CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals are purchased from commercial sources and used as received without further purification, unless noted otherwise.

1. Benzaldehyde : Merck
2. Boron triflouride diethyletherate ($BF_3 \cdot Et_2O$) : Fluka
3. Deuterated chloroform ($CDCl_3$) : Cambridge Isotope
4. 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU) : Sigma-Aldrich
5. 2,3-dichloro-5,6-dicyano benzoquinone (DDQ) : Sigma-Aldrich
6. Ethyl acetate : Distilled from commercial grade
7. Ethyl isocyanoacetate : Sigma-Aldrich
8. Hexanes : Distilled from commercial grade
9. 0.1 M Hydrochloric acid (HCl) : Merck
10. Anhydrous magnesium sulfate ($MgSO_4$) : Merck
11. Methanol : Distilled from commercial grade
12. 2-methoxyphenylboronic acid : Sigma-Aldrich
13. Methylene chloride (CH_2Cl_2) : Distilled from commercial grade
14. 1-nitrocyclohexene : Sigma-Aldrich
15. Pyrrole : Merck
16. Silica gel 60 particle size : Merck
17. Silica gel containing gypsum : Merck
18. Anhydrous sodium sulfate (Na_2SO_4) : Merck
19. Sodium bicarbonate ($NaHCO_3$) : Merck
20. 2-thiophene carboxaldehyde : Sigma-Aldrich
21. 2,2'-bithiophene-5-carboxaldehyde : Sigma-Aldrich
22. Toluene : RCI Lab-Scan
23. Triethylamine (NEt_3) : Fluka

25. Trifluoroacetic acid (TFA) : Fluka

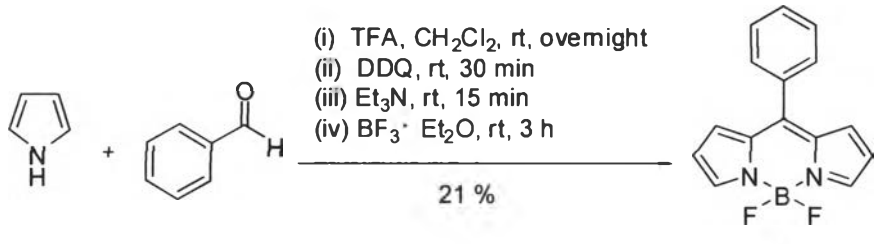
3.2 Analytical Instruments

^{1}H-NMR and ^{13}C-NMR spectra were obtained in $CDCl_3$ at 400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei (Varian Company, USA). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26 ppm for ^{1}H-NMR and 77.0 for ^{13}C-NMR). Coupling constant (*J*) is reported in Hertz (Hz). Mass spectra were obtained by high resolution electron spray ionization mass spectrometry (HR-ESI-MS) and matrix-assisted laser desorption ionization, MALDI (Bruker Daltonics, Germany) mass spectrometry with dithranol as a matrix. Absorption spectra were measured in toluene using a Hewlett-Packard 8453 spectrophotometer and absorption extinction coefficient (ε) was reported in $M^{-1}\cdot cm^{-1}$. Fluorescence spectra were measured in toluene using a Perkin-Elmer LS45 luminescence spectrometer.

3.3 Experimental procedure

Part 1: Synthesis of BODIPY-thiophene derivatives

3.3.1 Synthesis of compound 1

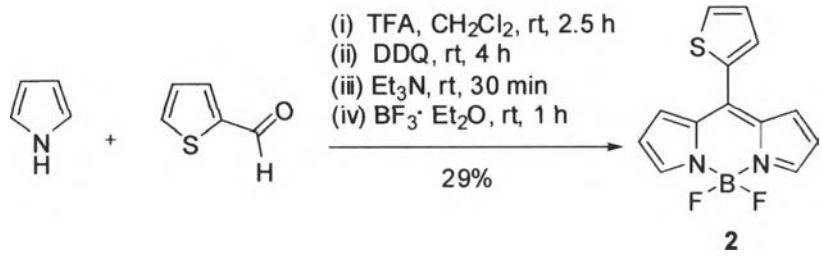


1

Following a previously published procedure [74], to benzaldehyde (0.531 g, 5.00 mmol) and pyrrole (0.671 g, 10.0 mmol) in deoxygenated CH_2Cl_2 (150 mL), TFA (0.050 mL, 0.65 mmol) was added and the mixture was stirred at room temperature for overnight under N_2. The resulting solution was treated with DDQ (1.1390 g, 5.018 mmol) stirring was continued at room temperature for 30 min, followed by the addition of Et_3N (15.33 mL, 0.1099 mol). After 15 min, $BF_3\cdot Et_2O$ (15.21 mL, 0.1200 mol) was added at 0°C, and the mixture was stirred at room temperature for additional 3 h. After washing with a saturated aqueous solution of $NaHCO_3$, the organic phase was collected, dried over $MgSO_4$, filtered, and concentrated to dryness. The residue was purified by silica gel column chromatography (ethyl

acetate/hexanes; 2:1) to afford **1** as an orange solid (113.6 mg, 21%). ^{1}H-NMR: δ_H 6.55 (d, *J* = 2.4 Hz, 2H), 6.94 (d, *J* = 3.2 Hz, 2H), 7.50—7.61 (m, 5H), 7.95 (s, 2H) (**Figure A-1**); MALDI-TOF-MS obsd 267.399 ($[M]^+$), calcd 268.0983 ($[M]^+$, M=$C_{15}H_{11}BF_2N_2$) (**Figure A-2**); λ_{abs} (ε) 344, 503 nm (0.5 × 10^5) (**Figures B-1** and **B-2**); λ_{em} (λ_{ex}= 470 nm) 521 nm (**Figure B-3**). Other spectroscopic data are consistent with those described in the literature.

3.3.2 Synthesis of compound 2

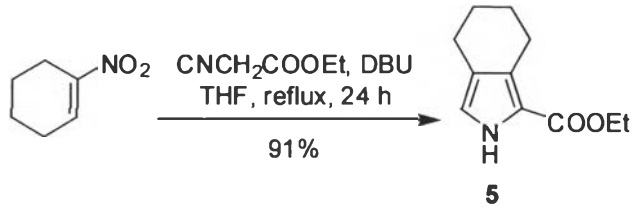


2

Following a previously published procedure [71], 2-thiophene carboxaldehyde (0.200 g, 1.79 mmol) was dissolved in pyrrole (1.79 mL, 25.0 mmol) and TFA (0.27 mL, 3.5 mmol) were added. The reaction was allowed to proceed at room temperature for 2.5 h. A solution of DDQ (0.405 g, 1.79 mmol) in dichloromethane (20 mL) was added and the reaction continued at room temperature for additional 4 h. NEt_3 (3.09 mL, 23.2 mmol) was added to the reaction mixture, which was stirred at room temperature for 30 min. After that, $BF_3{\cdot}OEt_2$ (3.85 mL, 30.4 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction mixture was then washed with H_2O (2×50 mL) and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to dryness. The resulting crude was purified by silica column chromatography (CH_2Cl_2/hexanes; 4:1) to afford **2** as an orange solid (175.0 mg, 29%). ^{1}H-NMR: δ_H 6.60 (d, *J* = 3.6 Hz, 2H), 7.26—7.35 (m, 3H), 7.60 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 5.2 Hz, 1H), 7.95 (s, 2H) (**Figure A-3**); ^{13}C-NMR δ_C 118.5, 128.2, 131.4, 131.5, 133.0, 134.3, 134.5, 139.5, 143.8 (**Figure A-4**); HR-ESI-MS obsd 297.0448 ($[M + Na]^+$), calcd 297.0445 ($[M + Na]^+$), 274.0548 ($[M]^+$, M=$C_{13}H_9BF_2N_2S$) (**Figure A-5**); λ_{abs} (ε) 393, 514 nm (0.5 × 10^5) (**Figures B-5** and **B-6**); λ_{em} (λ_{ex}= 480 nm) 617 nm (**Figure B-7**).

Past 2: Synthesis of benzoBODIPY-thiophene derivaatives

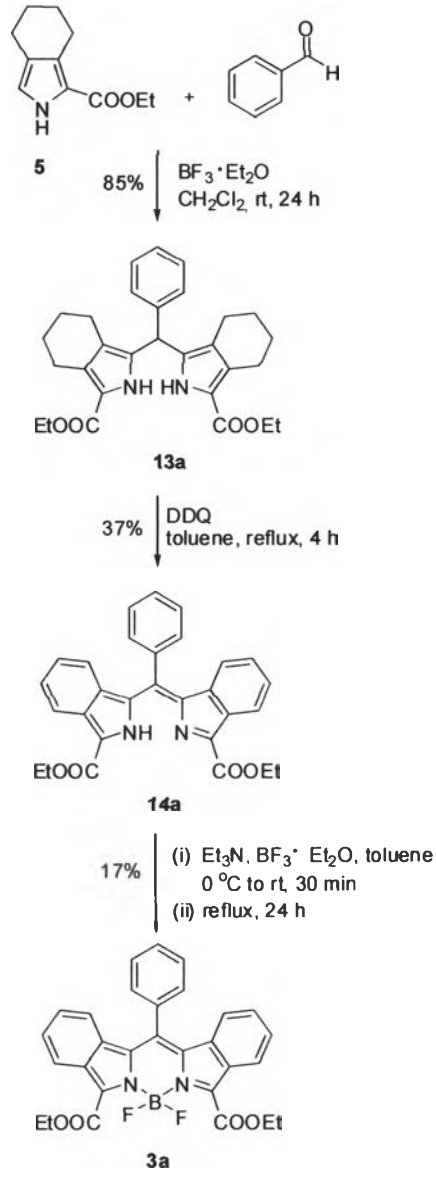
3.3.3 Synthesis of 2H-isoindole-4,5,6,7-tetrahydro-1-carboxylic ethyl ester (5)



5

Following a previously published procedure [55], a 3-neck-round bottom flask equipped with a condenser was purged with N_2. Then 1-nitrocyclohexene (4.40 mL, 39.2 mmol) and ethyl isocyanoacetate (4.30 mL, 39.2 mmol) were dissolved in dry THF (100 mL). To this solution, DBU (5.50 mL, 39.2 mmol) was slowly added and the reaction was refluxed for 24 h. The solvent was removed under reduced pressure and the crude product was purified on a silica column (CH_2Cl_2/hexanes; 4:1) to afford **5** as pale yellow crystals (6.853 g, 91%). ^{1}H-NMR: δ_H 1.34 (t, J = 6.8 Hz, 3H), 1.51—1.63 (m, 4H), 2.47—2.58 (m, 2H), 2.74—2.86 (m, 2H), 4.29 (q, J = 7.2 Hz, 2H), 6.64 (s, 1H), 8.76 (br s, 1H) (**Figure A-26**). Other spectroscopic data are consistent with those described in the literature.

3.3.4 Synthesis of compound 3a



Following a published procedure with slight modification [73], isoindole **5** (0.500 g, 2.59 mmol) and benzaldehyde (0.13 mL, 1.3 mmol) were dissolved in CH_2Cl_2 (50 mL). Then, $BF_3 \cdot Et_2O$ (0.032 mL, 0.26 mmol) was added dropwise and the solution was stirred at room temperature for 24 h. The solvent was evaporated under vacuum and the resulting residue was chromatographed on a silica column (CH_2Cl_2/hexanes, 4:1) to give **13a** as a white solid (0.523 g, 85%). ^{1}H-NMR: δ_H 1.29 (t, J = 7.0 Hz, 6H), 1.58—1.75 (m, 8H), 2.18 (m, 4H), 2.77 (m, 4H), 4.15—4.22 (m, 4H), 5.40 (s, 1H), 7.09 (d, J = 6.8 Hz, 2H), 7.27—7.35 (m, 3H), 8.46 (br s, 1H), 8.58 (br s, 1H) (**Figure**

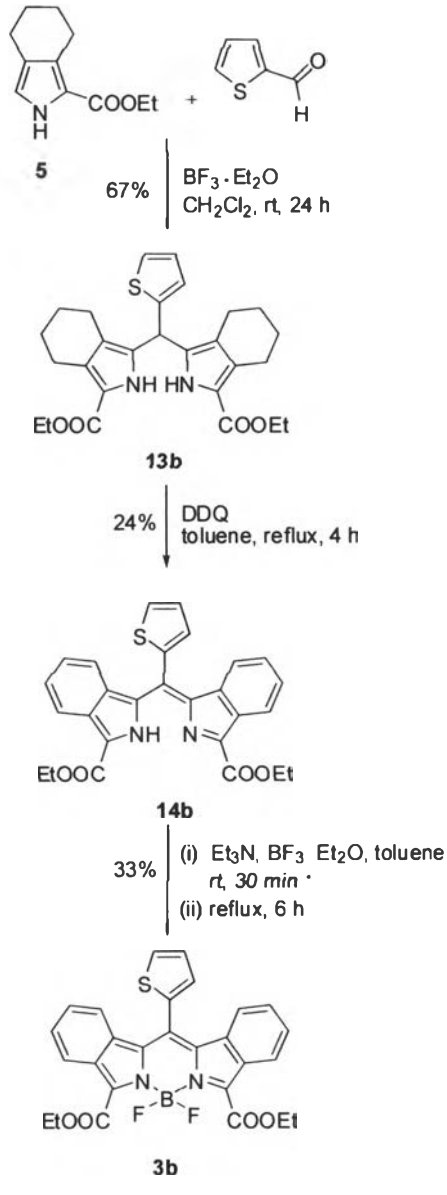
A-18); ^{13}C-NMR δ_C 14.5, 21.2, 23.1, 23.3, 40.6, 59.7, 116.7, 119.7, 127.3, 128.2, 128.9, 129.2, 130.8, 139.1, 161.8 (**Figure A-19**); λ_{abs} (ε) 289 nm (0.4 × 10^5) (**Figures B-25** and **B-26**). Other spectroscopic data are consistent with those described in the literature.

Following a previously published procedure [13], a solution of dipyrromethane **13a** (0.796 g, 1.68 mmol) in toluene (30 mL) was heated to 110°C. A solution of DDQ (2.666 g, 11.74 mmol) in toluene (20 mL) was then added and the mixture was refluxed for 4 h. After that, the solvent was removed under reduced pressure. The resulting residue was dissolved in ethyl acetate and extracted with a 0.1 M solution of HCl to remove traces of DDQ (3×50 mL), washed once with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2/hexanes, 4:1) to dipyrrin **14a** as a purple solid (0.285 g, 37%). ^{1}H-NMR: δ_H 1.57 (t, J = 7.2 Hz, 6H), 4.58 (q, J = 7.2 Hz, 4H), 6.12 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.0 Hz, 2H), 7.21—7.24 (m, 2H), 7.53 (d, J = 6.8 Hz, 2H), 7.63—7.71 (m, 3H), 8.19 (d, J = 8.0 Hz, 2H) (**Figure A-27**); ^{13}C-NMR δ_C 14.5, 61.3, 122.1, 122.9, 126.1, 127.0, 129.2, 129.5, 131.8, 135.1, 135.6, 136.5, 137.9, 138.3, 161.9 (**Figure A-28**); MALDI-TOF-MS obsd 463.710 ([M]$^+$), calcd 464.512 ([M]$^+$, M=$C_{29}H_{24}N_2O_4$) (**Figure A-29**); λ_{abs} (ε) 574 nm (0.4 × 10^5) (**Figures B-31** and **B-32**). Other spectroscopic data are consistent with those subscribed in the literature.

Following a previously published procedure [13], a solution of dipyrrin **14a** (0.285 g, 0.614 mmol) in toluene (20 mL) was treated with Et_3N (0.55 mL, 4.0 mmol) and BF_3·Et_2O (0.78 mL, 6.3 mmol) at 0°C and the mixture was stirred at room temperature for 30 min. The reaction mixture was then refluxed for additional 24 h. The solution was washed with a 10% aqueous solution of $NaHCO_3$ (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and purified by silica column (CH_2Cl_2/hexanes, 4:1) to give a mixture containing BODIPY **3a** as a blue solid. Due to impurity having a very similar R_f value, **3a** could not be completely purified (~90% purity, 53 mg, 17%). ^{1}H-NMR: δ_H 1.55 (t, J = 7.2 Hz, 6H), 4.62 (q, J = 7.2 Hz, 4H), 6.17 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 8.0 Hz, 2H), 7.23—7.27 (m, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.68—7.75 (m, 3H), 8.11 (d, J = 8.0 Hz, 2H) (**Figure A-6**); ^{13}C-NMR δ_C 14.2, 61.3, 121.8, 124.2, 126.5, 128.5, 129.2, 129.7, 129.8, 130.1, 131.3, 134.3, 134.7, 140.3, 141.2, 160.7 (**Figure A-7**); MALDI-TOF-MS obsd 511.842 ([M]$^+$), calcd 512.172 ([M]$^+$, M=$C_{29}H_{23}BF_2N_2O_4$) (**Figure A-8**); λ_{abs} (ε) 642 nm

(1.0×10^6) (**Figures B-9** and **B-10**); λ_{em} (λ_{ex}= 600 nm) 663 nm (**Figure B-11**). Other spectroscopic data are consistent with those subscribed in the literature.

3.3.5 Synthesis of compound 3b



Following a published procedure with slight modification [73], isoindole **5** (1.000 g, 5.17 mmol) and 2-thiophene carboxaldehyde (0.24 mL, 2.6 mmol) were dissolved in CH_2Cl_2 (70 mL). Then, $BF_3 \cdot Et_2O$ (0.065 mL, 0.52 mmol) was added dropwise and the solution was stirred 24 h at room temperature. The solvent was evaporated under vacuum and the resulting residue was chromatographed on a silica column (CH_2Cl_2/hexanes, 4:1) give **13b** as a white solid (1.669 g, 67%). ^{1}H-NMR: δ_H

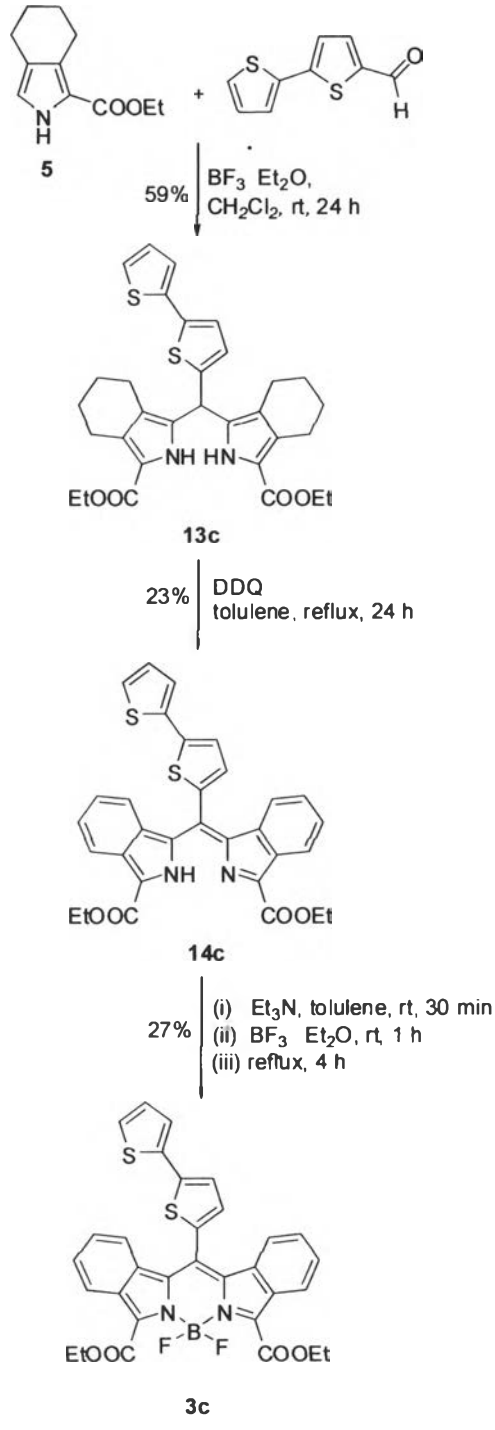
1.25 (t, *J* = 7.2 Hz, 6H), 1.73 (s, 8H), 2.38 (d, *J* = 5.6 Hz, 4H), 2.80 (s, 4H), 4.13 (q, *J* = 7.2 Hz, 4H), 5.69 (s, 1H), 6.73 (s, 1H), 6.83—6.89 (m, 1H), 7.16 (d, *J* = 4.6 Hz, 1H), 9.90 (br s, 2H), (**Figure A-20**); ^{13}C-NMR δ_C 14.4, 21.3, 23.2, 23.3, 23.4, 29.7, 35.7, 59.8, 117.1, 119.4, 124.8, 125.8, 126.8, 129.0, 130.9, 143.4, 161.1 (**Figure A-21**); HR-ESI-MS obsd 503.1975 ($[M + Na]^+$), calcd 503.1980 ($[M + Na]^+$), 480.2083 ($[M]^+$, $M=C_{27}H_{32}N_2O_4S$) (**Figure A-22**); λ_{abs} (ε) 288 nm (0.3×10^5) (**Figures B-27** and **B-28**).

Following a published procedure [13] with slight modification, a solution of dipyrromethane **13b** (0.488g, 1.02 mmol) in toluene (30 mL) was heated to 110°C. A solution of DDQ (2.077 g, 9.151 mmol) in toluene (20 mL) was then added and the mixture was refluxed for 4 h. After that, the solvent was removed under reduced pressure. The resulting residue was dissolved in ethyl acetate and extracted with a 0.1 M solution of HCl to remove traces of DDQ (50 mL), washed once with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2/hexanes, 4:1) to give dipyrrin **14b** as a purple solid (0.112 g, 24%). ^{1}H-NMR: δ_H 1.48 (t, *J* = 6.5 Hz, 6H), 4.49 (q, *J* = 6.8 Hz, 4H), 6.26 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 7.11—7.24 (m, 3H), 7.29 (s, 1H), 7.65 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J*=8.0 Hz, 2H) (**Figure A-30**); ^{13}C-NMR δ_C 14.4, 29.3, 29.6, 122.0, 122.9, 126.3, 127.2, 128.0, 128.2, 128.9, 161.7 (**Figure A-31**); HR-ESI-MS obsd 493.1202 ($[M + Na]^+$), calcd 493.1198 ($[M + Na]^+$), 470.1300 ($[M]^+$, $M=C_{27}H_{22}N_2O_4S$) (**Figure A-32**); λ_{abs} (ε) 579 nm (0.3×10^5) (**Figures B-33** and **B-34**).

Following a published procedure [13] with slight modification, a solution of dipyrrin **14b** (0.147 g, 0.314 mmol) in toluene (20 mL) was treated with Et_3N (0.56 mL, 4.0 mmol) and $BF_3{\cdot}Et_2O$ (0.79 mL, 6.4 mmol) at 0°C and the mixture was stirred at room temperature for 30 min. The reaction mixture was then refluxed for additional 6 h. The solution was washed with a 10% aqueous solution of $NaHCO_3$ (3×20 mL), brine (1×20 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and purified by a silica column (CH_2Cl_2/hexanes, 4:1) to give a mixture containing BODIPY **3b** as a blue solid. Due to impurity having a very similar R_f value, **3b** could not be completely purified (~90% purity, 54 mg, 33%). ^{1}H-NMR: δ_H 1.55 (t, *J* = 7.2 Hz, 6H), 4.61 (q, *J* = 7.2 Hz, 4H), 6.36 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.27—7.32 (m, 3H), 7.37—7.43 (m, 1H), 7.78 (d, *J* = 4.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 2H) (**Figure A-9**); ^{13}C-NMR δ_C 14.1, 62.3, 121.8, 124.2, 126.8, 128.5, 128.7, 128.9, 130.0, 160.5 (**Figure A-10**); HR-ESI-MS obsd 541.1181 ($[M + Na]^+$), calcd

541.1181 ([M + Na]$^+$), 518.1283 ([M]$^+$, M=$C_{27}H_{21}BF_2N_2O_4S$) (**Figure A-11**); λ_{abs} (ε) 656 nm (0.7 × 10^5) (**Figures B-13** and **B-14**); λ_{em} (λ_{ex}= 600 nm) 676 nm (**Figure B-15**).

3.3.6 Synthesis of compound 3c



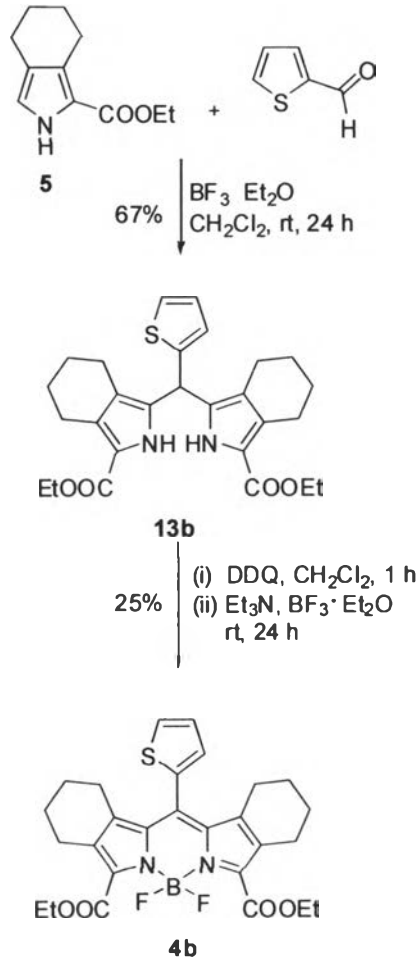
Following a published procedure [73] with slight modification, isoindole **5** (1.000 g, 5.175 mmol) and 2,2'-bithiophene-5-carboxaldehyde (0.503 g, 2.587 mmol) were dissolved in CH_2Cl_2 (100 mL). $BF_3 \cdot Et_2O$ (0.065 mL, 0.52 mmol) was added dropwise and the solution was stirred at room temperature for 24 h. The solvent was evaporated under vacuum and the resulting residue was chromatographed on a silica column (CH_2Cl_2/hexanes, 4:1) to give **13c** (1.715 g, 59%). ^{1}H-NMR: δ_H 1.20—1.26 (m, 6H), 1.68 (s, 8H), 2.39 (d, *J* = 8.8 Hz, 4H), 2.73 (s, 4H), 4.10—4.18 (m, 2H), 4.18—4.26 (m, 2H), 5.61 (s, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.8 Hz, 1H), 6.93—6.98 (m, 1H), 7.00 (s, 1H), 7.16 (d, *J* = 5.2 Hz, 1H), 9.91 (br s, 2H) (**Figure A-23**); ^{13}C-NMR δ_C 14.4, 21.2, 23.1, 23.2, 23.3, 24.6, 35.7, 36.6, 59.9, 76.7, 77.0, 77.3, 117.2, 119.6, 123.1, 123.5, 124.2, 126.5, 127.7, 129.1, 130.3, 137.1, 137.2, 142.3, 162.0 (**Figure A-24**); HR-ESI-MS obsd 585.1851 ($[M + Na]^+$), calcd 585.1858 ($[M + Na]^+$), 562.1960 ($[M]^+$, M=$C_{31}H_{34}N_2O_4S_2$) (**Figure A-25**); λ_{abs} (ε) 289 nm (0.4×10^5) (**Figures B-29** and **B-30**).

Following a published procedure [13] with slight modification, a solution of dipyrromethane **13c** (0.494 g, 0.877 mmol) in toluene (30 mL) was heated to 110°C. A solution of DDQ (1.792 g, 7.89 mmol) in toluene (20 mL) was then added and the mixture was refluxed 24 h. After that, the solvent was removed under reduced pressure. The resulting residue was dissolved in ethyl acetate and extracted with a 0.1 M solution of HCl to remove traces of DDQ (3×50 mL), washed once with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2/hexanes, 4:1) to give dibenzo-fused dipyrrin **14c** as a purple solid (0.109 g, 23%). ^{1}H-NMR: δ_H 1.56 (t, *J* = 7.2 Hz, 6H), 4.57 (q, *J* = 7.2 Hz, 4H), 6.69 (d, *J* = 8.0 Hz, 2H), 7.06 —7.15 (m, 3H), 7.19 (d, *J* = 3.2 Hz, 1H), 7.23—7.35 (m, 4H), 7.43 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), (**Figure A-33**); ^{13}C-NMR δ_C 14.4, 29.6, 61.3, 122.2, 122.9, 124.6, 125.4, 126.4, 127.4, 128.1, 129.9, 130.6, 131.7, 135.1, 135.3, 135.8, 136.6, 138.4, 140.5, 161.7 (**Figure A-34**); HR-ESI-MS obsd 575.1059 ($[M + Na]^+$), calcd 575.1075 ($[M + Na]^+$), 552.1177 ($[M]^+$, M=$C_{31}H_{24}N_2O_4S_2$) (**Figure A-35**); λ_{abs} (ε) 589 nm (0.2×10^5) (**Figures B-35** and **B-36**).

Following a published procedure [71] with slight modification, a solution of dipyrrin **14c** (0.121 g, 0.219 mmol) in toluene (20 mL) was stirred at room temperature. Et_3N (0.38 mL, 2.7 mmol) was added to the solution. After 30 min. $BF_3 \cdot Et_2O$ (0.46 mL, 3.6 mmol) was added, and the mixture was stirred was maintained for additional 1h. The reaction mixture was then refluxed for 4 h. After that, the solution was washed with a 10% aqueous solution of $NaHCO_3$ (20 mL), brine (20 mL)

and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and purified by a silica column (CH_2Cl_2/hexanes, 4:1) to give BODIPY **3c** as a blue solid (36.0 mg, 27%). ^{1}H-NMR: δ_H 1.55 (t, *J* = 7.2 Hz, 6H), 4.61 (q, *J* = 7.2, 4H), 6.70 (d, *J* = 8.0 Hz, 2H), 7.06—7.12 (m, 1H), 7.14—7.27 (m, 3H), 7.28—7.37 (m, 4H), 7.46 (d, *J* = 3.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H) (**Figure A-12**); ^{13}C-NMR: δ_C 14.1, 62.3, 122.0, 124.1, 124.3, 124.9, 125.5, 126.9, 128.0, 128.1, 129.7, 130.0, 131.2, 132.1, 132.7, 134.4, 136.0, 140.8, 141.1, 160.5 (**Figure A-13**); HR-ESI-MS obsd 623.1061 ([M + Na]$^+$), calcd 623.1058 ([M + Na]$^+$), 600.1160 ([M]$^+$, M=$C_{31}H_{23}BF_2N_2O_4S_2$) (**Figure A-14**); λ_{abs} (ε) 658 nm (0.5 × 10^5) (**Figures B-17** and **B-18**); λ_{em} (λ_{ex}= 600 nm) 676 nm (**Figure B-19**).

3.3.7 Synthesis of compound 4b



Following a published procedure [13] with slight modification, a solution of DDQ (0.567 g, 2.50 mmol) in CH_2Cl_2 (15 mL) was added to a solution of **13b** (1.00 g, 2.08 mmol) in CH_2Cl_2 (30 mL) at 0°C. After that, Et_3N (1.74 mL, 12.5 mmol) and $BF_3 \cdot Et_2O$ (2.64 mL, 20.8 mmol) were added and the solution was stirred at 0°C for 20 min and then at room temperature for overnight. The solution was wash with a 10% aqueous solution of $NaHCO_3$ (3×20 mL) and brine (1×20mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (ethyl acetate/hexanes; 1:4) to afford BODIPY **4b** (0.271 g, 25%). ^{1}H-NMR: δ_H 1.41 (t, J = 7.2 Hz, 6H), 1.44—1.50 (m, 4H), 1.60 (d, J = 5.6 Hz, 4H), 1.86 (s, 4H), 2.51—2.61 (m, 4H), 4.43 (q, J = 7.2 Hz, 4H), 6.94—6.98 (m, 1H), 7.13—7.18 (m, 1H), 7.56 (d, J = 4.8 Hz, 1H) (**Figure A-15**); ^{13}C-NMR δ_C 14.07, 14.08, 22.0, 22.3, 22.4, 22.6, 22.9, 23.0, 23.4, 23.5, 29.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.6, 31.9, 60.6, 61.7, 127.8, 128.0, 128.2, 132.7, 133.9, 134.0, 144.1, 161.4 (**Figure A-16**); HR-ESI-MS obsd 549.1776 ($[M + Na]^+$), calcd 549.1807 ($[M + Na]^+$), 526.1909 ($[M]^+$, M=$C_{27}H_{29}BF_2N_2O_4S$) (**Figure A-17**); λ_{abs} (ε) 439, 556 nm (0.4 × 10^5) (**Figures B-21** and **B-22**); λ_{em} (λ_{ex}= 500 nm) 582 nm (**Figure B-23**).