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Note added after first publication: This additional ESI document was added on November 9, 2016 at the authors request, as part of a correction to the original manuscript (DOI: 10.1039/C6CC90512A) to report improved synthetic and purification methods developed by the authors after first publication. An additional author, Dani M. Stoltzfus, has been added to the correction manuscript and this additional ESI in reflection of her considerable intellectual contribution and effort in the revised syntheses. The new methods reported in the correction and this additional ESI documents have undergone peer review before publication.

Erratum: Electronic Supplementary Information

Dielectric constant enhancement of non-polymeric organic semiconductors *via* side-chain modification

Jenny E. Donaghey,[a] Ardalan Armin,[a] Dani M. Stoltzfus,[a] Paul L. Burn,*[a] Paul Meredith*[a]

[a]*Centre for Organic Photonics & Electronics, School of Chemistry and Molecular Biosciences and School of Mathematics and Physics, The University of Queensland, St Lucia Campus, Brisbane 4072 (Australia)*

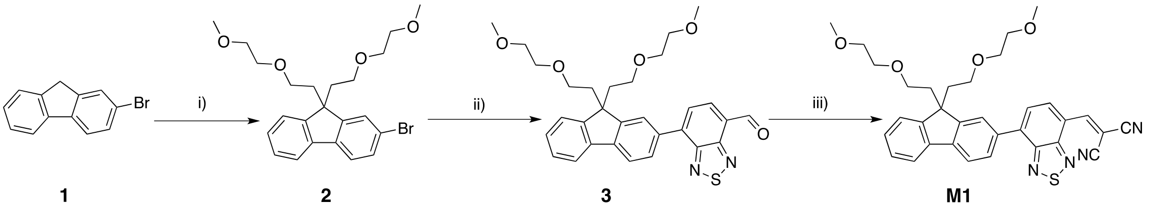
**Email: p.burn2@uq.edu.au; meredith@phys.uq.edu.au*

1. Experimental

Materials and synthesis

Cyclopenta[2,1-b;3,4-b']dithiophene[1,2] and 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde[3] were synthesized according to literature procedures. Tri(*n*-butyl)tin chloride was distilled under reduced pressure immediately before use. 2-Bromofluorene was obtained from Matrix Scientific with all other reagents purchased from Sigma-Aldrich or Alfa Aesar and used as received. Tetrahydrofuran was dried on a LC Systems solvent purification system prior to use. Solvents for chromatography were freshly distilled prior to use. Medium pressure liquid chromatography (MPLC) was performed on a Grace Reveleris X2 system with Grace silica cartridges. Thin layer chromatography (TLC) was performed using aluminum backed silica gel 60 F254 plates. ^{1}H and ^{13}C NMR were performed using Bruker AV-300, AV-400, AV-500 or AS-500 spectrometers in deuterated chloroform, referenced to 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C; or deuterated dichloromethane, referenced to 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C. Coupling constants (*J*) are quoted to the nearest 0.5 Hz. F H = fluorenyl H; CPDT H = cyclopentadithienyl H; BT H = benzothiadiazolyl H; VIN H = vinyl H. UV-visible spectroscopy was performed using a Cary 5000 UV-vis spectrophotometer as either a thin film on fused silica substrates or as a solution in distilled dichloromethane. Photoluminescence measurements were performed on a Fluoromax spectrophotometer as either a thin film on fused silica substrates or as a solution in distilled dichloromethane. FT-IR spectroscopy was performed on solid samples using a Perkin-Elmer Spectrum 100 spectrometer with an ATR attachment. Melting points (MP) were measured in a glass capillary on a Büchi B-545 melting point apparatus and are uncorrected. Microanalyses were performed using a Carlo Erba NA 1500 Elemental Analyzer. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker HCT 3D Ion Trap mass spectrometer. Thermal transitions were determined by using a Perkin-Elmer Diamond Differential Scanning Calorimeter. Thermal gravimetric analysis was undertaken using a Perkin-Elmer STA 6000 simultaneous thermal analyzer. Thermal decomposition value [$T_{d(5\%)}$] were reported as the temperature corresponding to a 5% mass reduction.

Synthesis of M1



Scheme S1. Synthesis of **M1**. Conditions and reagents: i) Tetra(*n*-butyl)ammonium bromide, aqueous NaOH (50% wt/wt), 2-(2-methoxyethoxy)ethyl bromide, MePh , 60 °C, overnight; ii) *n*-BuLi, THF, -78 °C 30 min; then B(*i*OPr)$_3$ -78 °C to r.t., 1 h; then 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde, Pd(PPh)$_3$)$_4$, MePh, EtOH, aqueous K_2CO_3, 100 °C, overnight; iii) Malononitrile, MePh, pyridine, 65 °C, 30 min.

7-[9,9-Bis(2-{2-methoxyethoxy}ethyl)-9H-fluoren-2-yl]benzo[c][1,2,5]thiadiazole-4-carbaldehyde **3**

A mixture of 2-bromofluorene (2.0 g, 8.16 mmol), tetra-*n*-butylammonium bromide (0.132 g, 0.41 mmol) and 2-(2-methoxyethoxy)ethyl bromide (3.30 mL, 24.5 mmol) in toluene (35 mL) and aqueous sodium hydroxide (50 wt%, 35 mL) was heated in an oil bath held at 60 °C under argon overnight. The solution was allowed to cool, and was diluted with water (200 mL). The mixture was extracted with ethyl acetate (3 x 50 mL), and the combined extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The crude material was purified by MPLC over silica, eluting with ethyl acetate:light petroleum spirit (3:7) to afford *2-bromo-9,9-bis[2-(2-methoxyethoxy)ethyl]fluorene* **2** as a pale yellow oil (0.56 g). Note: due to the instability of the material it should be used immediately in the subsequent reaction. A solution of **2** (0.56 g) in anhydrous tetrahydrofuran (2.5 mL) was cooled in a dry ice-acetone bath under argon. A solution of *n*-butyl lithium in cyclohexane (2.0 M, 0.75 mL) was added in one portion and the resulting solution was stirred for 30 min. Tri-*iso*-propylborate (0.43 mL, 1.88 mmol) was added and the solution was removed from the cold bath and was allowed to warm to rt. The reaction was quenched through the addition of water (20 mL) and the mixture was extracted with diethyl ether (3 x 20 mL). The combined extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo* to afford the boronic acid as a yellow oil. A solution of the boronic acid and 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.30 g, 1.25 mmol) in toluene (7 mL), ethanol (3.5 mL) and potassium carbonate solution (3.5 mL, 2.0 M) was subjected to one freeze-pump-thaw cycle, backfilling with argon. *Tetrakis*(triphenylphosphine)palladium(0) (0.072 g, 0.063 mmol) was added and the solution was heated in an oil bath at 100 °C overnight. The solution was allowed to cool, and the mixture was diluted with brine (50 mL). The solution was extracted with dichloromethane (4 x 20 mL) and the combined extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The crude material was purified by MPLC over silica, eluting with ethyl acetate:light petroleum spirit mixtures (3:7, 1:0) to afford **3** as a yellow oil which solidified on standing (0.20 g, 30%). MP = 95-96 °C; Found: C, 67.55; H, 6.1; N, 5.05; $C_{30}H_{32}N_2O_5S$ requires C, 67.7; H, 6.1; N, 5.3; IR (solid) υ/cm^{-1}: 1678 (C=O); λ_{max}(dichloromethane)/nm 328sh (logε/dm^3 mol^{-1} cm^{-1} 4.19), 416 (4.29); δ_H (300 MHz, CD_2Cl_2) 2.36-2.53 (4H, m, CH_2), 2.83-2.91 (4H, m, CH_2), 3.16-3.19 (10H, m, CH_2 and CH_3), 3.22-3.25 (4H, m, CH_2), 7.36-7.45 (2H, m, F H), 7.49-7.52 (1H, m, F H), 7.79-7.82 (1H, m, F H), 7.89 (1H, dd, *J* = 0.5 Hz, *J* = 8.0 Hz, BT H), 8.00 (1H, dd, *J* = 7.0 and 0.5 Hz, F H), 8.08 (1H, dd, 1.5 Hz, *J* = 8.0, BT H), 8.14 (1H, m, F H), 8.32 (1H, d, *J* = 7.0 Hz, F H), 10.81 (1H, d, *J* = 0.5 Hz, CHO); δ_C (75 MHz, CD_2Cl_2) 39.3, 51.3, 58.3, 66.8, 69.6, 71.5, 119.7, 120.1, 123.1, 124.4, 126.0, 126.7, 127.2, 127.8, 128.9, 131.9, 135.3, 139.5, 140.2, 141.7, 149.5, 149.6, 153.80, 153.83, 188.5; *m/z* [ESI]: Found: 555.2 (100%), 556.2 (35%), 557.2 (11%), 558.2 (3%). $C_{30}H_{32}N_2NaO_5S$ requires 555.2 (100%), 556.2 (35%), 557.2 (11%), 558.2 (3%).

2-[(7-{9,9-bis[2-(2-methoxyethoxy)ethyl)]-9H-fluoren-2-yl}benzo[c][1,2,5]thiadiazol-4-yl)methylene]malononitrile **M1**

A solution of **3** (0.20 g, 0.38 mmol) in toluene (8 mL), with pyridine (0.40 mL) and malononitrile (0.99 g, 15.0 mmol) was heated in an oil bath held at 65 °C for 30 min. The solution was allowed to cool and was diluted with toluene (50 mL). The solution was washed with water (2 x 20 mL), brine (20 mL), saturated sodium hydrogen carbonate solution (20 mL) then water (20 mL), and was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo.* The crude material was purified by MPLC over silica, eluting with ethyl acetate:light petroleum spirit (7:3) to give an orange oil. The oil was dissolved in diethyl ether (3 mL) and light petroleum spirit (1 mL) was added. The mixture was cooled in a dry ice/acetone bath, and the precipitate formed was collected via vacuum filtration, and was dried *in vacuo* to afford **M1** as a fluorescent orange powder (0.02 g, 10 %). MP = 101-102 °C; Found: C, 68.1; H, 5.6; N, 9.7; $C_{33}H_{32}N_4O_4S$ requires C, 68.3; H, 5.6; N, 9.7;

IR (solid) υ/cm^{-1}: 2224 (CN); λ_{max}(dichloromethane)/nm 326 (logε/dm^3 mol^{-1} cm^{-1} 4.26), 346sh (4.14), 455 (4.43); δ_H (500 MHz, CD_2Cl_2) 2.42-2.54 (4H, m, CH_2), 2.86-2.94 (4H, m, CH_2), 3.20-3.23 (10H, m, CH_2 and CH_3), 3.25-3.28 (4H, m, CH_2), 7.43-7.47 (2H, m, F H), 7.54-7.56 (1H, m, F H), 7.84-7.86 (1H, m, F H), 7.94 (1H, dd, J = 0.5 Hz, J = 8.0, BT H), 8.07 (1H, dd, J = 0.5 Hz, J = 7.5, F H), 8.13 (1H, dd, J = 0.5 Hz, J = 8.0, BT H), 8.23 (1H, dd, J = 0.5 Hz, J = 1.5, F H), 8.86 (1H, dd, J = 0.5 Hz, J = 7.5, F H), 8.94 (1H, dd, J = 0.5 Hz, J = 0.5 Hz, VIN H); δ_C (125 MHz, CD_2Cl_2) 39.9, 52.0, 58.9, 67.3, 70.2, 72.1, 83.6, 113.4, 114.3, 120.5, 120.8, 122.9, 123.8, 125.1, 127.7, 127.9, 128.5, 129.5, 131.1, 135.4, 140.0, 140.8, 142.7, 150.2, 150.3, 153.3, 153.5, 154.8; *m/z* [ESI]: Found: 603.2 (100%), 604.2 (40%), 605.2 (13%), 606.2 (3%). $C_{33}H_{32}N_4NaO_4S$ requires 603.2 (100%), 604.2 (38%), 605.2 (13%), 606.2 (3%); Td$_{(5\%)}$ = 320 °C; MP (DSC) = 104 °C; Tg (second cycle – after melt, scan rate 100 °C/min) = 13 °C.

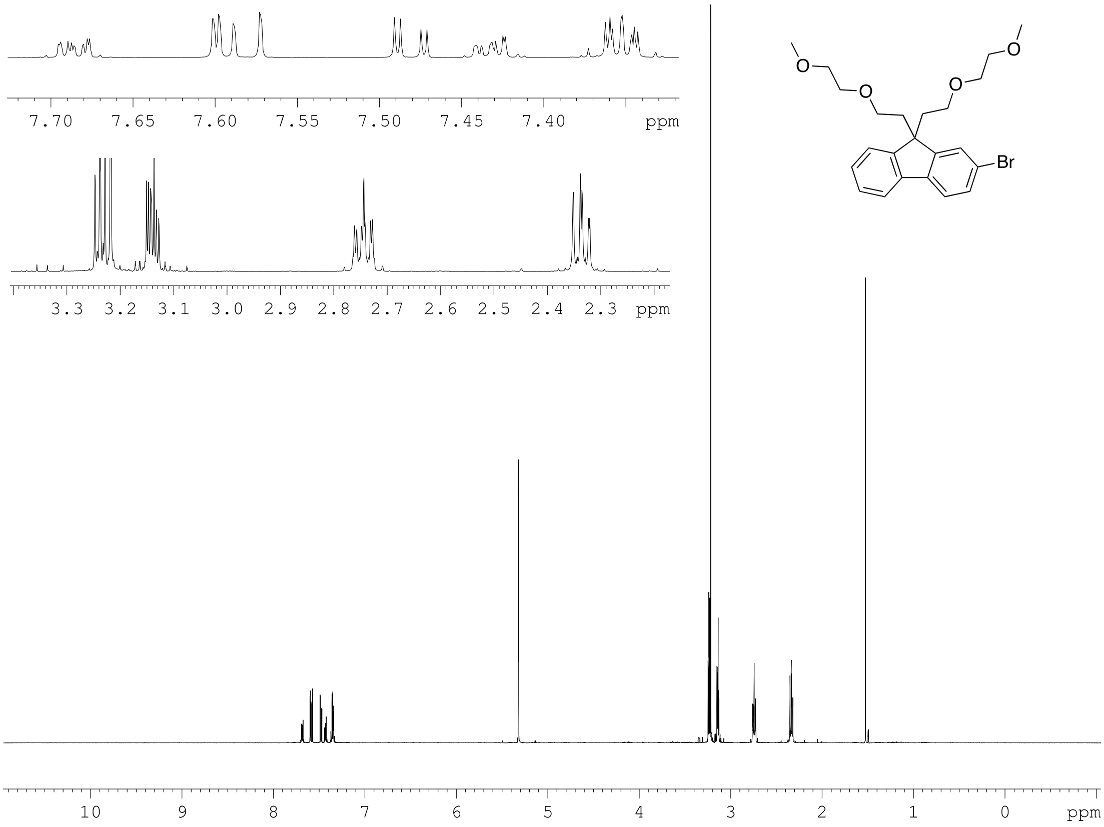


Figure S1. 500 MHz ^{1}H NMR spectrum of showing the peaks associated with **2** and common impurities due to its instablility.

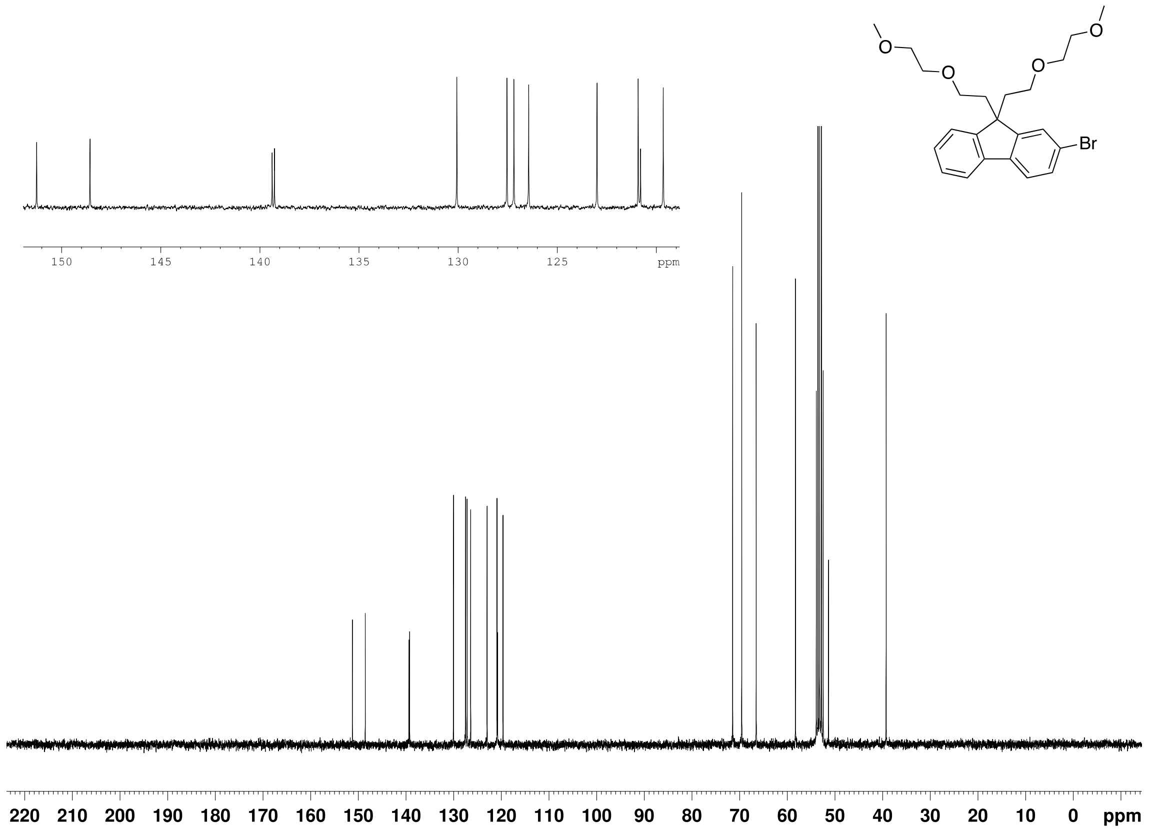


Figure S2. 300 MHz ^{13}C NMR spectrum showing the main peaks of **2**.

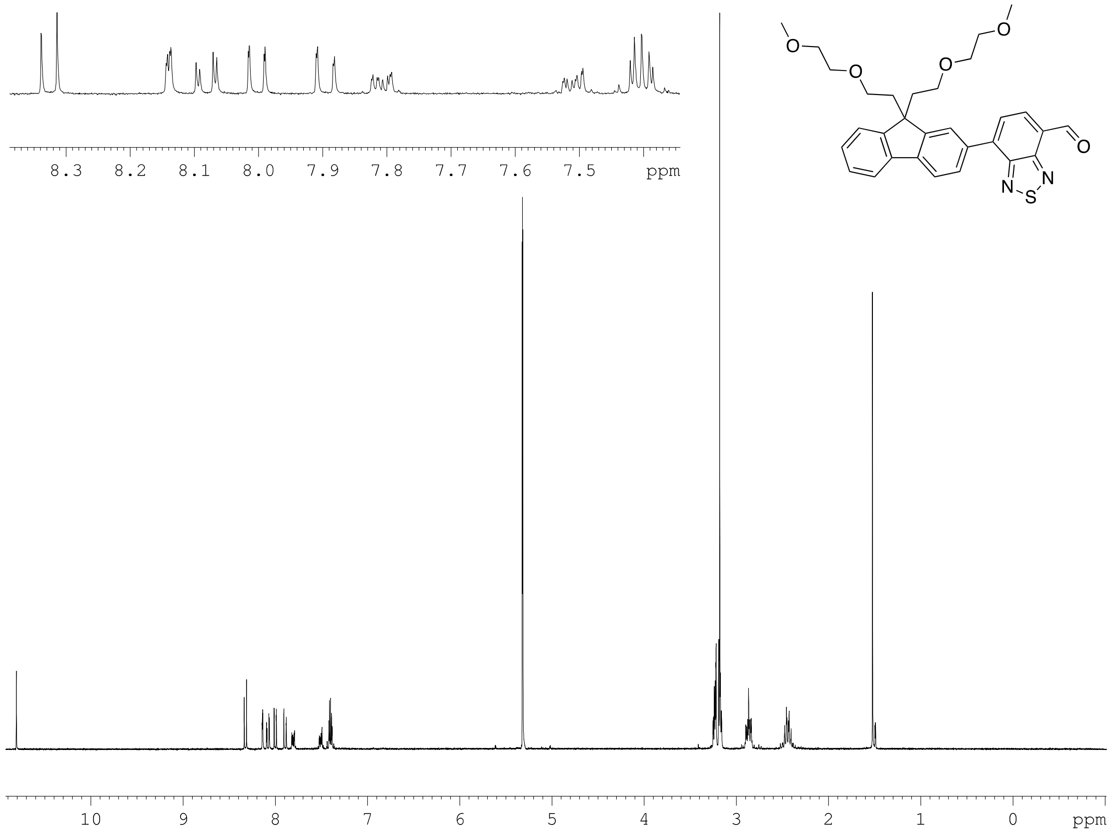


Figure S3. 300 MHz ^{1}H NMR spectrum of **3**.

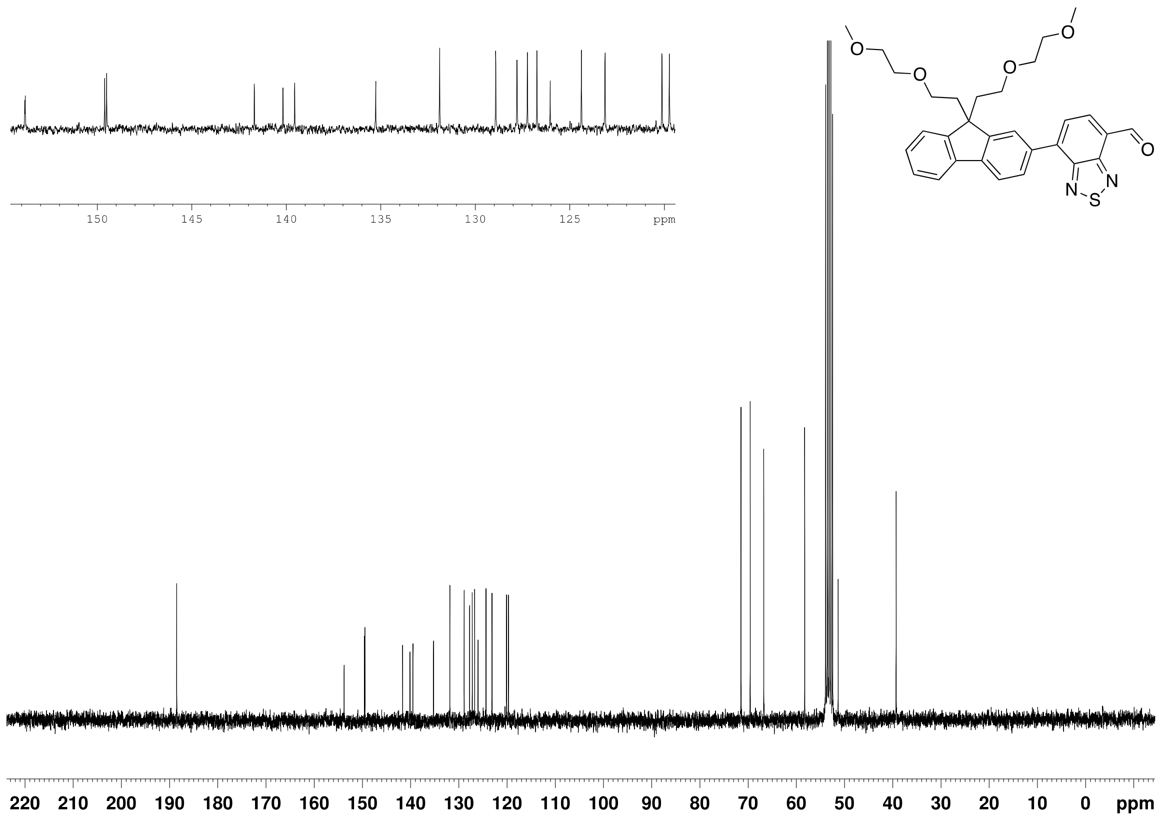


Figure S4. 75 MHz ^{13}C NMR spectrum of **3**.

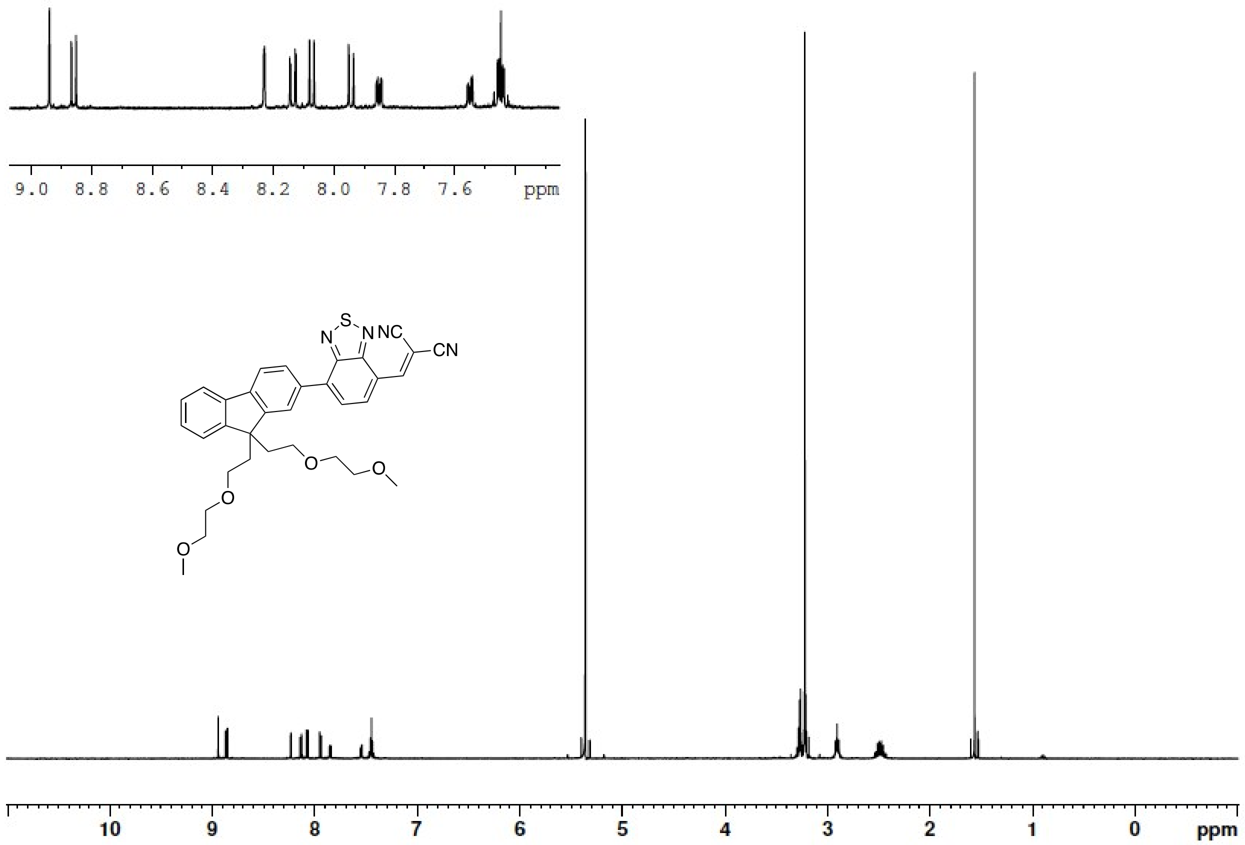


Figure S5. 500 MHz ^{1}H NMR spectrum of **M1**.

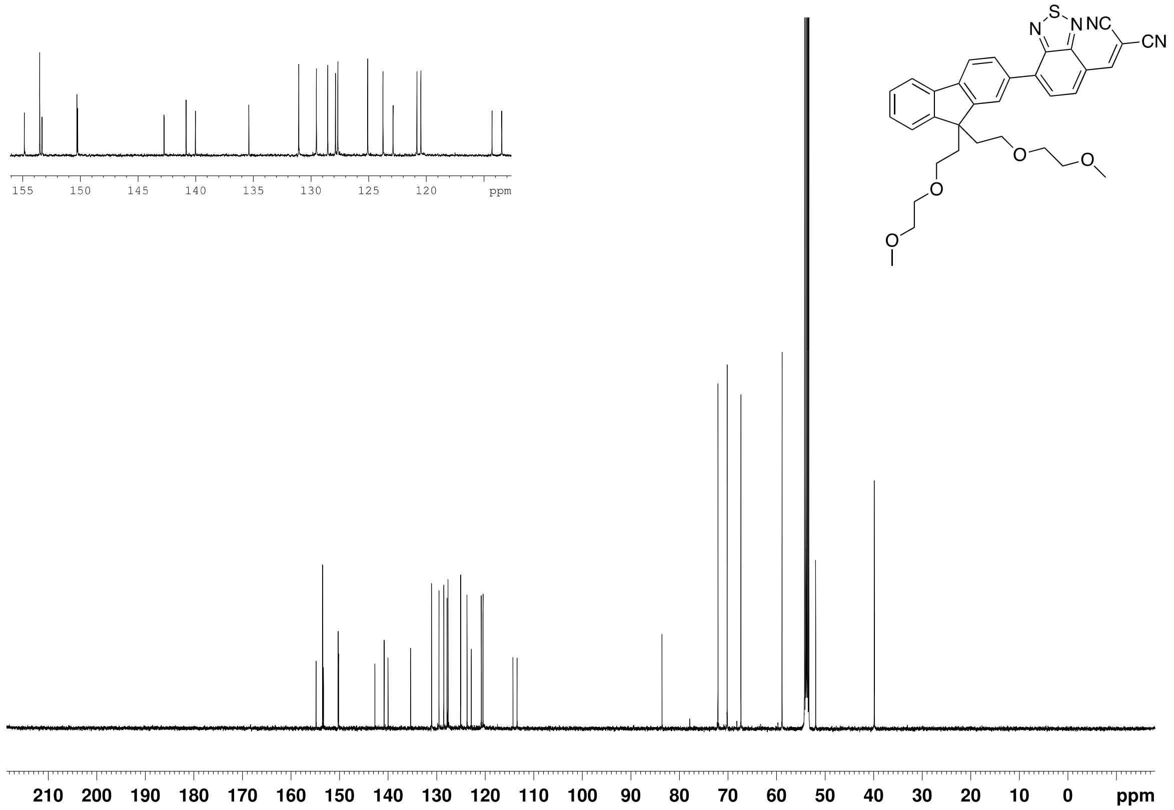
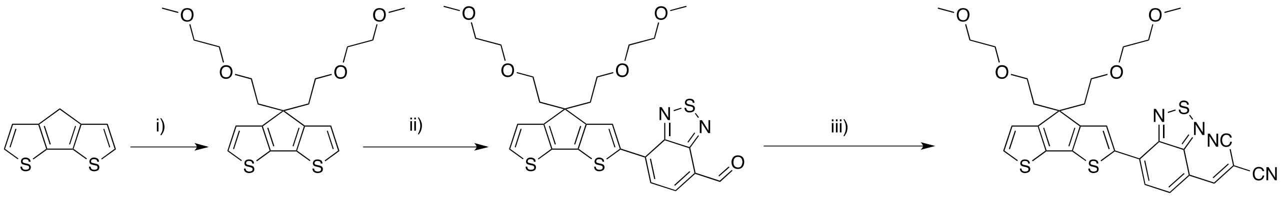


Figure S6. 125 MHz ^{13}C NMR spectrum of **M1**.

Synthesis of M2



Scheme S2. Synthesis of **M2**. Conditions and reagents: i) 1-bromo-2-(2-methoxyethoxy)ethane, KI, DMSO, r.t., overnight; ii) *n*-BuLi, THF, -78 °C, 30 min; then $(n\text{-Bu})_3$SnCl -78 °C to r.t.; then 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde, Pd(PPh$_3$)$_2$)Cl$_2$, THF, 70 °C 16 h; iii) malononitrile, pyridine, MePh, 65 °C, 30 min.

7-[4,4-bis(2-{2-methoxyethoxy}ethyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl]benzo[c][1,2,5]thiadiazole-4-carbaldehyde **6**

A solution of **4** (1.85 g, 10.4 mmol), potassium iodide (0.26 g, 1.56 mmol) and 1-bromo-2-(2-methoxyethoxy)ethane (4.2 mL, 31.2 mmol) in dimethylsulfoxide (10 mL) was subjected to two freeze-pump-thaw cycles, backfilling with argon. Potassium hydroxide (2.92 g, 52.0 mmol) was added and the suspension was stirred at rt under argon in the absence of light overnight. The solution was diluted with water (10 mL) and was extracted with ethyl acetate (4 x 10 mL). The combined extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The crude material was purified by column chromatography over silica eluting with ethyl acetate/light petroleum spirit mixtures (1:1), and then by MPLC over silica eluting with ethyl acetate/light petroleum spirit mixtures (1:1) to afford **5** as a pale yellow oil (2.12 g). Due to the instability of this material it was used without further purification in the subsequent reaction. A solution of **5** (2.12 g) in anhydrous tetrahydrofuran (60 mL) was cooled in a dry ice/acetone bath under argon. A solution of *n*-butyl lithium in cyclohexane (3.3 mL, 2.0 M) was added dropwise and upon completion of the addition the solution was stirred for 30 min. Freshly distilled tri(*n*-butyl)tin chloride (2.25 mL, 8.31 mmol) was added in one portion and the solution was allowed to warm to r.t., and was stirred for 1 h. The reaction was quenched through the addition of water (20 mL) and the layers were separated. The aqueous solution was extracted with ethyl acetate (3 x 20 mL) and the combined extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The crude material was used in the subsequent reaction immediately without purification. A solution of stannane (3.72 g) and 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (1.62 g, 6.65 mmol) in anhydrous tetrahydrofuran (77 mL) was subjected to two freeze-pump-thaw cycles, back-filling with argon. *Bis*(triphenylphosphine)palladium(II) dichloride (0.39 g, 0.55 mmol) was added and the solution was heated in an oil bath at 70 °C in the absence of light for 16 h. The solution was allowed to cool and the solvent was removed *in vacuo*. The crude material was purified by column chromatography over silica using ethyl acetate/light petroleum spirit (1:1) as the eluent, then by MPLC over silica eluting with ethyl acetate:light petroleum spirit (1:1) to afford **6** as a purple powder (1.14 g, 20% for three steps)/ MP = 131-132 °C; IR (solid) ν/cm^{-1}: 1678 (C=O); λ_{max}(dichloromethane)/nm 326sh (logε/dm^3 mol^{-1} cm^{-1} 4.25), 344 (4.26), 358sh (4.23), 513 (4.46); δ_H (400 MHz, CD_2Cl_2) 2.27-2.40 (4H, m, CH_2), 3.12 (4H, t, *J* = 7.0 Hz, CH_2), 3.22 (6H, s, CH_3), 3.27-3.33 (8H, m, CH_2), 7.08 (1H, d, *J* = 5.0 Hz, CPDT H), 7.36 (1H, d, *J* = 5.0 Hz, CPDT H), 8.02 (1H, d, *J* = 7.5 Hz, BT H), 8.21 (1H, d, *J* = 7.5 Hz, BT H), 8.32 (1H, s, CPDT H), 10.7 (1H, s, CHO). δ_C (100 MHz, $CDCl_3$) 37.5, 49.9, 59.0, 67.6, 70.1, 71.8, 121.9, 122.3, 124.7, 124.9, 127.8, 133.0, 134.0, 136.3, 138.6, 142.2, 152.0, 153.9, 157.7, 158.5, 188.4. LRMS (ESI-TOF-MS) For $C_{26}H_{29}N_2O_5S_3^+$ $(M+H)^+$ Calc.: 545.1 (100%), 546.1 (33%), 547.1 (19%), 548.1 (6%). Found 545.1 (100%), 546.1 (32%), 547.1 (23%), 548.0 (6%). Anal. Calc. for $C_{26}H_{28}N_2O_5S_3$: C, 57.3; H, 5.2; N, 5.1. Found. C, 57.2; H, 5.2; N, 5.1.

2-[(7-{4,4-bis[2-(2-methoxyethoxy)ethyl]-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl}benzo[c][1,2,5]thiadiazol-4-yl)methylene]malononitrile **M2**

A solution of **6** (0.040 g, 0.073 mmol) in toluene (2 mL) and pyridine (2 drops) was heated in an oil bath at 65 °C. Malononitrile (0.194 g, 2.94 mmol) was added and the solution was heated for 30 min.

The solution was allowed to cool and the solvent was removed *in vacuo*. The crude material was dissolved in dichloromethane (2 mL), light petroleum spirit (30 mL) was added, and the mixture was cooled in a dry ice-acetone bath. The precipitate formed was collected via vacuum filtration and was dried *in vacuo* to afford **M2** as a blue powder (0.029 g, 67%). MP = 138-139 °C; Found: C, 58.6; H, 4.7; N, 9.6; $C_{29}H_{28}N_4O_4S_3$ requires C, 58.6; H, 4.7; N, 9.6; IR (solid) υ/cm^{-1}: 2223 (CN); λ_{max}(dichloromethane)/nm 338sh (logε/dm^3 mol^{-1} cm^{-1} 4.02), 362 (4.09), 390 (4.04), 591 (4.52); δ_H (300 MHz, CD_2Cl_2) 2.26-2.42 (4 H, m, CH_2), 3.12 (4H, t, *J* = 7.0 Hz, CH_2), 3.22 (6H, s, CH_3), 3.27-3.34 (8H, m, CH_2), 7.09 (1H, d, *J* = 5.0 Hz, CPDT H), 7.39 (1H, d, *J* = 5.0 Hz, CPDT H), 8.02 (1H, dd, *J* = 0.5 Hz, *J* = 8.0, BT H), 8.36 (1H, s, CPDT H), 8.75 (1H, dd, *J* = 0.5 Hz, *J* = 8.0, BT H), 8.79 (1H, d, *J* = 0.5, VIN H); δ_C (125 MHz, CD_2Cl_2) 37.2, 49.8, 58.3, 67.2, 69.8, 71.5, 80.6, 113.4, 114.2, 120.5, 121.9, 122.5, 125.6, 128.3, 130.6, 134.0, 136.1, 138.5, 143.5, 150.7, 151.9, 154.4, 158.2, 159.3; *m/z* [ESI]: Found: 615.1 (100%), 616.1 (35%), 617.1 (18%), 618.1 (5%). $C_{29}H_{28}N_4NaO_4S_3$ requires 615.1 (100%), 616.1 (36%), 617.1 (20%), 618.1 (6%); Td$_{(5\%)}$ = 311 °C; MP (DSC) = 129 °C and 143 °C; Tg (second cycle – after melt, scan rate 100 °C/min) = 19 °C.

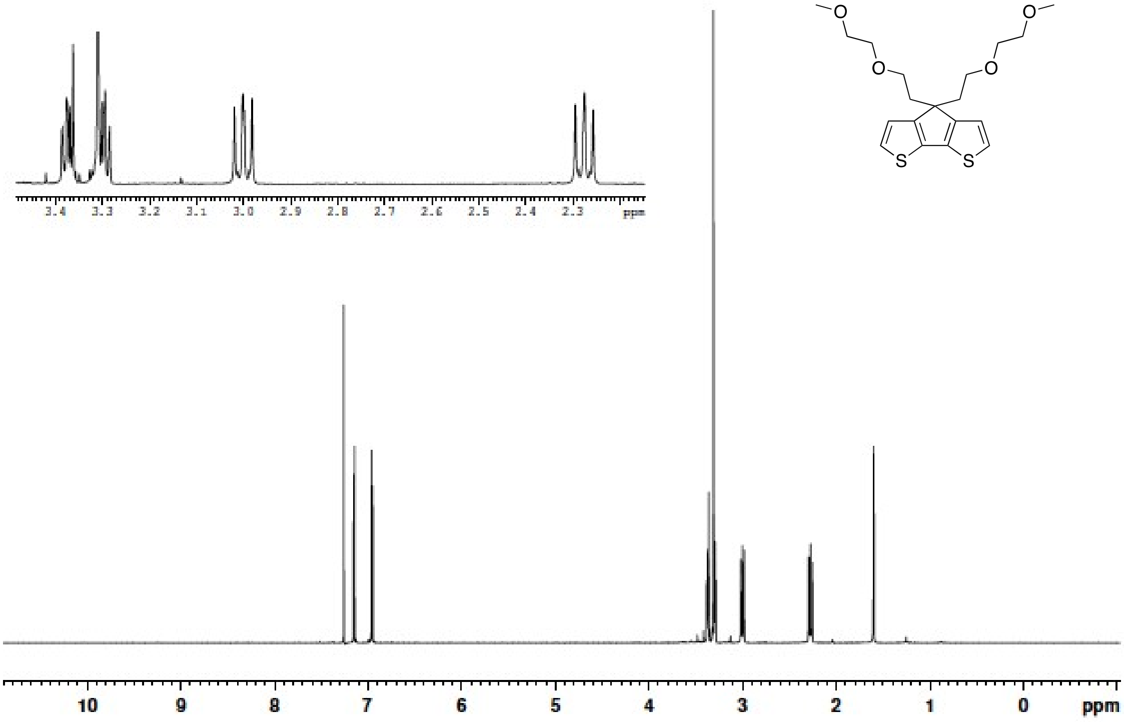


Figure S7. 400 MHz ^{1}H NMR spectrum of showing the peaks associated with **5** and common impurities due to its instablility.

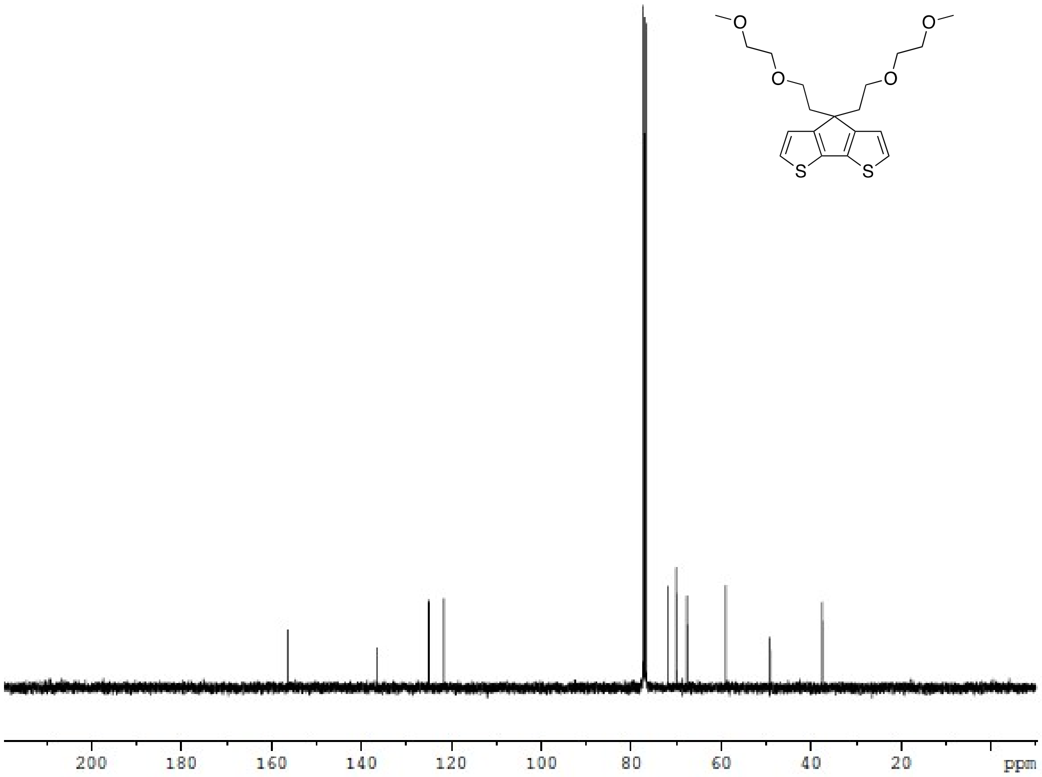


Figure S8. 100 MHz ^{13}C NMR spectrum showing the main peaks of **5**.

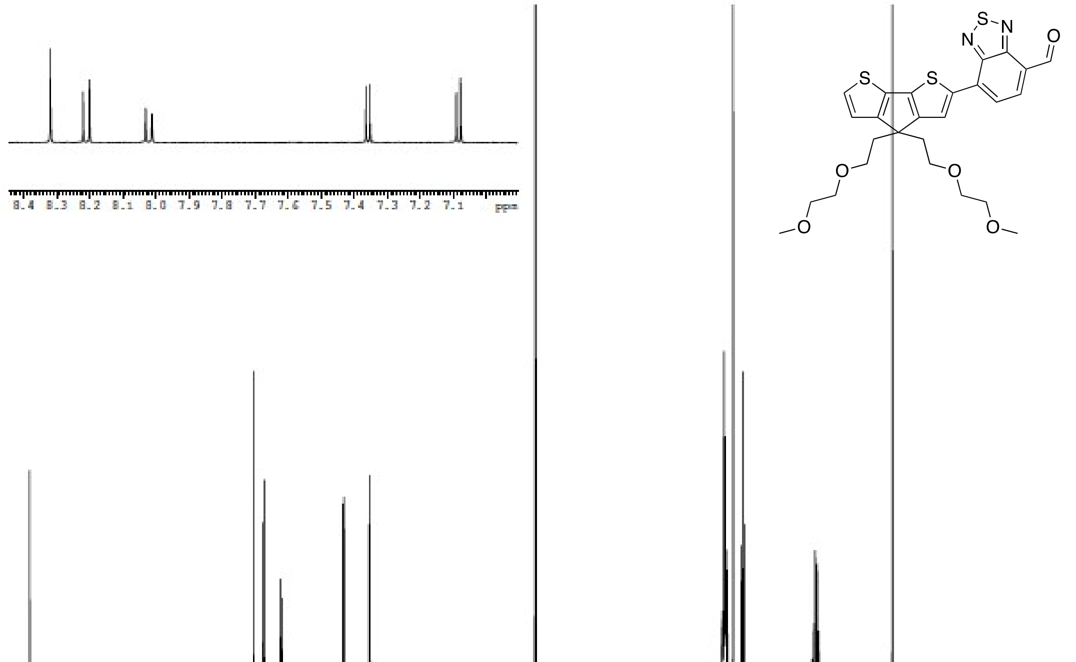


Figure S9. 400 MHz ^{1}H NMR spectrum of **6**.

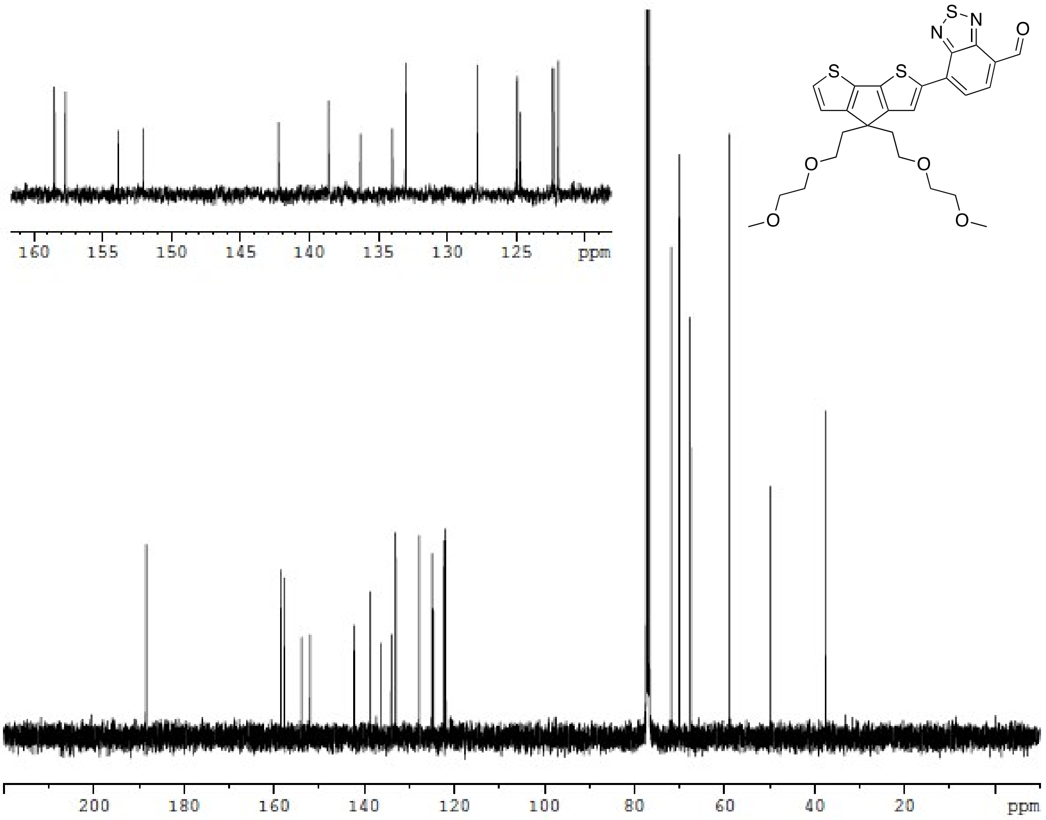


Figure S10. 100 MHz ^{13}C NMR spectrum of **6**.

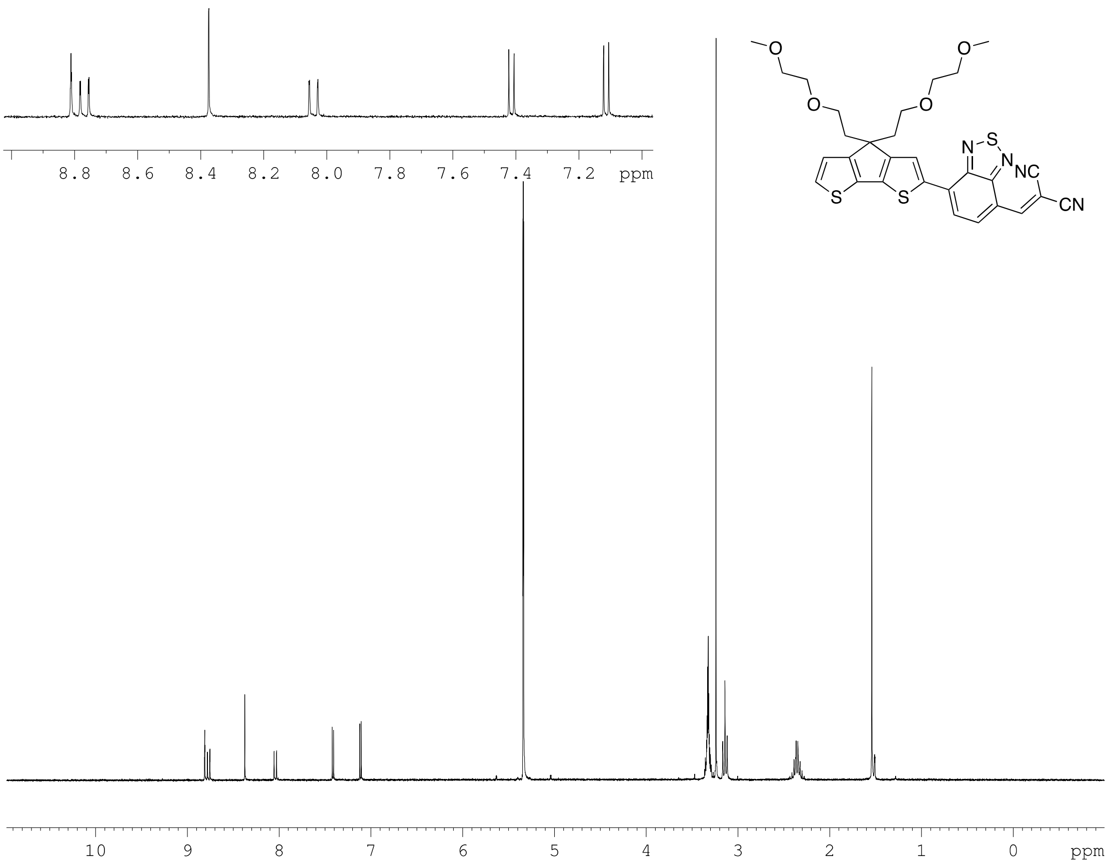


Figure S11. 300 MHz ^{1}H NMR spectrum of **M2**.

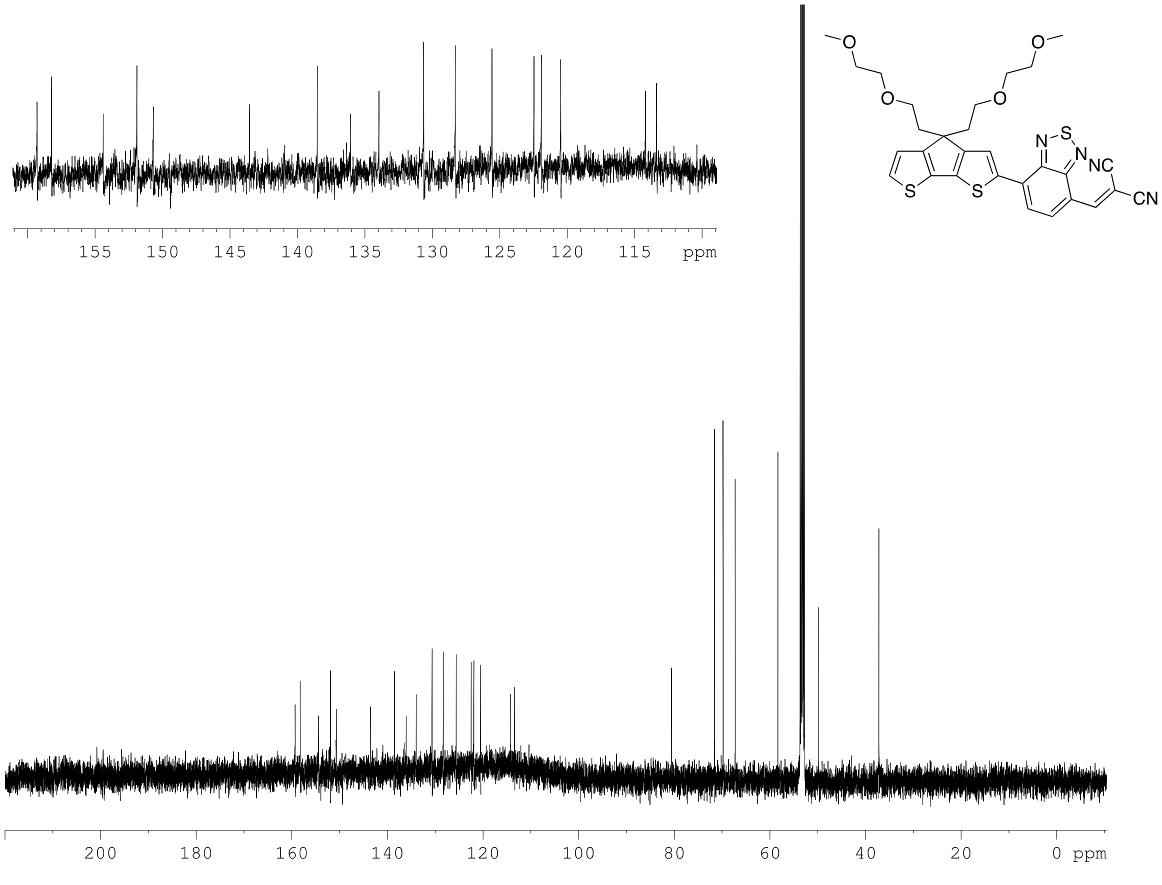
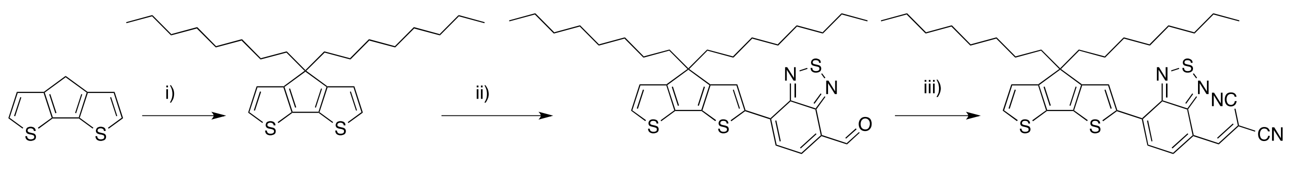


Figure S12. 125 MHz ^{13}C NMR spectrum of **M2**.

Synthesis of M3



4 **7** **8** **M3**

Scheme S3. Synthesis of **M3**. Conditions and reagents: i) *n*-octyl-*p*-toluenesulfonate, DMSO, r.t., overnight; ii) *n*-BuLi, THF, -78 °C, 30 min; then (n-Bu)$_3$SnCl -78°C to r.t.; then 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde, Pd(PPh$_3$)$_2$)Cl$_2$, THF, 60 °C 1h; iii) malononitrile, pyridine, MePh, 65 °C, 1 h.

7-[4,4-di-n-octyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl]benzo[c][1,2,5]thiadiazole-4-carbaldehyde **8**

A solution of **4** (0.19 g, 1.07 mmol), *n*-octyl-*p*-toluenesulfonate (0.91 g, 3.21 mmol) and potassium hydroxide (0.28 g, 4.92 mmol) in anhydrous dimethylsulfoxide (3 mL) was stirred at r.t. under argon, in the absence of light overnight. The reaction was quenched through the addition of water (50 mL) and the mixture was extracted with diethyl ether (4 x 20 mL). The combined extracts were washed with brine (4 x 20 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The crude material was purified by MPLC on silica, eluting with light petroleum spirit, to afford **7** as a colourless oil (0.20 g, 47%). The ^{1}H NMR spectrum matched that reported in the literature.[4] **7** was dissolved in anhydrous tetrahydrofuran (5.5 mL) and the solution was cooled in a dry ice/acetone bath under an atmosphere of argon. A solution of *n*-butyl lithium in cyclohexane (0.30 mL, 2.0 M) was added in one portion and the solution was stirred for 30 min. Freshly distilled tri(*n*-butyl)tin chloride (0.20 mL, 0.75 mmol) was added in one portion and the solution was removed from the dry ice/acetone bath and was allowed to warm to r.t.. The reaction was quenched through the addition of water (20 mL) and the mixture was extracted with diethyl ether (3 x 20 mL). The combined extracts were washed with brine (2 x 20 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo* to afford the stannane as a red oil. The crude material was used immediately in the next reaction. A solution of stannane (0.35 g) and 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.146 g, 0.60 mmol) in anhydrous tetrahydrofuran (7 mL) was subjected to one freeze-pump-thaw cycle, backfilling with argon. *Bis*(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.050 mmol) was added and the solution was heated in an oil bath held at 60 °C in the absence of light for 1 h. The solution was allowed to cool and the solvent was removed *in vacuo*. The crude material was purified by MPLC over silica eluting with dichloromethane:light petroleum spirit mixtures (1:1, 1:0) to afford **8** as a purple oil (0.14

g, 50% for the last two steps). IR (solid) ν/cm^{-1}: 1683 (C=O); λ_{max}(dichloromethane)/nm 336 (logε/dm^3 mol^{-1} cm^{-1} 4.28), 349 (4.29), 358sh (4.26), 537 (4.49); δ_H (300 MHz, $CDCl_3$) 0.81 (6H, t, J = 7.0 Hz, CH_3), 0.94-1.06 (4H, m, CH_2), 1.11-1.25 (20H, brm, CH_2), 1.90-1.96 (4H, brm, CH_2), 6.99 (1H, d, J = 5.0 Hz, CPDT H), 7.32 (1H, d, J = 5.0 Hz, CPDT H), 7.97 (1H, d, J = 7.5 Hz, BT H), 8.21 (1H, d, J = 7.5 Hz, BT H), 8.24 (1H, s, CPDT H), 10.69 (1H, s, CHO); δ_C (75 MHz, $CDCl_3$) 14.0, 22.5, 24.5, 29.2, 29.3, 29.9, 31.7, 37.7, 53.9, 121.8, 122.0, 124.3, 124.8, 127.5, 132.9, 134.1, 136.2, 138.3, 142.5, 152.0, 153.8, 159.4, 160.2, 188.2; HRMS (ESI-TOF-MS) For $C_{32}H_{41}N_2OS_3^+$ $(M+H)^+$ Calc.: 565.2381 (100%), 566.2412 (38%), 567.2376 (21%), 568.2384 (6%). Found 565.2369 (100%), 566.2400 (37%), 567.2360 (20%), 568.2373 (7%).

2-[(7-{4,4-di-n-octyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl}benzo[c][1,2,5]thiadiazol-4-yl)methylene]malononitrile **M3**

A solution of **8** (0.064 g, 0.11 mmol) in toluene (2 mL) and pyridine (2 drops) with malononitrile (0.30 g, 4.54 mmol) was heated in an oil bath at 65 °C for 1 h. The solution was allowed to cool and the solvent removed *in vacuo*. The crude material was dissolved in dichloromethane (40 mL) and the solution was washed with water (2 x 40 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo* to afford **M3** as a blue oil (0.059 g, 88%). IR (solid) υ/cm^{-1}: 2223 (C=O); λ_{max}(dichloromethane)/nm 340sh (logε/dm^3 mol^{-1} cm^{-1} 4.10), 361 (4.15), 397 (4.09), 611 (4.59); δ_H (300 MHz, $CDCl_3$) 0.81 (6H, t, J = 7.0 Hz, CH_3), 0.93-1.05 (4H, brm, CH_2), 1.11-1.27 (20H, brm, CH_2), 1.90-1.96 (4H, m, CH_2), 7.00 (1H, d, J = 5.0 Hz, CPDT H), 7.36 (1H, d, J = 5.0 Hz, CPDT H), 7.96 (1H, d, J = 8.5 Hz, BT H), 8.26 (1H, s, CPDT H), 8.74-8.77 (2H, m, VIN H and BT H); δ_C (125 MHz, $CDCl_3$) 14.0, 22.6, 24.6, 29.2, 29.3, 29.9, 31.8, 37.7, 54.0, 80.4, 113.6, 114.3, 120.3, 121.9, 122.4, 125.5, 128.5, 130.9, 134.5, 136.2, 138.5, 144.3, 150.8, 151.9, 154.6, 159.9, 161.0; *m/z* [ESI]: Found: 613.2491 (100%), 614.2519 (42%), 615.2462 (25%), 616.4632 (16%). $C_{35}H_{41}N_4S_3$ requires 613.2493 (100%), 614.2524 (42%), 615.2491 (22%), 616.2497 (7%); $Td_{(5\%)}$ = 318 °C; Tg (first cycle, scan rate 100 °C/min) = 13 °C.

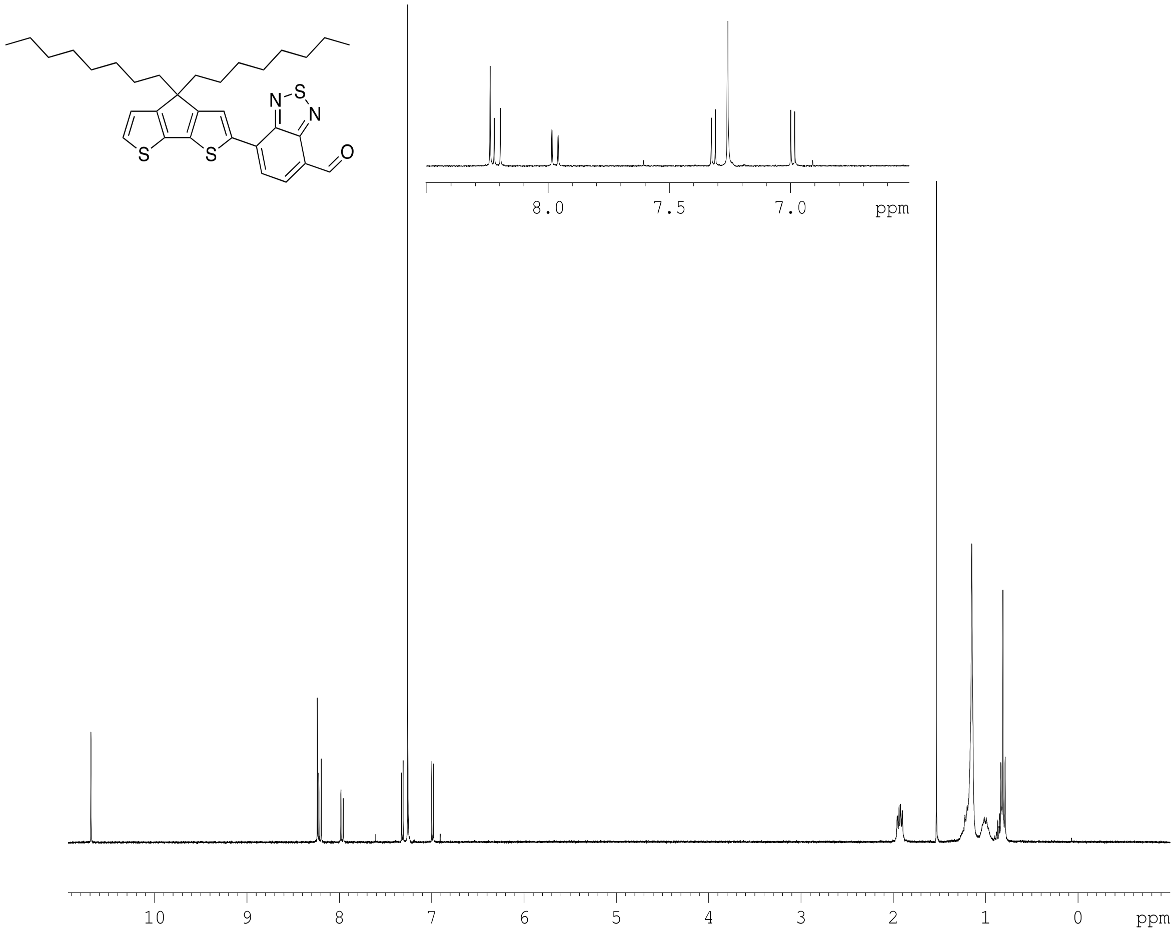


Figure S13. 300 MHz ^{1}H NMR spectrum of **8**.

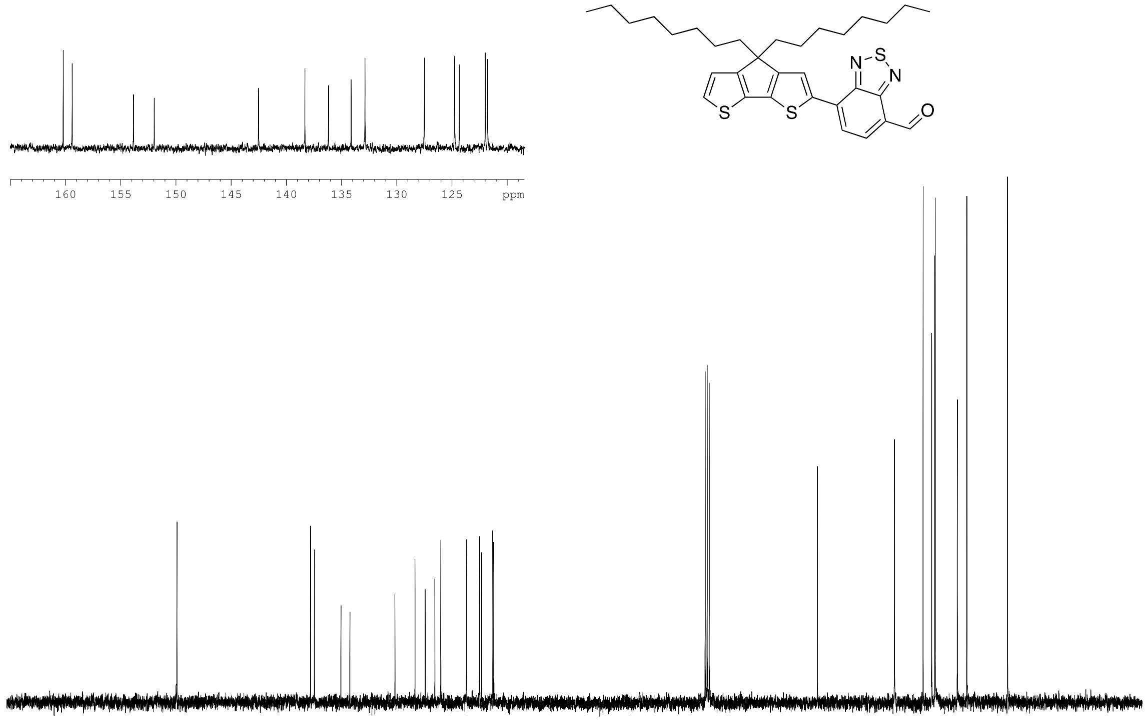


Figure S14. 75 MHz ^{13}C NMR spectrum of **3b**.

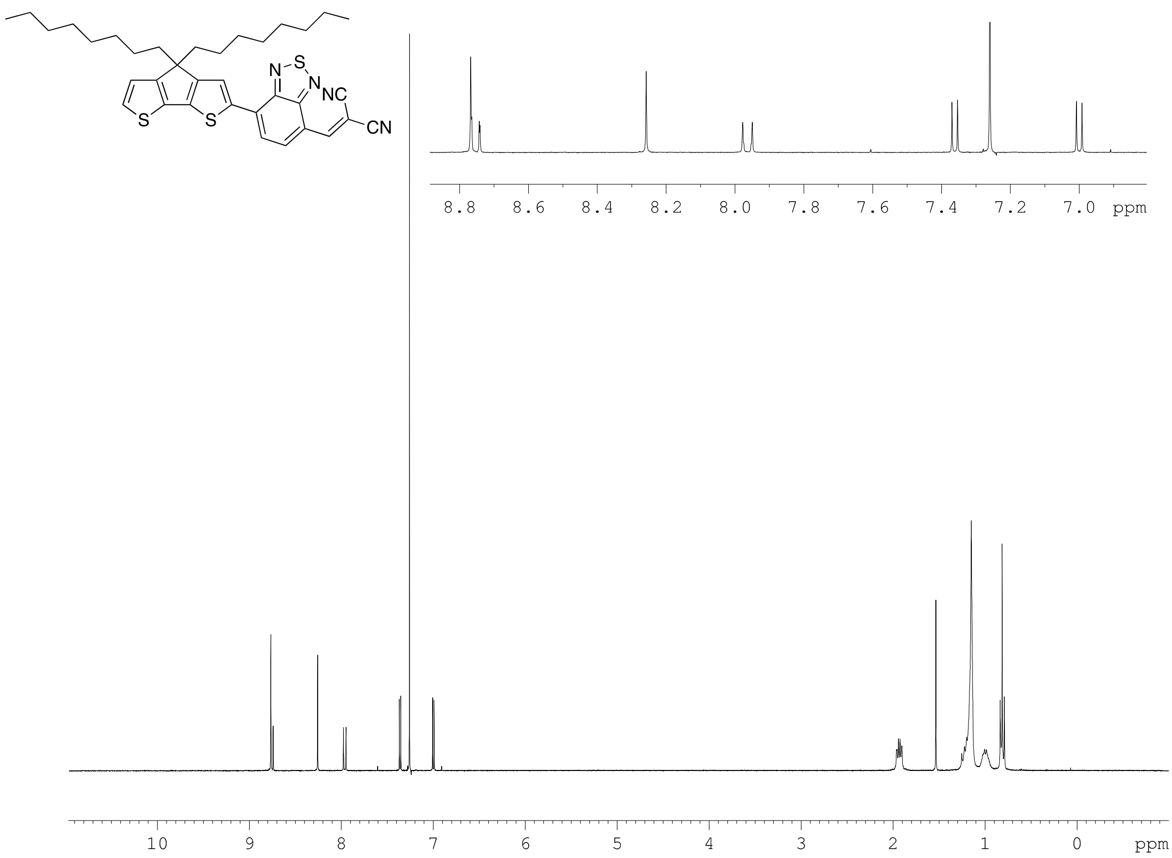


Figure S15. 300 MHz ^{1}H NMR spectrum of **M3**.

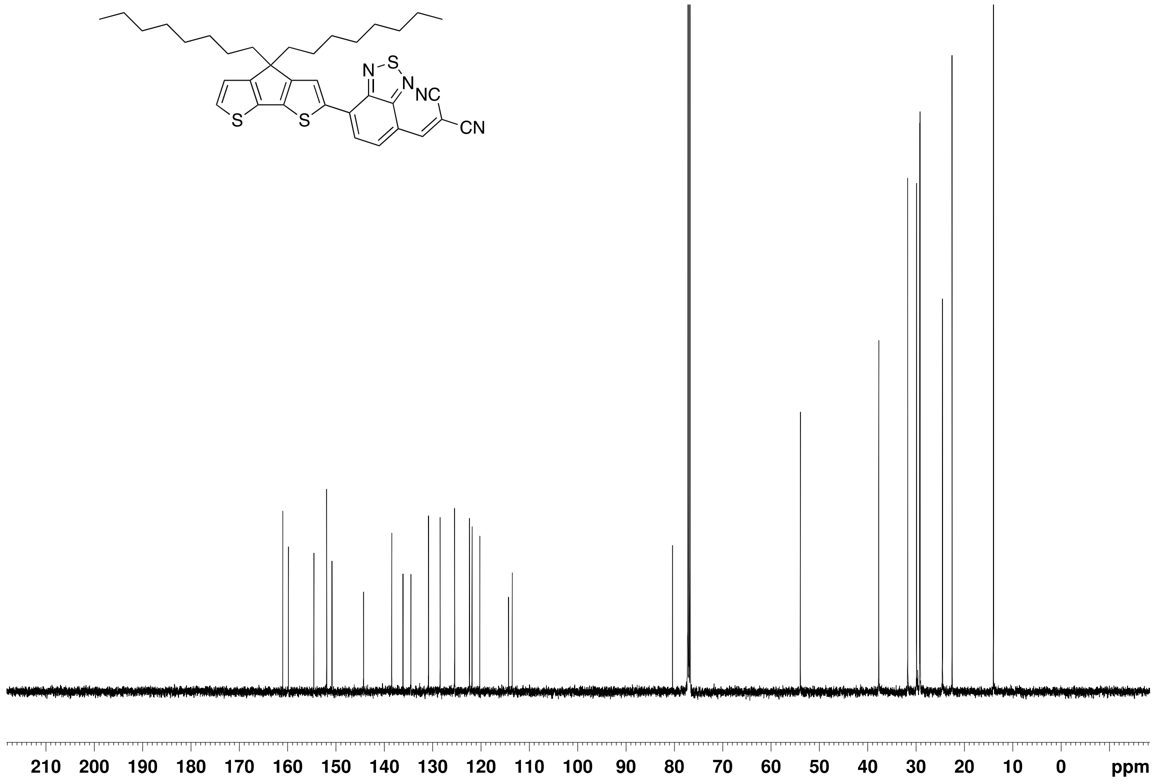


Figure S16. 125 MHz ^{13}C NMR spectrum of **M3**.

Device fabrication

Static and low frequency dielectric constant: 15 Ω/sq. indium tin oxide coated glass substrates (Kintec) patterned by photolithography were pre-cleaned with Alconox (detergent) solution and a soft cloth before being sonicated in sequence with Alconox, de-ionized water, acetone and 2-propanol for 10 minutes each. Each substrate was 2.5 cm x 2.5 cm with 6 pixels each 0.2 cm^2. The cleaned substrates were spin-coated with a solution of organic semiconductor with a concentration of 30 mg/mL in chloroform at a spin rate of 1000 rpm. For each material, films with thicknesses ~200 nm were deposited. The solution preparation and fabrication were carried out in a nitrogen atmosphere (O_2 <1 ppm, H_2O <1 ppm) at ~20 °C. The thicknesses of the films were measured by a Veeco Dektak150 profilometer. Finally, the devices were completed by depositing 100 nm silver (purity 99.99 %) by thermal evaporation under a 10^{-6} mbar vacuum. The dielectric constants at 20 Hz to ~106 Hz were measured using an Agilent E4980A LCR meter. The static dielectric constant was measured using the Charge Extraction by the Linearly Increasing Voltage (CELIV) technique as explained in detail in the citation.[5]

High frequency dielectric constant: The solutions described above were also used to form ~200 nm thick films on glass for the reflection/transmission measurements to the determine extinction coefficient (k). The same solutions were also diluted by a factor of three and spin-coated at 1000 rpm onto cleaned planar silicon substrates to perform spectroscopic ellipsometry. The films had a thicknesses of ~60 nm. The real part of the refractive index (n) was determined from the Kramers-Kronig transformations of the extinction coefficient (k) and base-lined with n (λ >1000 nm) extracted from the spectroscopic ellipsometry data collected on a J. A. Woollam VUV-VASE ellipsometer. Dielectric constants in the high frequency regime (~1014 Hz) were converted from the optical constants (n and k). Finally, the real part of the dielectric constant was calculated using n and k.

2. Optical gap estimation

To determine the optical gap the solution absorption and photoluminescence (PL) spectra (in dichloromethane) were plotted in energy and then the absorption was divided by energy and normalized while the PL was divided by energy cubed and normalized. The optical gap was then calculated from the intersection of the corrected absorption and PL spectra.

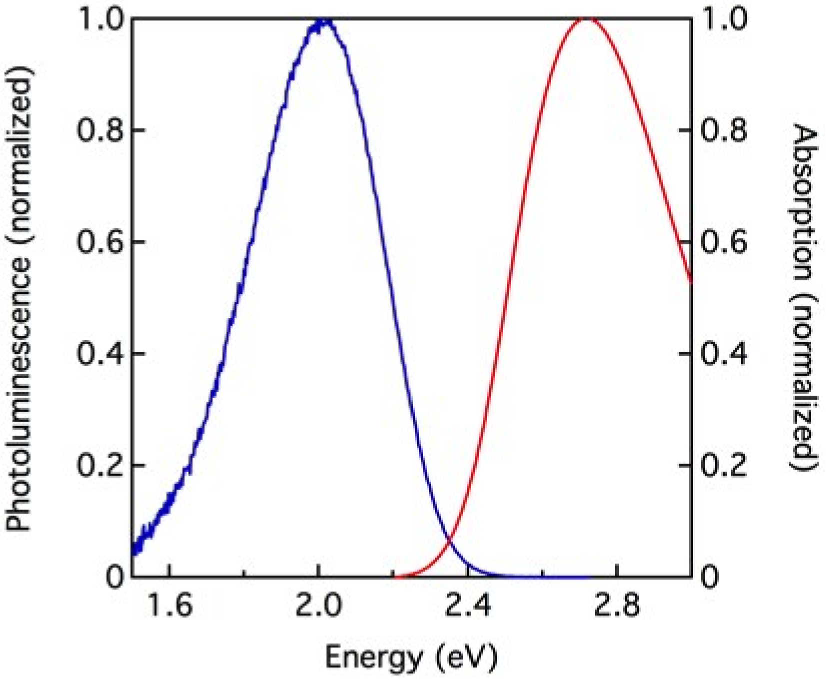


Figure S11. Optical gap estimation for **M1**. Absorption is red and PL is blue.

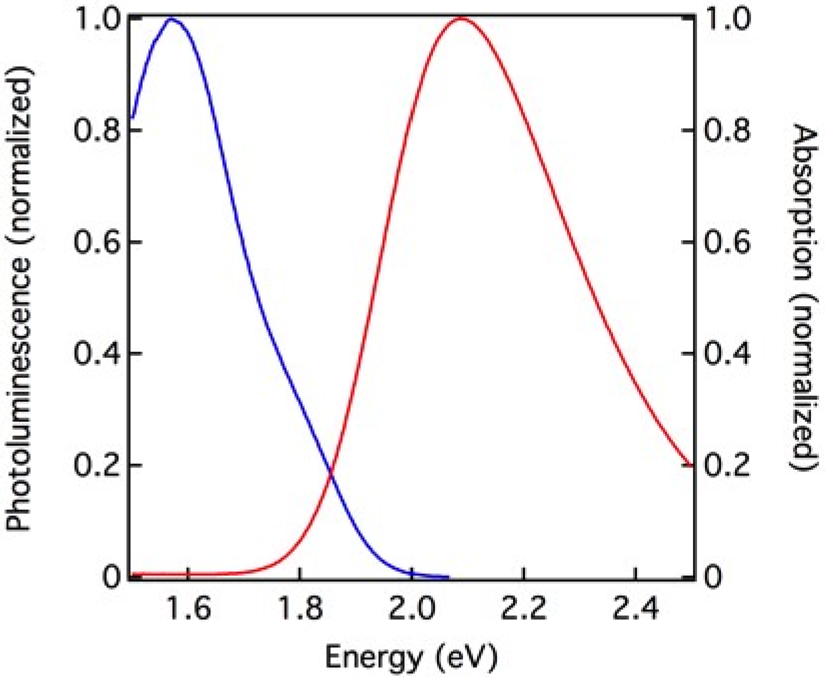


Figure S12. Optical gap estimation for **M2**. Absorption is red and PL is blue.

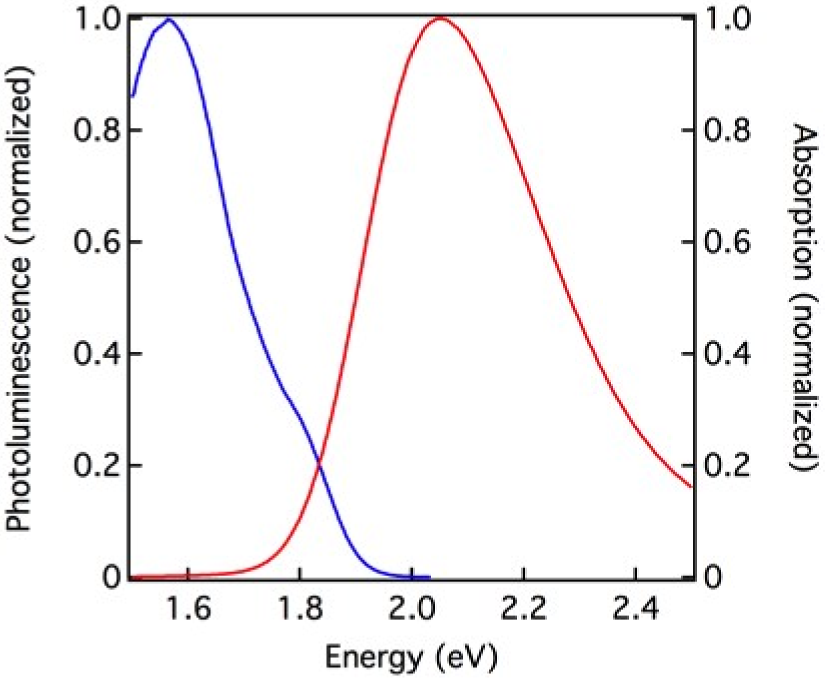


Figure S13. Optical gap estimation for **M3**. Absorption is red and PL is blue.

3. Thermal gravimetric analysis

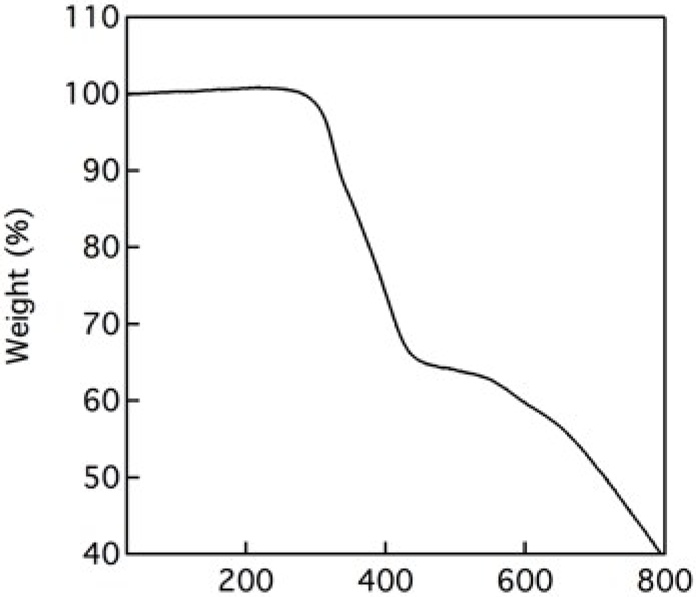


Figure S14. TGA thermogram of **M1** heated from 30-800 °C at 10 °C/min.

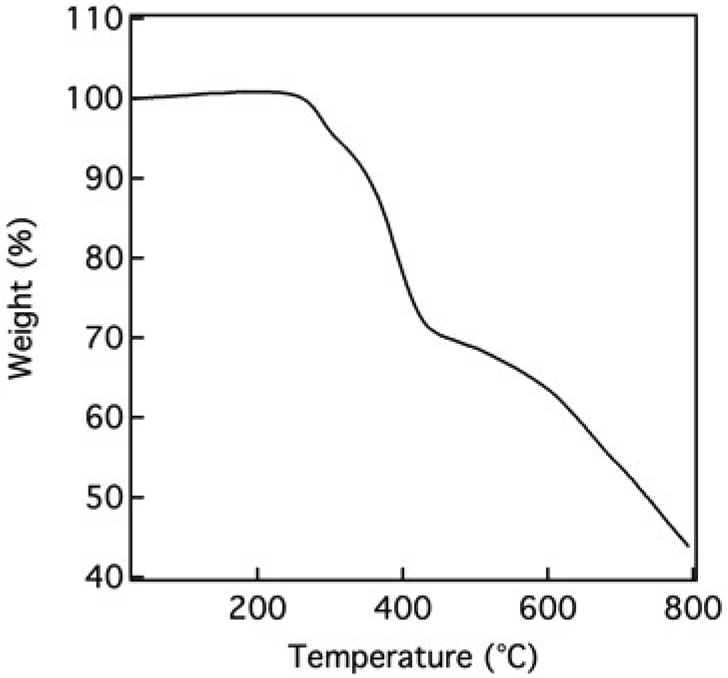


Figure S15. TGA thermogram of **M2** heated from 30-800 °C at 10 °C/min.

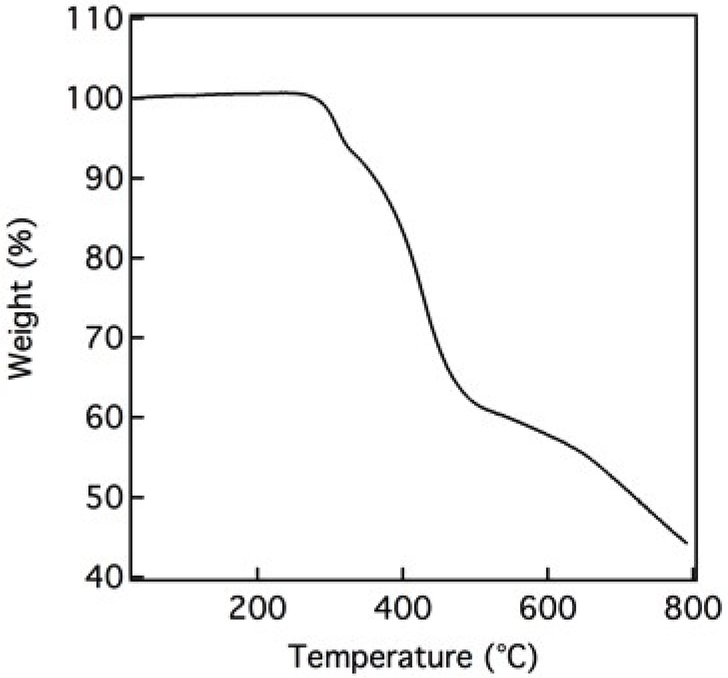


Figure S16. TGA thermogram of **M3** heated from 30-800 °C at 10 °C/min.

4. Differential scanning calorimetry

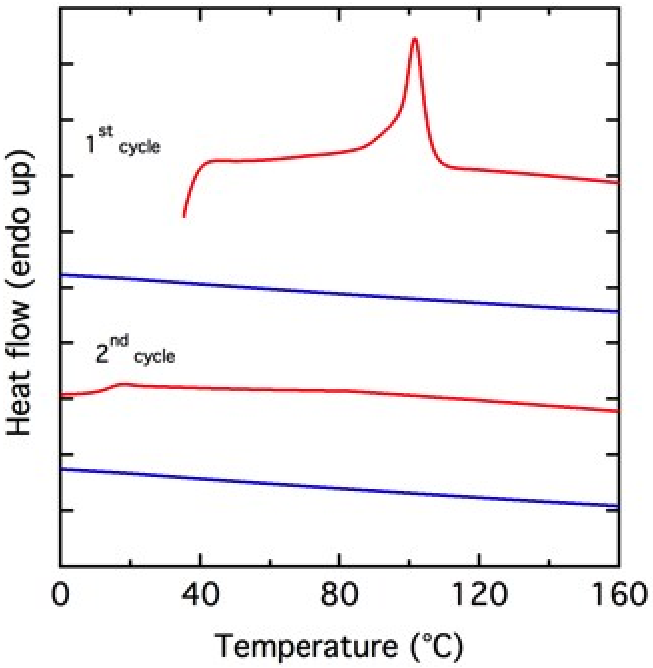


Figure S17. DSC thermogram of **M1** heated from -50 – 200 °C at a scan rate of 100 °C/min. The first scan begins at 30 °C and the scans have been plotted up to 160 °C to enable the transitions to be clearly seen.

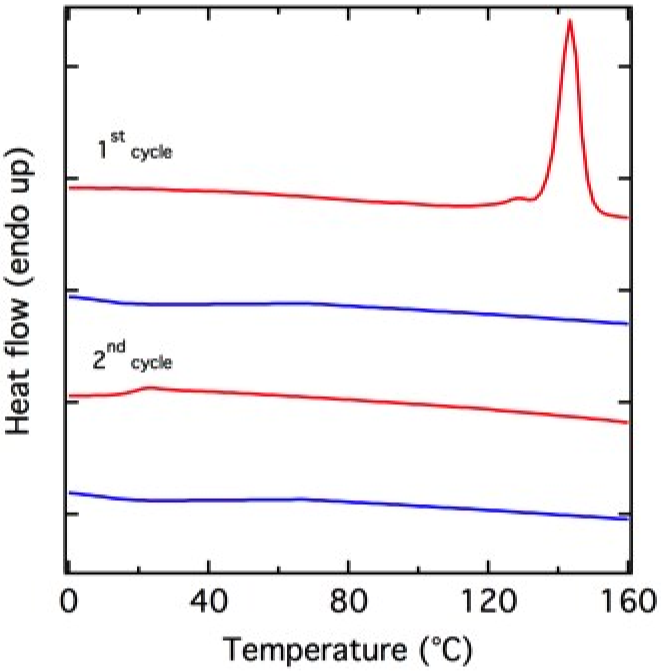


Figure S18. DSC thermogram of **M2** heated from -50 – 200 °C at a scan rate of 100 °C/min and the scans have been plotted up to 160 °C to enable the transitions to be clearly seen.

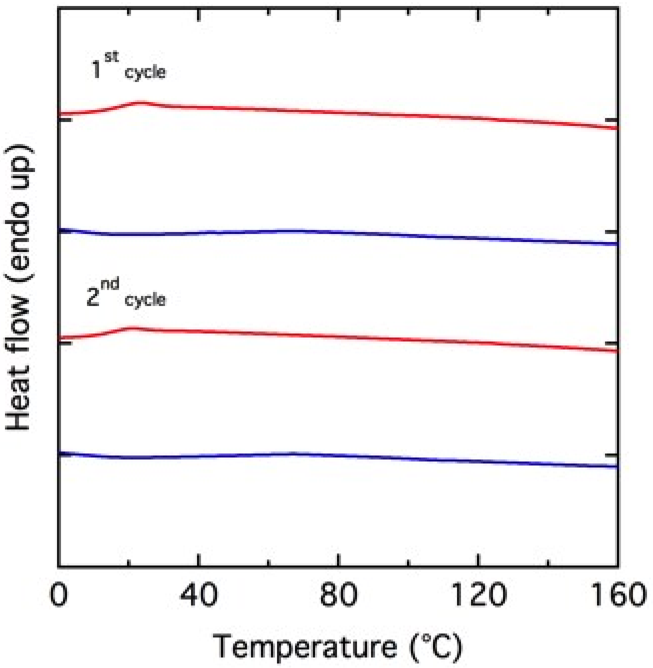


Figure S19. DSC thermogram of **M3** heated from -50 – 200 °C at a scan rate of 100 °C/min and the scans have been plotted up to 160 °C to enable the transitions to be clearly seen.

5. Cyclic voltammetry

Electrochemical measurements: Electrochemistry was performed using an Epsilon BASi C3 Cell Stand with a glassy carbon working electrode, platinum counter electrode and silver reference electrode in 0.01 M silver nitrate in acetonitrile. Oxidations were measured in freshly distilled dichloromethane [from calcium hydride (5%, w/v) under argon] and the reductions were measured in tetrahydrofuran [dried on a LC Systems solvent purification then distilled from lithium aluminum hydride under argon]. Samples (1 mM) were dissolved with electrochemical grade tetra-*n*-butylammonium perchlorate (0.1 M) as the supporting electrolyte and deoxygenated for 15 minutes with argon immediately prior to the electrochemical measurements. Oxidation and reduction potentials were calculated versus the ferrocene/ferrocinium couple,[6] which was measured on the same day under the same conditions.

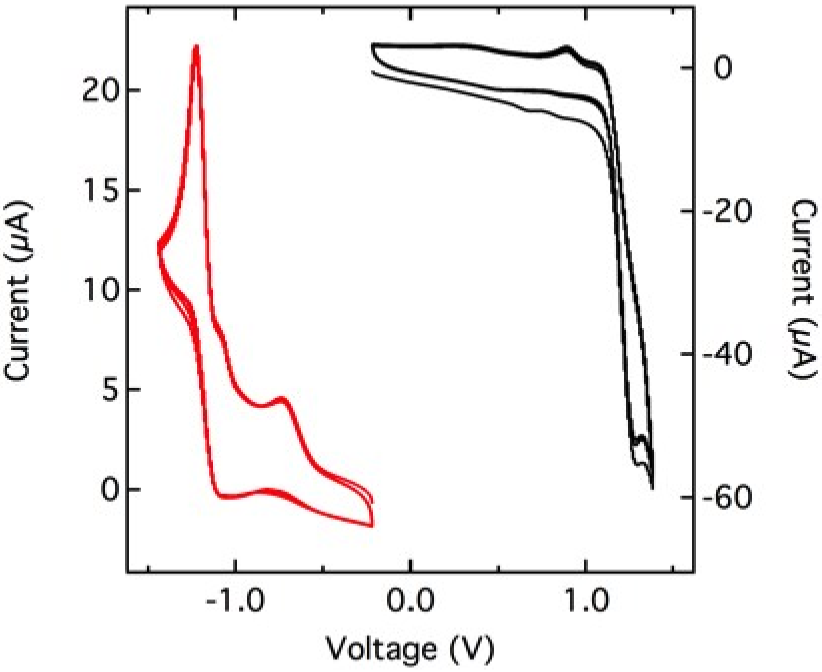


Figure S20. Cyclic voltammograms of **M1** (scan rate = 100 mV/s). Oxidation sweep is black, and reduction sweep is red. $E_{1/2}$(red) = -1.1 V, and $E_{1/2}$(ox) = 0.6 V.

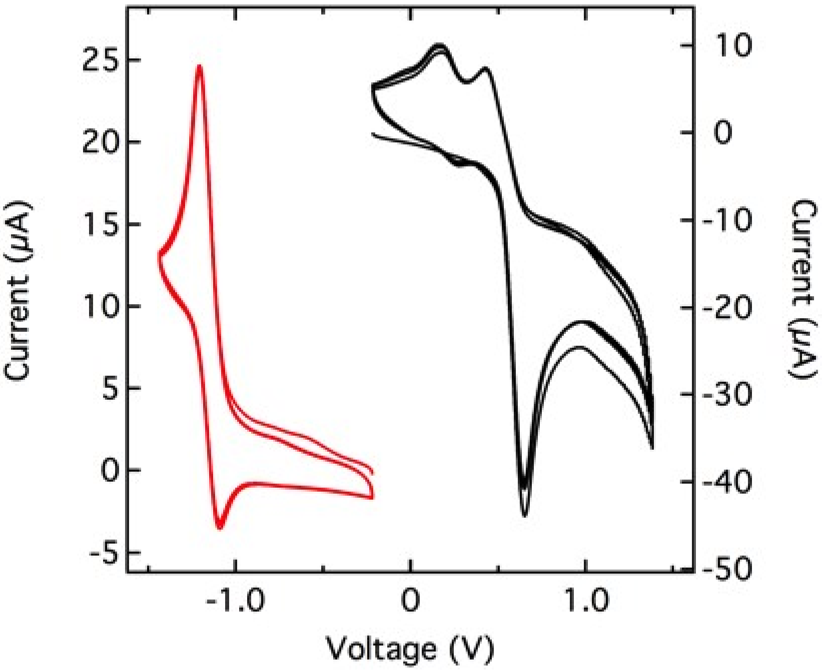


Figure S21. Cyclic voltammograms of **M2** (scan rate = 100 mV/s). Oxidation sweep is black, and reduction sweep is red. $E_{1/2}$(red) = -1.2 V, and $E_{1/2}$(ox) = 0.5 V.

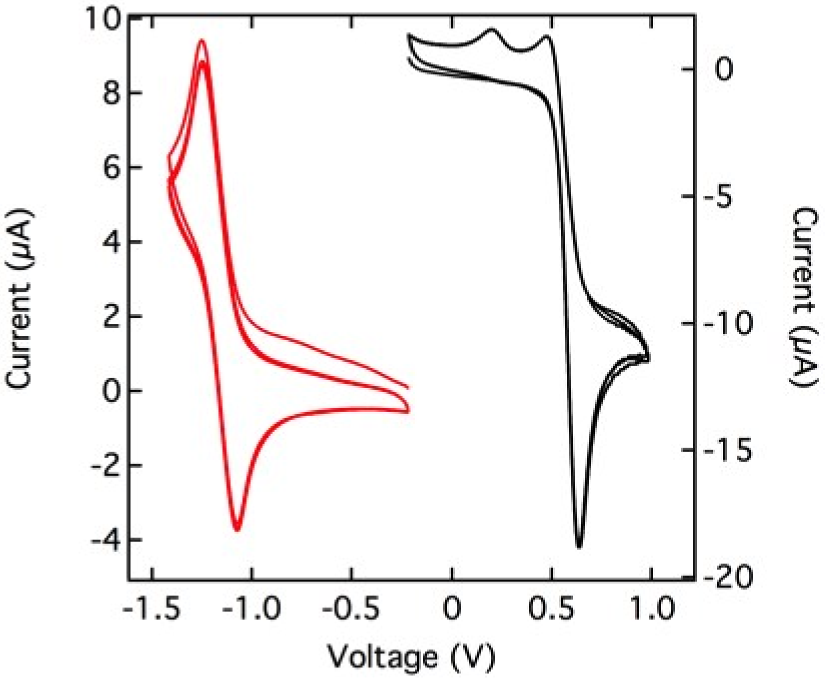


Figure S22. Cyclic voltammograms of **M3** (scan rate = 100 mV/s). Oxidation sweep is black, and reduction sweep is red. $E_{1/2}$(red) = -1.1 V, and $E_{1/2}$(ox) = 0.6 V.

6. Photoluminescence quenching

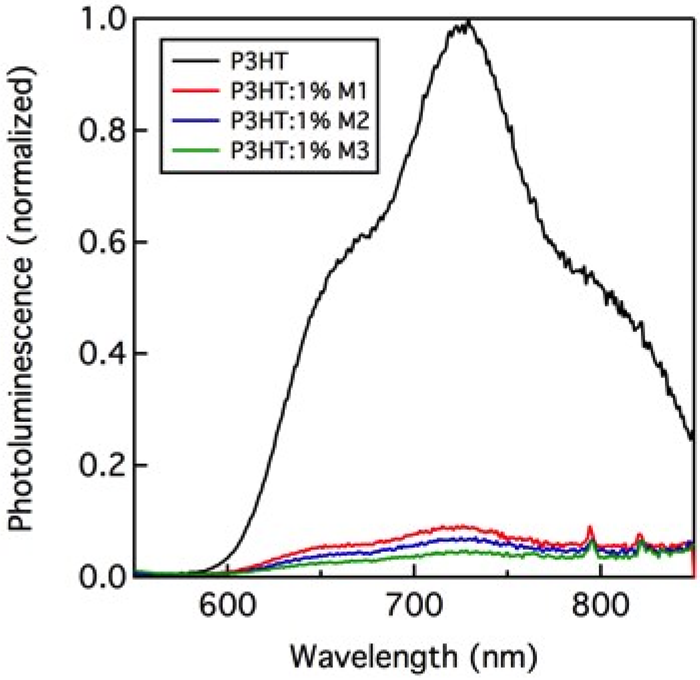


Figure S23. Photoluminescence spectra of neat P3HT (black), P3HT:1% **M1** (red), P3HT:1% **M2** (blue) and P3HT:1% **M3** (green). Films were excited at 535 nm, and the spectra are normalized with respect to the neat P3HT spectrum.

7. Mobility measurements

Electron mobility measurements were conducted by measuring the Space-Charge-Limited-Current (SCLC) and employing Mott-Gurney's law and Poole-Frenkel models:

$$J = E\sigma + \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}e^{\sqrt{\frac{E}{E_0}}},$$

where ε_0, ε_r, μ, E, σ, d and E_0 are the vacuum permittivity, relative permittivity, mobility, electric field, conductivity, film thickness, and field dependence coefficient, respectively. The device configuration used for the electron-only unipolar devices was ITO/PFN-OX (5 nm)/active layer/LiF (1 nm)/Al 100 nm.

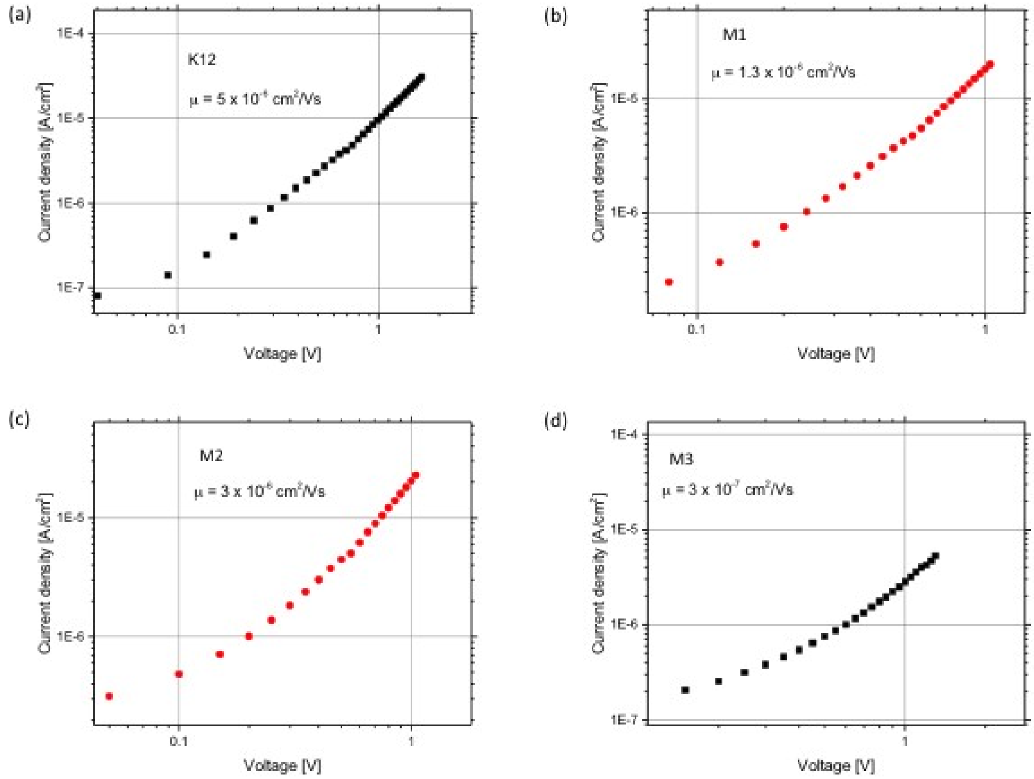


Figure S24. Current density-Voltage (*J*-*V*) curves of a) K12; b) **M1**; c) **M2** and d) **M3** for SCLC mobility estimation. The thickness of the active layers was ~350 nm.

8. OPV results

Experimental: First, 15 Ω/sq. indium tin oxide-coated glass substrates (Xinyan) patterned by photolithography were precleaned using Alconox (detergent) solution and a soft cloth before being sonicated in sequence with Alconox, deionized water, acetone, and 2- propanol for 10 min each. Each substrate was 2.5 cm x 2.5 cm, with 6 pixels each 0.2 cm^2. The cleaned substrates were coated with a 25 ± 5 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), purchased from Heraeus, by spin-coating at 5000 rpm for 60 s. The PEDOT:PSS layer was baked for

10 min at 170 °C. To obtain an 90 nm thick active layer, a 15 mg/mL solution of P3HT and a 15 mg/mL solution of the acceptor in *o*-DCB were mixed in a 1:1.5 w/w P3HT:Acceptor ratio and the blend solution was spin-coated at 1000 rpm for 25 s followed by slow drying. For non-crystalline **K12** a 15 mg/mL solution of **K12** in chloroform was blended with a 15 mg/mL solution of P3HT in a 1:1.5 w/w P3HT:**K12** ratio. The blend solution was then spin-coated at 1000 rpm. The fabrication was carried out in a nitrogen atmosphere (O_2 <1 ppm, H_2O <1 ppm) at ~20 °C. The thicknesses of the junctions were measured by a Veeco Dektak 150 profilometer. Finally, the devices were completed by depositing 20 nm of calcium and 80 nm of aluminum by thermal evaporation under a 10^{-6} mbar vacuum.

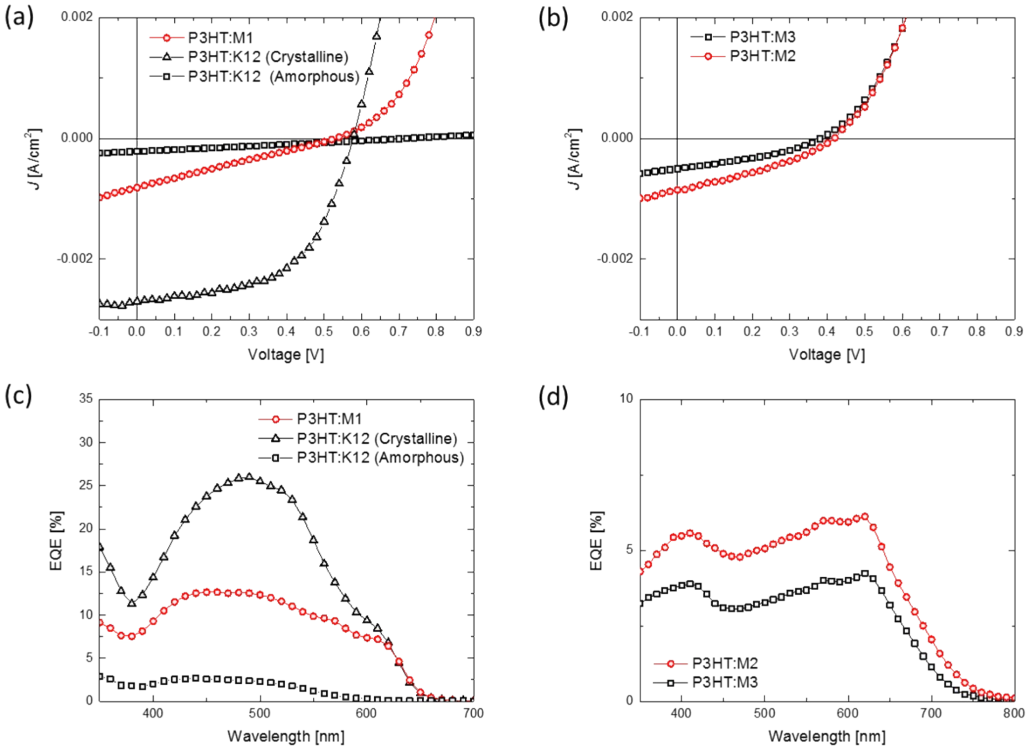


Figure S25. (a) Current density-voltage (*J*-*V*) curves for P3HT:**K12** and P3HT:**M1** bulk heterojunctions. As **M1** is amorphous, the relevant comparison is between P3HT:**M1** (from DCB solvent) and P3HT:**K12** from chloroform solvent which prevents formation of **K12** crystallites. (b) Shows *J*-*V* curve for P3HT:**M3** and P3HT:**M2**. The thickness of the junction was fixed at 90 nm (corresponding to the first interference peak of the solar cell cavity). (c) and (d) show corresponding external quantum efficiencies. The EQE of **M2** and **M3** series are extended beyond the P3HT absorption window (optical gap) indicating photoinduced hole transfer (Channel II) from the acceptor to the donor at wavelengths > 650 nm.

Table S1 OPV results for devices ITO/PEDOT:PSS/P3HT:Acceptor/Ca/Al where the acceptor is non-crystalline/crystalline **K12**, **M1**, **M2** or **M3**

Compound	J_{sc} **[mAcm^{-3}]**	V_{oc}**[V]**	**FF**	**PCE [%]**
K12	0.22	0.70	0.25	0.04
M1	0.81	0.52	0.25	0.10
M2	0.86	0.40	0.35	0.12
M3	0.51	0.38	0.35	0.07
K12 (cryst)	2.70	0.56	0.57	0.86

9. References

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