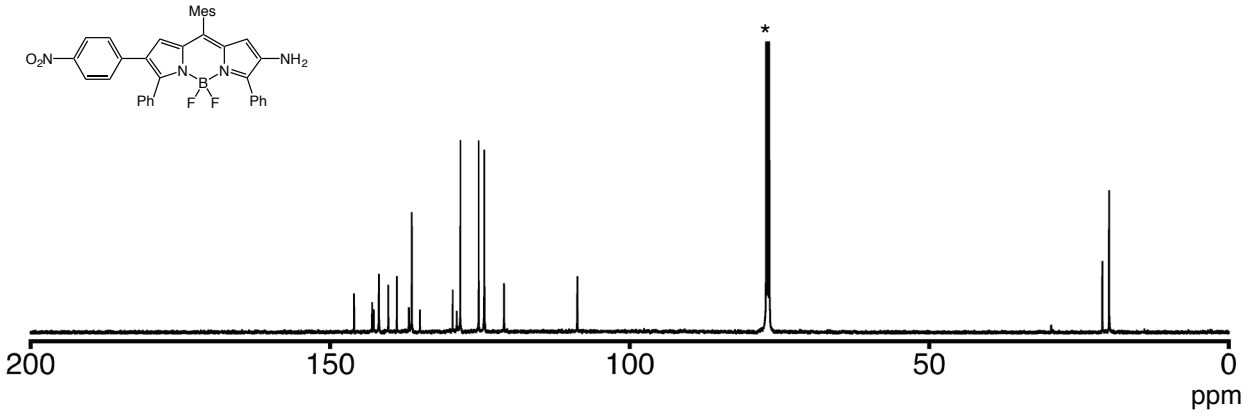


Fig. S6 ^{13}C NMR spectrum of **3b** in $CDCl_3$.

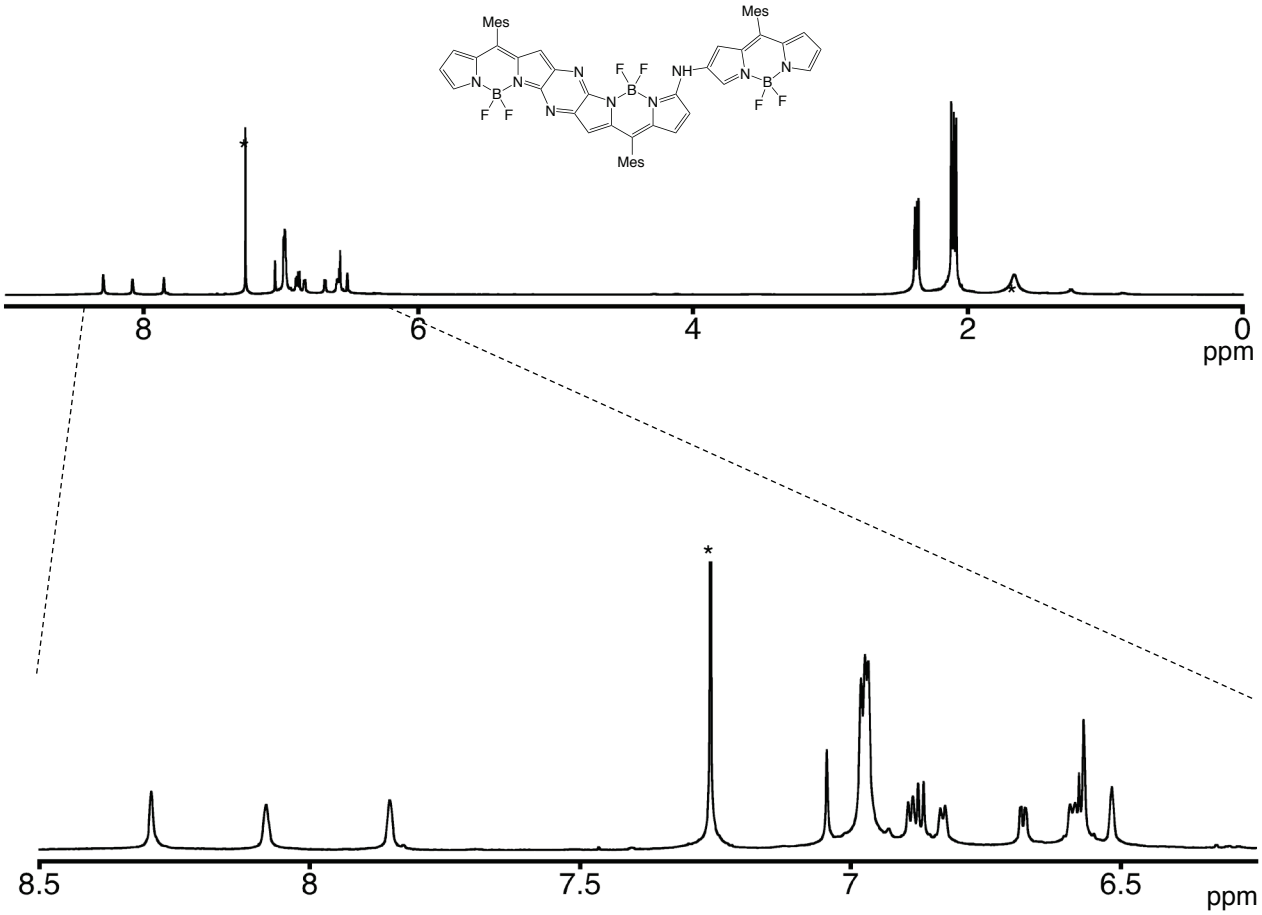


Fig. S7 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

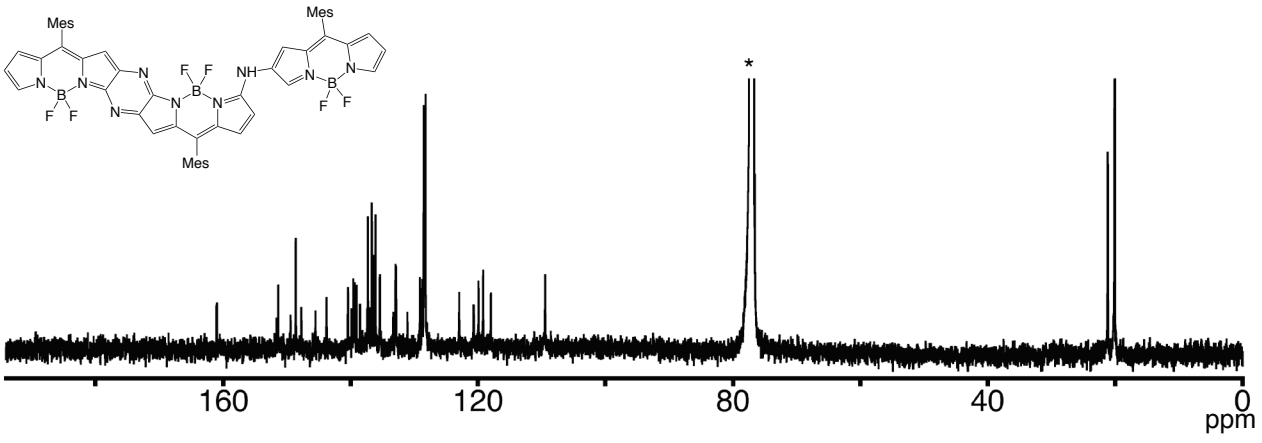


Fig. S8 ^{13}C NMR spectrum of **4a** in $CDCl_3$.

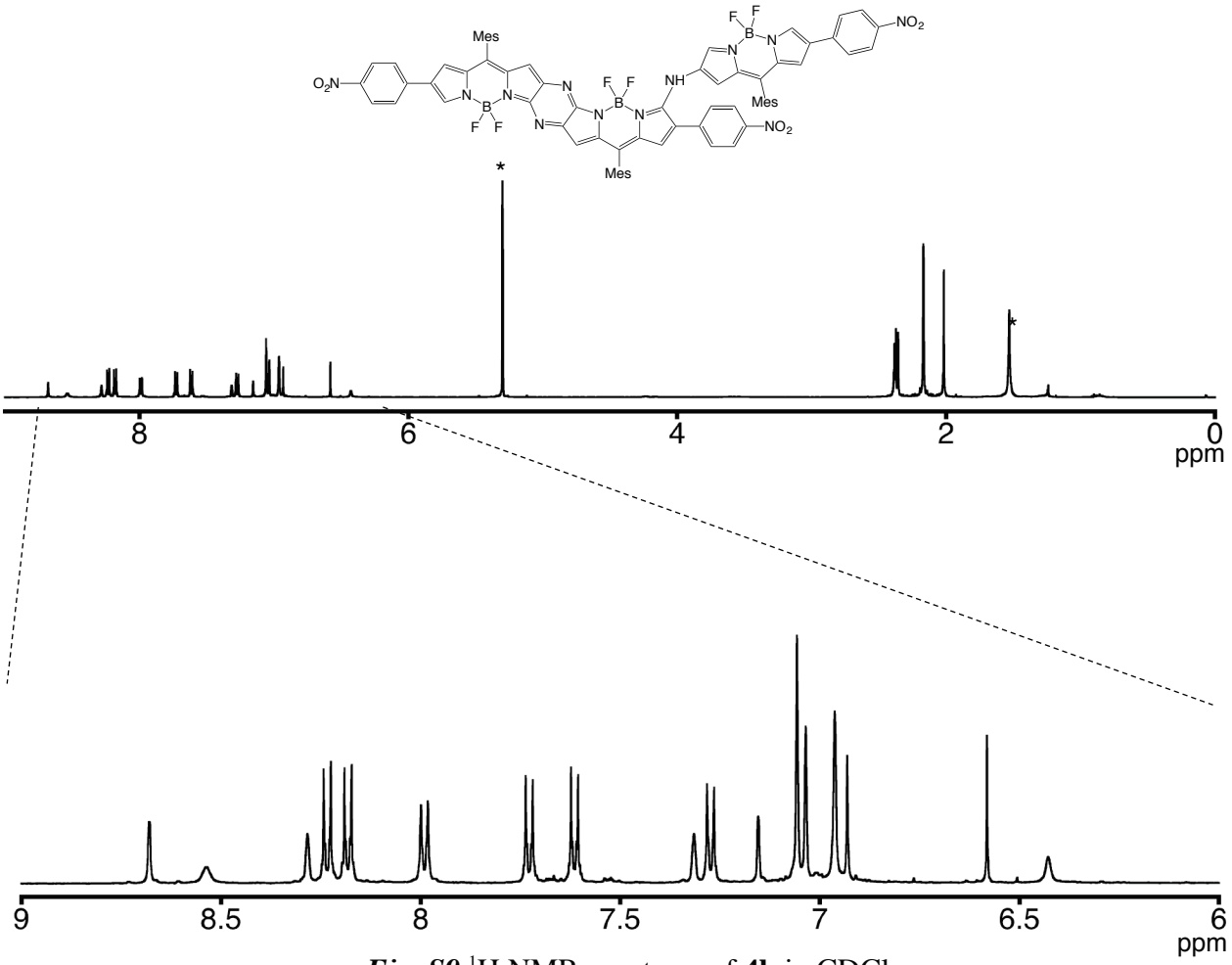


Fig. S9 ^{1}H NMR spectrum of **4b** in $CDCl_3$.

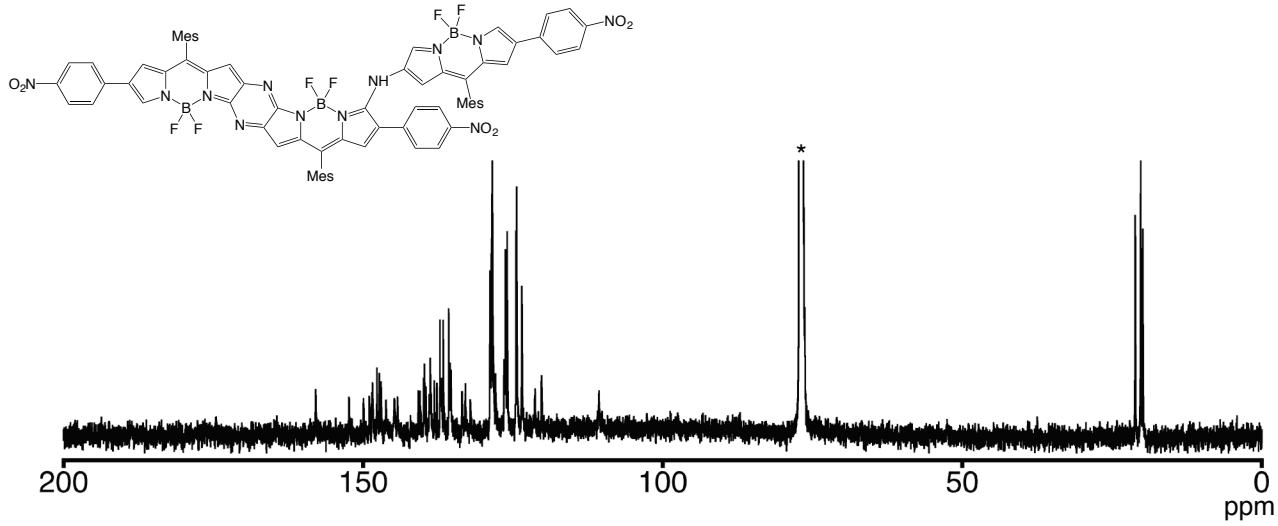
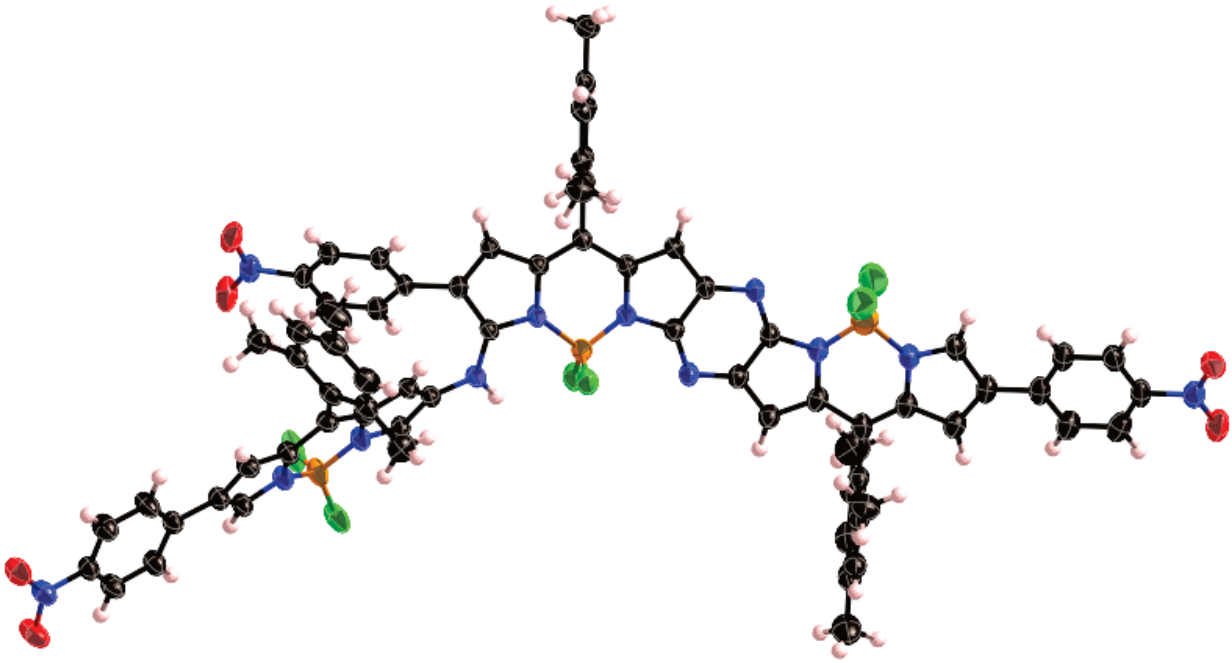


Fig. S10 ^{13}C NMR spectrum of **4b** in $CDCl_3$.

X-ray Diffraction analysis

A single crystal (0.20 mm × 0.20 mm × 0.20 mm) of **4a** for X-ray diffraction analysis was obtained by slow evaporation of chloroform solution. A single crystal (0.22 mm × 0.02 mm × 0.01 mm) of **4b** for X-ray diffraction analysis was obtained by slow evaporation of chlorobenzene solution. The data were collected at 103 K on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. Crystallographic data for **4a** and **4b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-971649 and CCDC-971650, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(a)



(b)

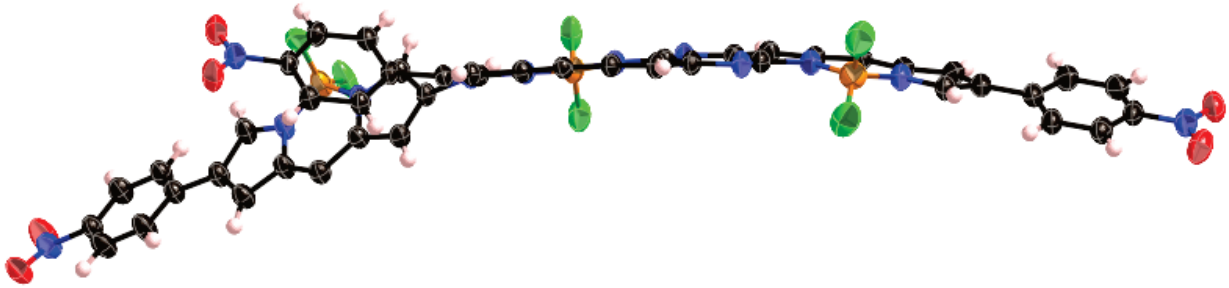


Fig. S11 X-ray crystal structure of **4b**. (a) top view and (b) side view. The thermal ellipsoids are scaled to the 50% probability level. The mesityl groups are omitted in the side view for clarity.

Cyclic voltammetry

Cyclic voltammograms of **4a**, **4b**, 5-mesitylBODIPY (**5a**), and 5-mesityl-2-(4-nitrophenyl)BODIPY (**5b**) were recorded on ALS electrochemical analyser 612C. Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three electrode system was used and consisted of a glassy carbon working electrode, a platinum wire and $Ag/AgClO_4$ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

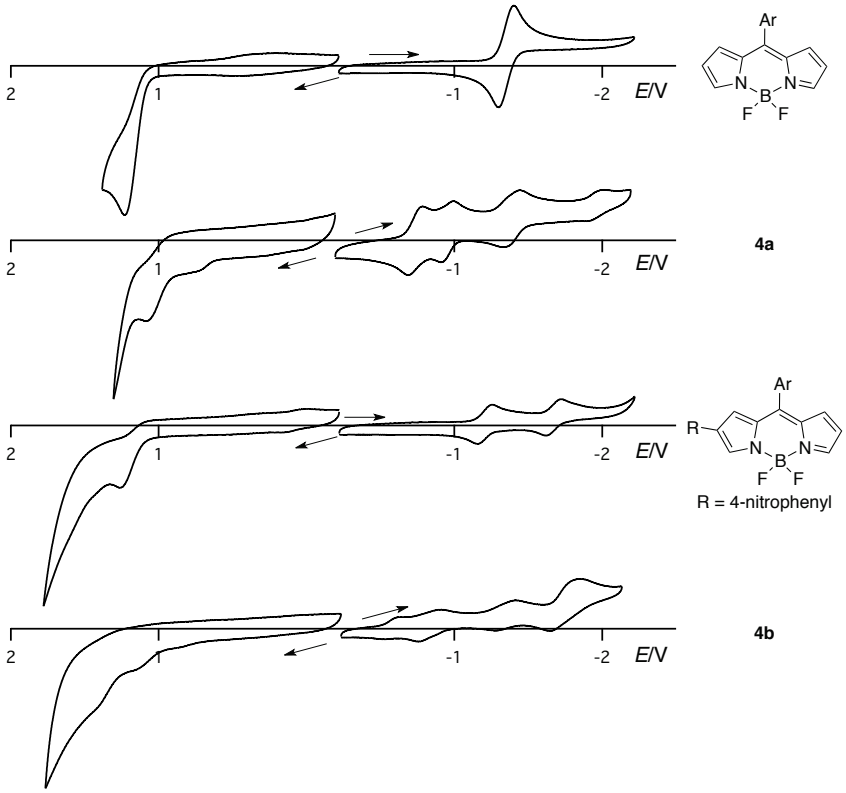


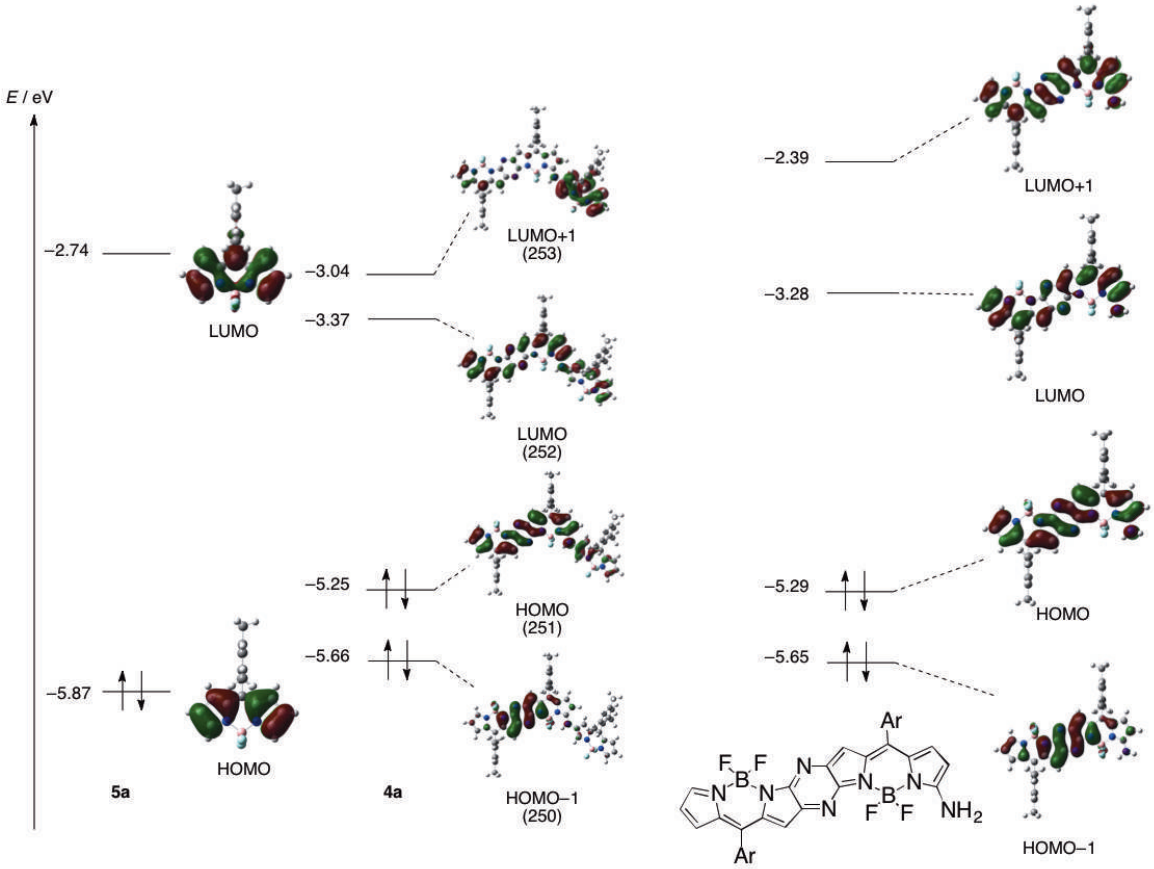
Fig. S12 Cyclic voltammograms of **5a**, **4a**, **5b** and **4b**.

Theoretical calculations

All calculations were carried out using the Gaussian 09 program.[1] The aminyl radical intermediate and the cation radical intermediate were optimized without any symmetry restriction based on DFT method using Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[2] and the 6-31G(d) basis set. The molecular orbitals were calculated by single point calculation at the B3LYP/6-31G(d) level using the geometry optimized at B3LYP/6-31G(d) level. The oscillator strength of the absorption spectrum of **4a** was calculated by the time-dependent (TD) DFT method based at the B3LYP/6-31G(d) level.

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[2] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.



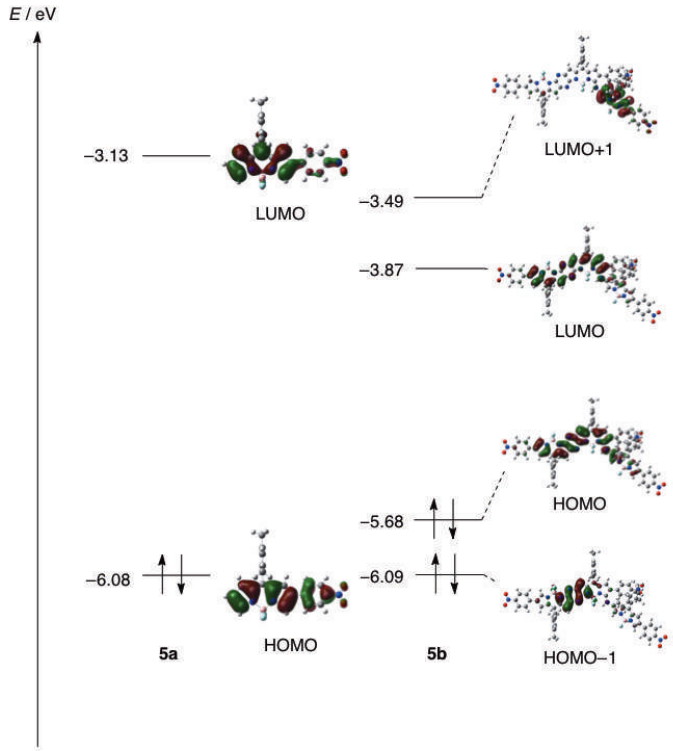
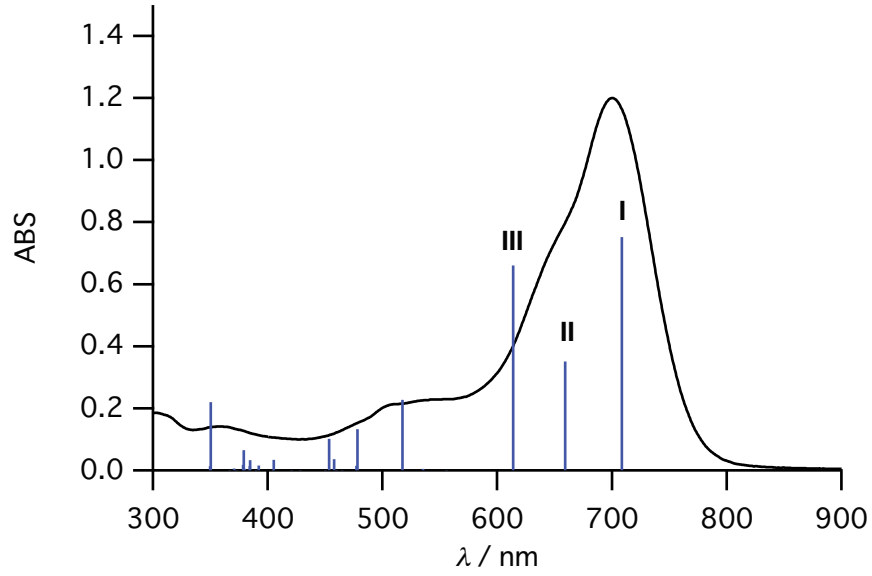


Fig. S13 Molecular orbitals of **4a**, **5a**, **4b**, **5b** and pyrazine-fused BODIPY dimer.



	transition	ratio
I	250 -> 252	-0.31378
	251 -> 252	0.60829
	251 -> 253	-0.15783
II	250 -> 252	0.54644
	251 -> 252	0.19552
	251 -> 253	-0.39236
III	249 -> 252	0.21219
	250 -> 252	0.30595
	251 -> 252	0.27526
	251 -> 253	0.53133

Fig. S14 Oscillator strength of the calculated absorption spectrum of **4a**.

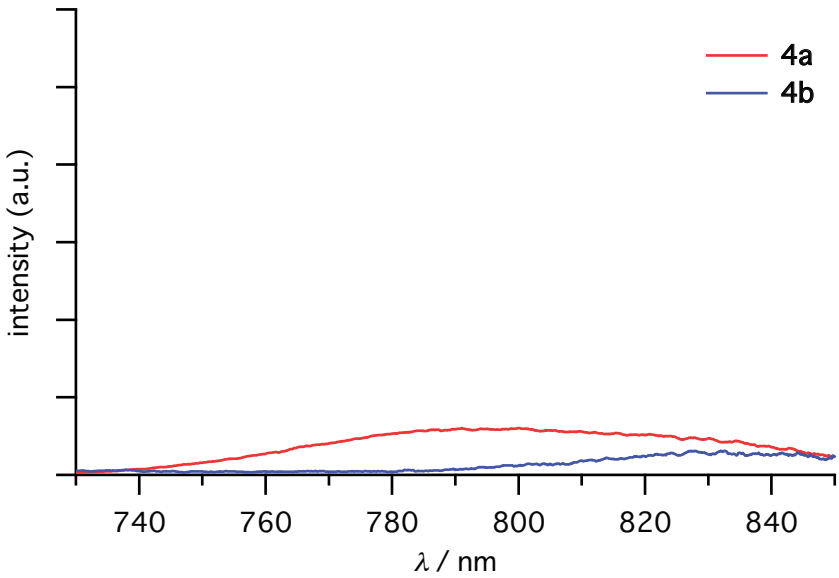


Fig. S15 Emission spectra of **4a** and **4b** in CH_2Cl_2. The data were obtained at the concentration of 6.0×10^{-6} M.