

## Electronic Supplementary Information

### Dielectric Constant Enhancement of Non-Fullerene Acceptors via Side-Chain Modification

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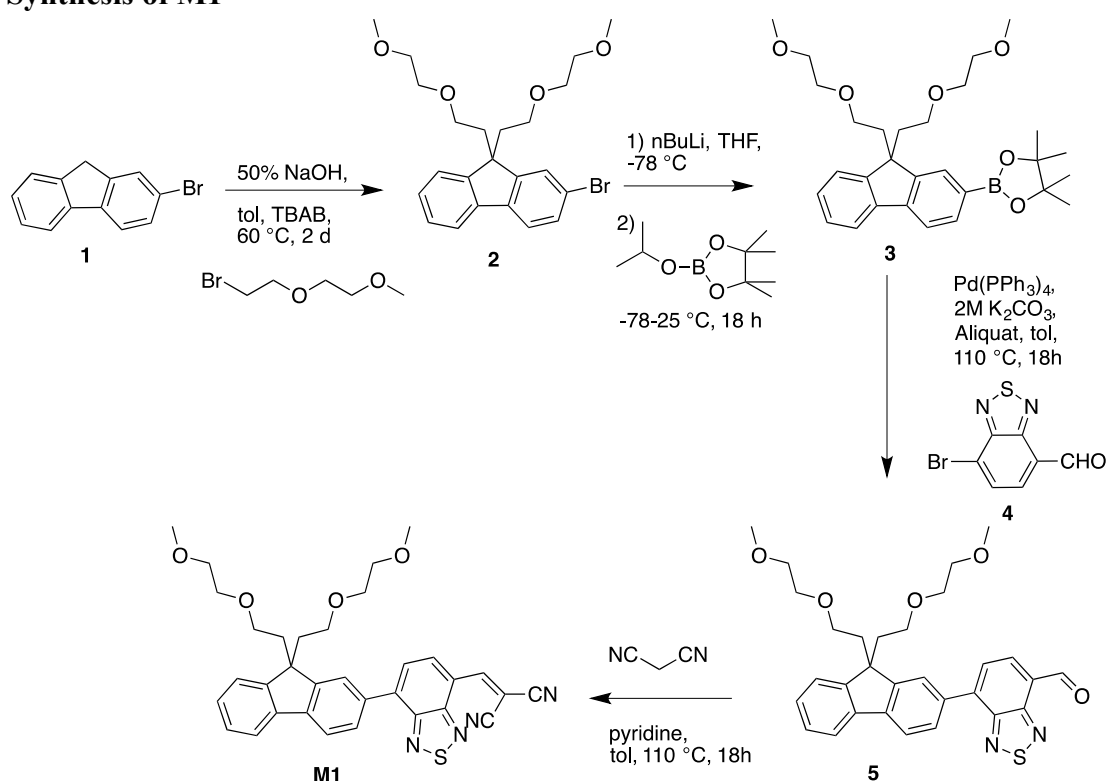
#### 1. Experimental

##### Materials and Synthesis

Cyclopenta[2,1-b;3,4-b']dithiophene<sup>1, 2</sup> and 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde<sup>3</sup> were synthesized according to literature procedures. 2-Bromofluorene was obtained from Matrix Scientific with all other reagents purchased from Sigma-Aldrich or Alfa Aesar and used as received. Tetrahydrofuran and toluene were dried on a LC Systems solvent purification system prior to use. All other solvents were freshly distilled prior to use. Hexane refers to light petroleum with a boiling point in the range 40-60 °C. Column chromatography was performed with Davisil LC60A 40–63 micron silica gel. Thin layer chromatography (TLC) was performed using aluminum backed silica gel 60 F254 plates. <sup>1</sup>H and <sup>13</sup>C NMR were performed using Bruker Advance AV-300, AV-400 or AV-500 MHz spectrometers in deuterated chloroform solvent; FH = fluorenyl H; CPDTH = cyclopentadithienyl H; BTH =

benzothiadiazolyl H. Coupling constants are given to the nearest 0.5 Hz. UV-visible spectroscopy was performed using a Cary 5000 UV-Vis spectrophotometer as either a thin film on glass substrates or as a solution in spectroscopic grade chloroform. Photoluminescence measurements were carried on a Fluoromax spectrophotometer as either a thin film on glass substrates or as a solution in spectroscopic grade chloroform. FT-IR spectroscopy was performed on solid samples using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with ATR attachment. Melting points (M.p.) 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 Analyser. 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 values [ $T_{d(5\%)}$ ] were reported as the temperature corresponding to a 5% mass reduction.

### Synthesis of M1



**Scheme S1** Synthesis of **M1**

#### *Synthesis of 2-bromo-9,9-bis[2-(2-methoxyethoxy)ethyl]fluorene 2*

2-Bromofluorene **1** (2.00 g, 8.16 mmol) and tetra-*n*-butylammonium bromide (0.13 g, 0.41 mmol) were dissolved in toluene (35 mL), followed by the addition of aqueous sodium hydroxide (50 % w/w, 35 mL). The mixture was deoxygenated by placing *in vacuo* and back filling with argon three times. Light was excluded and the reaction mixture was heated in an oil bath held at  $60\text{ }^\circ\text{C}$  for 2 d. The reaction mixture was

cooled to room temperature and the organic layer collected. The aqueous layer was extracted with ethyl acetate (2 x 20 mL) and the combined organic layers were washed with water (2 x 60 mL) and brine (60 mL). The organic layer was dried over anhydrous magnesium sulphate, filtered, and the solvent removed to give the crude product as a dark green oil. The residue was purified by column chromatography over silica using ethyl acetate:hexane (1:3) as eluent to yield **2** (2.4 g, 67%) as a pale yellow oil, which co-chromatographed with and had an identical <sup>1</sup>H nmr to an authentic sample.<sup>4</sup>

*Synthesis of 7-(9,9-bis[2-(2-methoxyethoxy)ethyl]fluoren-2-yl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde 5*

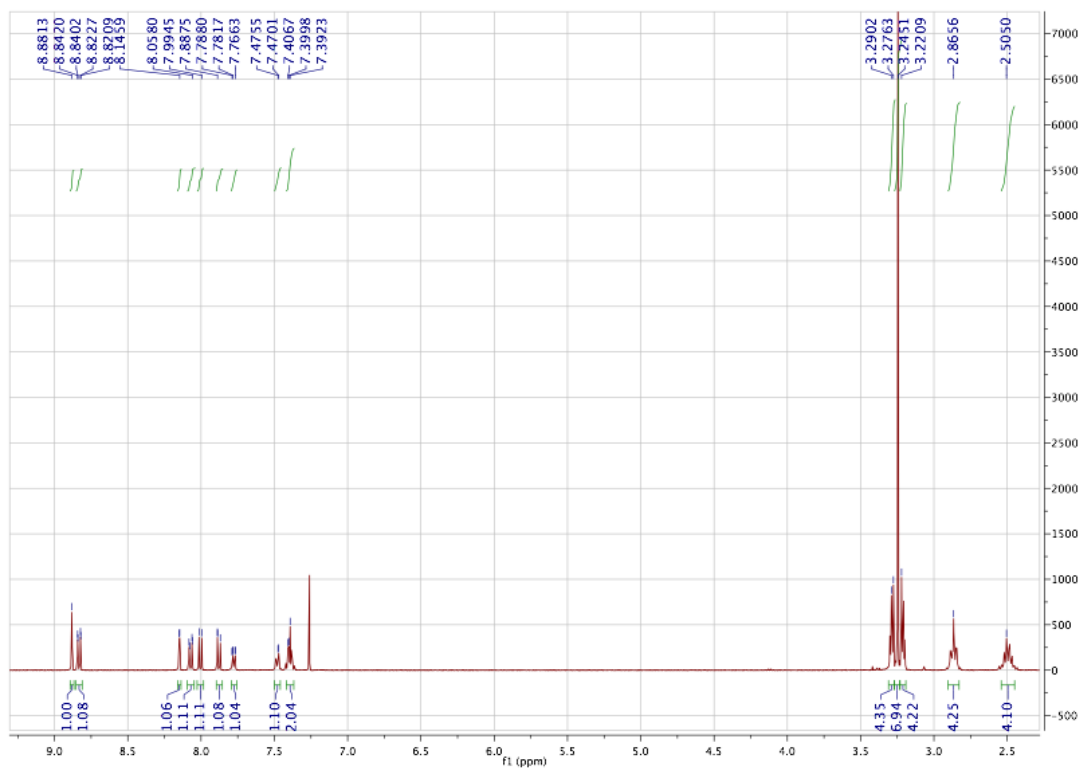
A solution of **2** (1.35 g, 3.00 mmol) in dry tetrahydrofuran (30 mL) under argon in a Schlenk tube was cooled in an acetone/dry ice bath. *n*-Butyllithium (1.6 M in hexanes, 2.6 mL, 4.21 mmol) was added dropwise, while maintaining the acetone/dry ice bath cooling. The reaction mixture was stirred for a further 30 min at this temperature, then 2-*iso*-propoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (1.0 mL, 4.80 mmol) was added dropwise to the reaction mixture. The mixture was stirred for 20 h during which time it was allowed to warm slowly to room temperature. Water (30 mL) was added to quench the reaction and the crude product was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous magnesium sulfate, filtered, the solvent was removed to give crude 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-9,9-bis[2-(2-methoxyethoxy)ethyl]fluorene **3** (1.15 g) as a colourless oil, which was used in the next step without further purification.

A Schlenk tube was charged with crude **3** (1.10 g, 2.22 mmol), 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde **4** (539 mg, 2.22 mmol) and tetrakis(triphenylphosphine)palladium(0) (128 mg, 0.11 mmol). The mixture was then placed under argon before adding deoxygenated toluene (14 mL) and Aliquat 336 (1 drop). After 5 min deoxygenated aqueous potassium carbonate (2M, 4.5 mL, 8.9 mmol) was added and the reaction mixture was heated in an oil bath held at 85 °C for 20 h. The reaction mixture was allowed to cool then water (20 mL) was added followed by ethyl acetate (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (80 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed to yield a red/brown oil. The crude product was purified by column chromatography over silica using ethyl acetate:hexane (3:1) as eluent to give **5** (970 mg, 61% over 2 steps based on moles of **2**) as a yellow/orange solid. M.p. = 94-96 °C; Found: C, 67.45; H, 6.35; N, 4.8; C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub>S requires C, 67.7; H, 6.1; N, 5.2;  $\bar{\nu}_{\max}/\text{cm}^{-1}$  1677 (C=O);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  292 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.26), 305sh (4.25), 321sh (3.93), 401 (4.09);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 2.42-2.57 (4H, m, CH<sub>2</sub>), 2.81-2.94 (4H, m, CH<sub>2</sub>), 3.19-3.26 (10H, m, CH<sub>2</sub> and CH<sub>3</sub>), 3.27-3.32 (4H, m, CH<sub>2</sub>), 7.34-7.44 (2H, m, FH), 7.45-7.50 (1H, m, FH), 7.74-7.79 (1H, m, FH), 7.85-7.90 (1H, m, FH), 7.98 (1H, dd, *J* = 0.5 Hz, *J* = 7.0 Hz, BTH), 8.05-8.09 (2H, m, FH), 8.34 (1H, d,

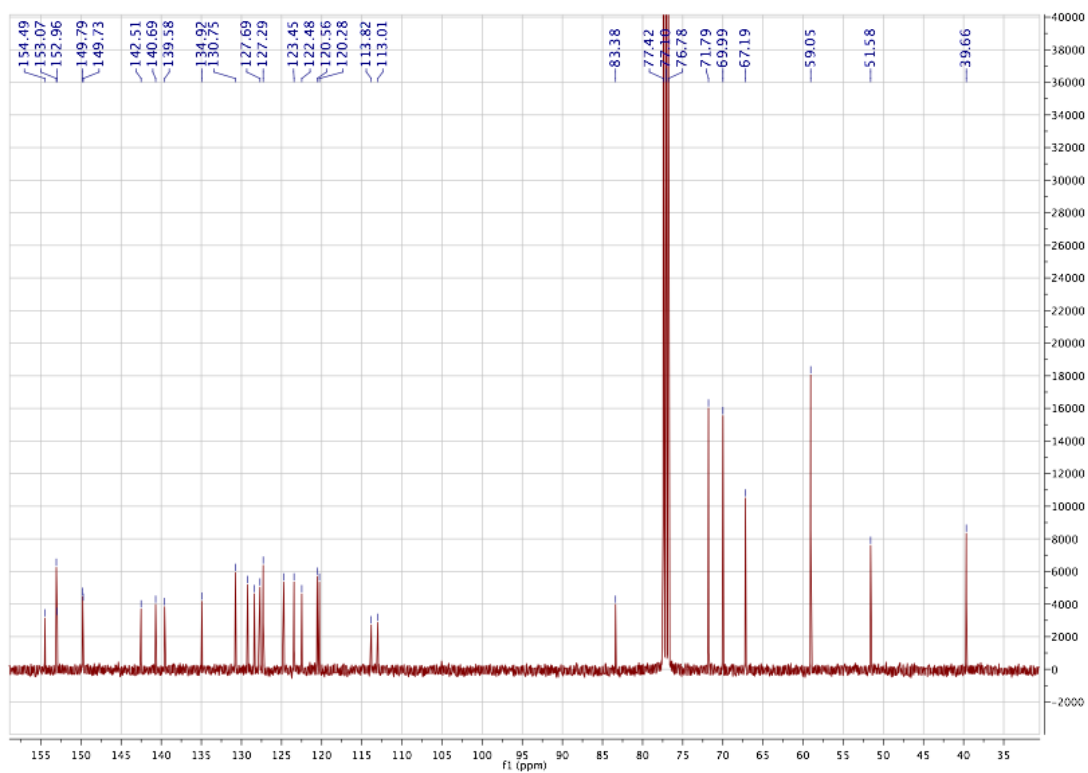
$J = 7.0$  Hz, BTH), 10.81 (1H, s, CHO);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 39.7, 51.5, 59.0, 67.2, 70.0, 71.8, 120.1, 120.5, 123.4, 124.6, 126.3, 126.9, 127.6, 129.3, 132.8, 135.4, 139.7, 140.6, 142.0, 149.6, 149.7, 153.9, 154.1, 189.1;  $m/z$  [ESI]: Found: 555.2 (100%), 556.2 (35%), 557.2 (12%), 558.2 (4%).  $C_{30}H_{32}N_2NaO_5S$  requires 555.2 (100%), 556.2 (32%), 557.2 (5%), 558.2 (3%).

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

Pyridine (6 drops) and then malononitrile (990 mg, 15 mmol) were added to a solution of **5** (800 mg, 1.50 mmol) in toluene (30 mL). The reaction mixture was heated at reflux overnight under argon. After cooling to room temperature the reaction mixture was washed with water (3 x 30 mL), brine (30 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent removed to give a dark red oil. The residue was dissolved in ethyl acetate (10 mL) and poured into hexane (150 mL). The red precipitate was collected by filtration and recrystallized from an ethyl acetate/hexane mixture to give **M1** (465 mg, 55%) as dark red crystals. M.p. = 102-104 °C; Found: C, 68.0; H, 5.5; N, 9.6;  $C_{33}H_{32}N_4O_4S$  requires C, 68.2; H, 5.6; N, 9.7;  $\bar{\nu}_{max}/cm^{-1}$  2223 (CN);  $\lambda_{max}(CHCl_3)/nm$  345sh ( $\log \epsilon/dm^3 mol^{-1} cm^{-1}$  3.86), 451 (4.16);  $\delta_H$  (500 MHz,  $CDCl_3$ ) 2.44-2.54 (4H, m,  $CH_2$ ), 2.83-2.91 (4H, m,  $CH_2$ ), 3.19-3.23 (4H, m,  $CH_2$ ), 3.25 (6H, s,  $CH_3$ ), 3.27-3.31 (4H, m,  $CH_2$ ), 7.37-7.43 (2H, m, FH), 7.46-7.49 (1H, m, FH), 7.76-7.80 (1H, m, FH), 7.88 (1H, dd,  $J = 0.5$  Hz,  $J = 8.0$  Hz, FH), 8.00 (1H, dd,  $J = 0.5$  Hz,  $J = 8.0$  Hz, BTH), 8.07 (1H, dd,  $J = 1.5$  Hz,  $J = 8.0$  Hz, FH), 8.15 (1H, dd,  $J = 0.5$  Hz,  $J = 1.5$  Hz, FH), 8.83 (1H, dd,  $J = 0.5$  Hz,  $J = 8.0$  Hz, BTH), 8.88 (1H, dd,  $J = 0.5$  Hz,  $J = 0.5$  Hz, vinylH);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 39.7, 51.6, 59.0, 67.2, 70.0, 71.8, 83.4, 113.0, 113.8, 120.3, 120.6, 122.5, 123.5, 124.7, 127.3, 127.7, 128.4, 129.2, 130.7, 134.9, 139.6, 140.7, 142.5, 149.7, 149.8, 153.0, 153.1, 154.5;  $m/z$  [ESI]: Found: 603.1 (100%), 604.1 (37%), 605.1 (13%), 606.1 (3%).  $C_{33}H_{32}N_4NaO_4S$  requires 603.1 (100%), 604.1 (36%), 605.1 (5%), 606.1 (4%);  $Td_{(5\%)} = 324$  °C; M.p. (DSC) = 104 °C; Tg (second cycle – after melt, scan rate 100 °C/min) = 11 °C.

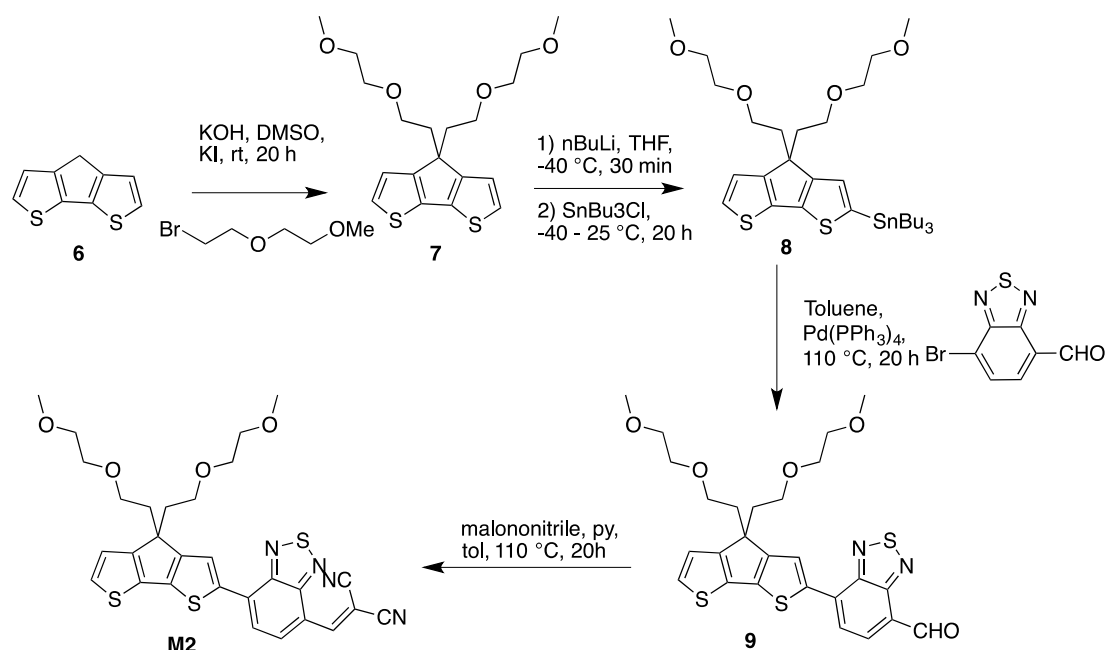


**Fig. S1**  $^1\text{H}$  NMR in  $\text{CDCl}_3$  of **M1**



**Fig. S2**  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **M1**

## Synthesis of **M2**



**Scheme S2** Synthesis of M2

*Synthesis of 4,4-bis[2-(2-methoxyethoxy)ethyl]-4H-cyclopenta[2,1-b;3,4-b']dithiophene 7*

A mixture of cyclopenta[2,1-b;3,4-b']dithiophene **6** (3 g, 16.8 mmol), potassium hydroxide (4.7 g, 84 mmol), potassium iodide (400 mg, 2.4 mmol) and deoxygenated dimethylsulfoxide (70 mL) was stirred at room temperature for 1 h under argon before 1-bromo-2-(2-methoxyethoxy)ethane (6.8 mL, 50.4 mmol) was added. Light was excluded and the reaction mixture was stirred overnight at room temperature. Water (100 mL) was added and the resulting aqueous solution was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were washed with water (300 mL), brine (300 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent removed to yield a brown oil. The residue was purified by column chromatography over silica using hexane:ethyl acetate mixtures (0:1-1:1) as eluent to give **7** (3.2 g, 50 %) as a yellow oil.  $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$  319 ( $\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.49), 333sh (4.37);  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 2.25-2.29 (4H, m,  $\text{CH}_2$ ), 2.98-3.01 (4H, m,  $\text{CH}_2$ ), 3.27-3.32 (10H, m,  $\text{CH}_2$  and  $\text{CH}_3$ ), 3.35-3.39 (4H, m,  $\text{CH}_2$ ), 6.95 (2H, d,  $J = 5.0$  Hz, CPDTH), 7.14 (2H, d,  $J = 5.0$  Hz, CPDTH);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 37.6, 49.2, 59.0, 67.6, 70.0, 71.8, 121.7, 125.0, 136.6, 156.4;  $m/z$  [HR-ESI]: Found 405.117 ( $\text{M}+\text{Na}^+$ );  $\text{C}_{19}\text{H}_{26}\text{O}_4\text{NaS}_2$  requires 405.117.

*Synthesis of 6-{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 9*

Anhydrous tetrahydrofuran (50 mL) was added to a Schlenk tube containing **7** (1.8 g, 4.7 mmol) under argon. The solution was cooled in an acetonitrile/dry ice bath and then *n*-butyllithium (3.5 mL, 5.7 mmol) was added dropwise over 10 min. The solution was stirred while cooled in an acetonitrile/dry ice bath for 30 min before the

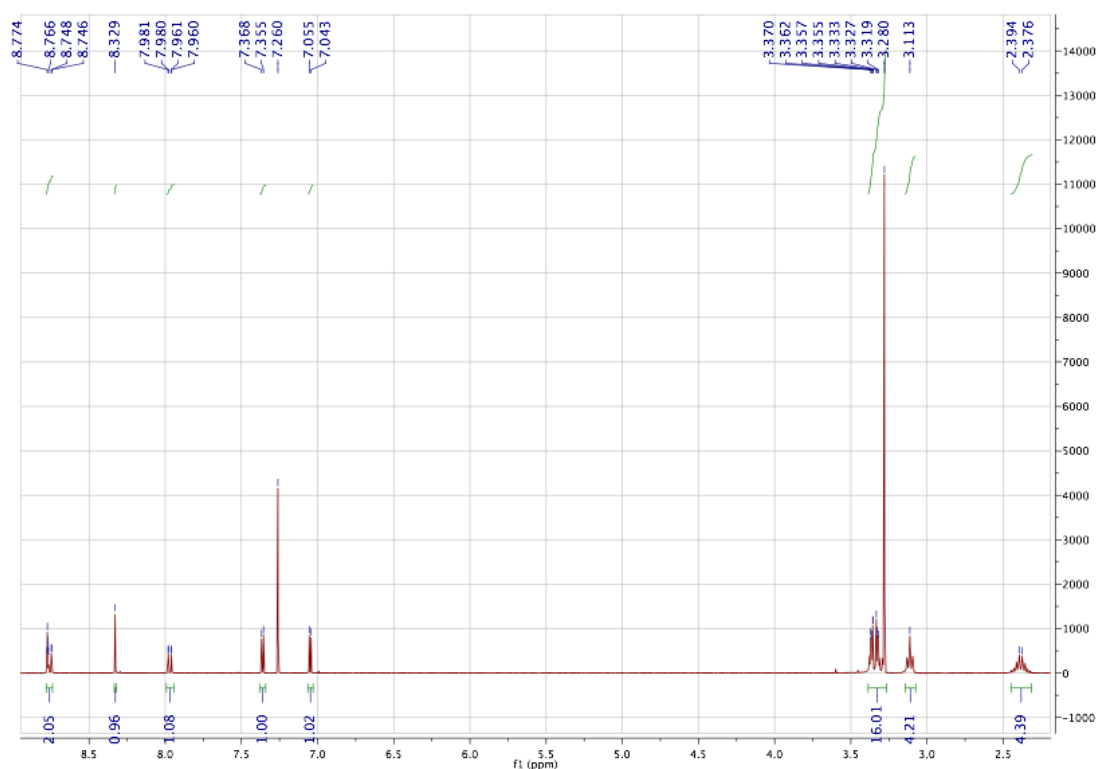
addition of tri-*n*-butyltin chloride (1.6 mL, 5.9 mmol). The reaction mixture was stirred and allowed to warm to room temperature overnight under argon. The reaction was quenched with water (50 mL) and extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed water (2 x 100 mL), brine (100 mL), dried over anhydrous magnesium sulphate, and the solvent removed to yield 2-tributylstannyl-4,4-bis[2-(2-methoxyethoxy)ethyl]-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene **8** as a brown oil (2.85 g), a portion of which was used without further purification in the next step.

A Schlenk tube containing **8** (2.6 g, 3.9 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.94 g, 3.9 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.22 g, 0.19 mmol) was placed under argon and then deoxygenated toluene (30 mL) was added. The reaction mixture was heated at reflux for 20 h and then allowed to cool. Water (30 mL) was added followed by ethyl acetate (30 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (120 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed to leave a dark purple solid. The crude product was purified by column chromatography over silica using hexane:ethyl acetate (1:1) as eluent to give **9** (670 mg, 27% over two steps based on moles of **7**) as dark purple solid. M.p. = 114-116 °C; Found: C, 57.1; H, 4.9; N, 5.3; C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>S<sub>3</sub> requires C, 57.3; H, 5.2; N, 4.9;  $\bar{\nu}_{\max}/\text{cm}^{-1}$  1678 (CH=O);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  323sh ( $\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  3.76), 341 (3.78), 361sh (3.73), 527 (4.01);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.33-2.45 (4H, m, CH<sub>2</sub>), 3.06-3.15 (4H, m, CH<sub>2</sub>), 3.28 (6H, s, CH<sub>3</sub>), 3.30-3.38 (8H, m, CH<sub>2</sub>), 7.03 (1H, d, *J* = 5.0 Hz, CPDTH), 7.32 (1H, d, *J* = 5.0 Hz, CPDTH), 7.98 (1H, d, *J* = 8.0 Hz, BTH), 8.22 (1H, d, *J* = 8.0 Hz, BTH), 8.28 (1H, s, CPDTH), 10.70 (1H, s, CHO);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 37.6, 50.0, 59.1, 67.6, 70.1, 71.9, 122.0, 122.4, 124.8, 125.0, 127.9, 133.1, 134.1, 138.7, 142.3, 152.1, 153.9, 157.8, 158.6, 188.5; *m/z* [ESI]: Found: 567.1 (100%), 568.1 (30%), 569.1 (16%), 570.1 (5%), 571.1 (2%). C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>NaO<sub>5</sub>S<sub>3</sub> requires 567.1 (100%), 568.1 (28%), 569.1 (14%), 570.1 (4%), 571.1 (2%).

2-[(6-{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**

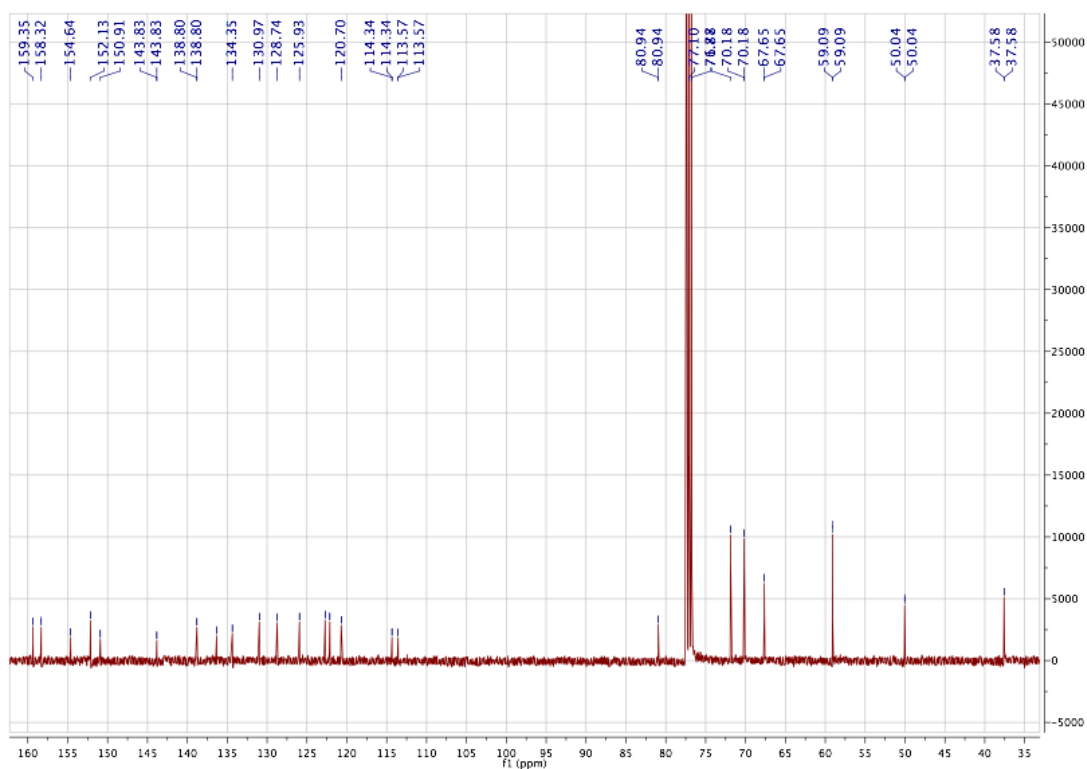
Pyridine (3 drops) followed by malononitrile (291 mg, 4.40 mmol) was added to a solution of **9** (240 mg, 0.44 mmol) in toluene (10 mL). The reaction mixture was heated at reflux overnight under an argon atmosphere. After cooling to room temperature ethyl acetate (10 mL) was added and the reaction mixture was washed with water (3 x 20 mL), brine (20 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent removed to give a dark blue oil. The oil was dissolved in ethyl acetate (5 mL) and precipitated in cold hexane (75 mL). The precipitate was collected by filtration and **M2** (165 mg, 63%) was isolated as dark blue powder. M.p. = 121-124 °C and 133-136 °C; Found: C, 58.4; H, 4.7; N, 9.4; C<sub>29</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>S<sub>3</sub> requires C, 58.8; H, 4.8; N, 9.5;  $\bar{\nu}_{\max}/\text{cm}^{-1}$  2222 (CN);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  595 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4.52);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.32-2.45 (4H, m, CH<sub>2</sub>), 3.07-3.16 (4H, m, CH<sub>2</sub>), 3.28

(6H,s, CH<sub>3</sub>), 3.31-3.38 (8H, m, CH<sub>2</sub>), 7.04 (1H, d, *J* = 5.0 Hz, CPDTH), 7.36 (1H, d, *J* = 5.0 Hz, CPDTH), 7.97 (1H, dd, *J* = 0.5 Hz, *J* = 8.0 Hz, BTH), 8.33 (1H, s, CPDTH), 8.76 (1H, dd, *J* = 1.0 Hz, *J* = 8.0 Hz, BTH), 8.77 (1H, dd, *J* = 0.5 Hz, *J* = 1.0 Hz, vinylH); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 37.6, 50.0, 59.1, 67.6, 70.2, 71.9, 80.9, 113.6, 114.3, 120.7, 122.1, 122.7, 125.9, 128.7, 131.0, 134.3, 136.3, 138.8, 143.8, 150.9, 152.1, 154.6, 158.3, 159.3; *m/z* [ESI]: Found: 614.9 (100%), 615.9 (40%), 616.9 (25%), 617.9 (7%), 618.9 (2%). C<sub>29</sub>H<sub>28</sub>N<sub>4</sub>NaO<sub>4</sub>S<sub>3</sub> requires 614.9 (100%), 615.9 (31%), 616.9 (14%), 617.9 (5%), 618.9 (4%); T<sub>d(5%)</sub> = 295 °C; M.p. (DSC) = 125 °C and 136 °C; T<sub>g</sub> (second cycle – after melt, scan rate 100 °C/min) = 14 °C.



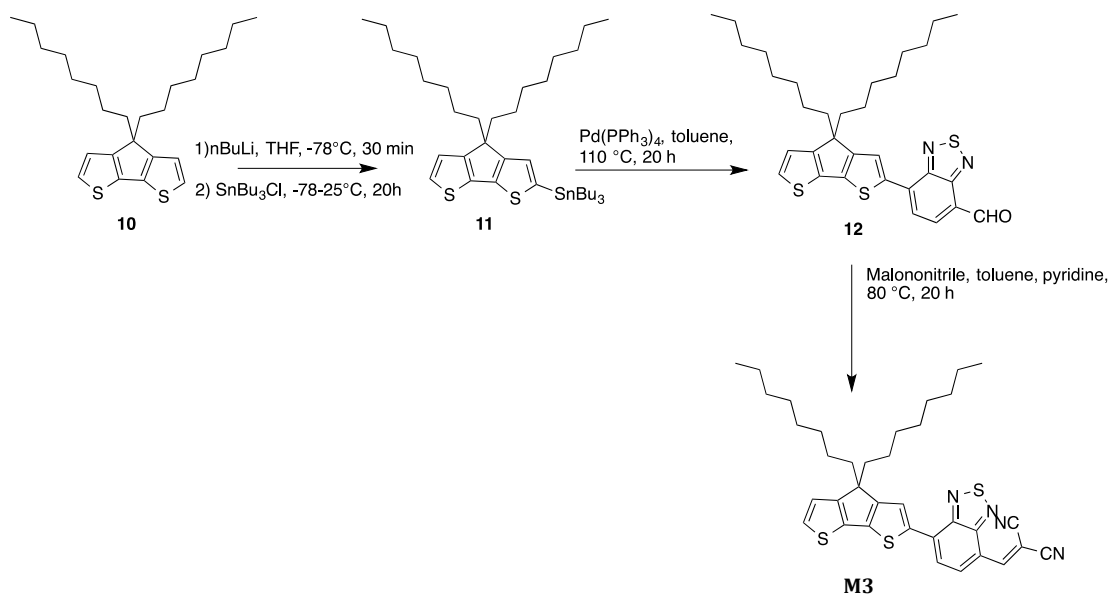
**Fig. S3** <sup>1</sup>H NMR in CDCl<sub>3</sub> of M2





**Fig. S4**  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **M2**

### Synthesis of **M3**



### Scheme S3 Synthesis of **M3**

Synthesis of 7-(4,4-di-*n*-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde **12**

An oven dried Schlenk tube was charged with 4,4-di-*n*-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene **10**<sup>5</sup> (2.5 g, 6.2 mmol) and filled with argon before adding anhydrous tetrahydrofuran (60 mL). The solution was cooled in a dry ice/acetone bath

and then *n*-butyllithium (4.1 mL, 6.52 mmol) was added dropwise over 10 min to the solution. The solution was stirred for a further 30 min before tri-*n*-butyltin chloride (1.6 mL, 5.9 mmol) was added. The reaction mixture was allowed to warm to room temperature overnight under argon. The reaction was quenched with water (50 mL) and extracted with ethyl acetate (2 x 50 mL). The organic layers were combined and washed with brine (100 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent removed to yield **11** as brown oil (4.2 g), which was used without further purification. A dry Schlenk tube was charged with **11** (2.3 g, 3.29 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (0.80 g, 3.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (190 mg, 0.16 mmol). The flask was back-filled with argon then deoxygenated toluene (25 mL) was added and the reaction mixture was heated at reflux for 20 h under argon. The reaction mixture was allowed to cool then it was passed through a plug of Celite using ethyl acetate as the eluent (150 mL). The filtrate was collected and the solvent removed to yield a dark purple oil. The crude product was purified by column chromatography over silica using hexane:ethyl acetate (4:1) as eluent to give **12** (1.4 g, 73% over two steps based on moles of **10**) as a dark purple oil. *m/z* [HR-ESI]: Found 565.2362 (M+H<sup>+</sup>); C<sub>32</sub>H<sub>41</sub>N<sub>2</sub>OS<sub>3</sub> requires 565.2376;  $\bar{\nu}_{\max}/\text{cm}^{-1}$  1683 (CH=O);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  325sh (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  3.97), 341 (3.98), 362sh (3.97), 534 (4.25);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 0.81 (6 H, t, *J* = 7.0 Hz, CH<sub>3</sub>), 0.93-1.08 (4 H, brm, CH<sub>2</sub>), 1.10-1.28 (24 H, brm, CH<sub>2</sub>), 1.88-1.99 (4 H, m, CH<sub>2</sub>), 6.99 (1 H, d, *J* = 5.0 Hz, CPDTH), 7.32 (1 H, d, *J* = 5.0 Hz, CPDTH), 7.97 (1 H, dd, *J* = 8.0 Hz, *J* = 0.5 Hz, BTH), 8.21 (1 H, d, *J* = 8.0 Hz, BTH), 8.24 (1H, s, CPDTH), 10.69 (1 H, d, *J* = 0.5 Hz, CHO);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 14.1, 22.7, 24.7, 29.3, 29.4, 30.1, 31.9, 37.9, 54.0, 121.9, 122.2, 124.5, 124.9, 127.6, 133.1, 134.3, 136.3, 138.4, 142.6, 152.1, 154.0, 159.5, 160.3, 188.4.

*Synthesis of 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***

Pyridine (1 drop) was added to a solution of **12** (100 mg, 0.18 mmol) in toluene (4 mL) followed by malononitrile (234 mg, 3.54 mmol). The reaction mixture was heated in an oil bath at 80 °C overnight under an argon atmosphere. After cooling to room temperature ethyl acetate (10 mL) was added and the reaction mixture was washed with water (3 x 10 mL) and brine (20 mL). The solution was dried over anhydrous magnesium sulfate, filtered and the removed to give **13** as a dark blue viscous oil (78 mg, 72 %). *m/z* [HR-ESI]: Found 613.2469; C<sub>35</sub>H<sub>41</sub>N<sub>4</sub>S<sub>3</sub> requires 613.2488;  $\bar{\nu}_{\max}/\text{cm}^{-1}$  2222 (CN);  $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$  358 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  3.56), 391 (3.52), 611 (4.03);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 0.78-0.87 (6 H, m, CH<sub>3</sub>), 0.93-1.07 (4 H, brm, CH<sub>2</sub>), 1.10-1.28 (20 H, brm, CH<sub>2</sub>), 1.88-1.98 (4 H, brm, CH<sub>2</sub>), 7.00 (1H, d, *J* = 5.0 Hz, CPDTH), 7.36 (1 H, d, *J* = 5.0 Hz, CPDTH), 7.97 (1 H, d, *J* = 8.0 Hz, BTH), 8.26 (1 H, s, CPDTH), 8.74-8.77 (2 H, m, BTH and vinylH);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 14.2, 22.7 24.7, 29.3, 29.4, 30.0, 31.9, 37.9, 54.1, 80.5, 113.7, 114.4, 120.4, 122.0, 122.5, 125.6, 128.6, 131.0, 134.7, 136.3, 138.6, 144.4, 151.0, 152.1, 154.7, 160.0, 161.1; Td<sub>(5%)</sub> = 308 °C.

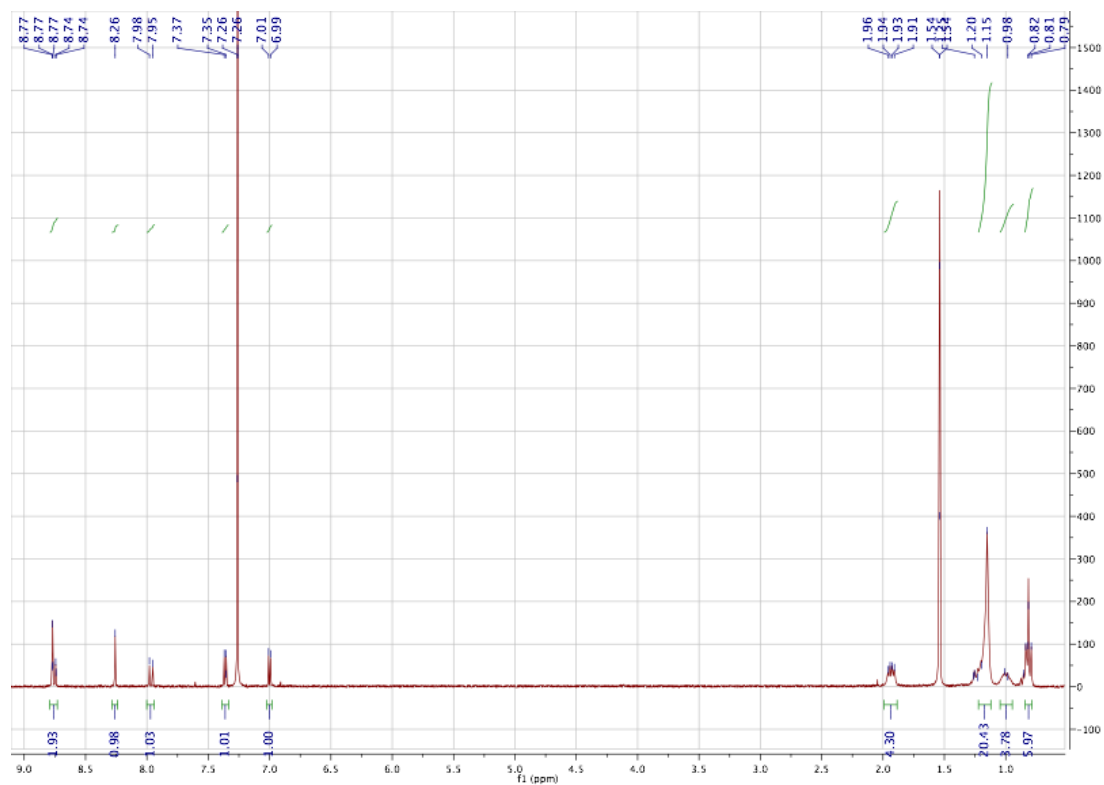


Fig. S5  $^1\text{H}$  NMR of M3 in  $\text{CDCl}_3$

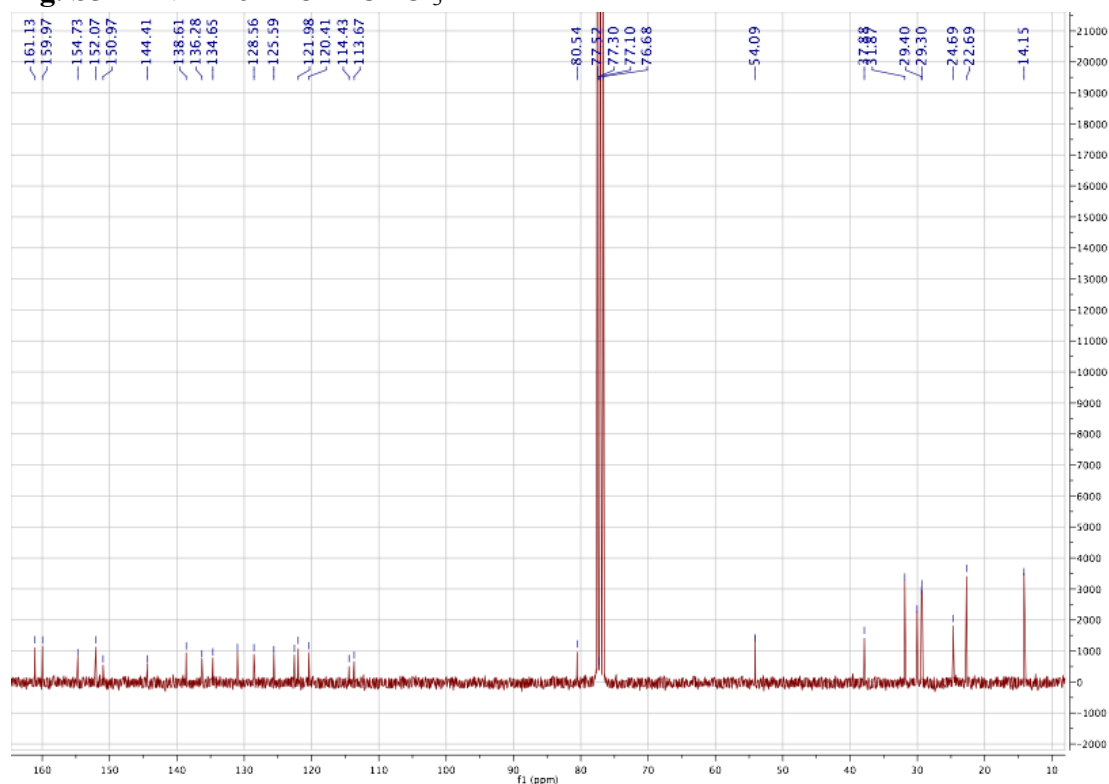


Fig. S6  $^{13}\text{C}$  NMR of M3 in  $\text{CDCl}_3$

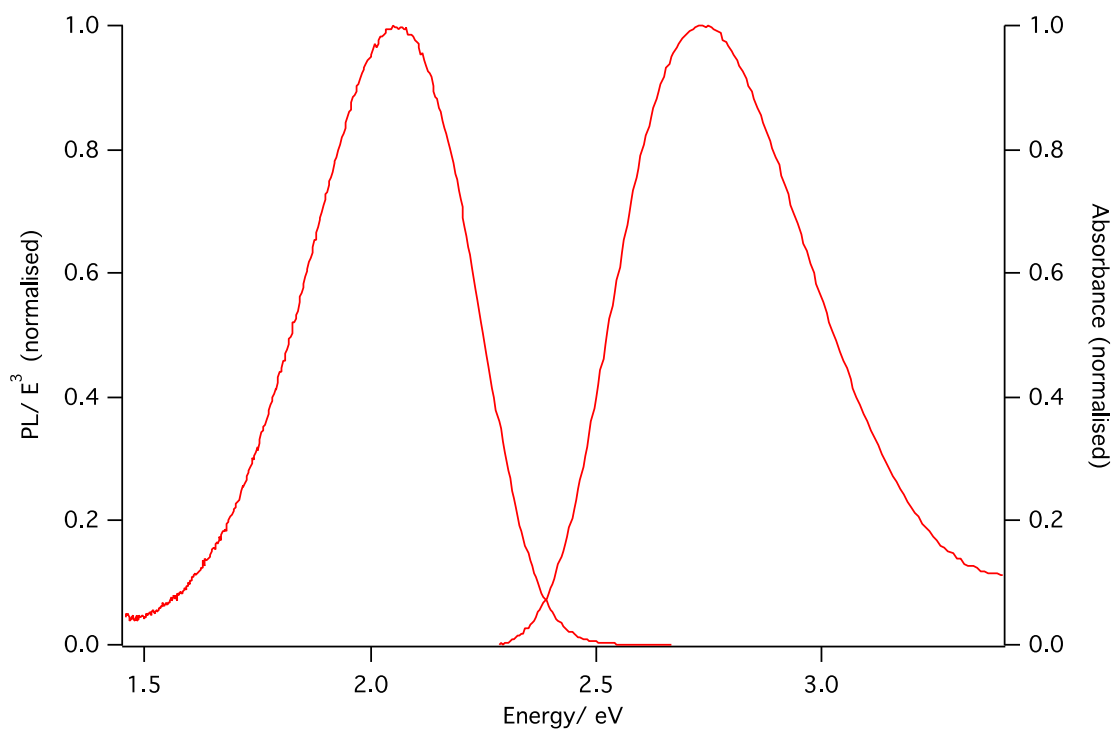
## Device Fabrication

*Static and low frequency dielectric constant:* 15  $\Omega/\text{sq}$ . indium tin oxide coated glass substrates (Kintec) patterned by photolithography were pre-cleaned with Alconox

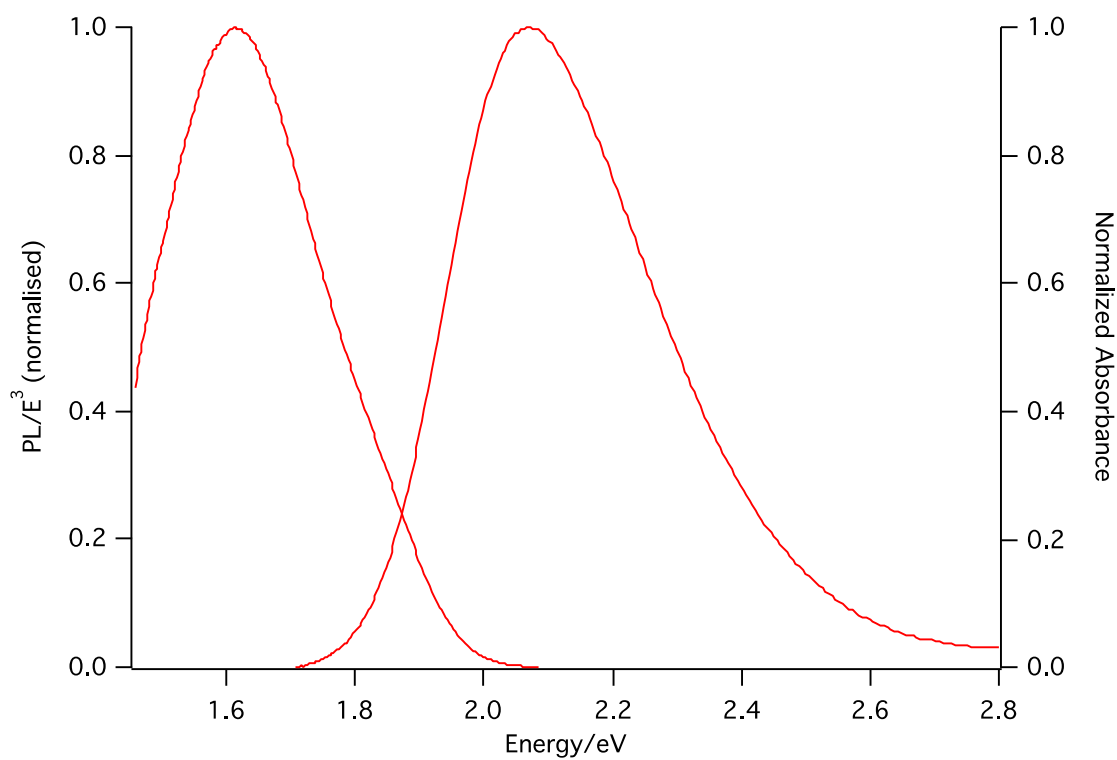
(detergent) solution and a soft cloth before being sonicated in sequence with Alconox, de-ionized water, acetone and 2-propanol for 10 minutes each. Each substrate was 2.5 cm x 2.5 cm with 6 pixels each 0.2 cm<sup>2</sup>. The cleaned substrates were spin-coated with a solution of organic semiconductor 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<sub>2</sub> <1 ppm, H<sub>2</sub>O <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<sup>-6</sup> mbar vacuum. The dielectric constants at 20 Hz to ~10<sup>6</sup> 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.<sup>5</sup>

*High frequency dielectric constant:* The solutions described above were also used to coat ~200 nm thick films on glass for the reflection/transmission measurements to determine extinction coefficient ( $k$ ). The same solutions were also diluted by a factor of three and spin-coated at 1000 rpm onto cleaned plane silicon substrates to perform spectroscopic ellipsometry. The films had a thicknesses ~60 nm. The real part of the refractive index ( $n$ ) was determined from *Kramers-Kronig* transformations of the extinction coefficient ( $k$ ) and base-lined with  $n$  ( $\lambda > 1000$  nm) extracted from the spectroscopic ellipsometry data collected on a J. A. Woollam VUV-VASE ellipsometer. Dielectric constants in the high frequency regime (~10<sup>14</sup> Hz) were converted from the optical constants ( $n$  and  $k$ ). Finally, the real part of the dielectric constant was calculated using  $n$  and  $k$ .

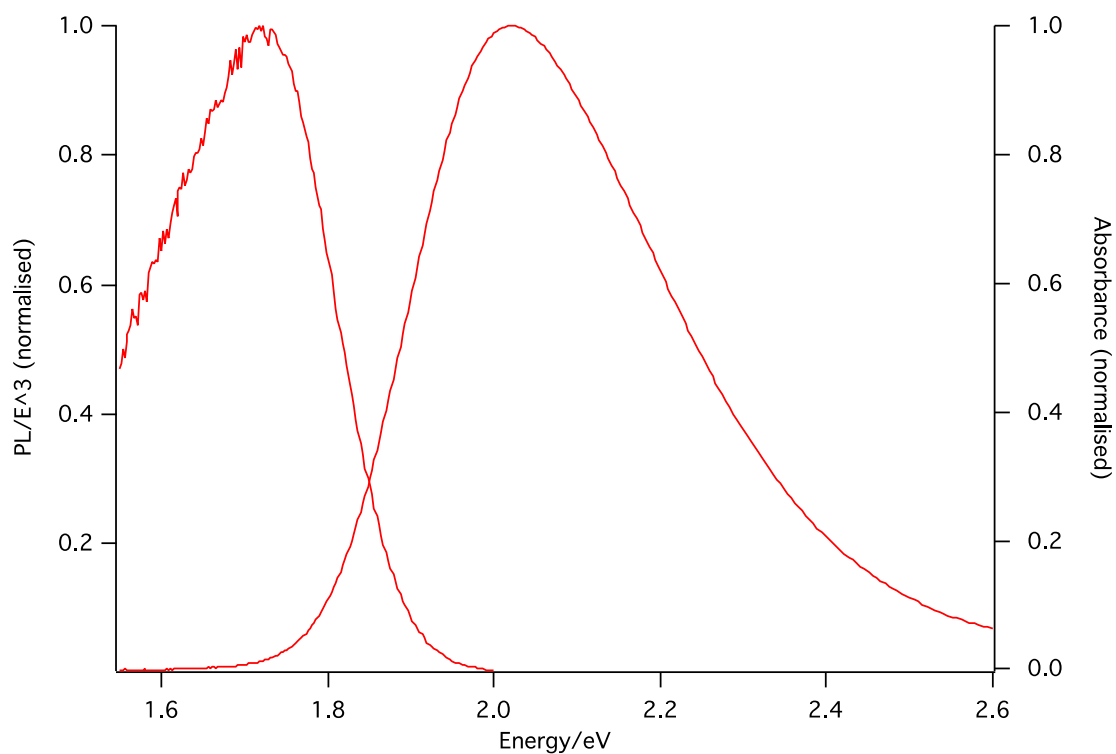
## **2. Optical gap estimation**



**Fig. S7** Optical gap estimation of **M1**.

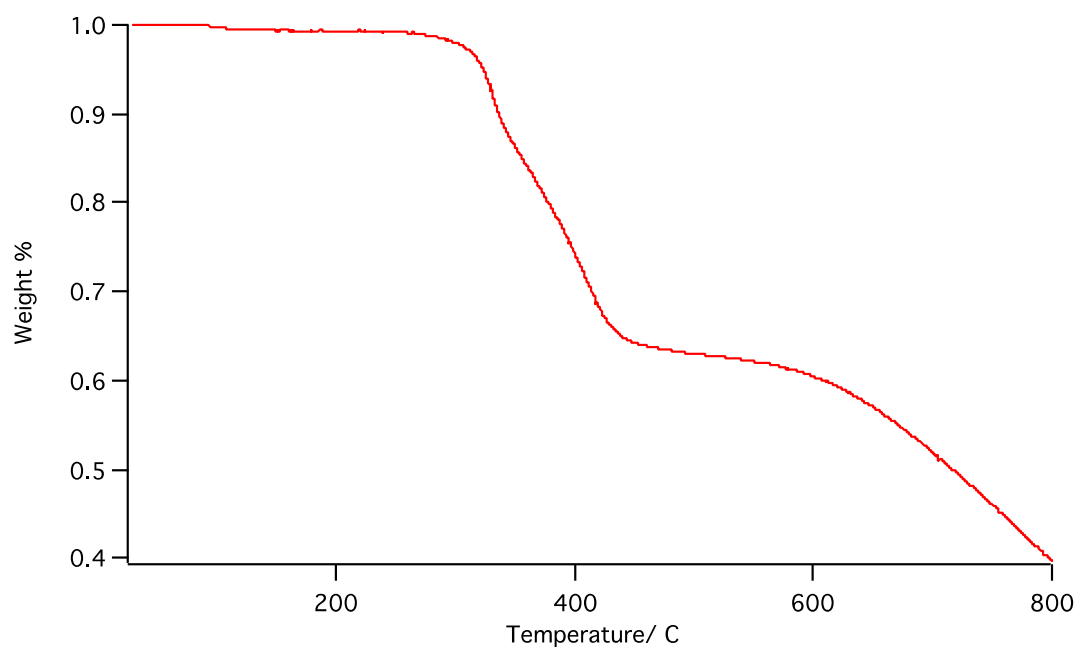


**Fig. S8** Optical gap estimation of **M2**.

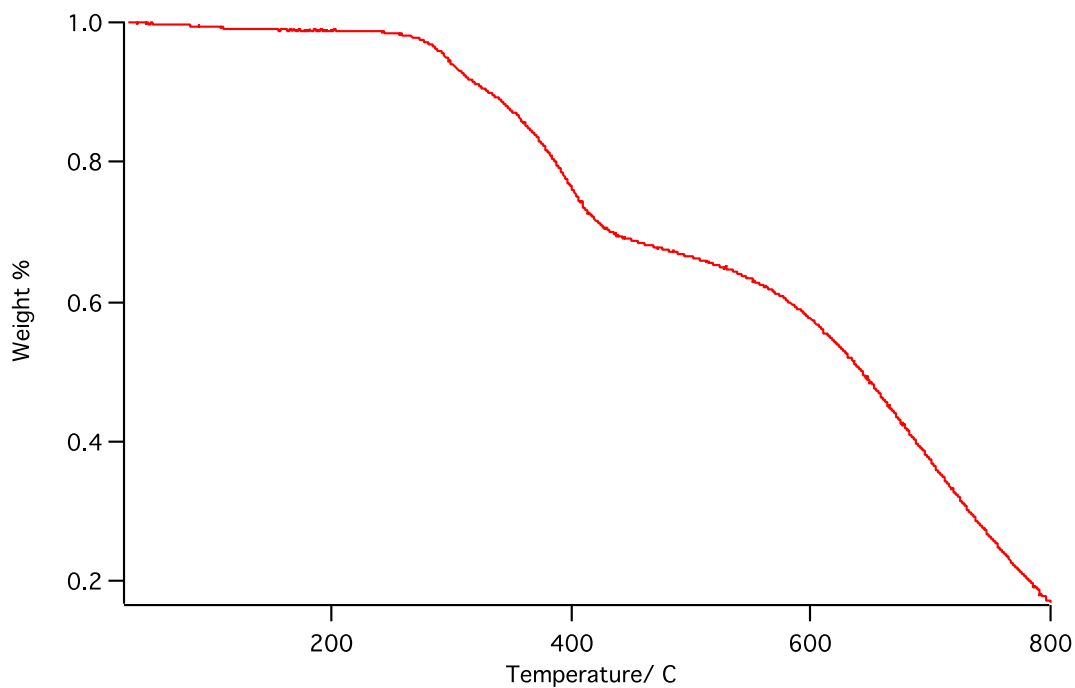


**Fig. S9** Optical gap estimation of **M3**

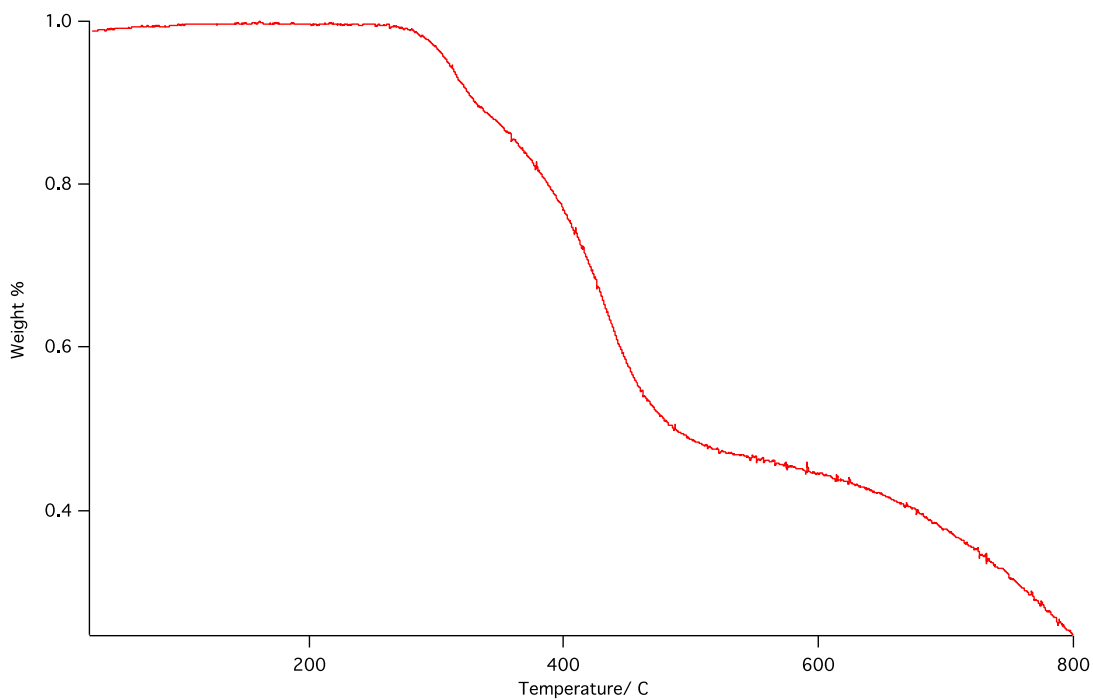
### 3. TGA



**Fig. S10** TGA trace of **M1** heated from 0-800 °C (scan rate = 10 °C/min).

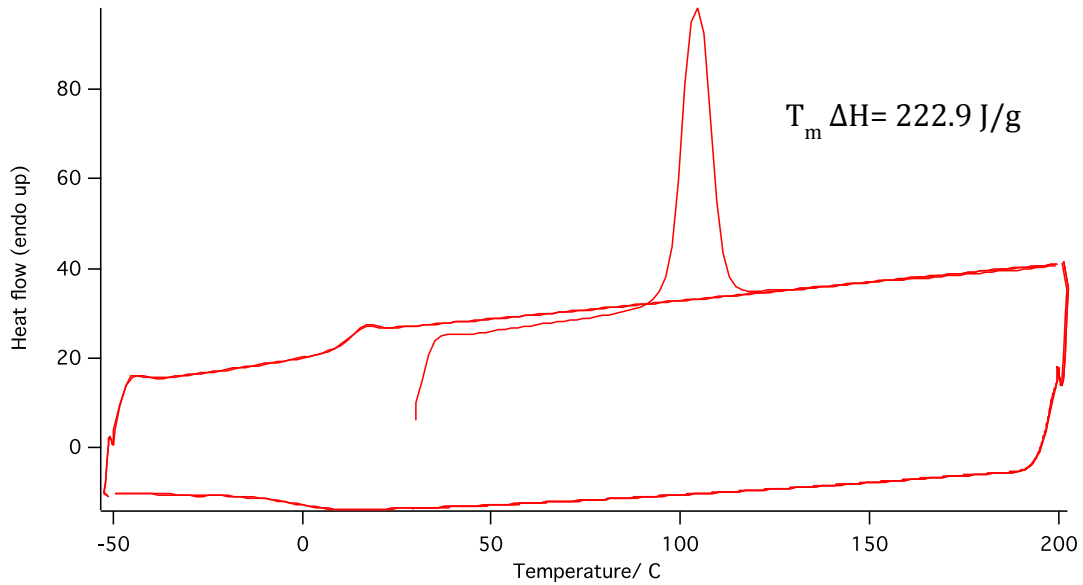


**Fig. S11** TGA trace of **M2** heated from 0-800 °C (scan rate = 10 °C/min).

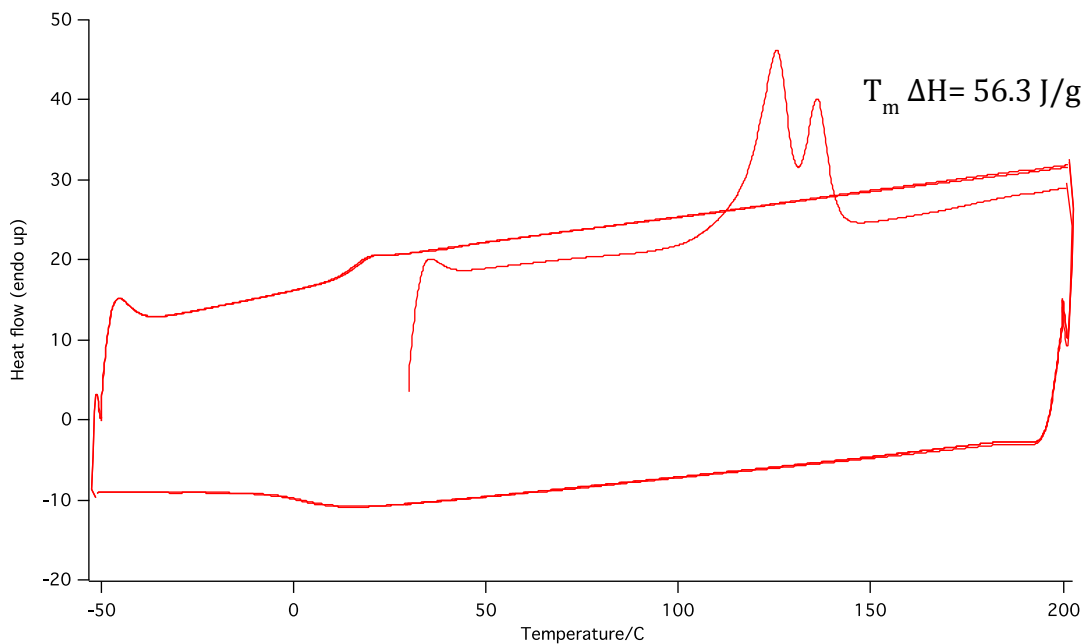


**Fig. S12** TGA trace of **M3** heated from 0-800 °C (scan rate = 10 °C/min).

#### 4. Differential Scanning Calorimetry

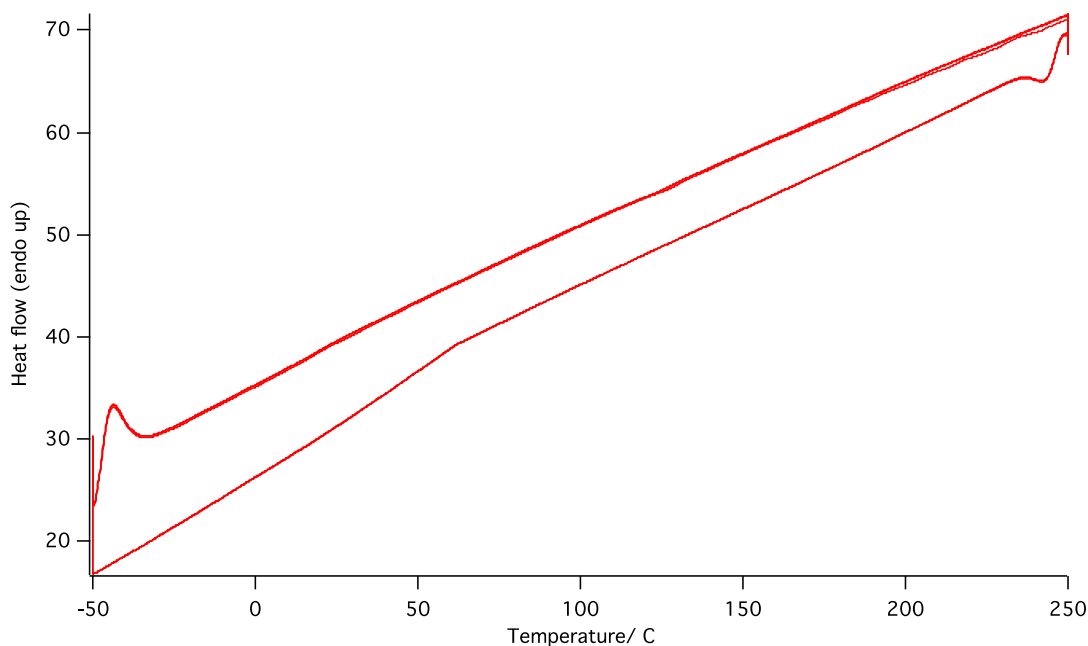


**Fig. S13** DSC trace of **M1** heated from -50 to 200 °C at a scan rate = 100 °C/min. The first cycle starts at 30 °C and at this scan rate crystallisation is not seen on cooling. The second and subsequent scans show a Tg.



**Fig. S14** DSC trace of **M2** heated from -50 to 200 °C at 100 °C/min at a scan rate = 100 °C/min. The first cycle starts at 30 °C and at this scan rate crystallisation is not seen on cooling. The second and subsequent scans show a Tg.



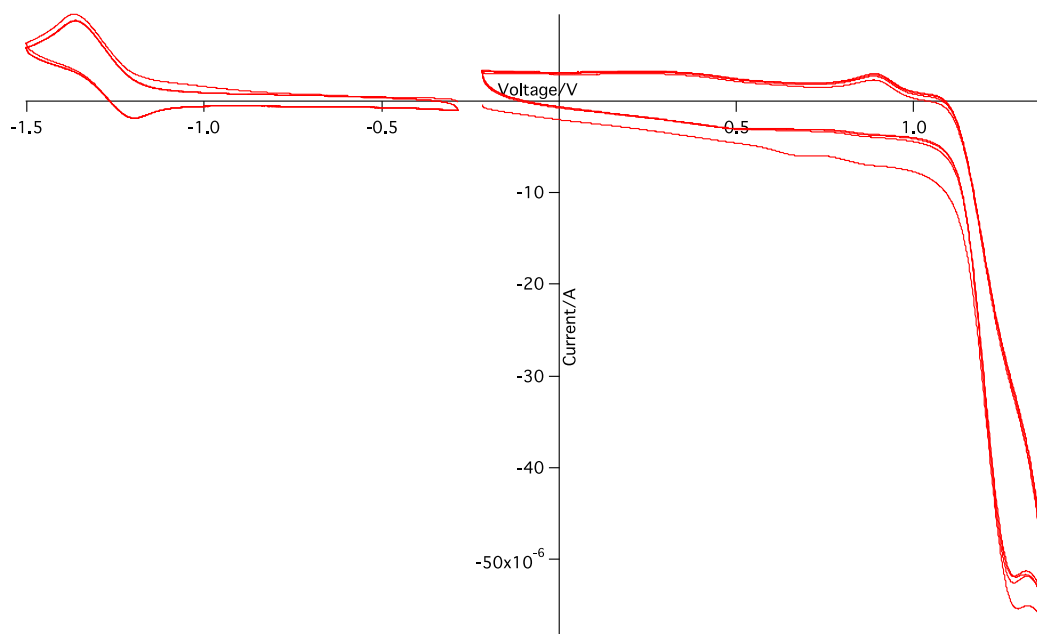


**Fig. S15** DSC trace of **M3** heated from -50 to 250 °C at 100 °C/min at a scan rate = 100 °C/min. The first cycle starts at -50 °C and at this scan rate no features are observed.

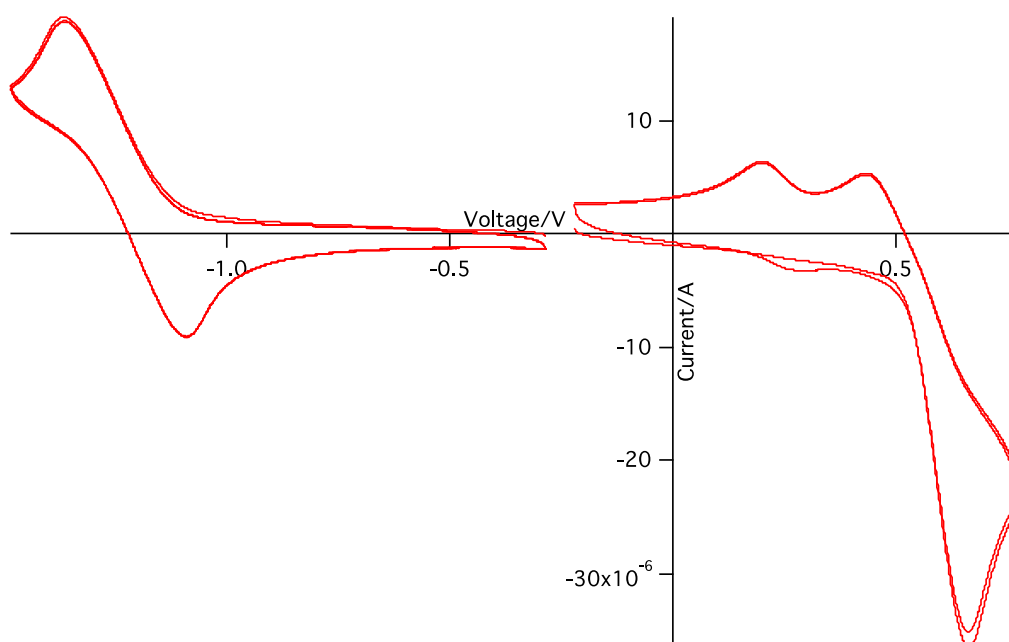
## 5. Cyclic Voltammetry

### *Electrochemical measurements*

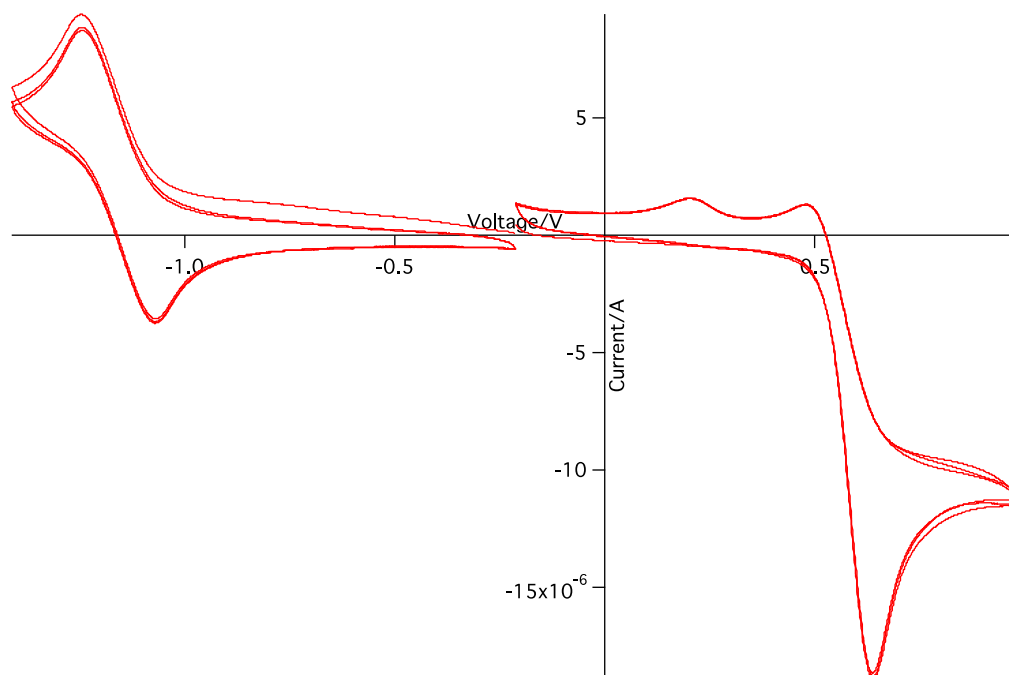
Electrochemistry was performed using an Epsilon BASi C3 Cell Stand with a glassy carbon working electrode, platinum counter electrode and silver reference electrode in 0.01 M silver nitrate in acetonitrile. Oxidations were measured in freshly distilled dichloromethane [from calcium hydride (5%, w/v) under argon] and the reductions were measured in tetrahydrofuran [dried on a LC Systems solvent purification then distilled from lithium aluminium hydride under argon]. Samples (1 mM) were dissolved with electrochemical grade tetra-*n*-butylammonium perchlorate (0.1 M, dried overnight under high vacuum at 50 °C) as the supporting electrolyte and deoxygenated for 15 minutes with argon immediately prior to the electrochemical measurements. Electrodes were polished between measurements. Oxidation and reduction potentials were calculated *versus* the ferrocene/ferrocinium couple,<sup>6</sup> which was measured on the same day under the same conditions.



**Fig. S16** Cyclic voltammograms of **M1** (scan rate = 100 mV/s).  $E_{1/2}(\text{red}) = -1.3$  V

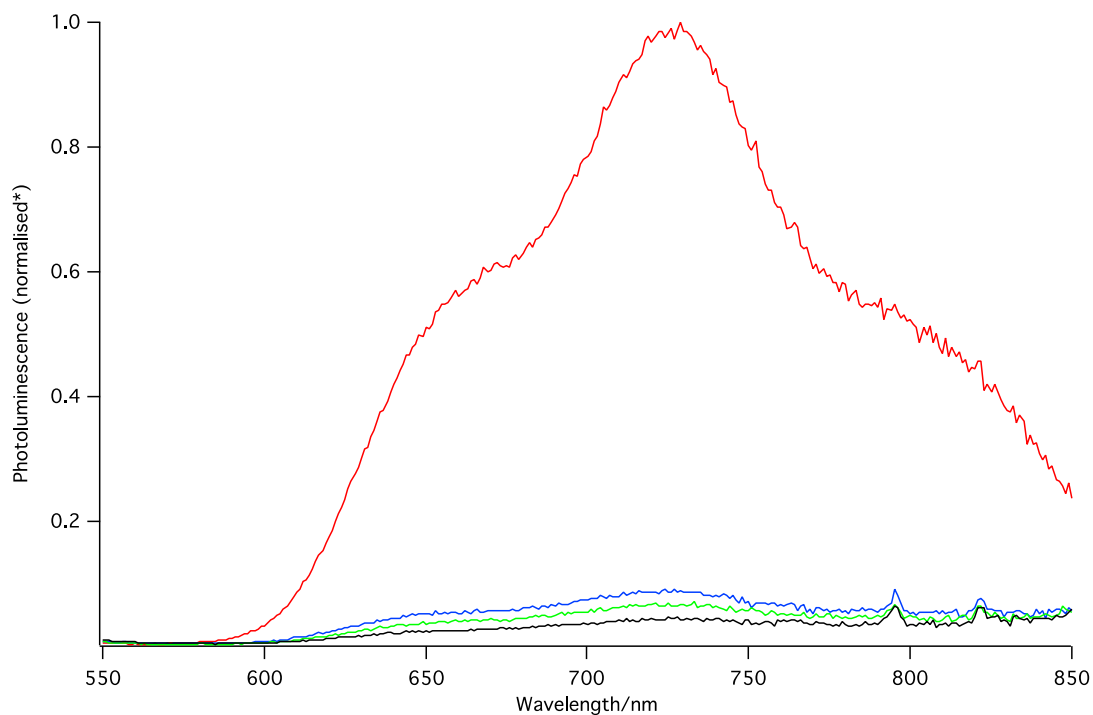


**Fig. S17** Cyclic voltammograms of **M2** (scan rate = 100 mV/s).  $E_{1/2}(\text{red}) = -1.2$  V;  $E_{1/2}(\text{ox}) = 0.5$  V



**Fig. S18** Cyclic voltammograms of **M3** (scan rate = 100 mV/s).  $E_{1/2}(\text{red}) = -1.1$  V;  $E_{1/2}(\text{ox}) = 0.6$  V

## 6. Photoluminescence Quenching



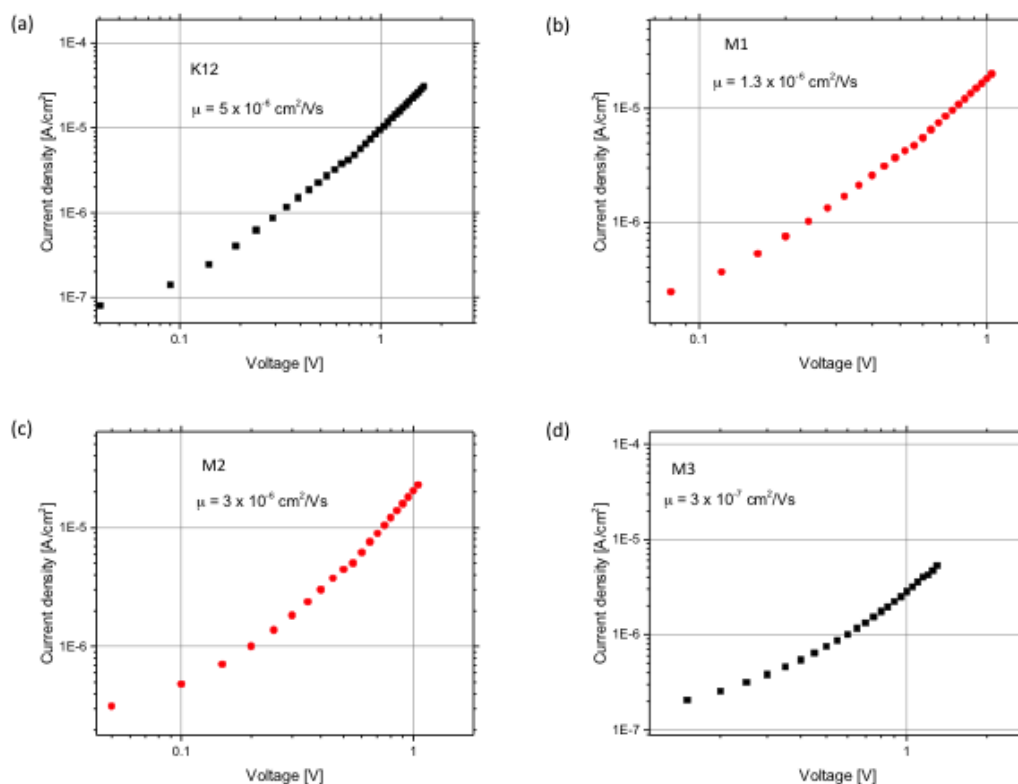
**Fig. S19** Photoluminescence spectrum of neat P3HT (red), P3HT:**M1** blend (blue), P3HT:**M2** blend (green) and P3HT:**M3** blend (black) when excited at 535 nm. All blends contain 1% w/w of acceptor. \*PL normalized with respect to neat P3HT PL maximum.

## 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:

$$J = E\sigma + \frac{9}{8}\epsilon_0\epsilon_r\mu\frac{V^2}{d^3}e\sqrt{\frac{E}{E_0}}$$

where  $\epsilon_0$ ,  $\epsilon_r$ ,  $\mu$ ,  $E$ ,  $\sigma$ ,  $d$  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.

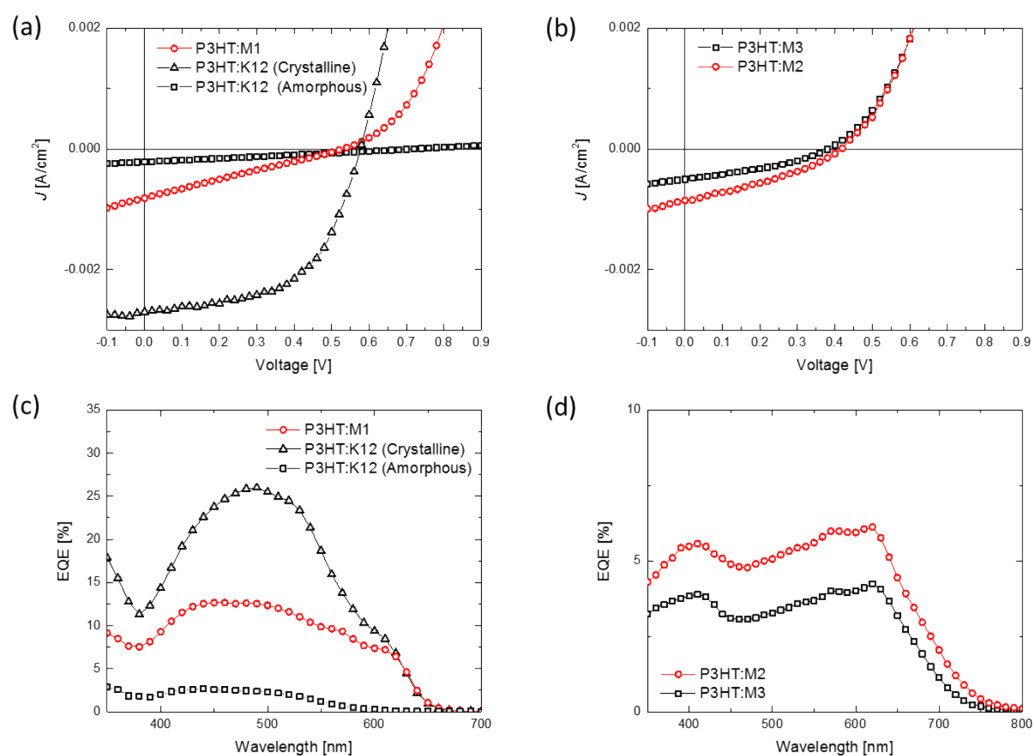


**Fig. S20** Current density-Voltage ( $J$ - $V$ ) curves of a) K12; b) M1; c) M2 and d) M3 for SCLC mobility estimation. The thickness of the active layers was  $\sim 350$  nm.

## 8. OPV results

### Experimental:

First, 15  $\Omega/\text{sq}$ . 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  $\text{cm}^2$ . The cleaned substrates were coated with a  $25 \pm 5$  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  $^\circ\text{C}$ . 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 ( $\text{O}_2 < 1$  ppm,  $\text{H}_2\text{O} < 1$  ppm) at  $\sim 20$   $^\circ\text{C}$ . 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.



**Fig. S21.** (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 <sup>-3</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
<b>K12</b>	0.22	0.70	0.25	0.04
<b>M1</b>	0.81	0.52	0.25	0.10
<b>M2</b>	0.86	0.40	0.35	0.12
<b>M3</b>	0.51	0.38	0.35	0.07
<b>K12 (cryst)</b>	2.70	0.56	0.57	0.86

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