CHAPTER 5

Experimental

GENERAL EXPERIMENTAL

All the chemicals were purchased from Aldrich and Alfa-Aesar and used without further purification. For reactions under anhydrous conditions, the glassware was dried in an oven at 130 °C. Dry solvents were collect through a PureSolv purification system.

^{1}H and ^{13}C NMR spectra were recorded, unless stated otherwise, at room temperature on a Bruker DRX500 at 500 and 125 MHz or a Bruker Avance 400 instrument at 400 and 100 MHz; chemical shifts are given in ppm and all *J* values are in Hz. Mass spectra (ES) were recorded on Thermo Finnigan LCQDuo system using direct infusion. MS MALDI-TOF were recorded on a Shimadzu Axima-CFR spectrometer (mass range 1-150000Da). Number-average (M_n) and weight-average (M_w) of the polymers were determined by gel permeation chromatography (GPC) in chloroform at room temperature with an OptiLab DSP (Interferometric Refractometre) and a MiniDawn (Wyatt Technology), and calibrated against narrow polydispersity polystyrene standards. Number-average (M_n) and weight-average (M_w) of **p(DPP-TTF)** were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards in the Department of Chemistry of Imperial College London. MALDI-TOF measurements of the polymers were carried out using a retinoic acid matrix; only the significant peaks are reported. Thermogravimetry analysis were recorded on a Perkin Elmer Thermogravimetric Analyzer TGA7 under nitrogen. Differential Scanning Calorimeter analysis were recorded on TA instruments DSCQ1000 Differential Scanning Calorimeter. HPLC analysis were carried out using a dual absorbance detector Waters 2487.

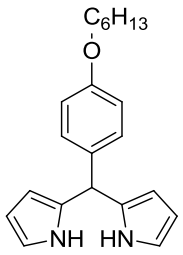
Alfa Aesar supplied the filer aid celite hyflo-super cel (dioxosilane) used for purification. Column chromatography was carried out on VWR silica gel (40-63µm mesh).

Solvents were removed using a rotary evaporator (vacuum supplied by low vacuum pump) and, where necessary, a high vacuum pump was used to remove residual

solvent. All distillations were performed on a Kugelrohr Z24 with high vacuum pump.

All novel compounds were fully characterised, while all the known compounds synthesised during this PhD are referenced at the end of the name of each compound.

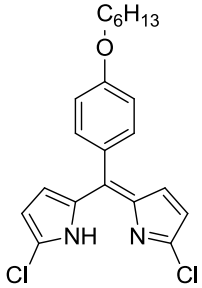
5-(4-*n*-Hexyloxyphenyl)dipyrromethane (10)



Freshly distilled pyrrole (50 ml, 0.727 mol) and 4-hexyloxy-benzaldehyde (5 g, 24.2 mmol) were added to a 250 ml round bottom flask, the mixture was purged with N_2 for 10 minutes and trifluoracetic acid (0.03 ml) was added. The mixture was stirred for 1 h at room temperature until all the benzaldehyde had been consumed (followed by TLC). The reaction mixture was washed with a solution of Na_2CO_3, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and evaporated. The crude product was purified by Kugelrohr vacuum distillation at 200 °C, 6.6 $x10^{-3}$ mbar, to give 5.7 g (73 %) of a yellow oil.

^{1}H NMR ($CDCl_3$) 7.92 (2H, d, *J* = 8.9); 7.13 (2H, d, *J* = 8.8), 6.86 (2H, d, *J* = 8.4), 6.69 (2H, d, *J* = 4.5), 6.17 (2H, m), 5.93 (2H, m), 5.43 (1H, s), 3.95 (2H, t, *J* = 6.5), 1.79 (2H, m) 1.47 (2H, m), 1.35 (4H, m) and 0.92 (3H, m); **^{13}C NMR** ($CDCl_3$) 158.2, 134.0, 133.0, 129.4, 117.2, 114.7, 108.5, 107.1, 68.1, 43.2, 31.7, 29.4, 25.9, 22.7, 14.1; **MS GC/EI** 322.06; **Elemental analysis** $C_{21}H_{26}N_2O$; C, 78.22; H, 8.13; N, 8.69; Found: C, 77.75; H, 8.13; N, 9.17.

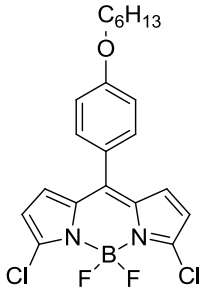
1,1-Dichloro-5-(4-n-hexyloxyphenyl)dipyrromethene (11)



Compound **10** (3.7g, 11.5 mmol) was dissolved in dry THF (80 mL) and cooled to -78 °C under N_2. A suspension of NCS (3.14 g, 23.5 mmol) in dry THF (60 mL) was added and the reaction mixture was stirred at -78 °C for 1.5 h and then warmed to room temperature overnight. The mixture was washed with water (3 x 150 ml) and extracted with CH_2Cl_2 (3 x 200 ml). The organic layer was dried over Na_2SO_4, filtered and evaporated. The residue was dissolved in CH_2Cl_2 (200mL), and DDQ (2.6 g, 12.5 mmol) was added and stirred at room temperature for 1.5 hour. The solvent was evaporated and the crude product was purified by column chromatography (dichloromethane:hexane, 3:7) to give 1.7 g (38%) of a green solid.

^{1}H NMR ($CDCl_3$) 12.48 (1H, bs), 7.37 (2H, d, *J* = 8.6), 6.96 (2H, d, *J* = 8.6), 6.60 (2H, d, *J* = 4.2), 6.27 (2H, d, *J* = 4.2), 4.03 (2H, t, *J* = 6.5), 1.84 (2H, m), 1.51 (2H, t, *J* = 6.5), 1.38 (4H, m) and 0.93 (3H, m); **^{13}C NMR** ($CDCl_3$) 160.5, 141.4, 140.2, 138.7, 132.5, 130.2, 127.7, 116.8, 113.9, 68.3, 31.7, 29.3, 25.8, 22.7, 14.1; **MS GC/EI** 389.07; **Elemental analysis** $C_{21}H_{22}Cl_2N_2O$; C 64.79; H 5.70; N 7.20; Found: C 64.79; H 5.98; N 7.25; **Melting point**: 78-80 °C.

3,5-Dichloro-8-(4-n-hexyloxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (12)

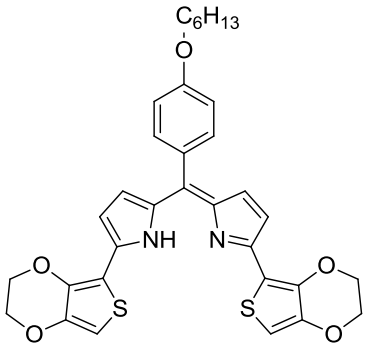


A solution of **11** (1 g, 2.57 mmol) and Et_3N (3.6 ml, 25.7mmol) in 100 ml dry CH_2Cl_2 was stirred under N_2 at room temperature for 10 min. Then $BF_3{\cdot}Et_2O$ (4.9 ml, 38.5 mmol) was added slowly over 10 min. The resulting solution was stirred for 22 h, then washed with water (3 x 70 ml), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The residue was loaded onto silica gel and purified by flash

column chromatography, eluting with ethyl acetate:hexane (1:4), (Rf = 0.28). Yielded 1.1 g, (95 %) of a violet oil.

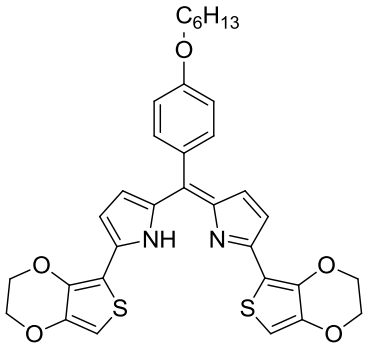
^{1}H NMR ($CDCl_3$) 7.43 (2H, d, *J* = 8.8), 7.03 (2H, d, *J* = 8.7), 6.89 (2H, d, *J* = 4.28), 6.44 (2H, d, *J* = 4.4), 4.05 (2H, t, *J* = 6.5), 1.85 (m, 2H), 1.51 (2H, t, *J* = 6.5), 1.36 (4H, m), 0.94 (3H, t, *J* = 7.0); **^{13}C NMR** ($CDCl_3$) 161.8, 144.2, 144.0, 133.6, 132.3, 131.4, 124.5, 118.5, 114.6, 68.4, 31.5, 29.1, 25.70, 22.60, 14.0; **MS MALDI TOF** 473 (hydrochloride salt); **Elemental analysis** $C_{21}H_{21}BCl_2F_2N_2O$; C 57.70; H 4.84; N, 6.41; found: C 57.95; H 4.49; N 5.99.

(Z)-2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5-((5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2H-pyrrol-2-ylidene)(4-(hexyloxy)phenyl)methyl)-1H-pyrrole (13) (*Microwave assisted synthesis*)



11 (350 mg, 0.9 mmol), trimethylstannane-EDOT (**22**) (603 mg, 1.9 mmol) and $Pd[(PPh_3)_4]$ (35 mg) were added to a 2.0-5.0 mL microwave vial. The vial was purged and vacuum five times and dry DMF (4 mL) was added. The reaction was stirred at 160 ^{o}C for 2 hours *via* microwave assisted heating. The reaction mixture was diluted in dichloromethane (30 mL) and washed with with water (50 mL), brine (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude mixture was purified by chromatography on silica (eluent mixture, hexane:ethyl acetate, 2:1) to give a dark green solid (64 mg, 12%). (Analysis see next)

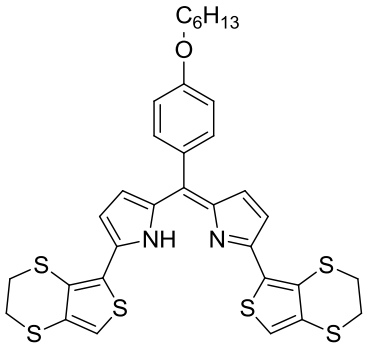
(Z)-2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5-((5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2H-pyrrol-2-ylidene)(4-(hexyloxy)phenyl)methyl)-1H-pyrrole (13)



11 (400 mg, 0.9 mmol), trimethylstannane-EDOT (**22**) (940 mg, 3 mmol) and $Pd[(PPh_3)_4]$ (40 mg) were dissolved in dry toluene (20 mL) and the reaction was stirred at reflux for 16 hours. The reaction mixture was diluted in dichloromethane (100 mL), washed with water (150 mL), brine (150 mL) and water (150 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude mixture was purified by chromatography on silica (eluent mixture, hexane:ethyl acetate, 2:1) to give a dark green solid (350 mg, 58%).

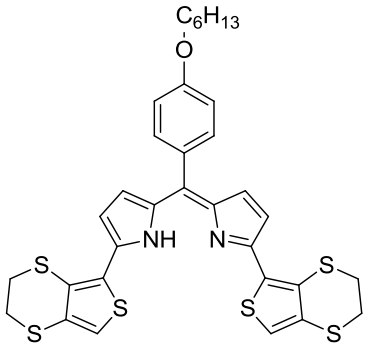
^{1}H NMR ($CDCl_3$): 13.02 (1H, s), 7.43 (2H, d, *J* = 8.6), 6.95 (2H, d, *J* = 8.6), 6.79 (2H, d, *J* = 4.2), 6.64 (2H, d, *J* = 4.2), 6.38 (2H, s), 4.43-4.40 (4H, m), 4.30-4.27 (4H, m), 4.04 (2H, t, *J* = 6.5), 1.90-1.80 (2H, m), 1.53-1.34 (6H, m), 0.94 (3H, t, *J* = 6.8); **^{13}C NMR** ($CDCl_3$) 159.7, 146.8, 142.1, 141.1, 140.0, 137.7, 132.5, 130.0, 129.2, 116.1, 113.6, 112.8, 99.9, 68.1, 65.1, 64.6, 31.6, 29.3, 25.8, 22.6, 14.1; **MS: m/z, MALDI**, M^+ 600.23; **Elemental analysis** $C_{33}H_{32}N_2O_5S_2$; C, 65.98; H, 5.37; N, 4.66; S, 10.68; found C, 63.41; H, 5.17; N, 4.41; S, 10.28; **Melting point**: 167-169 ^oC.

(Z)-2-(2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-5-((5-(2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-2H-pyrrol-2-ylidene)(4-(hexyloxy)phenyl)methyl)-1H-pyrrole (14) (*Microwave assisted synthesis*)



11 (290 mg, 0.7 mmol), trimethylstannane-EDTT (**23**) (603 mg, 1.9 mmol) and $Pd[(PPh_3)_4]$ (35 mg) were added to a 2.0-5.0 mL microwave vial. The vial was purged and vacuum five times and dry DMF (4 mL) was added. The reaction was stirred at 160 ^{o}C for 2 hours *via* microwave assisted heating. The reaction mixture was diluted in dichloromethane (30 mL) and washed with with water (50 mL), brine (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude mixture was purified by chromatography on silica (eluent mixture, hexane:dichloromethane, 1:2) to give a dark purple solid (50 mg, 10%). (Analysis see next)

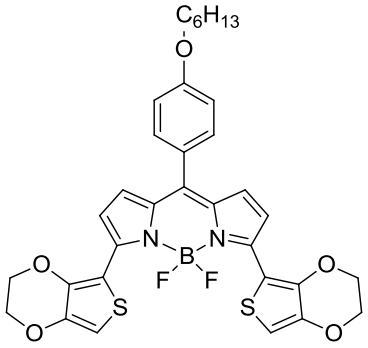
(Z)-2-(2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-5-((5-(2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-2H-pyrrol-2-ylidene)(4-(hexyloxy)phenyl)methyl)-1H-pyrrole (14)



11 (400 mg, 1.0 mmol) and trimethylstannane-EDTT (**23**) (1.0 g, 3 mmol) were dissolved in dry toluene (50 mL). The reaction was stirred at 120 ^{o}C under nitrogen for 16 hours. The reaction mixture was dissolved in dichloromethane (100 mL) and washed with water (3 x 100 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated. The mixture was purified by column chromatography on silica (eluent mixture, hexane:dichloromethane 1:2) to give a dark purple solid (0.350 g, 53 %).

^{1}H NMR ($CDCl_3$): 13.01 (1H, s), 7.45 (2H, d, *J* = 8.6), 7.03 (2H, s), 6.97 (2H, d, *J* = 8.6), 6.82 (2H, d, *J* = 4.3), 6.70 (2H, d, *J* = 4.3), 4.05 (2H, t, *J* = 6.5), 3.26 (8H, m), 1.90-1.80 (2H, m), 1.53-1.34 (6H, m), 0.94 (3H, t, *J* = 6.8); **^{13}C NMR** ($CDCl_3$) 160.0, 146.9, 141.9, 138.6, 132.5, 129.6, 129.3, 128.5, 126.7, 124.9, 118.5, 117.9, 113.7, 68.2, 31.6, 29.3, 28.3, 27.2, 25.8, 22.6, 14.1; **MS: m/z, MALDI**, M^+ 665.07; **Elemental analysis** $C_{33}H_{32}N_2OS_6$; C, 59.60; H, 4.85; N, 4.21; S, 28.93; found C, 58.95; H, 5.04; N, 4.02; S, 28.63; **Melting point**: 160-162 ^{o}C.

3,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,5-difluoro-10-(4-(hexyloxy)phenyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (15)

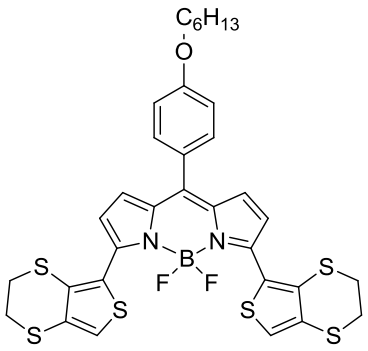


13 (250 mg, 0.4 mmol) was dissolved in dry dichloromethane (25 mL) and triethylamine (0.2 mL) was added. The reaction was stirred for 30 min and boron trifluoride diethyl etherate (1 mL) was slowly added. The reaction was stirred at room temperature under nitrogen overnight. The reaction mixture was washed with

water (50 mL), $NaHCO_3$ (aq) (50 mL), water (50 ml), dried over $MgSO_4$, filtered and the solvent was evaporated. Column chromatography on silica (eluent mixture, hexane:ethyl acetate 2:1) was carried out and a dark green solid was obtained (160 mg, 60 %).

^{1}H-NMR ($CDCl_3$): 7.52 (2H, d, *J* = 8.6), 7.18 (2H, d, *J* = 4.4), 7.01 (2H, d, *J* = 8.6), 6.82 (2H, d, *J* = 4.4), 6.65 (2H, s), 4.35-4.32 (4H, m), 4.27-4.24 (4H, m), 4.05 (2H, t, *J* = 6.5), 1.90-1.80 (2H, m), 1.53-1.35 (6H, m), 0.94 (3H, t, *J* = 6.8); **^{13}C NMR** ($CDCl_3$) 160.0, 147.3, 142.4, 140.6, 138.8, 135.3, 131.6, 128.3, 126.5, 120.6, 113.7, 109.2, 105.1, 67.8, 64.6, 63.7, 31.1, 29.2, 28.7, 25.2, 22.1, 13.5; **MS: m/z, MALDI**, M^+ 648.22; **Elemental analysis** $C_{33}H_{31}BF_2N_2O_5S_2$; C, 61.11; H, 4.82; N, 4.32; S, 9.89; found C, 59.32, H, 4.73, N, 4.02, S, 9.45; **Melting point**: 156-158 ^{o}C.

3,7-bis(2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-5,5-difluoro-10-(4-(hexyloxy)phenyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (16)



12 (440 mg, 0.9 mmol), trimethylstannane-EDTT (**23**) (1.02 g, 3 mmol) and $Pd[(PPh_3)_4]$ (40 mg) were dissolved in dry toluene (20 mL) and the reaction was stirred at reflux for 16 hours. The reaction mixture was dissolved in dichloromethane (100 mL) and washed with water (150 mL), brine (150 mL) and water (150 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude mixture was purified by chromatographic column on silica (eluent mixture, hexane : ethyl acetate

3:1) and a dark purple solid was obtained (470 mg, 65%).

^{1}H NMR ($CDCl_3$): 7.52 (2H, d, *J* = 8.6), 7.19 (2H, s), 7.04 (2H, d, *J* = 8.6), 6.93 (2H, d, *J* = 4.3), 6.90 (2H, d, *J* = 4.3), 4.07 (2H, t, *J* = 6.5), 3.21 (8H, m), 1.90-1.81 (2H, m), 1.54-1.33 (6H, m), 0.94 (3H, t *J* = 7.0); **^{13}C NMR** ($CDCl_3$): 160.7, 148.0, 142.8, 135.9, 131.8, 129.2, 127.8, 125.9, 125.2, 125.0, 121.9, 121.7, 113.9, 67.8, 31.1, 28.7, 27.9, 26.8, 25.2, 22.1, 13.5; **MS: m/z, MALDI**, M^+ 712.14; **Elemental analysis** $C_{33}H_{31}BF_2N_2OS_6$ C, 55.60; H, 4.38; N, 3.93; S, 26.99; found C, 55.39, H, 4.21, N, 3.30, S, 26.62; **Melting point**: 113-115 ^{o}C.

p(BDP-bis-EDTT) *via Sugimoto*

$FeCl_3$ (100 mg, 0.6 mmol) was placed in a 50 ml round bottom flask and evacuated then filled with nitrogen several times (the flask under high-vacuum is then slightly heated). Freshly distilled nitrobenzene (2.5 mL) was added to the flask. To the solution, a solution of **16** (100 mg, 0.14 mmol) in dry chloroform (12.5 mL) was added dropwise. The reaction was stirred under nitrogen at room temperature overnight. The reaction mixture was poured into methanol (300 mL), hydrazine (2%) was added and the mixture was stirred overnight. The black solids were filtered and consecutive soxhlet extractions (methanol, acetone, dichloromethane, chloroform and tetrahydrofuran) were performed. The main fractions were obtained from dichloromethane (41 mg).

^{1}H NMR ($CDCl_3$): 13.10 (0.3H, br), 11.67 (0.1H, br), 7.65-6.53 (8H, br), 4.00 (2H, br), 3.17 (8H, br), 1.93-1.70 (2H, br), 1.63-1.26 (6H, br) and 0.96 (3H, br).

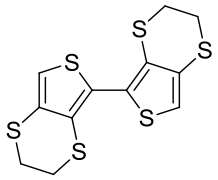
p(BDP-bis-EDTT) *via* oxidative polymerisation with nitrosonium

To a two-necked round bottom flask under nitrogen containing **16** (86 mg, 0.12 mmol), $NOBF_4$ (100 mg, 0.85 mmol) was added in a glovebox. The flask was maintained under nitrogen and dry dichloromethane (35 mL) was added. The

reaction was covered with foil and stirred at room temperature for two days. The reaction mixture was poured into methanol (200 mL) and the solids were filtered and dried (~65 mg). Consecutive soxhlet extractions were carried out (methanol, acetone, dichloromethane, chloroform and toluene). The main fractions were obtained from dichloromethane (20 mg).

^{1}H NMR ($CDCl_3$): 7.78-6.47 (8H, br), 4.07 (2H, br), 3.15 (8H, br), 1.97-1.70 (2H, br), 1.63-1.26 (6H, br) and 0.96 (3H, br).

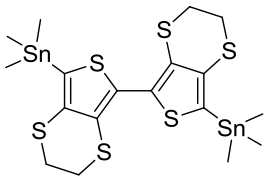
2,2',3,3'-Tetrahydro-5,5'-bithieno[3,4-b][1,4]dithiine (18)[1]



To a solution of EDTT (**17**) (3.83 g, 22 mmol) in dry THF (125 mL) cooled to -80°C, *n*-butyl-lithium (14 mL of 1.6 M solution in THF, 1.05 eq, 23 mmol) was slowly added. When the reaction temperature reached 0°C, the solution was stirred for an extra 2h at this temperature, before adding $CuCl_2$ (3.1 g, 1.05 eq, 23 mmol) in one portion. The reaction mixture was stirred overnight at 0°C. The solvent was then removed and the crude mixture was dissolved in CH_2Cl_2 (50 mL), washed with water (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The resulting mixture was loaded onto silica gel and purified by flash column chromatography, eluting with ethyl acetate hexane (1:3), to afford a yellow powder (1.9 g, 50%) that was used in the next stage without further purification.

^{1}H NMR ($CDCl_3$): 7.08 (2H, s) and 3.25 (8H, br s).

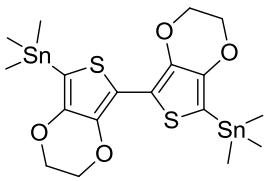
7,7'-bis(Trimethylstannyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dithiine (19)



To a solution of bis-EDTT (330 mg, 0.95 mmol) in dry THF (100 mL) and cooled to -80°C, *n*-butyl-lithium (1 mL of 2.5 M solution in hexane, 2.5 mmol) was slowly added. The reaction was stirred under nitrogen until the temperature reached -50°C, before being cooled down again to -80°C and Me_3SnCl (4 mL, 1 M in hexane, 4 mmol) was added. The reaction was stirred at room temperature overnight. The solvents were removed and the crude mixture dissolved in CH_2Cl_2 (50 mL), washed with water (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The crude mixture was recrystallised from hexane to give a pale brown solid (0.59 g, 91 %). The compound was used without further purification.

^{1}H NMR ($CDCl_3$): 3.15-3.20 (8H, m) and 0.45 (18H, s).

7,7'-bis(Trimethylstannyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine (21)[2]

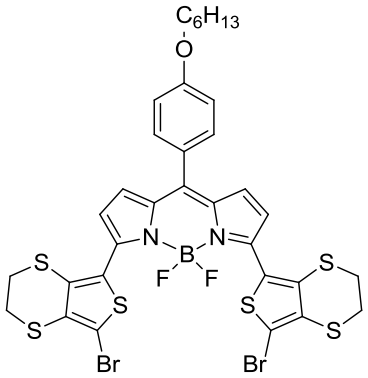


Bis-EDOT (**20**) (1.13 g, 4 mmol) was dissolved in dry THF (50mL) and cooled to -80°C. *n*-Butyl-lithium (4 mL, 2.5 M in hexanes, 10 mmol) was carefully added and the reaction was stirred for 30 min. Trimethyltin chloride (12 mL, 1 M in hexane, 12 mmol) was added keeping the reaction at -60 °C. The reaction was slowly warmed to

room temperature and left stirring under nitrogen overnight. The solvent was removed and the solid was dissolved in CH_2Cl_2 (50 mL), washed with water (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness to obtain a brown solid. The solid was recrystallised from hexane to obtain 2.2 g of a beige solid (81%). The compound was used in the next step without further purification.

^{1}H NMR ($CDCl_3$): 4.33-4.30 (4H, m), 4.24-4.21 (4H, m) and 0.38 (18H, s).

3,7-Bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dithiin-5-yl)-5,5-difluoro-10-(4-(hexyloxy)phenyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (32)



16 (0.20 g, 0.28 mmol) was dissolved in dry chloroform (50 mL) and NBS (0.110 g, 2.2 eq.) was added. The reaction was stirred in a nitrogen atmosphere overnight in the dark at room temperature. The reaction mixture was washed with water (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The resulting solids were loaded onto a chromatographic column (eluent mixture, hexane:ethyl acetate, 3:1) to give a dark green solid (0.140 g, 61%).

^{1}H NMR ($CDCl_3$): 7.51 (2H, d, *J* = 8.6), 7.19 (2H, s), 7.04 (2H, d, *J* = 8.8), 6.94 (2H, d, *J* = 4.8), 6.90 (2H, d, *J* = 4.0), 4.07 (2H, t, *J* = 6.6), 3.24 (8H, m), 1.90-1.81 (2H, m), 1.54-1.33 (6H, m), 0.94 (3H, t *J* = 7.0); **^{13}C NMR** ($CDCl_3$): 161.3, 1474, 143.4, 136.5, 132.8, 129.8, 126.6, 126.2, 125.7, 122.4, 114.4, 110.8, 68.3, 31.5, 29.1,

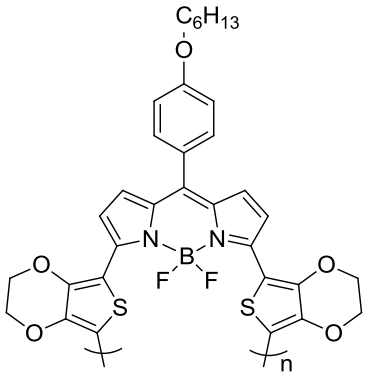
27.9, 27.5, 22.6, 14.0; **MS: m/z, MALDI**, M^+ 869.8; **Elemental analysis** $C_{33}H_{29}BBr_2F_2N_2OS_6$; C, 45.53; H, 3.36; N, 3.22; S, 22.10; found C, 43.53, H, 3.37, N, 3.05, S, 21.0.62; **Melting point**: 146-148 ^oC.

p(BDP-bis-EDTT) *via* Yamamoto

In a 50-mL-one-necked flask, $Ni(cod)_2$ (85 mg, 0.3 mmol) and 2,2'-bipyridine (48 mg, 0.3 mmol) were placed in a glovebox. The flask was kept under nitrogen and dry DMF was added (10 mL). A solution of **32** (0.20 g, 0.23 mmol) in anhydrous DMF (8mL) was added to the previous solution. 1,5-Cyclooctadiene (0.1 mL) was added and the reaction was stirred for two days at 60 °C in the dark. The reaction mixture was then poured into methanol (200 mL). After filtration, the black solids were subjected to subsequent soxhlet extractions (methanol, acetone, dichloromethane and chloroform). The main fractions were obtained from dichloromethane (86 mg).

^{1}H NMR ($CDCl_3$): 7.70-7.37 (2H, br), 7.20-6.47 (6H, br), 4.05 (2H, br), 3.17 (8H, br), 1.93-1.72 (2H, br), 1.61-1.19 (6H, br) and 0.96 (3H, br).

Copolymer p(BDP-bis-EDOT)

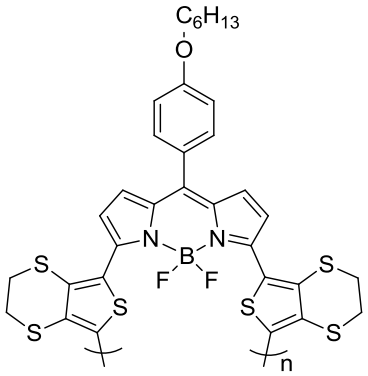


To a solution **21** (450 g, 0.7 mmol) in dry toluene (50 mL) was added a solution of **12** (332 mg, 0.7 mmol) in dry toluene (25 mL). $Pd[PPh_3]_4$ catalyst (30 mg) was added and the reaction was stirred under nitrogen at 110 °C for 48 h. The reaction

mixture was cooled down to room temperature and 2-bromothiophene (60 mg, 0.35 mmol) and $Pd[PPh_3]_4$ (10 mg) were added. The reaction was heated to 110 °C for 5h and cooled down again to room temperature to add stannylated-EDOT (100 mg, 0.35 mmol) and stirred at 110 °C again overnight. The crude product was precipitated into methanol and collected by filtration. Soxhlet purification was carried out using methanol, acetone and the main fractions were extracted from CH_2Cl_2 to give a black polymer (200 mg, 44%).

^{1}H NMR ($CDCl_3$): 7.48 (2H, br), 7.28 (2H, br), 7.01 (2H, br), 6.80 (2H, br), 4.28 (8H, br), 4.06 (2H, br), 1.85 (2H, br), 1.60-1.20 (6H, br) and 0.96 (3H, br); **GPC** (in chloroform *versus* polystyrene standard) M_n 170000, PDI 2.1; **TGA** T_d 285°C.

Copolymer p(BDP-bis-EDTT)

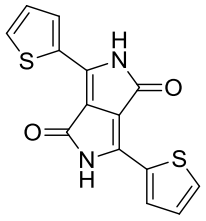


To a solution of **19** (360 g, 0.5 mmol) in dry toluene (50 mL) was added a solution of **12** (233 mg, 0.5 mmol) in dry toluene (25 mL). $Pd[PPh_3]_4$ catalyst (25 mg) was added and the reaction was stirred under nitrogen at 110°C for 48 h. The reaction mixture was cooled down to room temperature and 2-bromothiophene (50 mg, 0.25 mmol) and $Pd[PPh_3]_4$ (10 mg) were added. The reaction was heated to 110°C for 5h and cooled down again to room temperature to add stannylated-EDTT (125 mg, 0.35 mmol) and stirred at 110°C again overnight. The crude product was precipitated into methanol and collected by filtration. Soxhlet purification was carried out using

methanol, acetone and the main fractions were extracted from CH_2Cl_2 to give a black polymer (220mg, 33%).

^{1}H NMR ($CDCl_3$): 7.70-7.34 (4H, br), 7.13-6.73 (4H, br), 4.07 (2H, br), 3.21 (8H, br), 1.86 (2H, br), 1.63-1.26 (6H, br) and 0.96 (3H, br); **GPC** (in chloroform *versus* polystyrene standard) M_n 37000, PDI 5.4; **TGA** T_d 255°C.

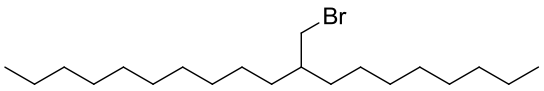
3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (33)[3]



To a 250 ml-two-necked-flask with tert-amyl-alcohol (175 mL), sodium (5.5 g, 0.239 mol) was slowly added in small pieces. The mixture was stirred at 90 ^oC until the sodium reacted completely. The temperature was decreased to 60 ^oC and thiophene-2-carbonitrile (13.1 mL, 15.3 g, 140 mmol) was added. The reaction was refluxed and a solution of dimethyl succinate (10.3 g, 70 mmol) in *tert*-amyl alcohol (40 mL) was added dropwise. The reaction was stirred at reflux overnight. Methanol (300 mL) and acetic acid (25 mL) was added and stirred at reflux for 30 min. The reaction was cooled to room temperature and the solid was filtrated with water and methanol to yield a dark purple solid. (14 g, 35%). This compound was used in the next step without further purification.

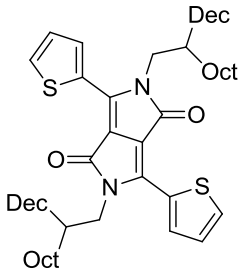
^{1}H-NMR (DMSO): 10.77 (2H, s), 7.76 (2H, d, J = 4.0), 7.51 (2H, d, J = 4.0), 6.85 (2H, t, J = 4.1).

9-(Bromomethyl)nonadecane (34)[4]



A solution of 2-octyl-1-dodecanol (10 g, 33.5 mmol, 1 eq.) and triphenylphosphine (16 g, 61 mmol, 1.8 eq) in dry tetrahydrofuran (300 mL) was cooled to 0 ^{o}C. Bromine (5 mL, 15 g, 2.7 eq.) was slowly added and the reaction was stirred for 4 hours. The solvent was removed and the remaining mixture was dissolved in dichloromethane (100 mL) and washed three times with water (100 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated. To the oily mixture hexane (300 mL) was added and filtered. The filtrate was concentrated and loaded onto a chromatographic column (eluent: hexane) to give a colourless oil. (10.8 g, 85%).
^{1}H-NMR ($CDCl_3$): 3.45 (2H, d, *J* = 4.8), 1.60 (1H, br), 1.39-1.20 (32H, m), 0.89 (6H, m).

2,5-Bis(2-octylundecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (35)[5]

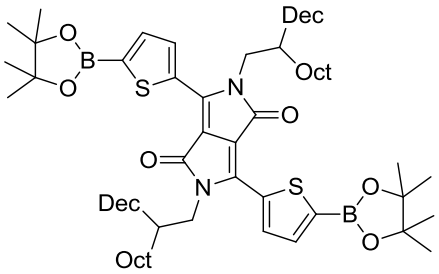


A mixture of **33** (2.32 g, 7.7 mmol) and anhydrous potassium carbonate (3.21 g, 2.3 mmol) in dry *N*,*N*-dimethylformamide (80 mL) was heated to 125 ^{o}C and 9-(bromomethyl)nonadecane (**34**) (11.5 g, 32 mmol) was added slowly. The reaction was stirred at 125 ^{o}C under nitrogen overnight. The reaction was cooled, diethyl ether (200 mL) was added and an aqueous work up was carried out (3 x 200 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated. After

chromatographic column (eluent mixture, hexane:ethyl acetate, 20:1), a dark purple powder was obtained (3.06 g, 46%).

^{1}H-NMR ($CDCl_3$): 8.87 (2H, d, *J* = 3.9), 7.62 (2H, d, *J* = 3.9), 7.23-7.30 (2H (masked by $CDCl_3$ peak), m), 4.02 (4H, d, *J* = 7.7), 1.91 (2H, br), 1.35-1.17 (64H, m) and 0.87 (12H, m).

2,5-Bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (36)

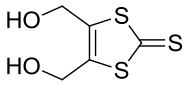


A solution of **35** (0.86 g, 1.0 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.61 ml, 0.56 g, 3.0 mmol) in dry THF (10 ml) was cooled to -25^{o}C and lithium diisopropylamide (1.43 ml, 1.6 M in tetrahydrofuran, 2.3 mmol) was added drop-wise. The reaction was stirred under nitrogen at 0^{o}C for 1 h. A solution of HCl (0.1 M, 10 ml) was added and the product was extracted with dichloromethane (3 x 25 ml), dried over $MgSO_4$ and the solvent evaporated. The crude mixture was dissolved in dichloromethane and poured into cold acetone. After filtration, the filtrate was washed with cold acetone and dried under low vacuum to give a dark pink powder (0.84 g, 75 %).

^{1}H NMR ($CDCl_3$): 8.91 (2H, d, *J* = 3.9), 7.71 (2H, d, *J* = 3.9), 4.05 (4H, d, *J* = 7.7), 1.89 (2H, br), 1.37 (24H, s), 1.30-1.17 (64H, m) and 0.86 (12H, m); **^{13}C NMR** ($CDCl_3$): 161.2, 140.0, 137.1, 135.6, 135.1, 108.2, 84.0, 45.7, 37.2, 31.4, 31.3, 30.7, 29.5, 29.1, 29.0, 29.04, 29.01, 28.8, 28.7, 25.8, 24.2, 22.1 and 22.1; **MS: m/z, MALDI**, M^+ 1112.51; **IR** υ_{max}/cm^{-1}: 2926, 2854, 1661, 1560, 1515, 1454, 1400,

1362, 1340, 1308, 1243, 1167, 1103, 1077, 1014, 852; **Elemental Analysis** $C_{66}H_{110}B_2N_2O_6S_2$; C, 71.20; H, 9.96; N, 2.52; S, 5.76; found: C, 71.60; H, 9.52; N, 2.43; S, 5.81. **Melting point**: 166-168^{o}C.

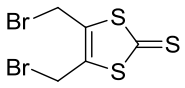
4,5-Bis(hydroxymethyl)-1,3-dithiole-2-thione (37) [6]



Dry THF (80 mL) and methanol (150 mL) were added to a 2 L Erlenmeyer flask. LiCl (1.51 g, 35.6 mmol) and sodium borohydride (15.05 g, 0.4 mol) was dissolved in the previous solvent mixture. The mixture was cooled to -10°C and a solution of the dicarboxylate **56** (14.92 g, 60 mmol) in dry THF (100 mL) was added dropwise. The solution was again cooled to -10°C before adding $NaBH_4$ (15.00 g, 0.4 mol). A small amount of effervescence was observed when adding $NaBH_4$. The mixture was stirred for 1 h at 0°C and then quenched with ice (1.25 L). The product was extracted with cold ethyl acetate (-10°C, 4 x 400 mL) and the organic phase was washed with brine (3 × 300 mL), dried with $MgSO_4$, filtered and the solvents evaporated. The product obtained was a bright yellow powder (8.24 g, 72%). It was used in the next step without further purification.

^{1}H NMR ($(CD_3)_2CO$): 4.63 (d, J = 5.6).

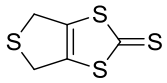
4,5-Bis(bromomethyl)-1,3-dithiole-2-thione (38)[6]



4,5-Bis(hydroxymethyl)-1,3-dithiole-2-thione (**37**) (6.50 g, 33 mmol) was dissolved in dry THF (250 mL) and cooled under nitrogen to 0°C. PBr_3 (6.42 mL, 66 mmoles) was carefully added over 30 min and the reaction was stirred overnight at room

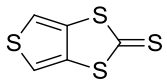
temperature. The solvent was removed and the crude mixture was recrystallised with CCl_4 (50 mL) yielding bright yellow crystalline needles (8.93 g, 85%).
^{1}H NMR ($CDCl_3$): 4.25 (s) ppm.

4,6-Dihydrothieno[3,4-d][1,3]dithiole-2-thione (39)[6]



4,5-Bis(bromomethyl)-1,3-dithiole-2-thione (4.01 g, 12 mmol) was dissolved in THF (200 mL) and ethanol (50 mL). $Na_2S{\cdot}9H_2O$ (3.01 g, 12 mmol) was dissolved in H_2O (200 mL) and ethanol (50 mL). Both solutions were added dropwise at an equal rate over 1 h to a 2-L-beaker with EtOH (200 mL), whilst stirring vigorously. The reaction mixture was stirred for another 30 min and the volume reduced to approximately 300 mL. The product was extracted with dichloromethane (4 × 200 mL), washed with water (4 × 250 mL), dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure to yield an orange-yellow solid (1.80 g). It was used in the next step without further purification.

Thieno[3,4-d][1,3]dithiole-2-thione (40)[6]

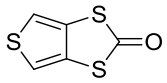


4,6-Dihydrothieno[3,4-d][1,3]dithiole-2-thione (**39**) (1.35 g, 7 mmol) was dissolved in dry toluene (130 mL) and DDQ (1.87 g, 8.2 mmoles) was added to the solution. The reaction was stirred under reflux under nitrogen for 2 h. The reaction was monitored by TLC (toluene) until no starting material was observed, adding additional DDQ if necessary. The reaction mixture was cooled and filtered through silica. Toluene was removed under reduced pressure and the crude product (*ca.* 1.3

g) was recrystallised from dichloromethane/hexane (25 mL/40 mL) to yield a brown yellow crystalline solid (0.90 g, 67%).

^{1}H NMR ($CDCl_3$): 7.25 (s) ppm.

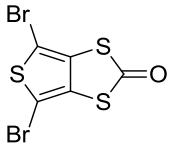
Thieno[3,4-d][1,3]dithiol-2-one (41)[6]



To a solution of thieno[3,4-d][1,3]dithiole-2-thione (**40**) (1.89 g, 10 mmol) in chloroform (75ml): acetic acid (25 mL), $Hg(AcO)_2$ (8.55 g, 27 mmol) was added and the reaction was kept reacting at room temperature under nitrogen for 16 h. The reaction was filtered through Celite, washed with water (3× 100mL), $NaHCO_3$ (2 × 100 mL) and water (2 × 100 mL). The organic phase was dried with $MgSO_4$, filtered and evaporated to yield white needles (1.55 g, 90%).

^{1}H NMR ($CDCl_3$): 7.20 (s) ppm.

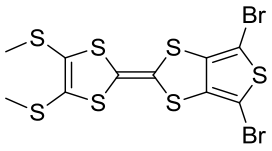
4,6-Dibromothieno[3,4-d][1,3]dithiol-2-one (42)[6]



To a suspension of thieno[3,4-d][1,3]dithiole-2-one (**41**) (1.55 g, 9 mmol) in dichloromethane (100 mL), was added bromine (10 mL, 86 mmol). The reaction was stirred at room temperature for 1 h before quenching it with a cold solution of Na_2SO_3 (10 g in 100 mL) and ice. The product was extracted with dichloromethane (5 × 125 mL), neutralised with saturated $NaHCO_3$ (2 × 125 mL), water (2 × 150 mL) and dried over $MgSO_4$. Charcoal was added, the solution was filtered through Celite and the solvent evaporated under reduced pressure. The crude mixture was

recrystallised from petroleum ether: dichloromethane to yield white-yellow crystalline needles (1.44 g, 48%).
Melting point: 125-127 ^{o}C (lit: 126-128 ^{o}C).

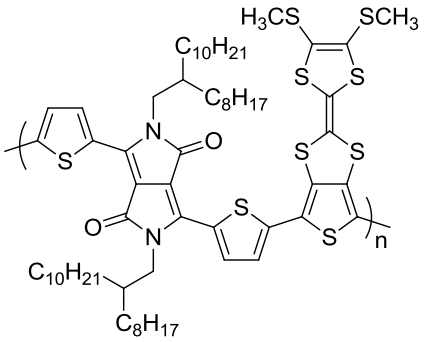
2-(4,5-Bis(methylthio)-1,3-dithiol-2-ylidene)-4,6-dibromothieno[3,4-d][1,3]dithiole (44)



To a mixture of **43** (0.25 g, 1.1 mmol) and **42** (0.26 g, 0.8 mmol), triethylphosphite (5 ml) was added and the reaction was stirred under nitrogen at 120^{o}C for 2 h. The reaction mixture was diluted in dichloromethane (200 ml) and filtered. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and precipitated in methanol. The precipitate was washed with cold methanol and dried at low pressure to give an orange powder (250 mg, 63 %).

^{1}H NMR ($CDCl_3$): 2.44 (6H, s); **^{13}C NMR** ($CDCl_3$): 136.5, 126.5, 116.2, 111.6, 96.5, 18.3; **MS: m/z, MALDI,** M^+ 509.42; **IR** υ_{max}/cm^{-1}: 2993, 2923, 1526, 1495, 1418, 1288, 1032, 967, 896, 762; **Elemental Analysis**: $C_{10}H_6Br_2S_7$; C 23.53; H, 1.18; S, 43.97 %; found: C 23.12; H 0.98; S, 43.50 %. **Melting point**: 170-172 ^{o}C.

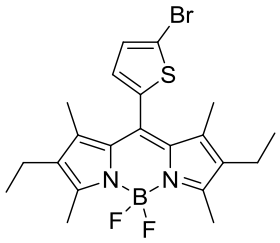
p(DPP-TTF)



Compound **36** (760 mg, 0.7 mmol), compound **44** (350 mg, 0.7 mmol), tris[dibenzylideneacetone]dipalladium(0) (50 mg, 0.05 mmol) and tri-*tert*-butyl phosphonium tetrafluoroborate (60 mg, 0.2 mmol) were dissolved in dry tetrahydrofuran (20 ml) and tripotassium phosphate (0.22 g, 1.0 mmol) dissolved in water (3 ml) was added to the solution. The reaction was stirred at 80^{o}C under nitrogen for 48 h and 2-bromothiophene (0.01 ml, 16 mg, 0.1 mmol) added after this time. The reaction was stirred at the same temperature for 6 h and 2-thienylboronic acid (19 mg, 0.15 mmol) was then added. At this point, the reaction was stirred for another 6 h before it was poured into methanol (500 mL) and filtered. The solids were purified by soxhlet extractions with methanol, acetone and chloroform. The chloroform fractions were redissolved in chloroform and precipitated in methanol to give 620 mg of a dark green-black powder (73 % yield).

^{1}H NMR ($CDCl_3$): 8.87-9.50 (2H, br), 7.40-6.80 (2H, br), 4.50-3.62 (4H, br), 2.73-2.40 (6H, br), 2.12-1.85 (2H, br), 1.49-1.10 (64H, br) and 0.94-0.80 (12H, br); **MALDI**: 5532.7(highest peak), 5372, 4840, 4139, 3645, 3281, 2922, 2422, 2462, 2071; **GPC** (in 1,2-dichlorobenzene *versus* polystyrene standard) M_n 9.6 kDa; M_w 31.4 kDa; PDI 3.2; **TGA** T_d 270 °C.

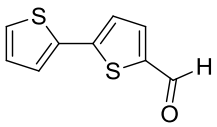
10-(5-Bromothiophen-2-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (58)[7]



5-Bromothiophene-2-carbaldehyde (1.7 g, 8.5 mmol) and 3-ethyl-2,4-dimethyl-1H-pyrrole (2.1 g, 17 mmol, 2 eq.) were dissolved in dry dichloromethane (600 ml). The reaction vessel was covered with foil and TFA (6 drops) were added. The reaction was stirred at room temperature for 24 h. Then, DDQ (2.12 g, 1 eq.) was added and the reaction was stirred an extra 24 h. Et_3N (6.0 ml, 43 mmol) was added and after 30 min, $BF_3.Et_2O$ (10.6 ml, 86 mmol) was added dropwise. The reaction was stirred overnight at room temperature. The reaction volume was reduced to 100 ml (approx.) and washed with water (100 mL), $NaHCO_3$ (aq) (100 mL), water (100 ml), dried over $MgSO_4$, filtered and the solvent was evaporated. Column chromatography on silica (eluent mixture, hexane:dichloromethane, 2:3) was carried out and a dark purple powder was obtained (1.35 mg, 33 %).

^{1}H NMR ($CDCl_3$): 7.10 (1H, d, *J* = 3.6), 6.77 (2H, d, *J* = 3.7), 2.53 (6H, s), 2.34 (4H, m, *J* = 7.6), 1.60 (6H, s), 1.01 (6H, t *J* = 7.6); **Melting point**: 190-192 ^{o}C (lit: 194-196 ^{o}C).

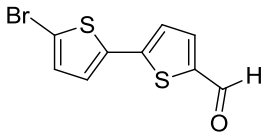
[2,2'-Bithiophene]-5-carbaldehyde (60)[8]



2,2'-Bithiophene (4.0 g, 24 mmol) and DMF (2.6 g, 36 mmol, 1.5 eq.) were dissolved in dichloroethane (150 ml) and cooled to -10 ^{o}C. Phosphoryl chloride (4.4 g, 2.7 ml, 29 mmol, 1.2 eq.) was added to the previous solution dropwise. The reaction was left to reach room temperature and the reaction was stirred at 50 ^{o}C overnight. A solution of sodium acetate was added to the reaction mixture and it was vigorously stirred for 1 h. The reaction mixture was washed with water (3 x 100 ml), dried over $MgSO_4$, filtered and the solvent evaporated. The residue was chromatographed on silica gel (eluent mixture, dichloromethane : hexane, 2:1) to yield **60** (4.2 g, 90%).

^{1}H NMR ($CDCl_3$): 9.87 (1H, s), 7.68 (1H, d, *J* = 4.0), 7.38 (2H, d, *J* = 4.0), 7.38 (1H, hidden by the solvent peak), 7.08 (1H, t, *J* = 4.0).

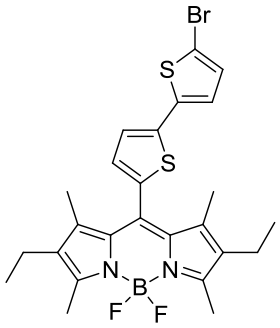
5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (61)[9]



[2,2'-Bithiophene]-5-carbaldehyde (3.0 g, 15.5 mmol) was dissolved in dry DMF (30 ml) and cooled to -15 ^{o}C. NBS (2.89 g, 1.05 eq) was added in one portion and the reaction was stirred overnight at room temperature. The reaction mixture was poured into ice and stirred till the ice had melted. The solid was filtered and recrystallised from hot dichloromethane and petroleum ether. A pale yellow solid was obtained (3.7 g, 88 %).

^{1}H NMR ($CDCl_3$): 9.88 (1H, s), 7.67 (1H, d, *J* = 4.0), 7.19 (1H, d, *J* = 4.0), 7.12 (1H, d, *J* = 4.0), 7.05 (1H, d, *J* = 4.4).

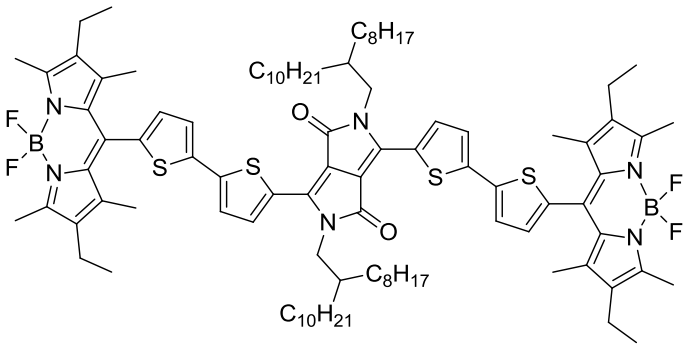
10-(5'-Bromo-[2,2'-bithiophen]-5-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (62)[7]



5'-Bromo-[2,2'-bithiophene]-5-carbaldehyde (**61**) (1.45 g, 5.31 mmol) and 3-ethyl-2,4-dimethyl-1H-pyrrole (1.44 g, 11.7 mmol, 2 eq.) were dissolved in dry dichloromethane (300 ml) and the reaction vessel was covered with aluminium foil. TFA (4 droplets) was added and the reaction was stirred at room temperature overnight. DDQ (1.2 g, 1 eq.) was added and the reaction was stirred overnight before adding Et_3N (2.7 g, 3.7 ml, 26.5 mmol, 5 eq.). After 30 min, BF_3Et_2O (7.5 ml, 8.6 g, 60 mmol) was added dropwise and the reaction was stirred overnight. The reaction volume was reduced to 50 ml (approx.) and washed with water (50 mL), $NaHCO_3$ (aq) (50 mL), water (50 ml), dried over $MgSO_4$, filtered and the solvent was evaporated. Column chromatography (eluent mixture, hexane:dichloromethane, 2:1) was carried out and a slightly contaminated dark red solid was obtained. After precipitation with methanol, **62** was obtained (0.350, 12 %).

^{1}H NMR ($CDCl_3$): 7.25 (1H, d, *J* = 3.6), 7.02 (1H, d, *J* = 4.0), 6.99 (1H, d, *J* = 4.0), 6.90 (1H, d, *J* = 3.6), 2.55 (6H, s), 2.35 (4H, d, *J* = 7.5), 1.65 (6H, s), 1.03 (3H, t, *J* = 7.5); **Melting point**: 226-228 ^{o}C (lit: 228-230 ^{o}C).

10,10'-(5',5'''-(2,5-Bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide) (63)

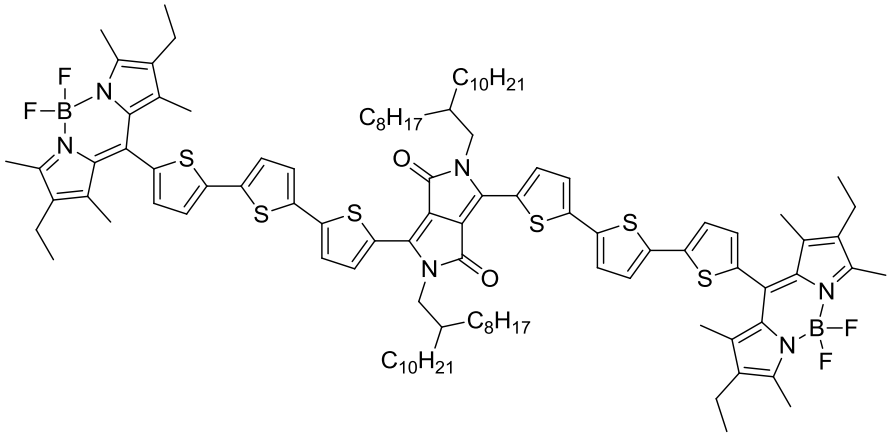


DPP **36** (100 mg, 0.09 mmol, 3 eq), Bodipy **58** (124 mg, 0.3 mmol, 1 eq), $Pd_2(dba)_3$ (20 mg, 0.02 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (20 mg, 0.06 mmol) were dissolved in dry THF (10 mL). A solution of of tripotassium phosphate (84 mg, 0.4 mmol) in water (3 ml) was added to the previous solution. The reaction was refluxed for 48 hours under nitrogen. Dichloromethane was added to the reaction mixture and washed with water (50 mL), brine (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvents evaporated. Column chromatography on silica (eluent mixture, hexane:dichloromethane, 1:1) was carried out. The main fractions were recrystallized by dissolving in dichloromethane and precipitating with methanol. The precipitate was dissolved in hot hexane and the beaker was left in the fridge. The precipitate was filtered and a dark purple product was obtained (83 mg, 55%).

^{1}H NMR ($CDCl_3$): 8.88 (2H, d, *J* = 4.1), 7.37 (4H, m), 6.96 (2H, d, *J* = 3.6), 4.05 (4H, d, *J* = 6.8), 2.55 (12H, s), 2.35 (8H, m), 1.98 (2H, br s), 1.66 (12H, s), 1.40-1.15 (64H, m), 1.02 (12H, t), 0.85 (12H, m); **^{13}C NMR** ($CDCl_3$): 161.1, 154.4, 141.1, 138.9, 137.9,137.6, 135.9, 135.8, 132.9, 131.0, 130.1, 128.7, 128.1, 124.7, 124.6, 108.2, 45.8, 37.5, 31.4, 31.3, 30.8, 29.5, 29.1, 29.09, 29.04, 28.8, 28.7, 25.8, 22.1,

16.6, 14.0, 13.5, 12.1, 10.8; **MS: m/z, MALDI,** M^+ 1628.3;. **Elemental Analysis**: $C_{96}H_{134}B_2F_4N_6O_2S_4$; C, 70.74; H, 8.29; N, 5.16; S, 7.87; found: C, 68.78; H, 8.05; N, 5.56; S, 8.09; **Melting point**: 165-167 ^oC.

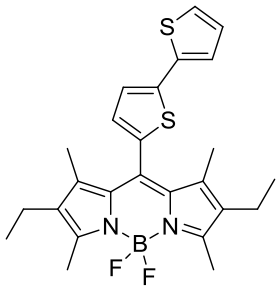
10,10'-(5'',5'''''-(2,5-Bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2':5',2''-terthiophene]-5'',5-diyl))bis(2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide) (64)



BDP **62** (278 mg, 0.5 mmol, 2.5 eq), DPP **36** (218 mg, 0.2 mmol, 1 eq), $Pd_2(dba)_3$ (40 mg, 0.04 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (40 mg, 0.1 mmol) were dissolved in dry THF (20 mL). To the previous solution, a solution of tripotassium phosphate (84 mg, 0.4 mmol) in water (3 ml) was added. The reaction was refluxed for 48 hours under nitrogen. Dichloromethane (50 mL) was added to the reaction mixture and washed with water (50 mL), brine (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvents evaporated. The resulting solids were loaded onto a silica column (eluent mixture, hexane:dichoromethane, 2:1). The product was subjected to further chromatographic columns in silica (eluent mixture, hexane:ethyl acetate, 7:3). Preparative HPLC (isocratic) was then carried out (eluent mixture, hexane : dichoromethane, 2:1) to obtain pure **64** (120 mg, 34%).

^{1}H NMR ($CDCl_3$): 8.93 (2H, d, *J* = 4.1), 7.35 (4H, m), 7.27-7.24 (4H, (masked by $CDCl_3$ peak)), 7.19 (2H, d, *J* = 3.8), 6.93 (2H, d, *J* = 3.6), 4.06 (4H, d, *J* = 7.5), 2.56 (12H, s), 2.35 (8H, m), 1.98 (2H, br s), 1.66 (12H, s), 1.42-1.16 (64H, m), 1.02 (12H, t), 0.85 (12H, m); **^{13}C NMR** ($CDCl_3$): 161.1, 154.2, 141.5, 138.8, 138.1, 138.0, 136.7, 136.1, 134.9, 134.7, 132.8, 131.1, 130.4, 128.5, 127.9, 125.3, 124.6, 124.4, 123.6, 108.1, 45.8, 37.4, 31.4, 30.8, 29.5, 29.1, 29.0, 28.9, 28.8, 25.9, 22.1, 16.6, 14.0, 13.6, 12.1, 10.8; **MS: m/z, MALDI,** M^+ 1794.2; **Elemental Analysis**: $C_{104}H_{138}B_2F_4N_6O_2S_6$ C, 69.62; H, 7.75; N, 4.68; S, 10.72; found: C, 67.33; H, 7.60; N, 4.87; S, 11.00; **Melting point**: 109-111 ^{o}C.

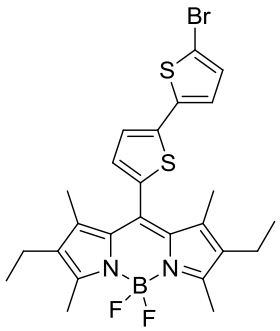
10-([2,2'-bithiophen]-5-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (75)[7]



58 (0.50 g, 1.07 mmol, 1 eq), 2-thienyl-boronic acid (165 mg, 1.3 mmol, 1.2 eq) and $Pd[PPh_3]_4$ catalyst (36 mg) were dissolved in dry THF (50 mL). A 1M solution of sodium carbonate (3.21 mmol, 3 mL water, 3 eq) was added to the reaction mixture and the reaction was refluxed overnight under nitrogen. The THF was removed and the crude mixture was dissolved in dichloromethane (50 mL). The organic phase was washed with water (3 x 50 ml), dried over $MgSO_4$, filtered and the solvent was evaporated. Chromatographic column on silica (eluent mixture, hexane:dichloromethane, 1:1) was carried to yield a solid compound **75** (425 mg, 85%).

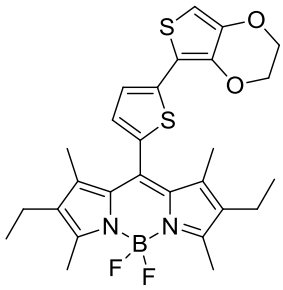
^{1}H NMR ($CDCl_3$): 7.25 (1H, m), 7.22 (1H, d, *J* = 4.0), 7.07 (1H, m), 6.90 (1H, d, *J* = 3.6), 2.55 (6H, s), 2.36 (4H, d, *J* = 7.5), 1.66 (6H, s), 1.02 (3H, t, *J* = 7.5).

10-(5'-Bromo-[2,2'-bithiophen]-5-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide



75 (0.43 g, 0.9 mmol) and NBS (0.21 g, 1.18 mmol) were dissolved in dichloromethane (30 mL) and the reaction was stirred under nitrogen at room temperature overnight in the absence of light. The reaction mixture was washed with water (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The mixture was purified by column chromatography on silica (eluent mixture, hexane:dichloromethane, 1:2). No fraction of the desired product was recovered.

10-(5-(2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (76)

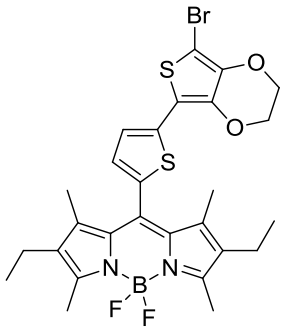


58 (0.60 g, 1.3 mmol), trimethyl-stannylated-EDOT (0.60 g, 1.9 mmol) and $Pd[PPh_3]_4$ catalyst (35 mg) were dissolved in dry toluene (40 mL). The reaction was

refluxed overnight under nitrogen. The reaction mixture was washed with water (3 x 50 mL) and the organic fraction was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The solids were loaded onto a silica column (eluent mixture, hexane:dichloromethane, 1:1) and a dark red solid was isolated (350 mg, 51%).

^{1}H NMR ($CDCl_3$): 7.24 (1H, d, *J* = 3.6), 6.86 (1H, d, *J* = 3.6), 6.28 (1H, s), 4.36-4.27 (4H, m), 2.53 (6H, s), 2.33 (4H, d, *J* = 7.5), 1.63 (6H, s), 1.01 (3H, t, *J* = 7.5); **^{13}C NMR** ($CDCl_3$): 154.7, 142.3, 139.1, 138.3, 137.4, 133.7, 133.4, 132.3, 132.3, 128.3, 122.7, 111.9, 97.6, 65.4, 64.9, 17.4, 14.9, 12.9, 11.6; **MS: m/z, MALDI,** M^+ 526.04; **Elemental Analysis**: C, 61.60; H, 5.55; N, 5.32; S, 12.18; found: C, 61.20; H, 5.46; N, 5.37; S, 12.61; **Melting point**: 225-227 ^{o}C.

10-(5-(7-Bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide



76 (300 mg, 0.57 mmol) and NBS (0.11 g, 0.59 mmol) were dissolved in dichloromethane (30 mL) and the reaction was stirred under nitrogen at room temperature overnight in the absence of light. The reaction mixture was washed with water (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The mixture was purified by column chromatography on silica (eluent mixture, hexane:dichloromethane, 1:2). No fraction of the desired product was recovered.

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