

Linear Oligofluorene-BODIPY structures for fluorescence applications

Neil J. Findlay,^a Clara Orofino-Peña,^a Saadeldin E. T. Elmasly,^a Sasikumar Arumugam,^a Anto R. Inigo,^a
Alexander L. Kanibolotsky,^a Jochen Bruckbauer,^b Robert W. Martin^b and Peter J. Skabara^{*a}

peter.skabara@strath.ac.uk

^a *WestCHEM, Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, Glasgow, G1 1XL, UK*

^b *Department of Physics, SUPA, University of Strathclyde, Glasgow, G4 0NG, UK*

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Experimental

General experimental

Tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) was prepared prior to use and stored under nitrogen. Unless otherwise stated, all other reagents were sourced commercially and used without further purification. Dry solvents were obtained from a solvent purification system (SPS 400 from Innovative Technologies) using alumina as the drying agent. ^1H and ^{13}C NMR spectra were recorded on either a Bruker DRX 500 apparatus at 500.13 and 125.76 MHz, or a Bruker Avance DPX400 apparatus at 400.13 and 100.6 MHz. Chemical shifts are given in ppm; all J values are in Hz. Elemental analyses were obtained on a Perkin-Elmer 2400 analyser. MS LDI-TOF spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1-150000 Da). Accurate mass measurements (HRMS) were recorded using ASAP mode on an Orbitrap instrument at the EPSRC National Mass Spectrometry Service Centre in Swansea. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Thermogravimetric Analyzer TGA7 under a constant flow of helium. Melting points were taken using a TA instruments DSC QC1000 Differential Scanning Calorimeter, or a Stuart Scientific apparatus, and are uncorrected.

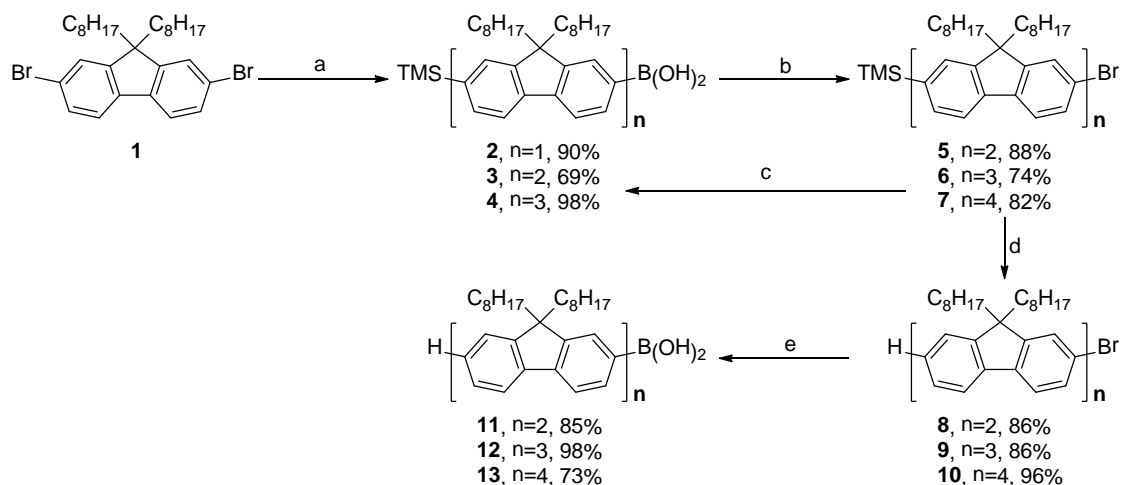
Cyclic voltammetry (CV) measurements were performed on a CH Instruments 660A electrochemical workstation with iR compensation using anhydrous dichloromethane as the solvent. The electrodes were glassy carbon, platinum wire and silver wire as the working, counter and reference electrodes, respectively. All solutions were degassed (Ar) and contained monomer substrates in concentrations of *ca.* 10^{-4} M, together with $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) as the supporting electrolyte. All measurements are referenced against the $E_{1/2}$ of the Fc/Fc^+ redox couple. Absorption spectra and CIE coordinates were recorded on a Unicam UV 300 instrument. Photoluminescence measurements were recorded using a Perkin-Elmer LS 50 B fluorescence spectrometer in a quartz cuvette (path length 10 mm). For PLQY measurements, absorption and photoluminescence measurements were performed using a Jasco V-660 spectrophotometer and a Jasco FP 6500 spectrofluorometer, respectively.

Electroluminescence (EL) measurements of the light-emitting diodes (LEDs) were carried out at room temperature using a Keithley source measure unit. The light was dispersed by an Oriel 1/8 m spectrograph before being collected by an Andor charge-coupled device. The UV LEDs (XSL 365 class) were purchased from Roithner Lasertechnik and were used with the glass lens removed.

Synthesis

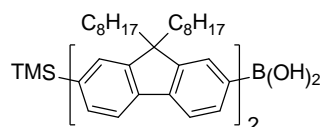
Compounds **2**,¹ **14**,² **17**³ and **18**⁴ were prepared according to literature procedures.

Scheme 1: formation of the oligofluoreneboronic acids **11** - **13**.



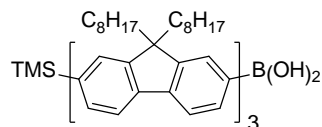
Reaction conditions: a) (i) *n*BuLi, THF, -78 °C; (ii) TMSCl, -78 °C-rt, 1 h; (iii) *n*BuLi, -78 °C; (iv) B(O*i*Pr)₃, -100 °C-rt, 18 h, Ar; b) **1**, Pd(PPh₃)₄, 2M Na₂CO₃(aq.), PhMe, 110 °C, 18 h; c) (i) *n*BuLi, -78 °C; (ii) B(O*i*Pr)₃, -78 °C-rt, 18 h, Ar; d) TFA, CH₂Cl₂, 2 h; e) (i) *n*BuLi, -78 °C; (ii) B(O*i*Pr)₃, -78 °C-rt, 18 h, Ar.

Synthesis of 9,9,9',9'-tetraoctyl-2,2'-bifluorene-7-trimethylsilyl-2-boronic acid **3**



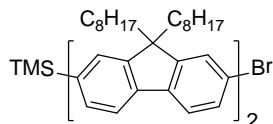
To a solution of 7'-bromo-9,9,9',9'-tetraoctyl-2,2'-bifluorene-7-yl) trimethylsilane (**5**) (8.957 g, 9.619 mmol) in dry tetrahydrofuran (100 mL), *n*-BuLi (1.95 M solution in *n*-hexanes, 6.41 mL, 12.51 mmol) was added dropwise under a N₂ atmosphere at -80 °C over the span of 2 min. The system was stirred at -80 °C for 10 min and then cooled down to -100 °C. Triisopropylborate (6.7 mL, 28.86 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. The reaction mixture was washed with water (500 mL), and extracted with diethyl ether (4 x 100 mL). The combined organic fractions were washed with water (300 mL), dried over anhydrous MgSO₄ and the solvent evaporated to yield 8.587 g of crude product. The residue was purified by flash chromatography on a silica gel column with elution first by toluene to remove by-products and then with diethyl ether to recover the product as a white foamy solid (5.940 g, 6.63 mmol, 69 %); ¹H NMR (CDCl₃): δ 8.38 (1 H, d, *J* = 7.6 Hz), 7.96 (1 H, d, *J* = 7.6 Hz), 7.93 (1 H, d, *J* = 8.0 Hz), 7.84 (1 H, d, *J* = 7.6 Hz), 7.77-7.68 (5 H, m), 7.56 (2 H, d, *J* = 8.8 Hz), 2.30-2.04 (8H, m), 1.26-1.07 (40 H, m), 0.88-0.75 (20 H, m), 0.36 (9 H, s). The analysis was comparable with the literature.⁵

Synthesis of 9,9,9',9'',9'',9''-hexaoctyl-2,2'-terfluorenyl-7-trimethylsilyl-boronic acid **4**



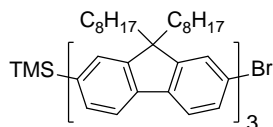
To a solution of 2-bromo-9,9,9',9'',9'',9''-hexaoctyl-2,2'-terfluorenyl-7-trimethylsilane (**6**) (8 g, 5.73 mmol) in dry tetrahydrofuran (170 mL), *n*-BuLi (2.39 M solution in *n*-hexanes, 3.11 mL, 7.446 mmol) was added dropwise under a N₂ atmosphere at -80 °C over the span of 2 min. The system was stirred at -80 °C for 45 min and then cooled down to -100 °C. Triisopropylborate (4 mL, 17.85 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. The reaction mixture was washed with water (500 mL) and extracted with diethyl ether (3 x 300 mL). The combined organic fractions were washed with water (500 mL), dried over anhydrous MgSO₄ and the solvent evaporated to yield a yellow crude product. It was purified by flash chromatography on a silica gel column with elution first by toluene to remove by-products and then with diethyl ether to recover the product as a white foamy solid (1.61 g, 1.33 mmol, 98 %); m.p. 66-68 °C; ¹H NMR (CDCl₃): δ 8.41-8.15 (2 H, m), 8.00-7.64 (14 H, m), 7.57-7.51 (2 H, m), 2.31-2.00 (12 H, m), 1.32-1.07 (60 H, m), 0.92-0.70 (30 H, m), 0.36 (9 H, s); ¹³C NMR (CDCl₃): δ 150.47, 145.59, 141.77, 141.71, 140.90, 140.67, 140.61, 140.50, 140.23, 139.27, 136.07, 135.03, 132.13, 130.07, 127.95, 126.53, 126.47, 126.32, 125.81, 121.86, 121.80, 120.95, 120.27, 119.64, 119.29, 55.65, 55.53, 55.40, 40.68, 40.44, 32.08, 30.62, 30.38, 30.33, 30.23, 29.51, 29.45, 29.41, 24.22, 24.11, 22.90, 14.41, 14.35; (MALDI/TOF, *m/z*): [M⁺] 1238.9; Anal. calc. for C₉₀H₁₃₁BO₂Si: C, 84.19; H, 10.28; Found: C, 84.63; H, 9.95.

Synthesis of 7'-bromo-9,9,9',9''-tetraoctyl-2,2'-bifluorenyl-7-yl) trimethylsilane **5**



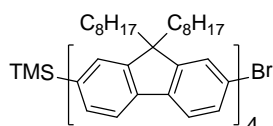
A solution of 2,7-dibromo-9,9-dioctylfluorene **1** (19.740 g, 36 mmol) and Pd(PPh₃)₄ (0.416 g, 0.36 mmol) in dry toluene (40 mL) was stirred under a N₂ atmosphere for 20 min. A solution of 9,9-dioctyl-7-trimethylsilylfluorene-2-ylboronic acid (**2**) (6.05 g, 12 mmol) in dry toluene (20 mL) was added to the mixture. The flask previously containing **2** was washed with an additional portion of dry toluene (20 mL) and added to the reaction mixture. An aqueous 2M solution of Na₂CO₃ (14 mL, 28 mmol) was added and the system was stirred under N₂ refluxing at 80 °C for 18 h. The reaction mixture was washed with water (200 mL) and extracted with dichloromethane (5 x 200 mL). The combined organic fractions were washed with water (3 x 300 mL), dried over anhydrous MgSO₄ and the solvent evaporated to yield the crude product (25.41 g) as a yellow oil. The residue was purified by column chromatography on silica gel eluting with petroleum ether to afford the product as a white solid (8.06 g, 8.67 mmol, 88 %); ¹H NMR (CDCl₃): δ 7.78 (1 H, d, *J* = 8.0 Hz), 7.73 (2 H, t, *J* = 6.0 Hz), 7.66-7.59 (5 H, m), 7.53-7.47 (4 H, m), 2.05-1.93 (8 H, m), 1.20-1.09 (40 H, m), 0.84-0.66 (20 H, m), 0.34 (8 H, m); (MALDI/TOF, *m/z*): [M⁺] 930.59. The analysis was comparable with the literature.⁶

Synthesis of 2-bromo-9,9,9',9'',9''',9'''-hexaoctyl-2,2'-terfluorenyl-7-trimethylsilane **6**



A solution of 2,7-dibromo-9,9-dioctylfluorene (**1**) (17.77 g, 32.40 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.374 g, 0.03 mmol) in dry toluene (60 mL) was stirred under a N_2 atmosphere for 20 min. A solution of 9,9,9',9'-tetraoctyl-2,2'-bifluorene-7-trimethylsilylboronic acid **3** (9.710 g, 10.80 mmol) in dry toluene (40 mL) was added to the mixture. The flask previously containing **3** was washed with an additional portion of dry toluene (40 mL) and added to the reaction mixture. An aqueous 2M solution of Na_2CO_3 (12.96 mL, 25.92 mmol) was added and the system was stirred under N_2 refluxing at 80 °C for 18 h. The reaction mixture was washed with water (200 mL) and extracted with dichloromethane (5 x 200 mL). The combined organic fractions were washed with water (300 mL), dried over anhydrous MgSO_4 and the solvent evaporated yielding the crude product (30.180g) as a yellow oil. The residue was purified by column chromatography on silica gel eluting with petroleum ether and then crystallised in acetone to afford the product as a white crystalline solid (10.976 g, 8.014 mmol, 74 %); m.p. 100-102 °C; ^1H NMR (CDCl_3): δ 7.84-7.74 (5 H, m), 7.67-7.61 (9 H, m), 7.55-7.49 (4 H, m), 2.14-1.97 (12 H, m), 1.28-1.60 (60 H, m), 0.89-0.67 (30 H, m), 0.35 (9 H, s); ^{13}C NMR (CDCl_3): δ 140.91, 140.53, 140.09, 139.82, 139.75, 139.68, 139.40, 139.36, 138.71, 138.49, 131.35, 129.50, 127.16, 125.78, 125.73, 125.66, 125.52, 120.99, 120.92, 120.57, 120.47, 119.49, 119.46, 118.51, 55.04, 54.84, 54.61, 39.86, 38.78, 39.65, 31.28, 29.52, 29.45, 28.70, 28.62, 23.40, 23.31, 23.27, 22.10, 13.56, -1.34; (MALDI/TOF, m/z): $[\text{M}^+]$ 1318.3; Anal. calc. for $\text{C}_{90}\text{H}_{129}\text{BrSi}$: C, 81.95; H, 9.86, Br, 6.06; Found: C, 82.11; H, 9.75; Br, 6.50.

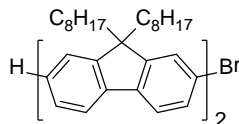
Synthesis of 7-bromo-9,9,9',9'',9''',9'''-octaoctyl-2-trimethylsilylquaterfluorene **7**



A solution of 2,7-dibromo-9,9-dioctylfluorene (**1**) (7.476 g, 13.63 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.158 g, 0.136 mmol) in dry toluene (60 mL) was stirred under a N_2 atmosphere for 20 min. A solution of 9,9,9',9'',9''',9'''-hexaoctyl-2,2'-terfluorenyl-7-trimethylsilyl-boronic acid **4** (6.06 g, 0.454 mmol) in dry toluene (50 mL) was added to the mixture. The flask previously containing **4** was washed with an additional portion of dry toluene (50 mL) and added to the reaction mixture. An aqueous 2M solution of Na_2CO_3 (6.8 mL, 13.63 mmol) was added and the system was stirred under N_2 refluxing at 80 °C for 18 h. The reaction mixture was washed with water (250 mL) and extracted with dichloromethane (3 x 250 mL). The combined organic fractions were washed with water (200 mL), dried over anhydrous MgSO_4 and the solvent evaporated yielding the crude product (18.58 g) as a yellow oil. The residue was purified by column chromatography on silica gel eluting first with petroleum ether and then 30:1 petroleum ether:toluene to recover the product, which was crystallised in acetone to afford a creamy solid (6.317 g, 3.71 mmol, 82 %); ^1H NMR (CDCl_3): δ 7.86-7.61 (20 H, m), 7.57-7.48 (4 H, m), 2.19-1.96

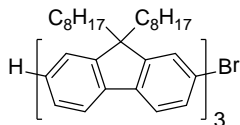
(15 H, m), 1.32-1.07 (80 H, m), 0.91-0.67 (40 H, m), 0.36 (9 H, s); The analysis was comparable with the literature.⁶

Synthesis of 7-bromo-9,9,9',9'-tetraoctyl-2,2'-bifluorene **8**



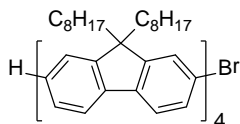
To a solution of 7'-bromo-9,9,9',9'-tetraoctyl-2,2'-bifluoren-7-yl) trimethylsilane (**5**) (3.06 g, 3.29 mmol) in dichloromethane (60 mL), CF₃COOH (6 mL) was added and the mixture stirred at room temperature for 2 h. Basic work up was carried out with water (2 x 60 mL), saturated NaHCO₃ solution (3 x 60 mL) and final washing with water (2 x 60 mL). The organic fraction was dried over anhydrous MgSO₄ and filtered through a silica plug to remove polar by-products and crystallised from acetone to yield the product as a white crystalline solid (2.120 g, 2.47 mmol, 86 %); ¹H NMR (CDCl₃): δ 7.79-7.74 (3 H, m), 7.66-7.59 (5 H, m), 7.49-7.47 (2 H, d, *J* = 8.0 Hz), 7.38-7.32 (4 H, m), 2.05-1.93 (8 H, m), 1.21-1.03 (40 H, m), 0.84-0.79 (12 H, m), 0.77-0.63 (8 H, m). The analysis was comparable with the literature.⁷

Synthesis of 7-bromo-9,9,9',9'',9'',9'''-hexaethyl-2,2'-terfluorene **9**



To a solution of 2-bromo-9,9,9',9'',9'',9'''-hexaethyl-2,2'-terfluorenyl-7-trimethylsilane **6** (4 g, 2.921 mmol) in dichloromethane (68 mL), CF₃COOH (3.1 mL) was added and the mixture stirred at room temperature for 2 h. Basic work up was carried out with water (2 x 100 mL), saturated NaHCO₃ solution (2 x 60 mL) and final washing with water (100 mL). The organic fraction was dried over anhydrous MgSO₄ and filtered through a silica plug to remove polar by-products and crystallised from acetone to yield the product as a white crystalline solid (2.120 g, 2.47 mmol, 86 %); ¹H NMR (CDCl₃): δ 7.87-7.75 (5 H, m), 7.69-7.60 (9 H, m), 7.49 (2 H, d, *J* = 8.0 Hz), 7.39-7.31 (3 H, m), 2.13-1.98 (12 H, m), 1.26-1.50 (60 H, m), 0.85-0.65 (30H, m). The analysis was comparable with the literature.⁷

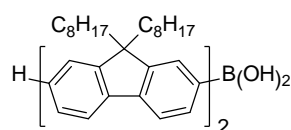
Synthesis of 7-bromo-9,9,9',9'',9'',9''',9'''-octaethyl-2,2'-quaterfluorene **10**



To a solution of 7-bromo-9,9,9',9'',9'',9''',9'''-octaethyl-2-trimethylsilylquaterfluorene **7** (2.96 g, 1.74 mmol) in dichloromethane (56 mL), CF₃COOH (1.8 mL) was added and the mixture stirred at room temperature for 2 h. Basic work up was carried out with water (2 x 100 mL), saturated NaHCO₃ solution (2 x 70 mL) and final washing with water (100 mL). The organic fraction was dried over anhydrous MgSO₄ and filtered through a

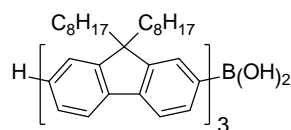
silica plug to remove polar by-products and crystallised from acetone to yield the product as a white crystalline solid (2.743 g, 1.68 mmol, 96 %); ^1H NMR (CDCl_3): δ 7.86-7.59 (20 H, m), 7.52-7.30 (5 H, m), 2.18-1.95 (15 H, m), 1.29-1.05 (80 H, m), 0.90-0.65 (40 H, m); ^{13}C NMR (CDCl_3): δ 140.78, 140.75, 140.68, 140.56, 140.48, 140.38, 140.27, 140.19, 140.16, 140.07, 139.44, 130.22, 129.00, 127.43, 127.21, 127.01, 126.50, 126.38, 126.26, 123.15, 121.70, 121.62, 121.29, 121.21, 120.21, 120.10, 119.94, 55.76, 55.56, 55.39, 40.61, 40.51, 32.02, 30.26, 30.18, 29.45, 24.13, 24.05, 23.99, 22.86, 22.80, 14.30; TOF/MALDI [M^+] 1635; HRMS (ASAP Orbitrap) calc. for $\text{C}_{116}\text{H}_{161}\text{Br}$ 1633.1776, found 1633.1771.

Synthesis of 9,9,9',9'-tetraoctyl-2,2'-bifluorene-7-ylboronic acid **11**



To a solution of 7-bromo-9,9,9',9'-tetraoctyl-2,2'-bifluorene (**8**) (3.744 g, 4.35 mmol) in dry tetrahydrofuran (50 mL), was added dropwise $n\text{-BuLi}$ (1.68 M solution in $n\text{-hexanes}$, 3.1 mL, 4.35 mmol) under a N_2 atmosphere at -80°C over the span of 2 min. The system was stirred at -80°C for 10 min and then cooled down to -100°C . Triisopropylborate (3 mL, 13 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. The reaction mixture was washed with water (500 mL), acidified with HCl until a pH of 2-3 was reached and extracted with diethyl ether (4 x 100 mL). The combined organic fractions were washed with water (300 mL), dried over anhydrous MgSO_4 and the solvent evaporated to yield 3.784 g of crude product. The residue was purified by flash chromatography on a silica gel column with elution first by toluene to remove by-products and then with diethyl ether to recover the product as a white foamy solid (3.05 g, 3.70 mmol, 85 %); ^1H NMR (CDCl_3): δ 8.38-7.95 (2.64 H, m), 7.93-7.64 (7.28 H, m), 7.41-7.30 (3 H, m), 2.30-1.98 (8 H, m), 1.28-1.04 (40 H, m), 0.88-0.73 (20 H, m); the analysis was comparable with the literature.⁷

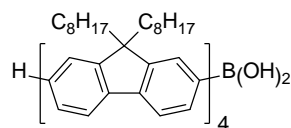
Synthesis of 9,9,9',9'',9'',9''-hexaethyl-2,2'-terfluorene-7-ylboronic acid **12**



To a solution of 7-bromo-9,9,9',9'',9'',9''-hexaethyl-2,2'-terfluorene (**9**) (1.701 g, 1.36 mmol) in dry tetrahydrofuran (20 mL), was added dropwise $n\text{-BuLi}$ (2.5 M solution in $n\text{-hexanes}$, 0.7 mL, 1.79 mmol) under a N_2 atmosphere at -80°C over the span of 2 min. The system was stirred at -80°C for 45 min and then cooled down to -100°C . Triisopropylborate (1 mL, 4.15 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. The reaction mixture was washed with water (300 mL), acidified with HCl until a pH of 2-3 was reached and extracted with diethyl ether (7 x 100 mL). The combined organic fractions were washed with water (300 mL), dried over anhydrous MgSO_4 and the solvent evaporated to yield a yellow crude product. It was purified by flash chromatography on a silica gel column with elution first by toluene to remove by-products and then with diethyl ether to recover the product as a white foamy solid

(1.61 g, 1.33 mmol, 98 %); ^1H NMR (CDCl_3): δ 8.39-7.94 (3 H, m), 7.92-7.65 (13 H, m), 7.39-7.33 (3 H, m), 2.28-1.98 (12 H, m), 1.27-1.04 (60 H, m), 0.90-0.65 (30 H, m); the analysis comparable with literature.⁷

Synthesis of 9,9,9',9'',9''',9''''-octaoctyl-2,2'-quaterfluorene-7-ylboronic acid **13**



To a solution of 7-bromo-9,9,9',9'',9''',9''''-octaoctyl-2,2'-quaterfluorene (**10**) (0.406 g, 0.25 mmol) in dry tetrahydrofuran (6 mL), was added dropwise $n\text{-BuLi}$ (2.45 M solution in $n\text{-hexanes}$, 0.15 mL, 0.32 mmol) under a N_2 atmosphere at -80°C . The system was stirred at -80°C for 45 min and cooled down to -100°C . Triisopropylborate (0.2 mL, 0.75 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. The reaction mixture was washed with water (200 mL), acidified with HCl until a pH of 2-3 was reached and extracted with diethyl ether (5 x 100 mL). The combined organic fractions were washed with water (200 mL), dried over anhydrous MgSO_4 and the solvent evaporated to yield 0.472 g of a white solid. The crude product was purified by flash chromatography on a silica gel column with elution first by toluene to remove by-products and then with diethyl ether to recover the product as a white foamy solid (0.37 g, 0.23 mmol, 73 %); ^1H NMR (CDCl_3): δ 8.39 (1 H, d, $J = 8.0$ Hz), 8.31 (1 H, s), 8.10-7.62 (20 H, m), 7.41-7.30 (3 H, m), 2.32-1.98 (16 H, m), 1.28-1.02 (80 H, m), 0.92-0.67 (40 H, m); (MALDI/TOF, m/z): $[\text{M}^+]$ 1601.01; Anal. calc. for $\text{C}_{116}\text{H}_{163}\text{BO}_2\text{Si}$: C, 87.06; H, 10.27; Found: C, 87.32; H, 10.20; the analysis was comparable with the literature.⁷

Figure S1: oxidation of *meso*-TFBOD.

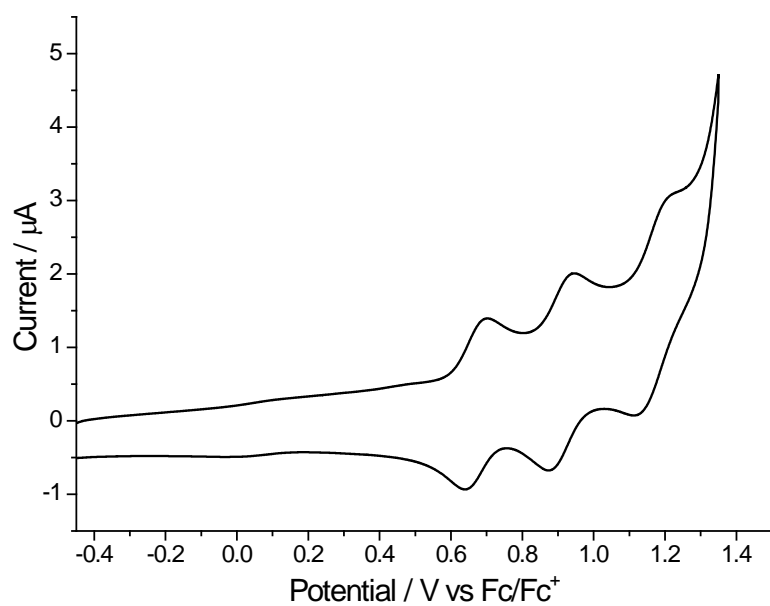


Figure S2: reduction of *meso*-TFBOD.

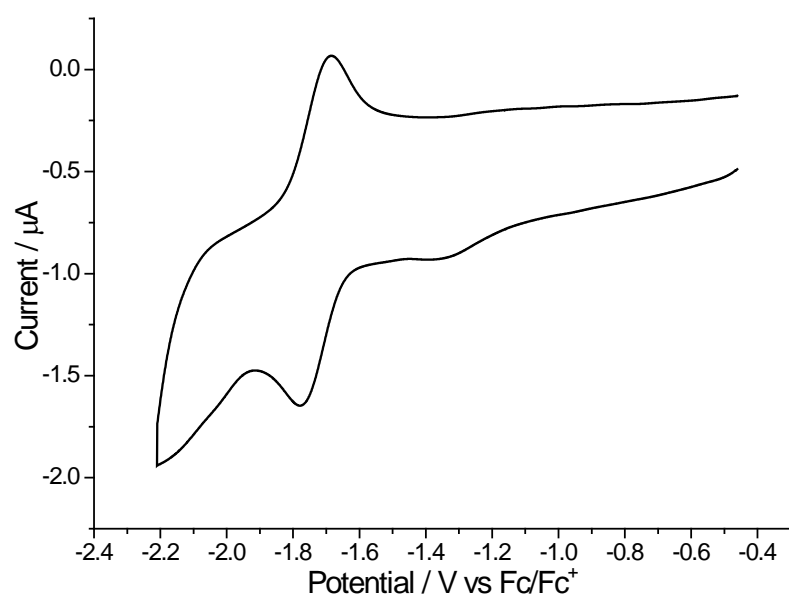


Figure S3: oxidation of *meso*-QFBOD.

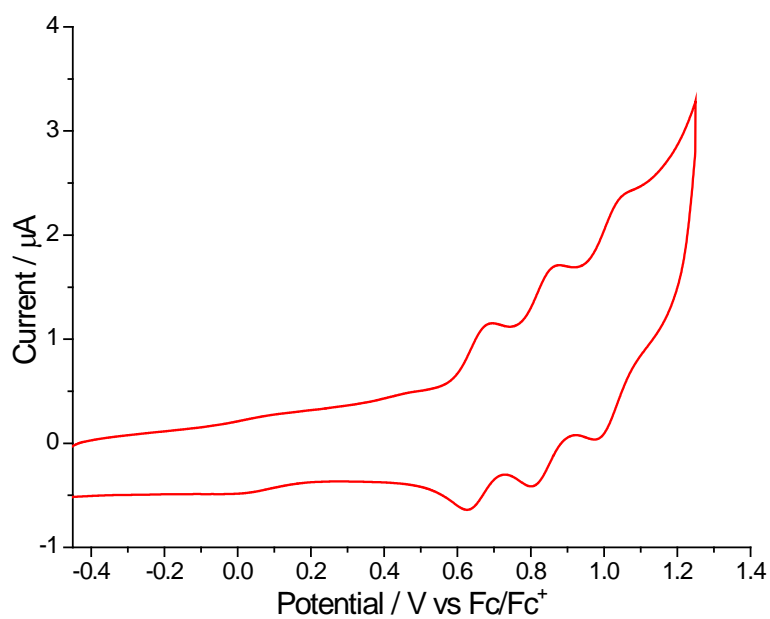


Figure S4: reduction of *meso*-QFBOD.

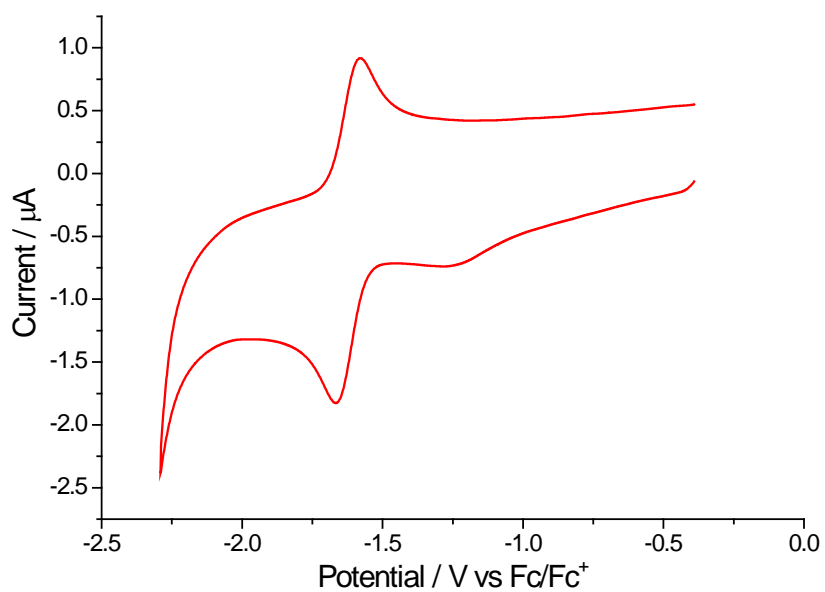


Figure S5: oxidation of ***beta*-TFBOD**.

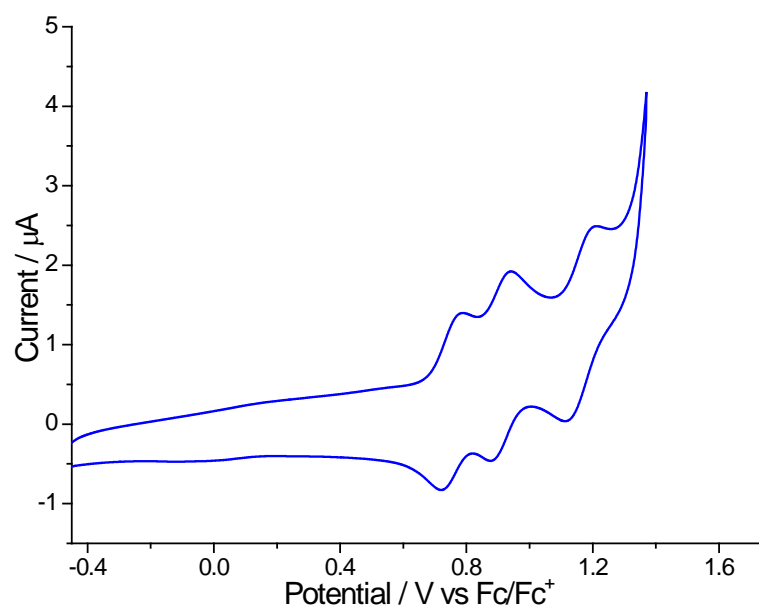


Figure S6: reduction of ***beta*-TFBOD**.

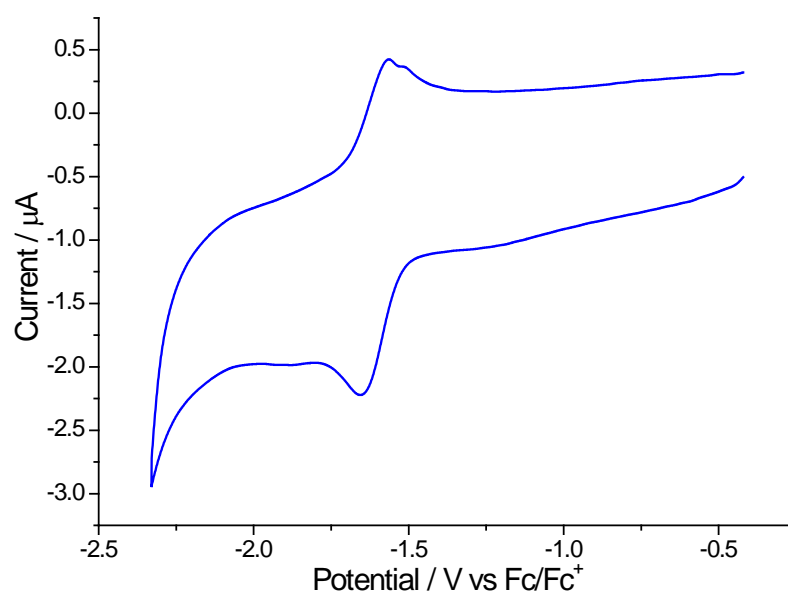


Figure S7: oxidation of **beta**-QFBOD.

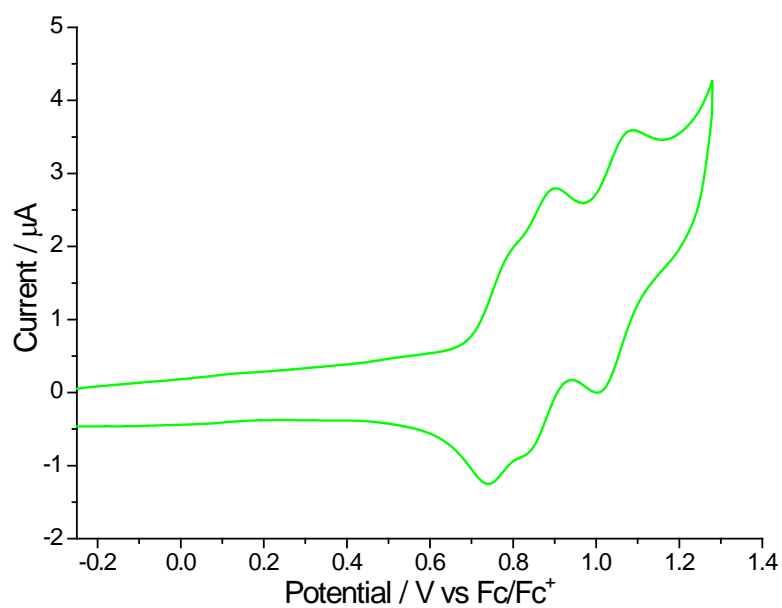


Figure S8: reduction of **beta**-QFBOD.

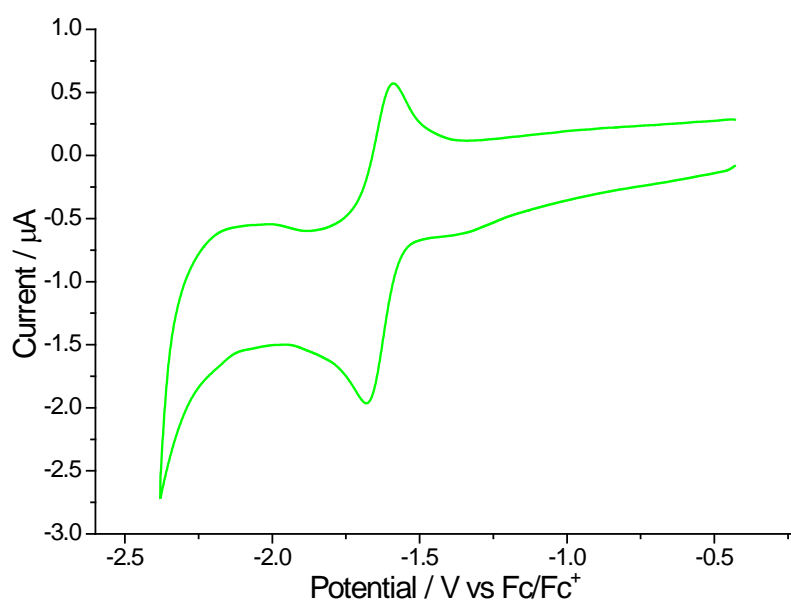


Figure S9: UV-vis absorbance spectra used for the relative PLQY measurement of **meso-QFBOD** against a BODIPY reference⁸ in dichloromethane. At 365 nm, the optical densities of the solutions varied from 0.01 to 0.1.

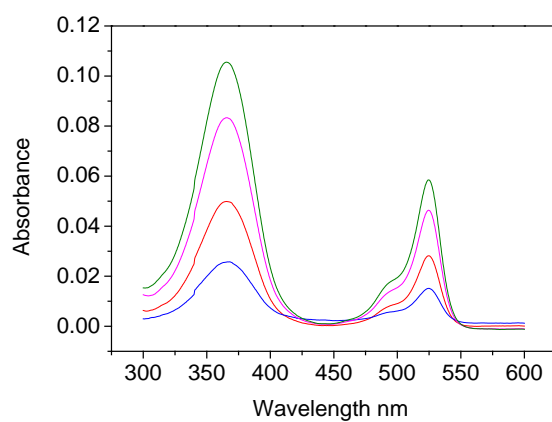


Figure S10: Photoluminescence spectra for the relative PLQY measurement of **meso-QFBOD** in dichloromethane, when excited at 366 nm. **meso-QFBOD** solutions of differing optical density (as shown above) were used.

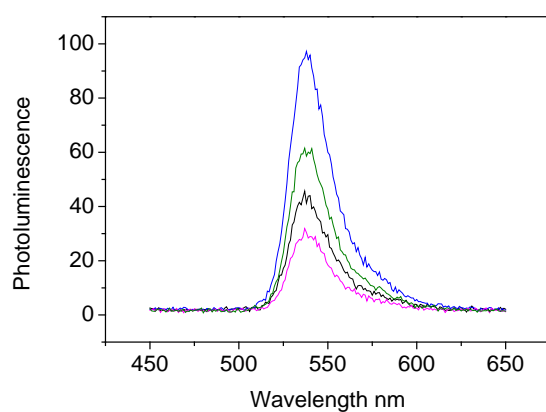


Figure S11: DSC plot for *meso*-TFBOD.

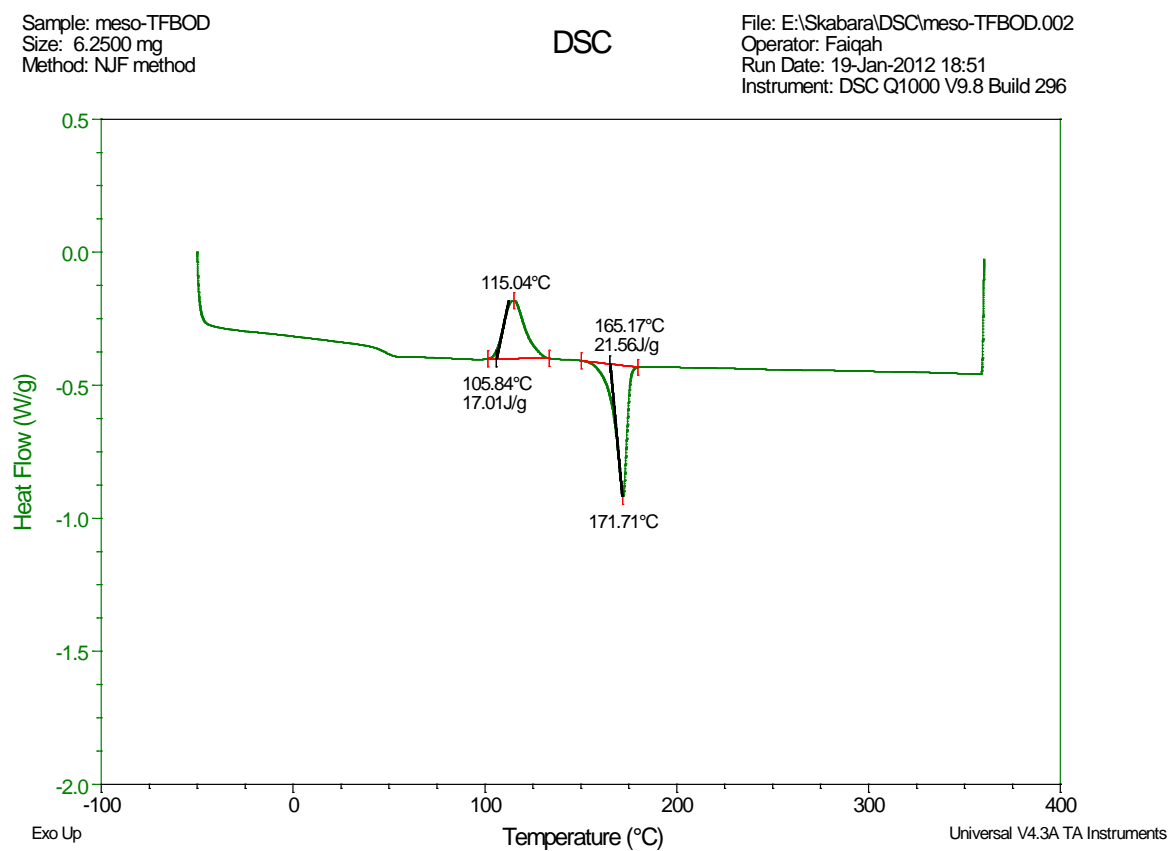
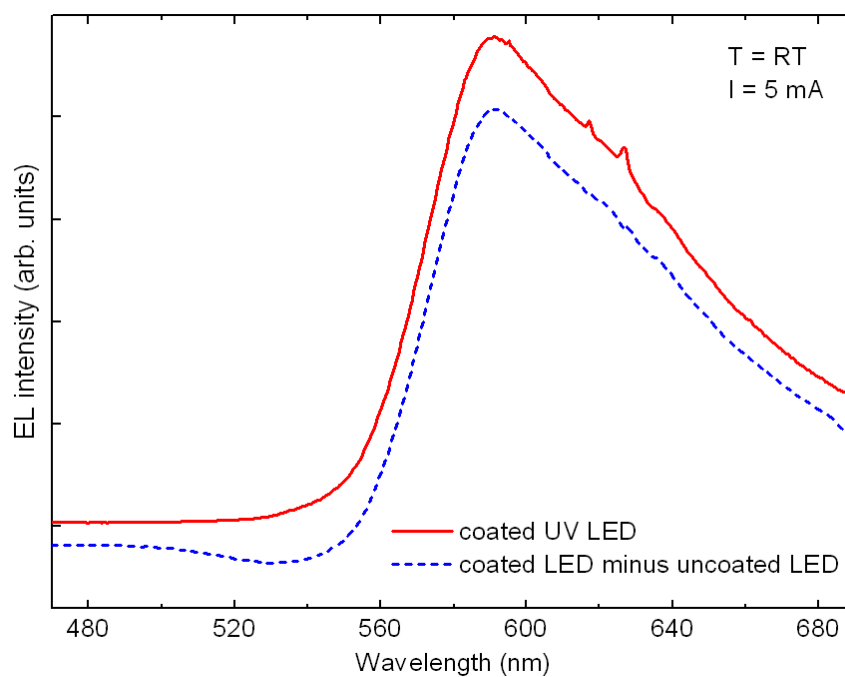


Figure S12: spectrum of the uncoated LED subtracted from the spectrum of the *meso*-QFBOD coated LED (blue dashed line) compared to the spectrum of the coated LED (red line).



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