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Supporting Information
For

A structural study of p-type A-D-A oligothiophenes: Effects of regi-oregular alkyl sidechains on annealing processes and photovoltaic performances

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S1 Materials and Methods

Unless noted, all materials were reagent grade and used as received without further purification. Anhydrous solvents were prepared by drying HPLC grade solvents using freshly activated molecular sieves. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick).

IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV–vis spectra were recorded using a Cary 50 UV–vis spectrometer, a Perkin Elmer Lambda 1050 UV–vis-NIR spectrophotometer, or an Agilent 8453 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were carried out on either a Varian 400 MHz spectrometer, an Agilent 500 MHz spectrometer, or a Varian 600 MHz spectrometer. All NMR data was referenced to the chloroform signal, unless stated otherwise, and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). MALDI–TOF mass spectrometry was performed on a Bruker microflex instrument, using chloroform as solvent and DCTB or terthiophene as the assisted matrix. ESI mass spectrometry was performed on a Thermo Scientific Q Exactive Plus Orbitrap LC-MS/MS instrument, using 50% acetonitrile/ 0.1% formic acid as the solvent. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE–440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC at a ramp rate of 10 °C min^{-1} unless otherwise noted. Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mVs^{-1}. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag^{+} pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate in acetonitrile. The solutions were deoxygenated by sparging with nitrogen prior to each scan and blanketed with nitrogen during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the materials were drop-casted on the electrode from dichloromethane solution to form a film. A ferrocene/ferrocenium redox couple was used as the internal standard.

S1.1 Device fabrication and characterization:

Organic photovoltaic devices were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. The devices were fabricated with a conventional device geometry of glass/ITO/PEDOT:PSS/active layer/Ca/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone and isopropyl alcohol for 15 minutes each and subsequently treated in UV–Ozone for 15 minutes. A thin layer (30 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 µm) was spin-coated onto the ITO surface. After being baked at 150 °C for 10 minutes, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated from a blended chloroform solution (20 mg/mL) with weight ratio of oligothiophene and $PC_{71}BM$ at 1:1 and the active layer thicknesses of all films were measured as 210–260 nm. Then, the substrates were placed in a glass Petri dish containing 1 mL THF for solvent vapour annealing (SVA) or thermally annealed, as specified in the text. After treatment, the films were transferred to a metal evaporation chamber and a bilayer cathode consisted of Ca (30 nm) capped with Al (100 nm) was deposited through a shadow mask (active area was 0.1 cm2) at approximately 1 $\times 10^{-6}$ Torr. Film thickness was determined by a Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions.

S1.2 Thin-film fabrication and GIWAXS characterization

Samples were prepared for GIWAXS by spin-coating solutions of the oligothiophenes onto PEDOT:PSS coated Si substrates using the same deposition condition and annealing conditions as for the photovoltaic devices. The Si wafers had been sonicated in acetone and isopropanol for 30 minutes each followed by 15 minutes of UV/Ozone treatment. GIWAXS experiments were performed at the Australian Synchrotron on the SAXS/WAXS beamline under ambient conditions.[1] A Pilatus 200K detector was used for 2D diffraction pattern collection. The energy of the incident beam was 11 kEV at a range of incident angles from $\theta = 0.02 - 0.20°$. The sample-to-detector range was 29.6 cm for the thermally-annealed films and 23.9 cm for all other films. Data from GIWAXS experiments was analysed using a customized version of NIKA 2D based in IgorPro.[2] Single-crystal data was gathered from the MX1 beamline at the Australian synchrotron.[3] Atomic force microscopy images were acquired using an Asylum Research Cypher scanning probe microscope operated in tapping mode.

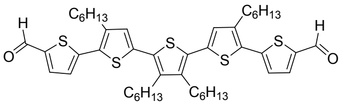
S.1.3 SCLC charge mobility measurements

The space charge limited current (SCLC) of molecular semiconductors (MN/HR/CHR (5T/6T^x)) were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of active layer sandwiched between a PEDOT:PSS coated ITO electrode and MoO_3/Ag counter-electrode as the electron-blocking contact, were fabricated as shown in Figure S10.1. From the current density as a function of voltage data, the hole mobility in the space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation, $J=9(\varepsilon_r\varepsilon_0\mu)/8 \times (V^2/d^3)$, where J is the current density, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, V_{bi} is the built-in potential resulting from workfunction difference between two electrodes, ε_r is the dielectric constant of molecular semicondurctor, ε_0 is the permittivity of vacuum, μ is the hole mobility, d is the sample thickness.

S2 Synthesis

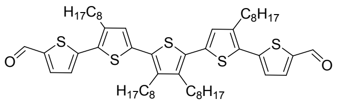
The end-group acceptor **6** was purchased from Sigma-Aldrich, while the synthesis of **7** and **8** have been previously described in the literature.[4-5] The synthesis of the other known intermediates are found in references in the main text.

S2.1 *Synthesis of 3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3a)**



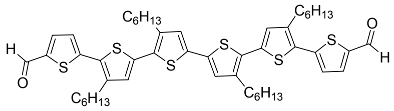
1a (0.24 g, 0.48 mmol), **2a** (0.40 g, 0.99 mmol) and P(o-tolyl)$_3$ (0.03 g, 0.1 mmol) were dissolved in THF (4 mL), and K_3PO_4 (1 mL, 2M aqueous solution), and the solution was bubbled for 30 minutes. Pd$_2$(dba)$_3$ (0.02 g, 0.02 mmol) was then added and the reaction stirred at 60 ^{o}C overnight. The organic layer was precipitated in isopropanol and then purified via column chromatography in hexanes/dichloromethane (1:1) to give **3a** as an orange solid (282 mg, 0.36 mmol, 75%).^{1}H NMR (CDCl$_3$, 600 MHz) δ 9.89 (s, 2H); 7.72 (d, *J* = 4.0 Hz, 2H); 7.23 (d, *J* = 4.0 Hz, 2H); 7.02 (s, 2H); 2.82 (t, *J* = 7.8 Hz, 4H); 2.72 (t, *J* = 8.4 Hz, 4H); 1.69 (q, *J* = 7.6 Hz, 4H); 1.61 – 1.51 (m, 4H), 1.48 – 1.39 (m, 8H), 1.37 – 1.29 (m, 16H), 0.92 – 0.87 (m, 12H). ^{13}C NMR (CDCl$_3$, 151 MHz) δ 182.53, 146.10, 142.47, 142.17, 141.04, 136.83, 136.15, 129.70, 129.40, 129.09, 125.82, 31.63, 31.47, 30.57, 30.20, 29.76, 29.57, 29.21, 28.27, 22.61, 22.57, 14.06, 14.05. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm^{-1}. MS (MALDI$^+$) calculated for $C_{46}H_{60}O_2S_5$ [M$^+$] = 804.32 , found = 804.26. Elemental analysis calculated for $C_{46}H_{60}O_2S_5$ (%).C, 68.61; H, 7.51; S, 19.91. Found, C, 68.82; H, 7.70; S, 19.72.

S2.2 *Synthesis of 3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3b)**



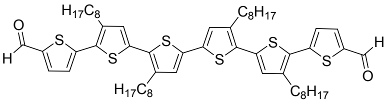
1b (0.78 g, 1.39 mmol), **3b** (1.5 g, 3.46 mmol) and P(o-tolyl)$_3$ 106 mg, 0.35 mmol) were dissolved in THF (12 mL), and K_3PO_4 (3 mL, 2M aqueous solution), and the solution was bubbled for 30 minutes. Pd$_2$(dba)$_3$ (90 mg, 0.09 mmol, 2.5%) was then added and the reaction stirred at 60 ^{o}C overnight. The organic layer was precipitated in isopropanol and then purified via column chromatography in 2:1 DCM/petroleum spirits, then 1:10 ethyl acetate:petroleum spirits to give **3b** as an orange solid (1.08 g, 1.19 mmol, 85%). ^{1}H NMR (CDCl$_3$, 600 MHz) δ 9.89 (s, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 5.9 Hz, 4H), 2.82 (t, *J* = 7.8 Hz, 4H), 2.77 (t, *J* = 7.9 Hz, 4H), 1.70 (m, 8H), 1.68 (m, 8H), 1.30 (m, 30H), 0.88 (m, 12H). ^{13}C NMR (CDCl$_3$, 151 MHz) δ 182.52, 146.09, 142.54, 142.15, 141.16, 136.82, 136.06, 135.12, 129.32, 129.14, 128.92, 126.83, 125.82, 31.88, 31.86, 30.39, 30.24, 29.76, 29.59, 29.55, 29.42, 29.41, 29.25, 29.24, 22.67, 14.11. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm^{-1}. MS (MALDI$^+$) calculated for $C_{54}H_{76}O_2S_5$ = 916.44, found = 916.363. Elemental analysis calculated for $C_{54}H_{76}O_2S_5$ (%): C, 70.69; H, 8.35; O, 3.49; S, 17.47. Found, C: 70.86; H: 8.15

S2.3 *Synthesis of 3',3'',4''',4''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(5a)**



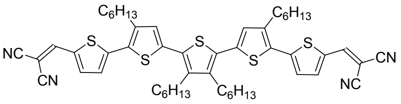
A solution of Ni(COD)$_2$ (0.35 g, 1.26 mmol), 2,2-bipyridine (0.19 g, 1.26 mmol) and COD (0.14 g, 1.26 mmol) in anhydrous DMF/toluene (5 mL, 1:1 mixture) were stirred at 80°C for 30 minutes. **4a** (0.72 g, 1.26 mmol) in anhydrous toluene (5 mL) was added in 1 portion and stirred for 4 hours. 30 mL of H_2O was added, and the organic layer was extracted in DCM (3 x 30 mL). The crude material was precipitated in isopropanol, then purified via column chromatography in DCM:hexanes (2:1) to get **5a** (0.46 g, 0.52 mmol, 86 %) as a red solid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.84 (s, 2H); 7.67 (d, *J* = 4.0 Hz, 2H); 7.20 (d, *J* = 5.0 Hz, 2H); 6.97 (d, *J* = 3.8 Hz, 2H); 2.77 (t, *J* = 7.8 Hz, 4H); 2.77 (t, *J* = 8.0 Hz, 4H); 1.64 (qq, *J* = 7.2 Hz; 8H); 1.45-1.25 (m, 25H); 0.85 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 182.54, 146.09, 142.55, 142.16, 141.17, 136.84, 136.06, 135.13, 129.33, 129.13, 128.94, 126.84, 125.84, 31.64, 30.37, 30.21, 29.76, 29.59, 29.22, 22.59, 22.58, 14.08, 14.06. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm^{-1}. HRMS (ESI-LTQ-FTICP) calculated for $C_{50}H_{62}O_2S_6$ = 886.3069, found = 886.3101 m/z. Elemental analysis calculated For $C_{50}H_{62}O_2S_6$ (%): C, 67.67; H, 7.04. Found C, 67.66; H, 7.07.

S2.4 *Synthesis of 3',3'',4''',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(5b)**



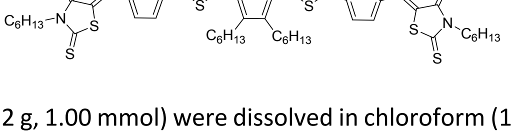
A solution of Ni(COD)$_2$ (0.20 g, 0.72 mmol), 2,2-bipyridine (0.11 g, 0.72 mmol) and COD (78 mg, 0.72 mmol) in anhydrous DMF/toluene (2 mL, 1:1 mixture) were stirred at 80 C for 30 minutes. **4b** (0.3 g, 0.48 mmol) in anhydrous toluene (2 mL) was added in 1 portion and stirred for 4 hours. 30 mL of H_2O was added, and the organic layer was extracted in DCM (3 x 30 mL). The crude material was precipitated in isopropanol, then purified via column chromatography (2:1 DCM:hexanes) to yield the product **5b** as a red solid (0.18 g, 0.18 mmol, 75%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.89 (s, 2H), 7.71 (d, J= 4.0 Hz, 2H), 7.24 (d, J= 4.0 Hz, 2H), 7.01 (d, J= 5.9 Hz, 4H), 2.82 (t, J= 7.8 Hz, 4H), 2.77 (t, J= 7.8 Hz, 4H), 1.68 (m, 8H), 1.42 (m, 8H), 1.29 (m, 32H), 0.88 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 182.52, 146.09, 142.54, 142.15, 141.16, 136.82, 136.06, 135.12, 129.32, 129.14, 128.92, 126.83, 125.82, 31.88, 31.86, 30.39, 30.24, 29.76, 29.59, 29.55, 29.42, 29.41, 29.25, 29.24, 22.67, 14.11. IR (neat): ν = 2952, 2852, 1665, 1436, 1228, 1059 cm^{-1}. MS (MALDI^{+}) calculated for $C_{58}H_{78}O_2S_6$ = 998.43, found = 998.49 m/z. Elemental analysis calculated For $C_{58}H_{78}O_2S_6$ (%): C, 69.69; H, 7.86; O, 3.20; S, 19.25. Found C, 69.70; H: 7.68.

S2.5 *Synthesis of 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T^{6})**



3a (0.1 g, 0.12 mmol) and **6** (0.08 g, 1.24 mmol), were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred at room temperature for 3 hours. The reaction was stopped, and the crude material precipitated in isopropanol before being purified by column chromatography in toluene followed by size exclusion chromatography in toluene to get **MN5T^{6}** (80 mg, 0.08 mmol, 74%) as a green solid. ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.75 (d, *J* = 0.4 Hz, 2H), 7.71 (d, *J* = 4.2 Hz, 2H), 7.26 (d, *J* = 4.2 Hz, 2H), 7.04 (s, 2H), 2.86 – 2.82 (t, *J* = 8.4 Hz, 4H), 2.76 – 2.71 (m, 4H), 1.70 (qq, *J* = 7.5 Hz, 4H), 1.61 – 1.54 (m, 4H), 1.45 (m, 8H), 1.39 – 1.29 (m, 16H), 0.94 – 0.86 (m, 12H). ^{13}C NMR (CDCl$_3$,151 MHz) δ 149.76, 148.25, 143.91, 141.58, 139.01, 137.38, 133.93, 129.87, 129.42, 128.96, 126.04, 114.35, 113.51, 75.86, 31.61, 31.45, 30.48, 30.14, 30.10, 29.55, 29.19, 28.32, 22.60, 22.55, 14.06, 14.05. IR (neat): ν = 2956, 2926, 2858, 2215, 1717, 1582, 1528, 1420, 1387, 1359, 1127, 1065. HRMS (ESI-LTQ-FTICP) [M^{+}] calculated for $C_{52}H_{60}N_4S_5$ = 900.34, found = 900.3447 m/z. Elemental analysis calculated for $C_{52}H_{60}N_4S_5$ (%):C, 69.29; H, 6.71; N, 6.22; S, 17.78. Found, C, 69.49; H, 6.76; N, 6.13; S, 17.66.

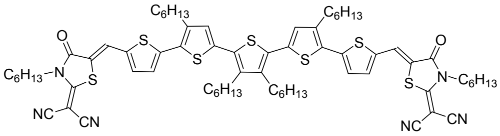
S2.6 *Synthesis of (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR5T^{6})**



3a (0.08 g, 0.10 mmol) and **7** (0.22 g, 1.00 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) was added and the reaction stirred overnight. The crude material precipitated in isopropanol before being purified by column chromatography in a hexane/dichloromethane mixture (2:1), followed by size exclusion chromatography (SX1 beads) in toluene to get **HR5T^{6}** as a green solid (75 mg, 0.07 mmol, 67%).^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.85 (s, 2H); 7.36 (d, *J* = 4.0 Hz, 2H); 7.22 (d *J* = 4.0 Hz, 2H); 7.02 (s, 2H); 4.11 (t, *J* = 7.6 Hz, 4H); 2.83 (t, *J* = 8.0 Hz, 4H); 2.74 (t, *J* = 8.2 Hz, 4H); 1.71 (pentet; *J* = 6.8 Hz, 8H); 1.65-1.55 (m, 4H); 1.52-1.42 (m, 8H); 1.42-1.26 (m, 28H); 0.99-0.80 (m, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 192.16, 167.51, 144.32, 141.89, 140.98, 137.08, 135.84, 134.67, 129.77, 129.57, 129.08, 126.54, 124.99, 120.25, 44.88, 31.69, 31.48, 31.33, 30.55, 30.29, 29.83, 29.59, 29.28, 28.30, 26.93, 26.44, 22.64, 22.49, 14.11, 12.99. IR (neat): ν = 2928, 2855, 2217, 1568, 1412, 1354, 1267, 1068 cm^{-1}. HRMS (ESI-LTQ-FTICP) [M^{+}] calculated for $C_{64}H_{86}N_2O_2S_9$ = 1202.47, found = 1202.4161 m/z.

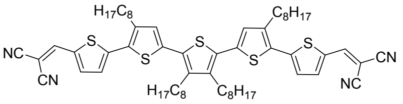
Elemental analysis calculated for $C_{64}H_{86}N_2O_2S_9$ (%): C, 63.85; H, 7.20; N, 2.33; S, 23.97. found C, 63.68; H, 7.20; N, 2.11; S, 24.11.

S2.7 *Synthesis of 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T^6)**



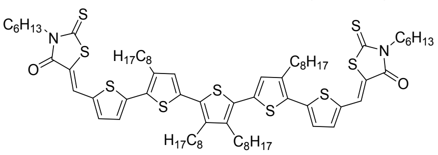
3a (0.1 g, 0.12 mmol) and **8** (0.31 g, 1.24 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred at room temperature for three hours. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in toluene and size exclusion chromatography (SX1 beads) in toluene to get **CHR5T^6** (100 mg, 0.08 mmol, 64%) as a green solid. ^{1}H NMR ($CDCl_3$, 600 MHz) *δ* 8.00 (s, 2H), 7.41 (d, *J* = 4.1 Hz, 2H), 7.22 (d, *J* = 4.0 Hz, 2H), 7.01 (s, 2H), 4.18 (t, *J* = 7.8 Hz, 4H), 2.80 (t, *J* = 8.2 Hz, 4H), 2.72 (t, *J* = 8.2 Hz, 4H), 1.78 – 1.67 (m, 8H), 1.58 (m, 4H), 1.52 – 1.29 (m, 36H), 0.96 – 0.86 (m, 18H). ^{13}C NMR ($CDCl_3$,151 MHz) *δ* 165.92, 165.28, 145.27, 142.61, 141.19, 136.42, 135.68, 135.62, 129.81, 129.09, 129.00, 128.34, 126.65, 113.33, 113.11, 112.27, 55.83, 45.31, 31.63, 31.45, 31.22, 30.42, 30.19, 30.00, 29.57, 29.24, 28.73, 28.36, 25.60, 22.62, 22.55, 22.41, 14.10, 13.92. IR (neat): ν = 2954, 2927, 2856, 2216, 1568, 1415, 1353, 1267, 1066, 792. HRMS (ESI-LTQ-FTICP) [M$^+$] calculated for $C_{70}H_{86}N_6O_2S_7$ = 1266.45, found = 1266.4853 m/z. Elemental analysis calculated For $C_{70}H_{86}N_6O_2S_7$ (%): C, 66.31; H, 6.84; N, 6.63; S, 17.70. Found, C, 66.53; H, 6.84; N, 6.66; S, 17.51.

S2.8 *Synthesis of 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T^8)**



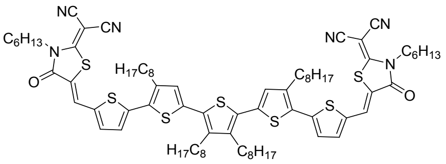
3b (0.15g, 0.15 mmol) and **6** (99 mg, 1.5 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in 2:1 DCM:hexanes and and size exclusion chromatography (SX1 beads) in toluene, then precipitated in methanol to yield **MN5T^8** as a dark purple solid (0.1 g, 0.14 mmol, 94%). ^{1}H NMR ($CDCl_3$, 600 MHz) *δ* 7.76 (s, 2H), 7.72 (d, *J* = 4.2 Hz, 2H), 7.28 (d, *J* = 4.2 Hz, 2H), 7.05 (s, 2H), 2.87 – 2.82 (t, *J* = 8.4 Hz, 4H), 2.76 – 2.71 (m, 4H), 1.64-1.56 (pentet, *J* = 7.5 Hz, 4H), 1.50 – 1.42 (m, 8H), 1.38 – 1.22 (m, 32H), 0.94 – 0.86 (m, 12H). ^{13}C NMR ($CDCl_3$,151 MHz) δ 149.77, 148.27, 143.92, 141.59, 138.97, 137.38, 133.94, 129.87, 129.46, 128.96, 126.08, 114.36, 113.51, 77.31, 76.99, 76.68, 75.90, 31.87, 31.84, 30.53, 30.14, 29.88, 29.52, 29.41, 29.26, 29.21, 28.31, 22.68, 22.66, 14.11. IR (neat): ν = 2952, 2925, 2854, 2218, 1567, 1416, 1067 cm^{-}1. MS (MALDI$^+$) calculated for $C_{60}H_{76}N_4S_5$ = 1012.47, found = 1012.354 m/z. Elemental analysis calculated for $C_{60}H_{76}N_4S_5$: C, 71.10; H, 7.56; N, 5.53; S, 15.82. Found: C, 70.99; H, 7.67; N, 5.34; S, 15.72

S2.9 *Synthesis of (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR5T^8)**



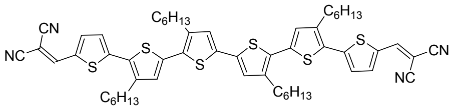
3b (0.15 g, 0.16 mmol) and **7** (0.35 g, 1.60 mmol) were dissolved in chloroform (5 mL). DBU (1 drop) was added and the reaction stirred for 5 hours in the dark. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in a petroleum spirits/DCM mixture (1:2), followed by a size exclusion column (SX1 beads) in toluene to yield **HR5T^8** as a green solid (110 mg, 0.84 mmol, 56%). ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.85 (s, 2H), 7.37 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.02 (s, 2H), 4.13 (t, J = 7.6 Hz, 4H), 2.83 (t, J = 8.0 Hz, 4H), 2.74 (t, J = 8.2 Hz, 4H), 1.75-1.65 (p, J = 6.8 Hz, 8H), 1.65 – 1.58 (m, 4H), 1.48 – 1.42 (m, 8H), 1.40 – 1.25 (m, 44H), 0.99 – 0.80 (m, 18H). ^{13}C NMR (CDCl3,151 MHz) δ 192.15, 167.52, 144.31, 141.89, 140.98, 137.09, 135.84, 134.64, 129.77, 129.58, 129.09, 126.56, 124.99, 120.25, 44.87, 31.89, 31.33, 30.57, 30.32, 29.91, 29.81, 29.61, 29.48, 29.29, 29.26, 28.29, 26.94, 26.44, 22.69, 22.49, 14.12, 13.99. IR (neat): ν = 2954, 2924, 2855, 1698, 1578, 1424, 1329 cm^{-1}. MS (MALDI$^+$) calculated for $C_{72}H_{102}N_2O_2S_9$ = 1314.54, found = 1314.322 m/z. Elemental analysis calculated for $C_{72}H_{102}N_2O_2S_9$: C, 65.70; H, 7.81; N, 2.13; O, 2.43; S, 21.93. Found: C, 65.85; H, 7.99; N, 2.04; S, 21.78

S2.10 *Synthesis of 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T^8)**



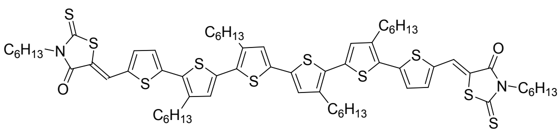
3b (0.15 g, 0.16 mmol) and **8** (0.4 g, 1.60 mmol) were dissolved in chloroform (5 mL). DBU (1 drop) was added and the reaction stirred for 3 hours in the dark. The crude material was precipitated in isopropanol before being purified by column chromatography in toluene, followed by a size exclusion column (SX1 beads) in toluene to yield **CHR5T^8** as a green solid (0.15 g, 0.11 mmol, 68%). ^{1}H NMR (CDCl$_3$, 600 MHz) δ 8.03 (s, 2H), 7.44 (d, J = 4.0 Hz, 2H), 7.26 (d, *J* = 4.0 Hz, 2H), 7.03, (d, J = 4.0 Hz, 2H), 4.23 (t, J = 7.6 Hz, 4H), 2.83 (t, J = 8.0 Hz, 4H), 2.75 (t, J = 8.2 Hz, 4H), 1.74 (m, 4H), 1.69 (m, 4H), 1.59 (m, 4H), 1.44 (m, 16H), 1.35-1.20 (m, 38H), 0.88 (m, 18H). ^{13}C NMR (CDCl$_3$,151 MHz) δ 166.25, 165.61, 145.58, 142.86, 141.46, 136.73, 136.00, 135.91, 130.06, 129.39, 128.73, 127.06, 122.63, 113.61, 113.38, 112.54, 56.12, 45.60, 32.13, 31.49, 30.79, 30.50, 30.15, 29.78, 29.67, 29.52, 29.45, 29.01, 28.55, 25.86, 22.93, 22.66, 14.36. IR (neat): ν = 2955, 2925, 2855, 2217, 1697, 1581, 1541, 1421, 1387, 1357, 1131, 764, 750 cm^{-1}. MS (MALDI$^+$) calculated for $C_{78}H_{102}N_6O_2S_7$ = 1378.61, found = 1378.41 m/z. Elemental analysis calculated for $C_{78}H_{102}N_6O_2S_7$: C, 67.88; H, 7.45; N, 6.09; O, 2.32; S, 16.26. Found: C, 67.54; H, 7.47; N, 5.96; S, 16.32

S2.11 *Synthesis of 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^6)**



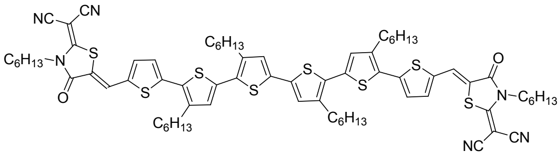
5a (0.1 g, 0.11 mmol) and **6** (0.07 g, 1.13 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred overnight. The crude material was precipitated in isopropanol before being purified by column chromatography in chloroform, followed by a size exclusion column (SX1 beads) in toluene to yield **MN6T^6** as a green solid (80 mg, 0.08 mmol, 73 %).^{1}H NMR (CDCl$_3$, 600 MHz) *δ* 7.25 (d, *J* = 3.5 Hz, 2H), 7.20 (s, 2H), 6.99 (m, 4H), 6.96 (s, 2H), 2.68 (m, 8H), 1.65-1.50 (m, 8H), 1.38 – 1.25 (m, 8H), 1.22-1.10 (m, 17H), 0.75 (m, 12H). ^{13}C NMR (CDCl$_3$,151 MHz) *δ* 148.69, 148.54, 147.64, 143.74, 141.65, 138.48, 138.35, 137.34, 135.54, 133.72, 125.81, 125.56, 114.02, 113.34, 75.89, 31.56, 31.54, 30.24, 30.09, 30.04, 29.74, 29.32, 29.18, 22.52, 22.50, 13.89, 13.74. IR (neat): ν = 2926, 2854, 1688, 1579, 1420, 1332 cm^{-1}. HRMS (ESI-LTQ-FTICP) [M$^+$] calculated for $C_{56}H_{62}N_4S_6$ = 1982.33, found = 982.3603 m/z. Elemental analysis calculated for $C_{56}H_{62}N_4S_6$ (%): C, 68.39; H, 6.35; N, 5.70; S, 19.56. Found, C, 68.27; H, 6.32; N, 5.50

S2.12 *Synthesis of (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T^6)**



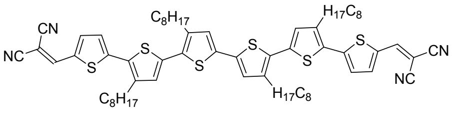
5a (0.2 g, 0.23 mmol) and **7** (0.49 g, 2.25 mmol) were dissolved in chloroform (20 mL), DBU (2 drops) were added and the reaction stirred overnight. The crude material was precipitated in isopropanol before being passed through a silica plug in chloroform, then purified multiple times by a size exclusion chromatography (SX1) in toluene to get a green solid which was recrystallized from 1,4-dioxane to get **HR6T^6** as a green solid (200 mg, 1.58 mmol, 70 %). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.84 (s, 2H); 7.37 (d, *J* = 4.1 Hz, 2H); 7.22 (d, *J* = 4.0 Hz, 2H); 7.01 (d, *J* = 6.9 Hz, 4H); 4.11 (t, *J* = 7.8 Hz, 4H); 2.82 (t, *J* = 8.1 Hz, 4H); 2.77 (t, *J* = 8.1 Hz, 4H); 1.75-1.66 (m, 12H); 1.50-1.40 (m, 8H); 1.40-1.30 (m, 30H); 0.95-0.85 (m, 18H). ^{13}C NMR ($CDCl_3$,125 MHz) δ 192.18, 167.51, 144.33, 141.96, 141.08, 137.08, 135.76, 135.08, 134.68, 129.52, 129.25, 128.93, 126.83, 126.54, 124.99, 120.24, 44.88, 31.70, 31.67, 31.34, 30.35, 30.30, 29.84, 29.70, 29.65, 29.31, 29.26, 26.95, 26.45, 22.66, 22.62, 22.51, 14.13, 14.00. IR (neat): ν = 2955, 2926, 2855, 1696, 1578, 1412, 1329, 1182, 1140 cm^{-1}. HRMS (ESI-LTQ-FTICP) [M$^+$] calculated for $C_{68}H_{88}N_2O_2S_{10}$ = 1984.41, found =1284.4031 m/z. Elemental analysis calculated for $C_{68}H_{88}N_2O_2S_{10}$ (%): C, 63.50; H, 6.90; N, 2.18; O, 2.49; S, 24.93. Found, 63.88; H, 6.94; N, 2.06; S, 24.75.

S2.13 *Synthesis of 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T^6)**



5a (0.22 g, 0.25 mmol) and **8** (0.62 g, 0.47 mmol) were dissolved in chloroform (20 mL). DBU (4 drops) was added and the reaction stirred at room temperature for 3 hours. The crude material was precipitated in isopropanol then purified with silica gel chromatography in toluene to get **CHR6T^6** (240 mg, 0.36 mmol, 80%) as a green solid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.02 (s, 2H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 7.01 (d, *J* = 3.0 Hz, 4H), 4.22 (t, *J* = 7.8 Hz, 4H), 2.83 (t, *J* = 7.8 Hz, 4H), 2.76 (t, *J* = 4.0 Hz, 2H), 1.78 – 1.66 (m, 12H), 1.48 – 1.39 (m, 12H), 1.38) δ 165.96, 165.26, 145.26, 142.64, 141.35, 136.48, 135.86, 135.42, 135.33, 129.22, 129.04, 128.99, 128.29, 126.88, 126.83, 113.58, 113.02, 112.18, 56.02, 45.37, 31.59, 31.57, 31.18, 30.26, 30.20, 29.89, 29.64, 29.15, 28.71, 25.59, 22.52, 22.48, 22.33, 13.96, 13.94, 13.78. IR (neat): ν = 2955, 2927, 2856, 2217, 1695, 1576, 1541, 1412, 1386, 1356, 1168, 1133, 1065, 842 cm^{-1}. HRMS (ESI-LTQ-FTICP) [M+H$^+$] calculated for $C_{74}H_{88}N_6O_2S_8$ = 1341.48, found =1349.4693 m/z. Elemental analysis calculated for $C_{74}H_{88}N_6O_2S_8$ (%): C, 65.83; H, 6.57; N, 6.22; O, 2.37; S, 19.00. Found, C, 65.80; H, 6.75; N, 6.31.

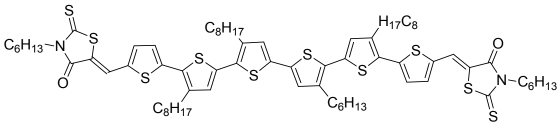
S2.14 *Synthesis of 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^8)**



5b (90 mg, 0.9 mmol) and **6** (59 mg, 9 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The solvent was removed and the crude solid purified via precipitation in isopropanol and silica coloumn chromatography in chloroform, then size exclusion column in toluene to get **MN6T^8** as a green solid (90 mg, 0.08 mmol, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.74 (d, 2H, J = 4.2 Hz), 7.30 (d, J = 4.2 Hz, 2H), 7.05 (s, 4H), 2.88 (t, J = 7.8 Hz, 4H), 2.81 (t, J = 7.8 Hz, 4H), 1.74 (m, 8H), 1.46 (m, 8H), 1.38 – 1.29 (m, 32H), 0.88, (m, 12H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 149.75, 148.33, 143.98, 141.69, 139.00, 137.41, 135.42, 133.89, 129.24, 129.05, 128.79, 127.06, 126.03, 114.37, 113.52, 75.81, 31.86, 31.83, 30.30, 30.14, 30.11, 29.65, 29.52, 29.40, 29.23, 29.20, 22.66, 14.10. IR (neat): ν = 2952, 2925, 2852, 1698, 1587, 1422, 1260, 1275, 764 cm^{-1}. MS (MALDI$^+$) calculated for $C_{64}H_{78}N_4S_6$ = 1094.46, found =

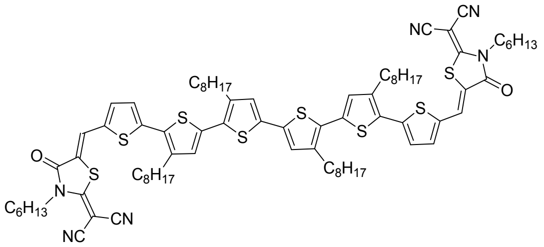
1094.759 m/z. Elemental analysis calculated for $C_{64}H_{78}N_4S_6$ (%): C, 68.93; H, 7.48; N, 4.76; S, 18.83. Found: C, 68.61; H, 7.03; N, 4.47; S, 18.65

S2.15 *Synthesis of (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T^8)**



5b (0.16g, 0.16 mmol) and **7** (347 mg, 1.6 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The solvent was removed and the crude precipitated in isopropanol then purified via silica gel column chromatography in chloroform and size-exclusion chromatography in toluene, then precipitated in methanol to yield **HR6T^8** as a dark purple solid (170 mg, 0.12 mmol, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.37 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.01 (d, J = 7.1 Hz, 4H), 4.13 (dd, J = 8.8, 6.5 Hz, 4H), 2.80 (t, J = 7.8 Hz, 4H), 2.78 (t, J = 7.8 Hz, 4H), 1.70 (m, 12H), 1.42 (m, 8H), 1.36 – 1.29 (m, 44H), 0.88 (m, 18H). ^{13}C NMR (101MHz, $CDCl_3$) δ 149.77, 148.34, 143.99, 141.69, 139.03, 137.41, 135.41, 133.88, 129.24, 129.06, 128.79, 127.06, 126.03, 114.39, 113.53, 75.78, 31.87, 31.84, 30.31, 30.14, 29.66, 29.53, 29.41, 29.24, 29.21, 22.66, 14.11. IR (neat): ν = 2952, 2925, 2852, 1698, 1587, 1422, 1275, 1260, 764 cm^{-1}. MS (MALDI$^+$) calculated for $C_{76}H_{104}O_2N_2S_{10}$ = 1094.46, found = 1396.504 m/z. Elemental analysis calculated for $C_{76}H_{104}O_2N_2S_{10}$ (%): C, 65.28; H, 7.50; N, 2.00; O, 2.29; S, 22.93. Found: C, 65.32; H, 7.71; N, 1.98; S, 23.05.

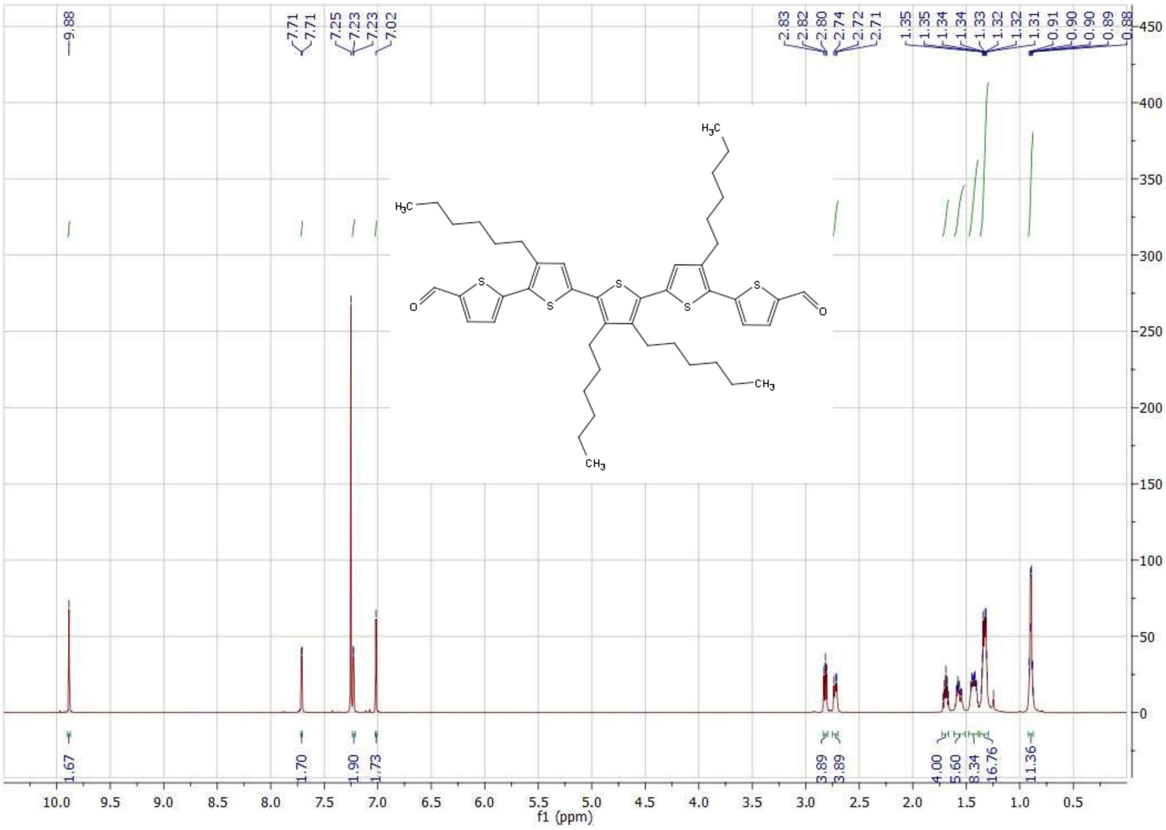
S2.16 *Synthesis of 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T^8)**

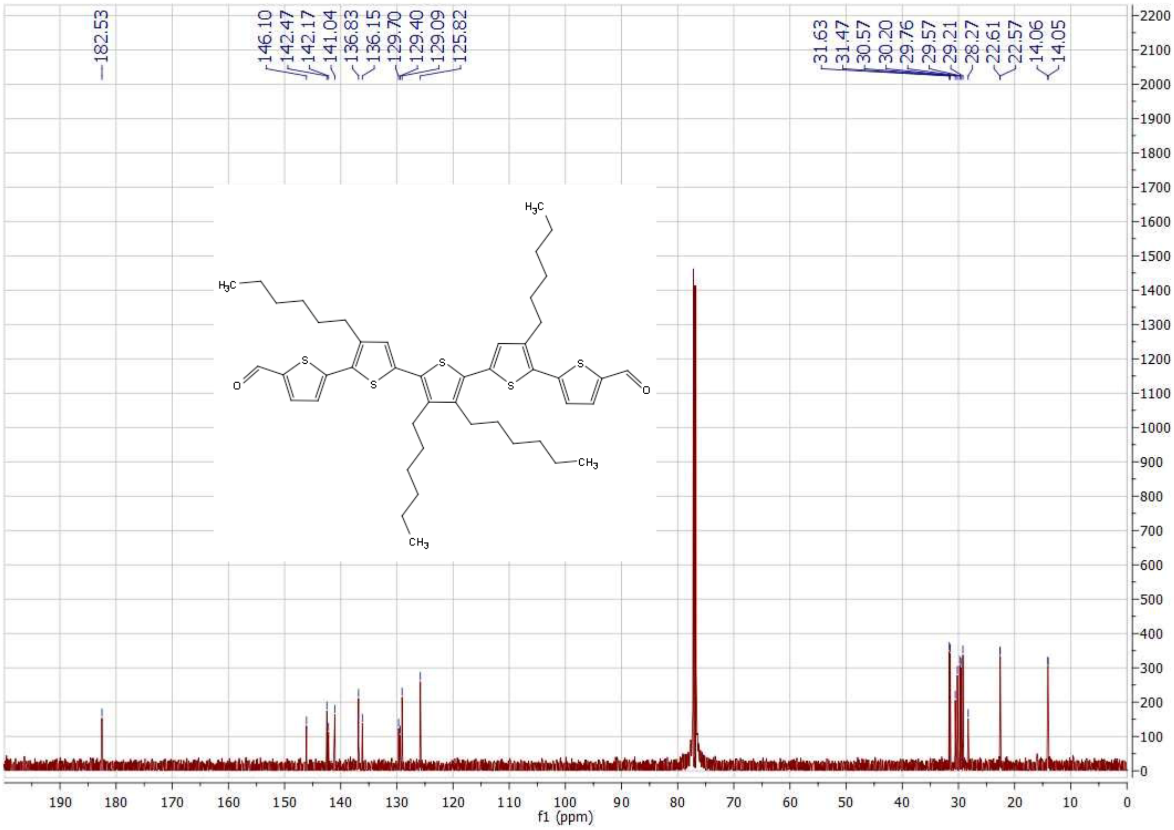


5b (0.16g, 0.16 mmol) and **8** (0.40 g, 1.6 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at 60°C in the dark for 2 hours. The solvent was removed and the crude solid purified via silica gel column chromatography in chloroform and size-exclusion chromatography in toluene, then precipitated in methanol to yield **CHR6T^8** as a dark purple solid (131 mg, 0.09 mmol, 56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 s, 2H), 7.45 (d, J = 4.0 Hz, 2H), 7.26 (d, J = 4.0 Hz, 2H), 7.03 (m, 4H), 4.24 (t, J = 7.9 Hz, 4H), 2.85 – 2.76 (m, 8H), 1.75 (m, 12H), 1.36-1.25 (m, 54 H) 0,88 (m, 18H). ^{13}C NMR (151MHz, $CDCl_3$) δ 165.98, 165.36, 145.34, 142.65, 141.30, 136.41, 135.71, 135.66, 135.21, 129.15, 128.98, 128.95, 128.46, 126.89, 126.78, 113.32, 113.13, 112.28, 55.84, 45.33, 31.86, 31.84, 31.22, 30.32, 30.30, 30.27, 30.23, 29.89, 29.68, 29.62, 29.52, 29.48, 29.44, 29.40, 29.36, 29.24, 29.22, 29.18, 29.16, 28.74, 25.60, 22.66, 22.64, 22.40, 14.10, 13.91. IR (neat): ν = 2954, 2923, 2853, 2217, 1693, 1575, 1540, 1421, 1386, 1355, 1336, 1132, 1062, 764, 750 cm^{-1}. MS (MALDI$^+$) calculated for $C_{82}H_{104}N_6O_2S_6$ = 1460.60, found =1460.996 m/z. Elemental analysis calculated for $C_{82}H_{104}N_6O_2S_6$ (%): C, 66.35; H, 7.17; N, 4.75; O, 3.19; S, 18.54. Found: C, 65.97; H, 7.51; N, 4.95; S, 18.31.

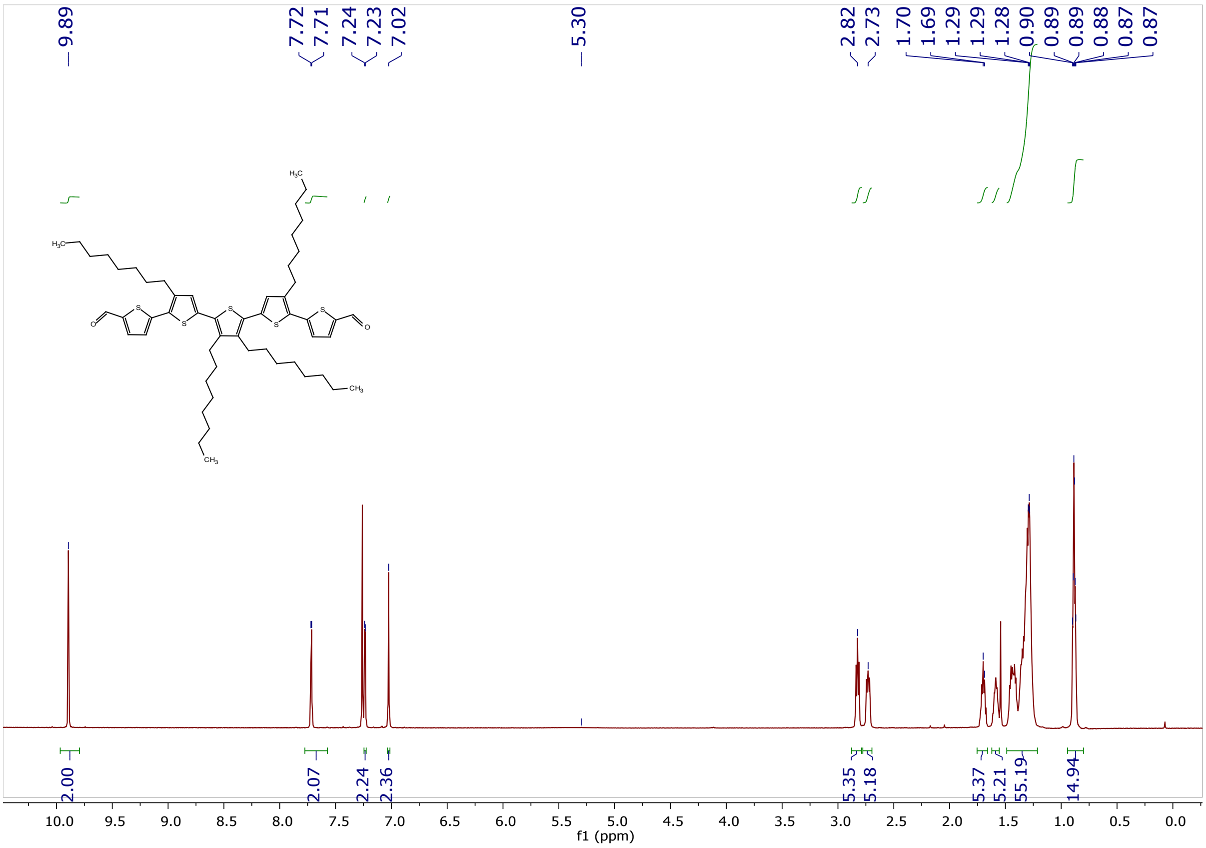
S3 ^{1}H and ^{13}C spectra

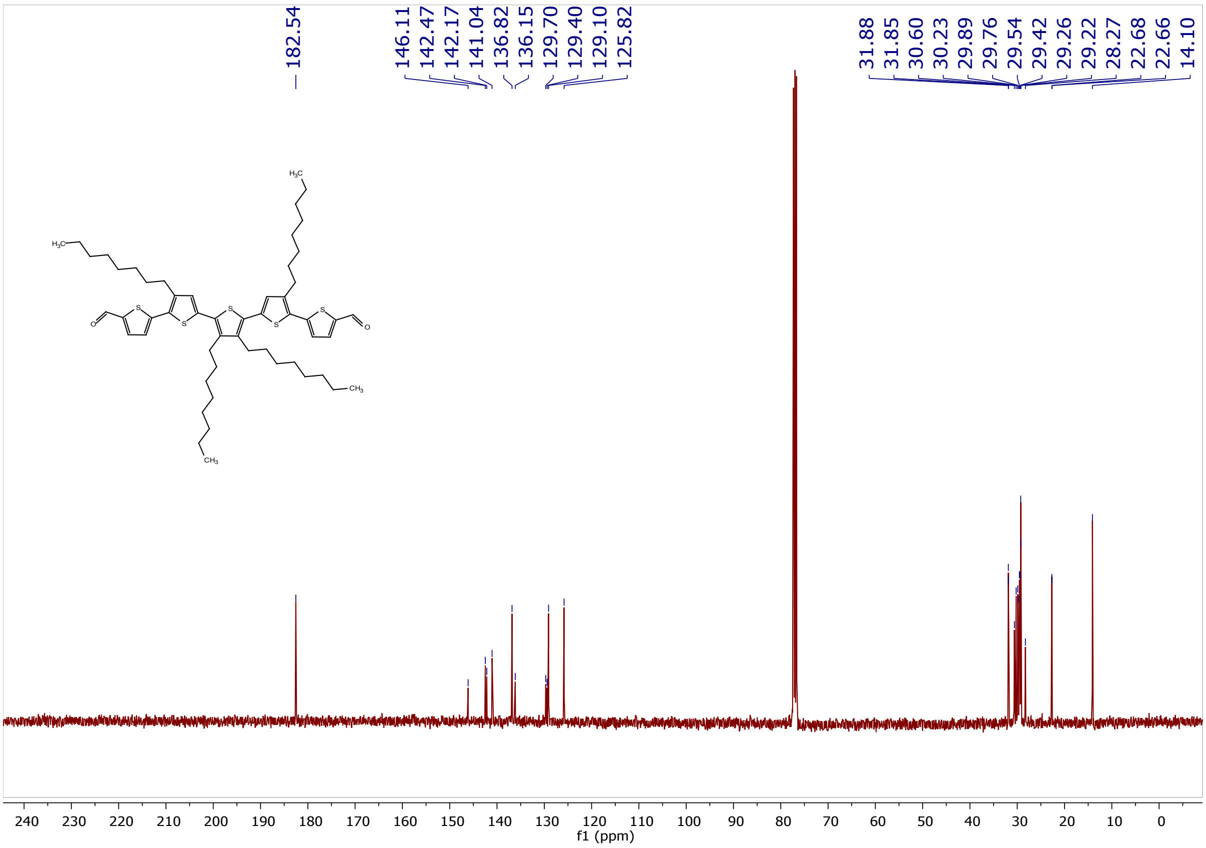
S3.1 *3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3a)**



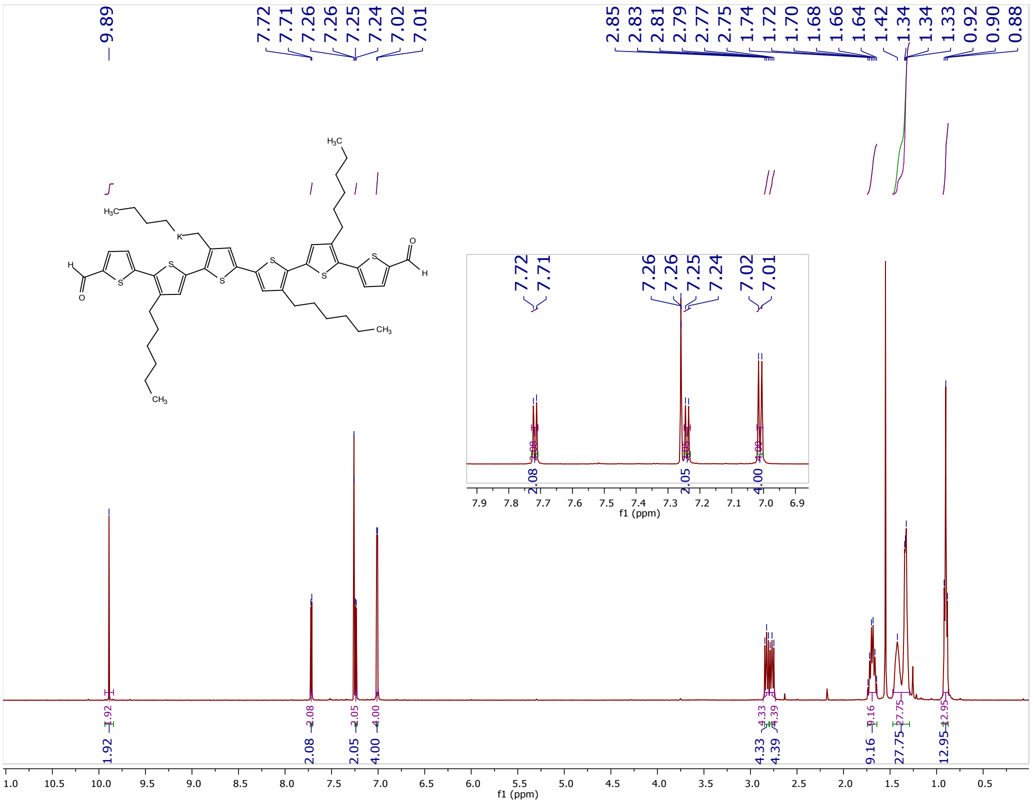


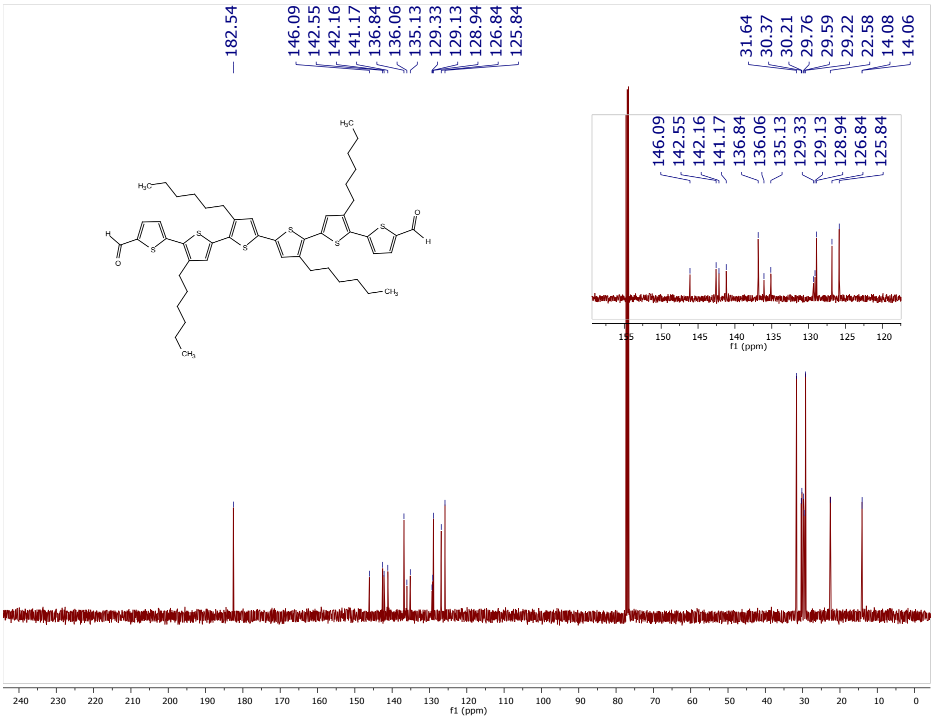
S3.2 *3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3b)**



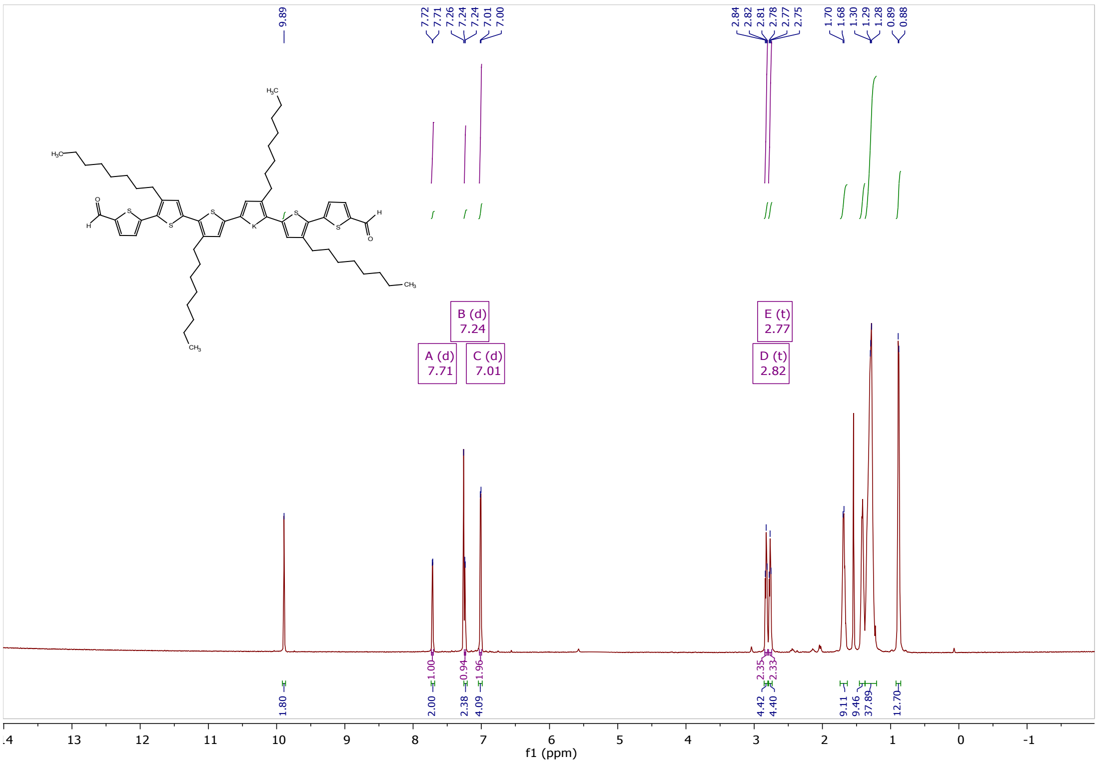


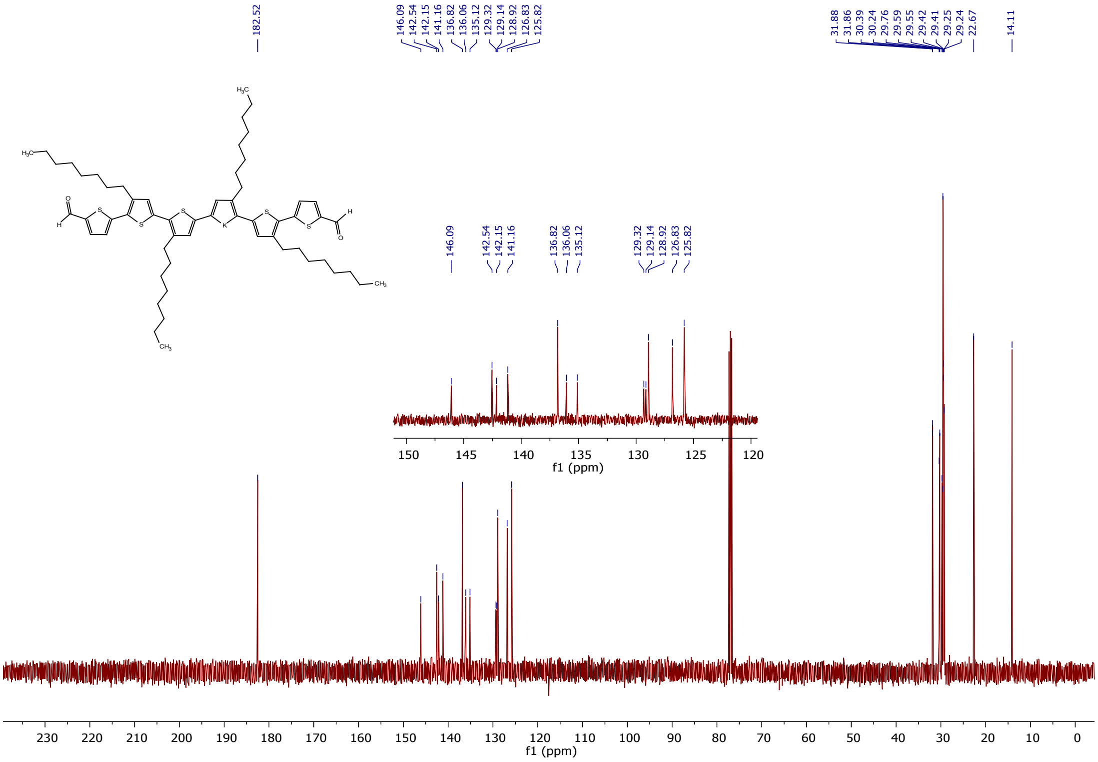
S3.3 *3',3'',4''',4''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(4a)**



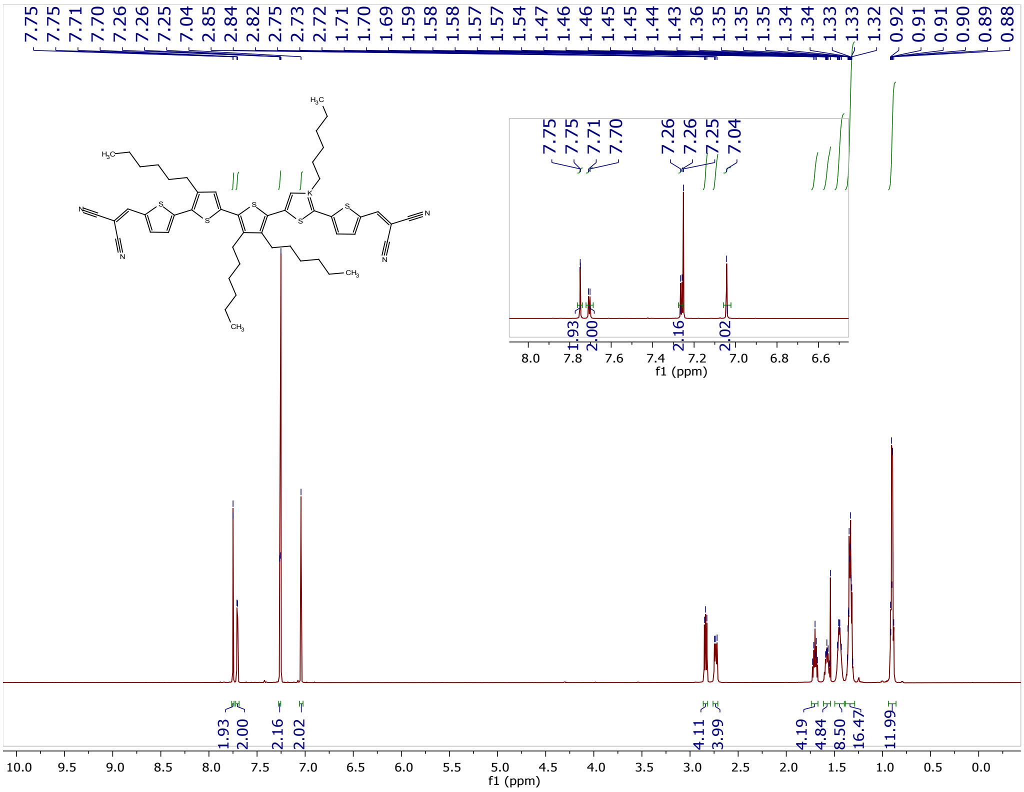


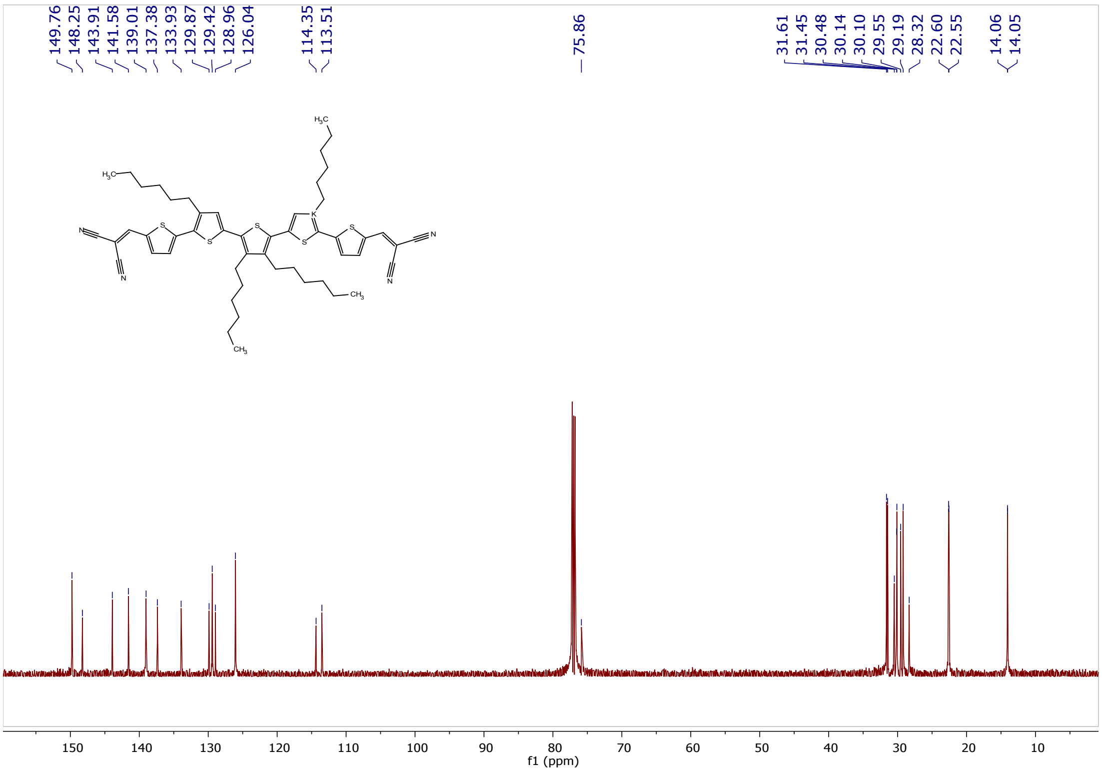
S3.4 *3',3'',4''',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(4b)**



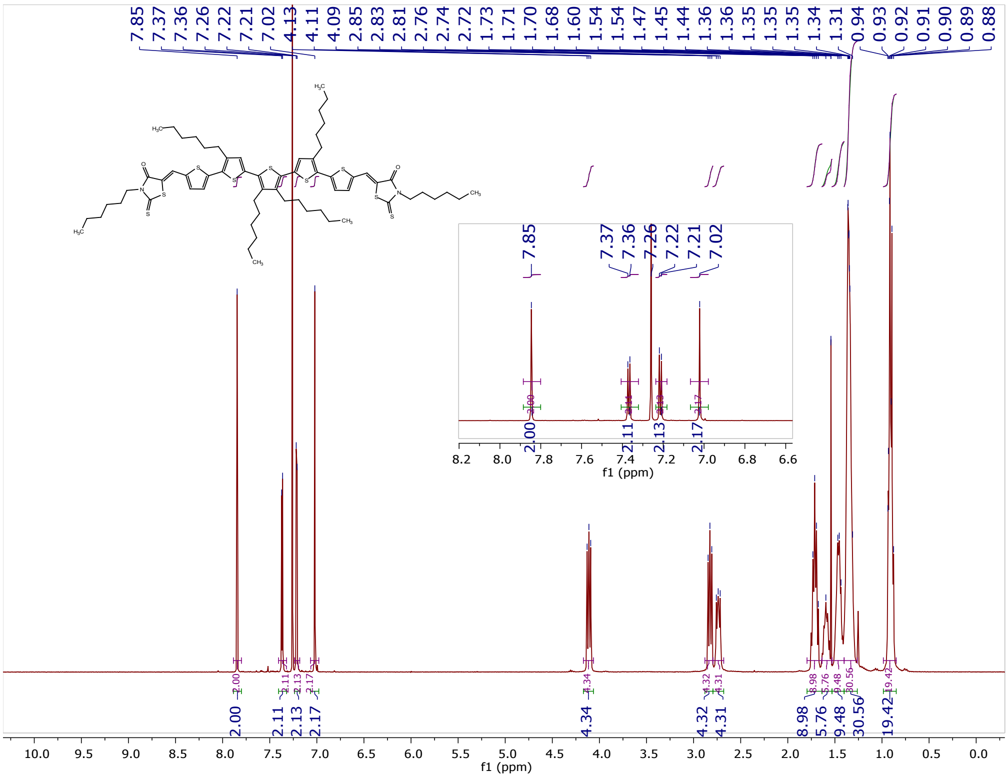


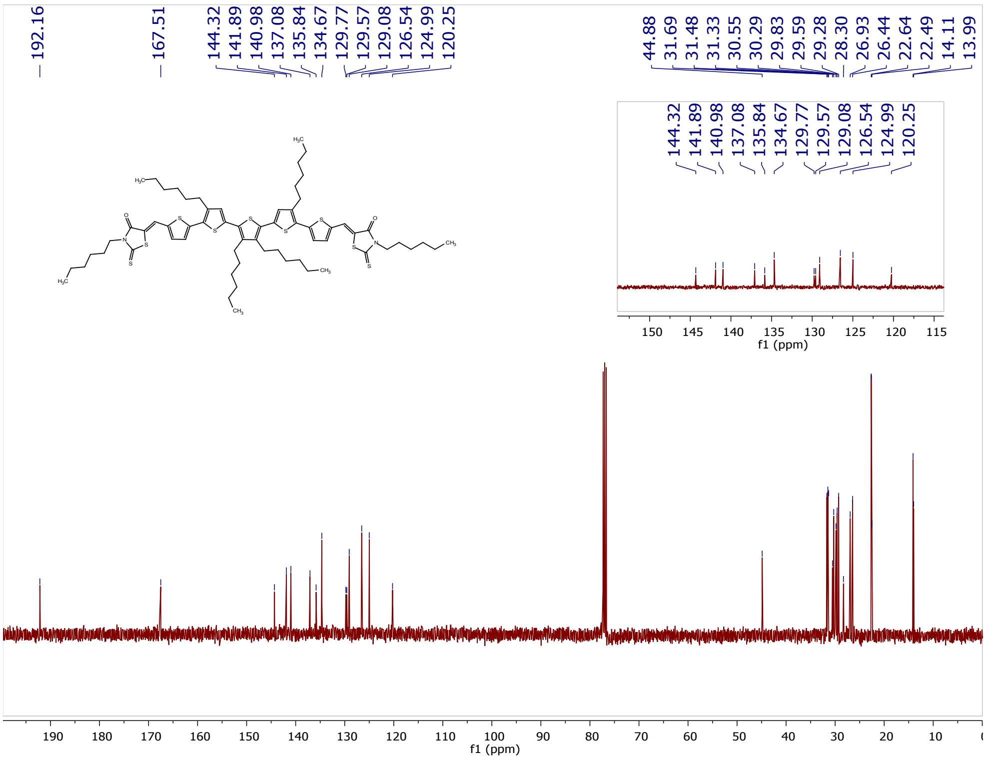
S3.5 *2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T^{6})**



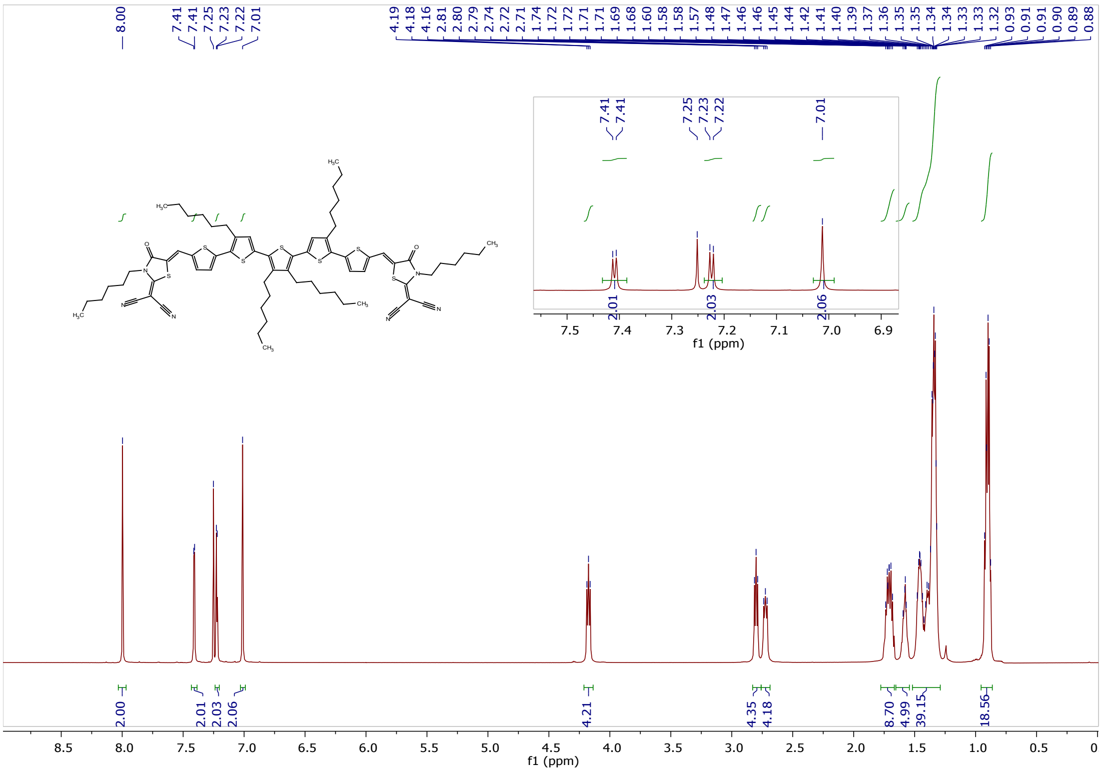


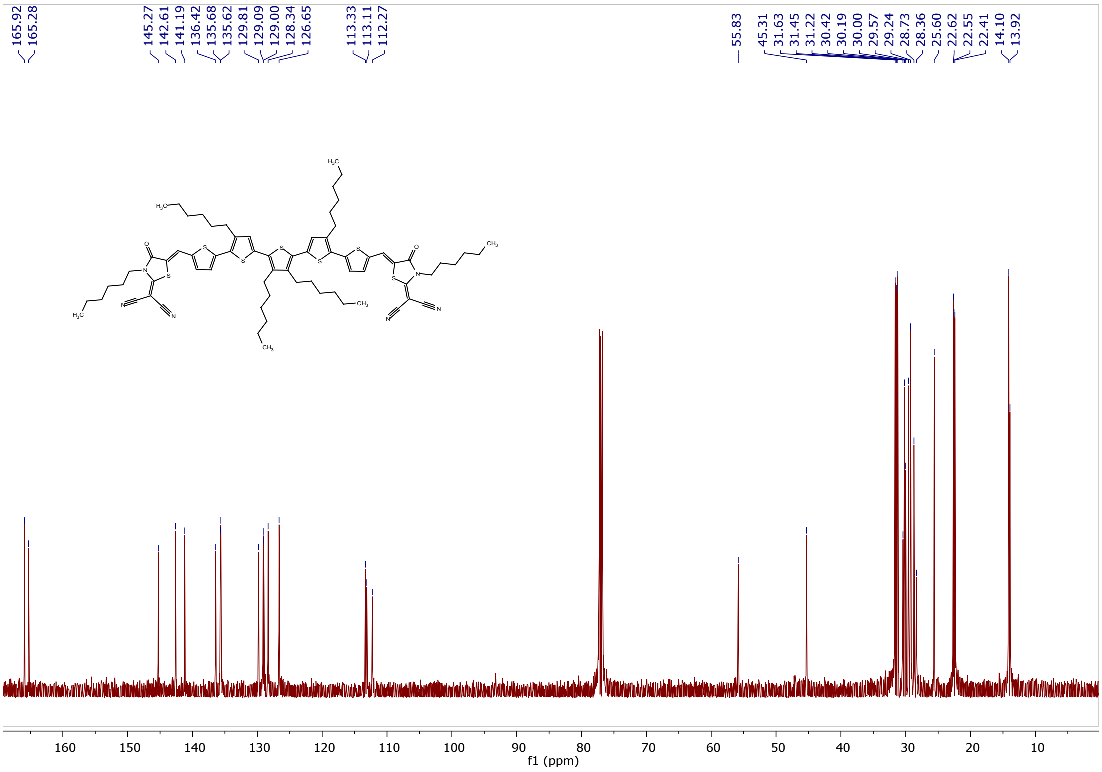
S3.6 (*5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR5T[6])**



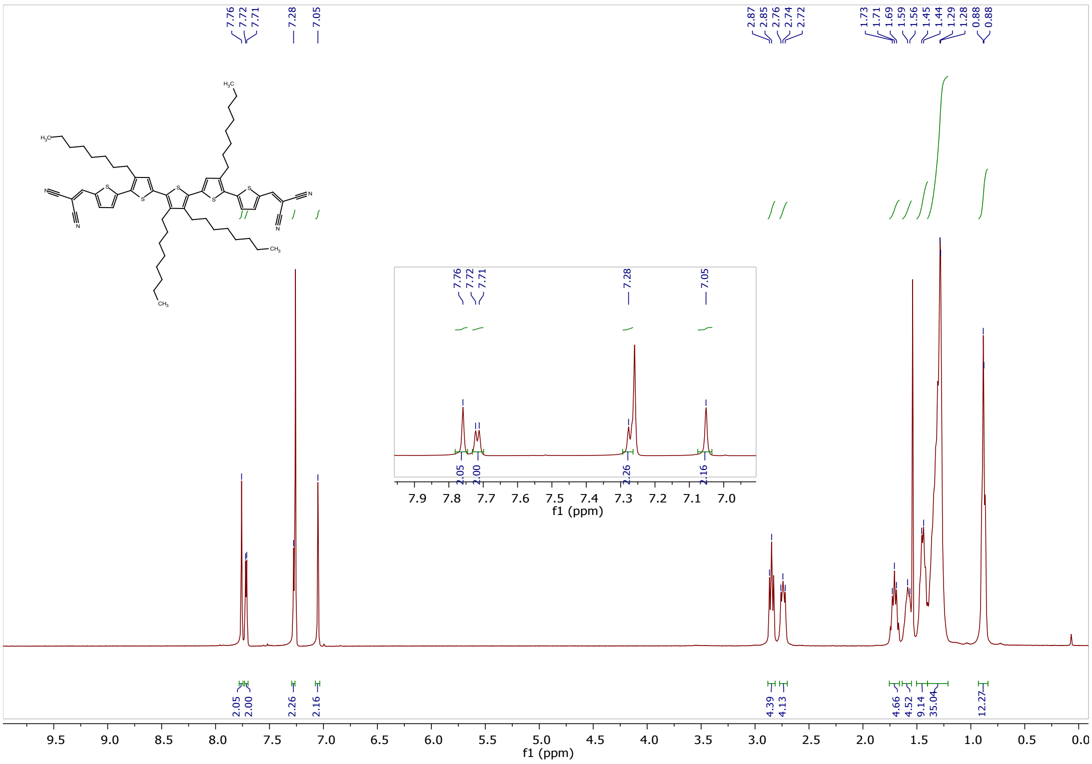


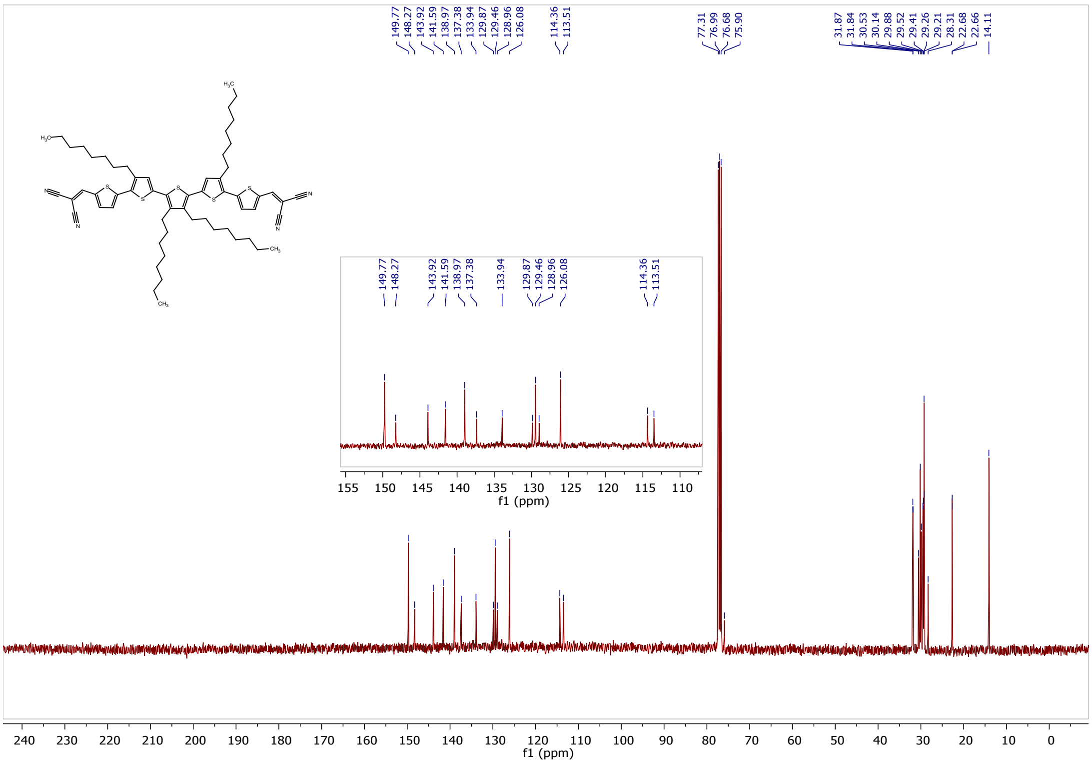
S3.7 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T^6)**



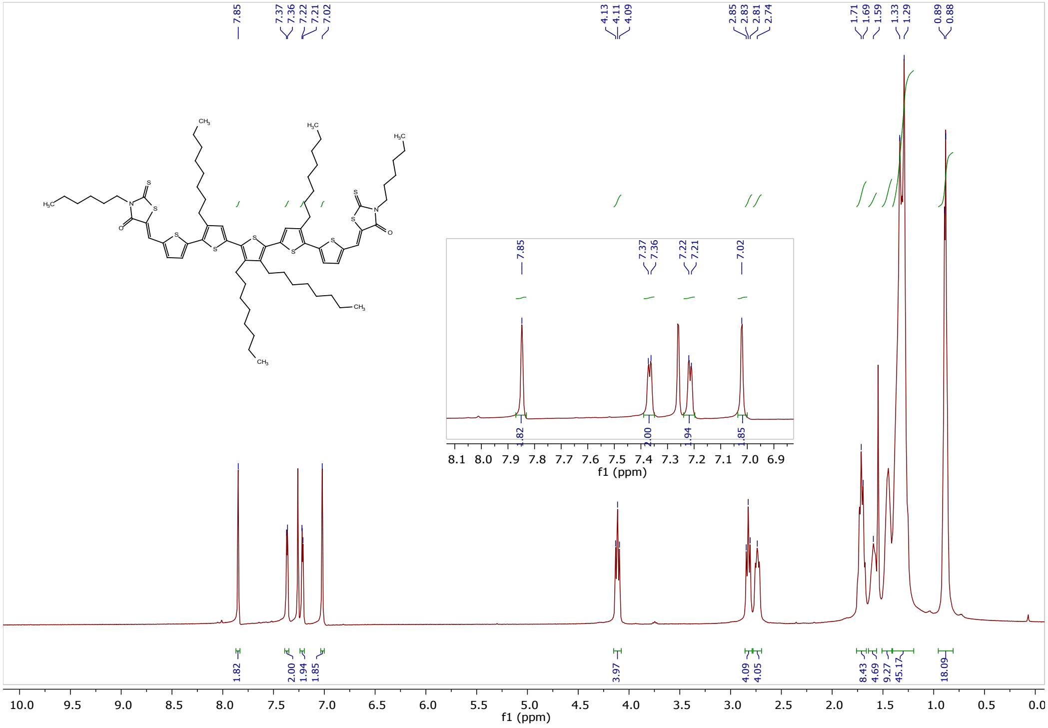


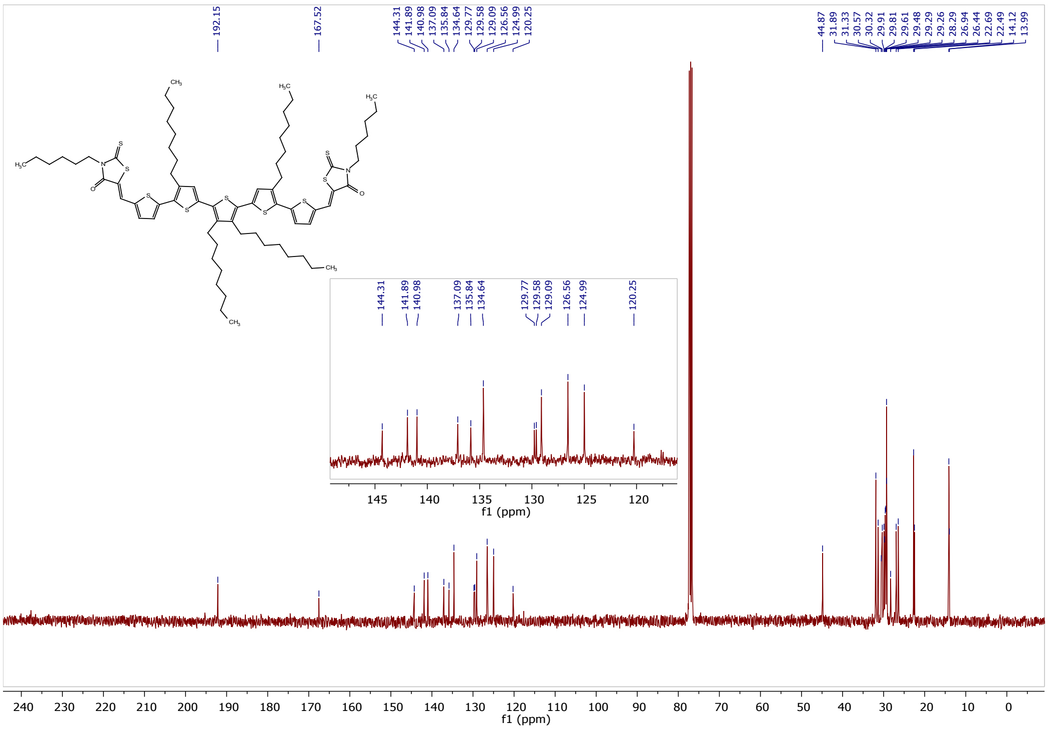
S3.8 *2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T^8)**



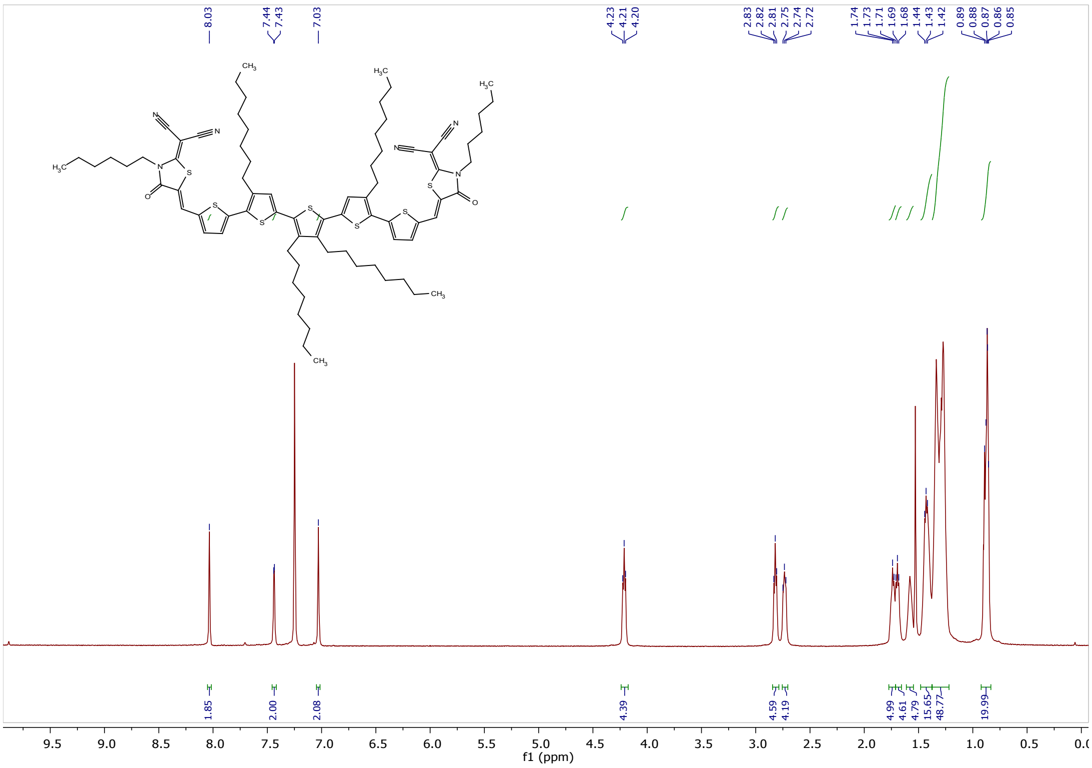


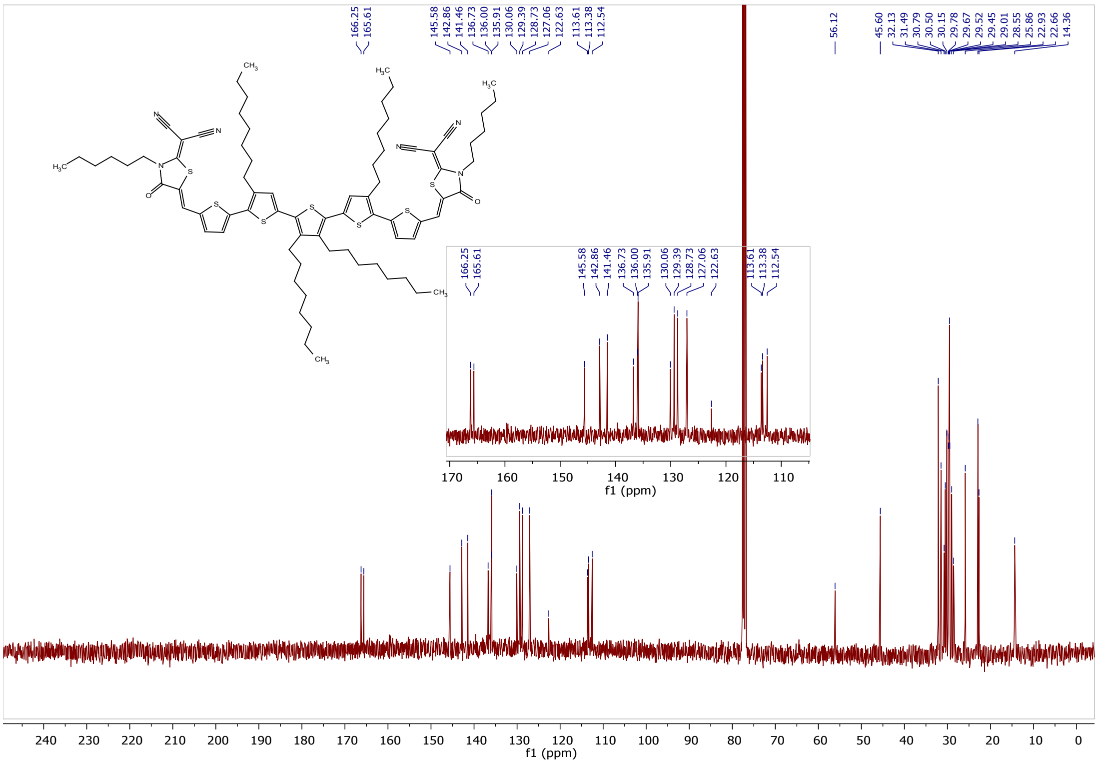
S3.9 ***(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)*** (HR5T^{8})



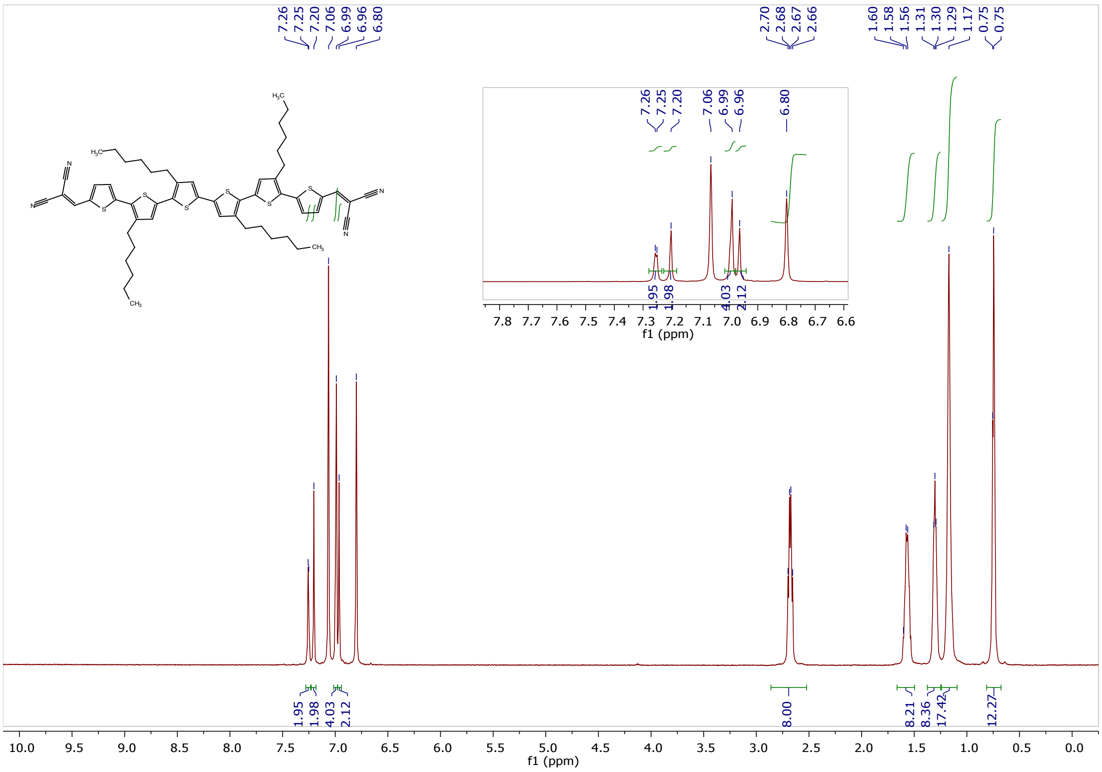


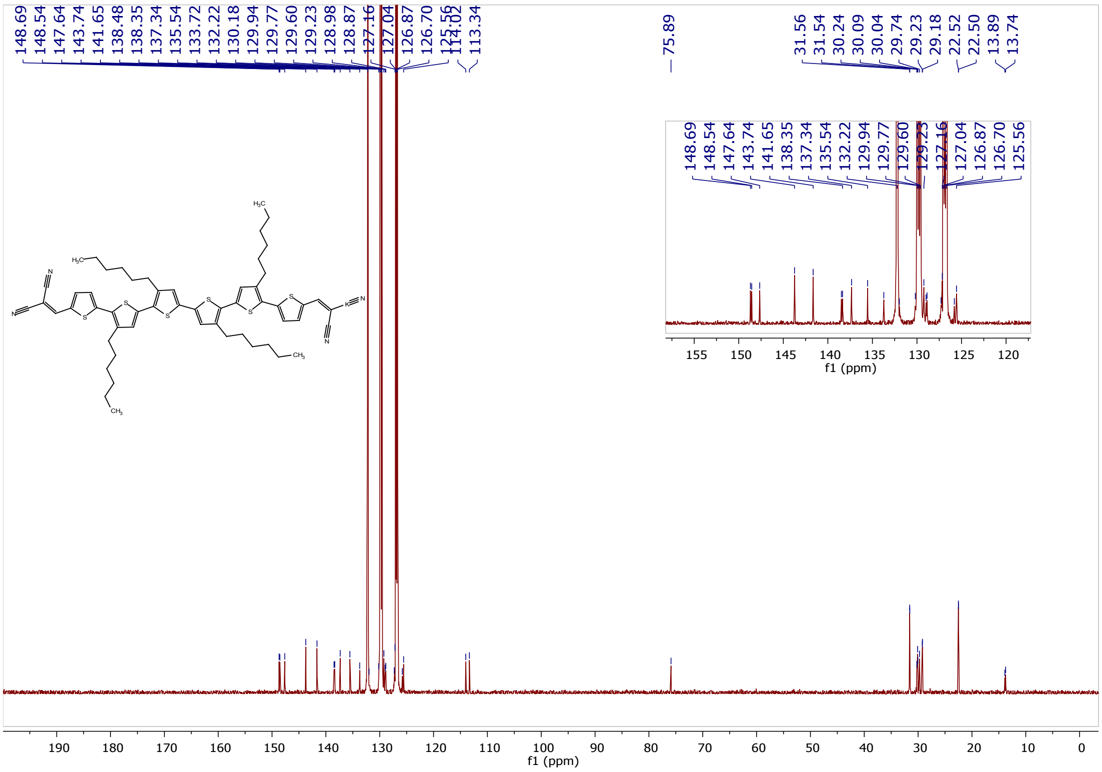
S3.10 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T^{8})**



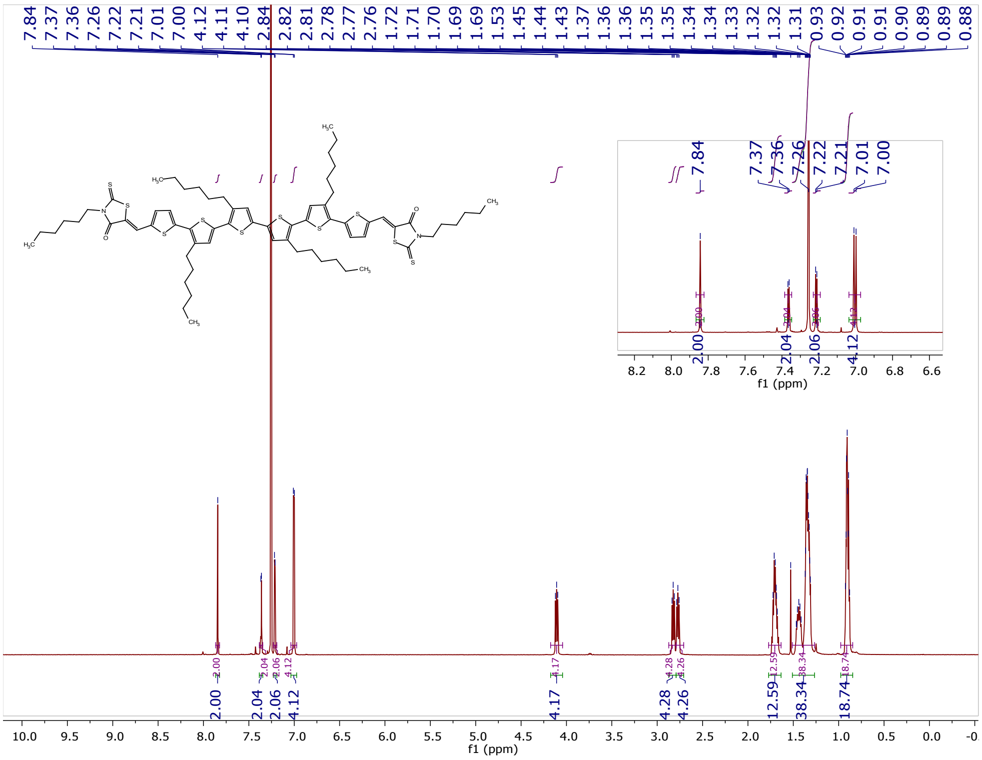


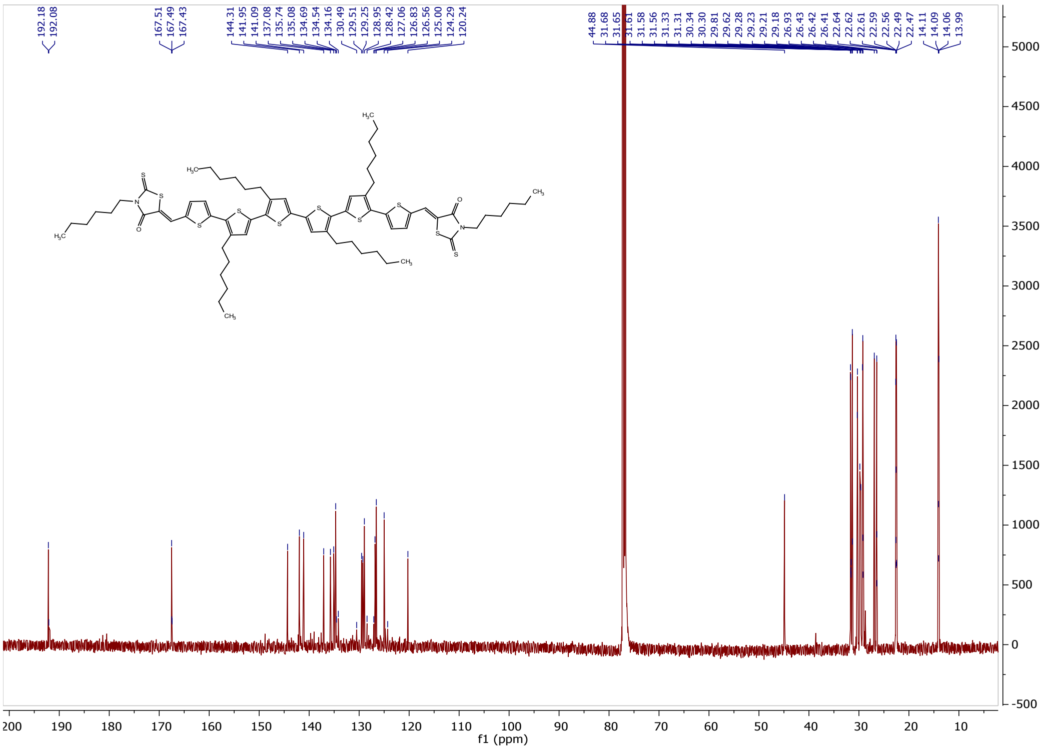
S3.11 *2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^6)**



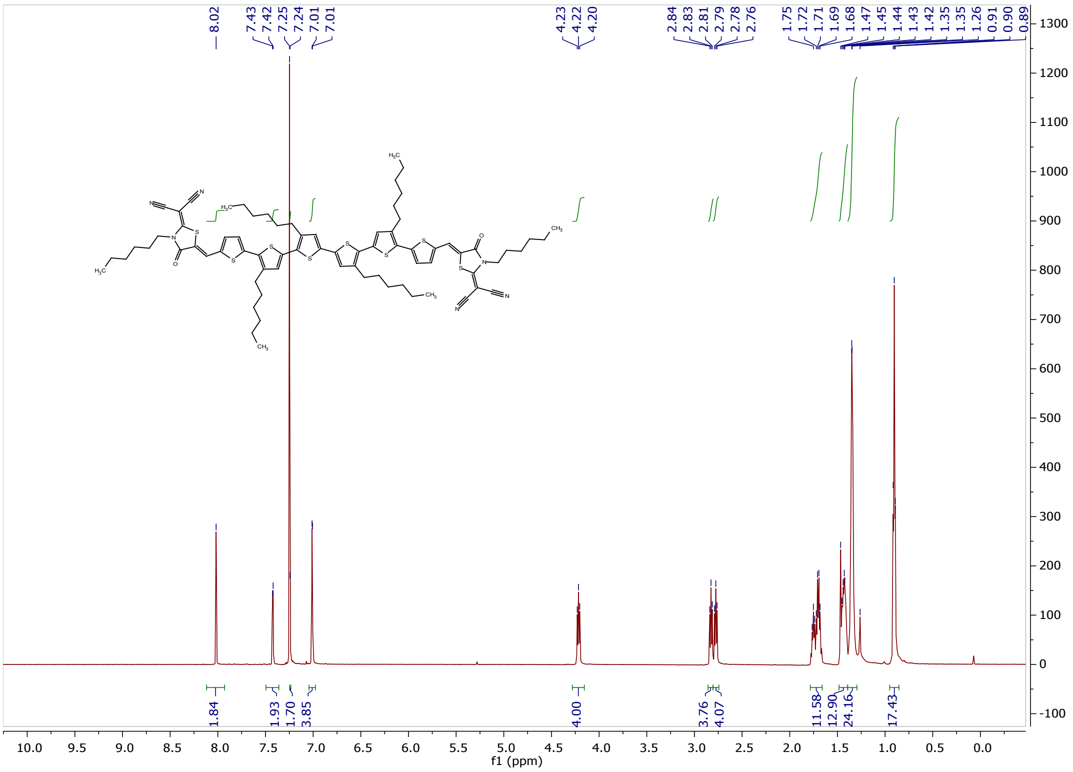


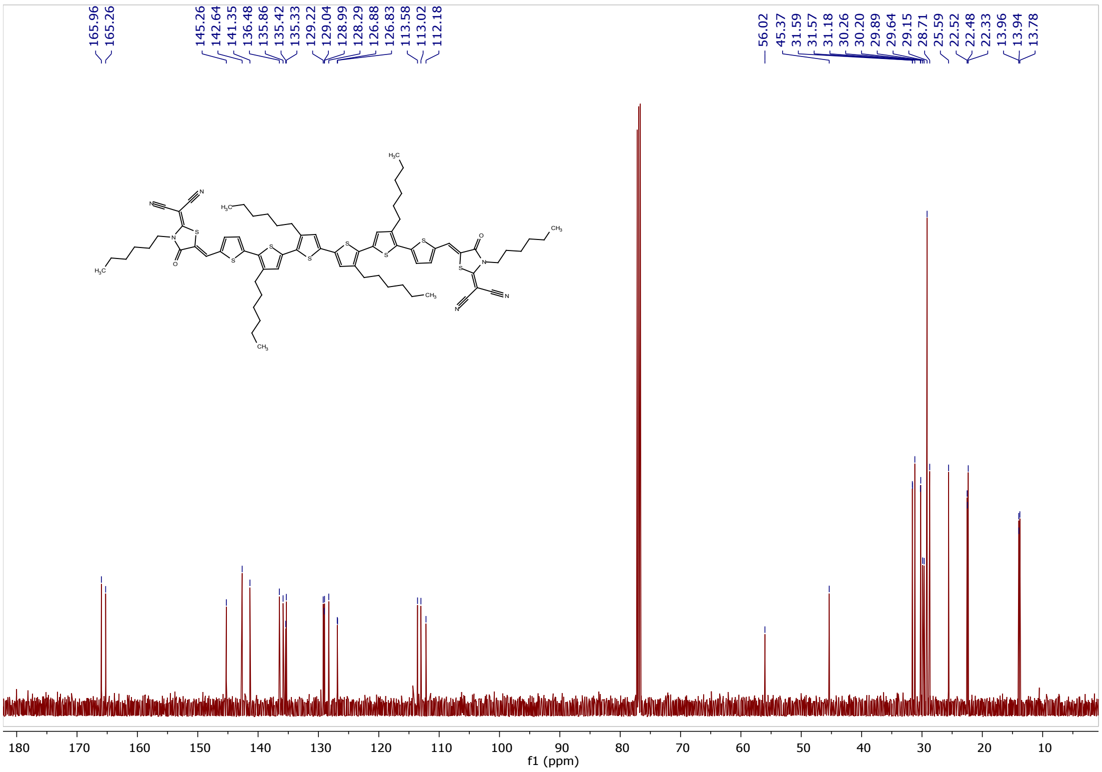
S3.12 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T^6)**



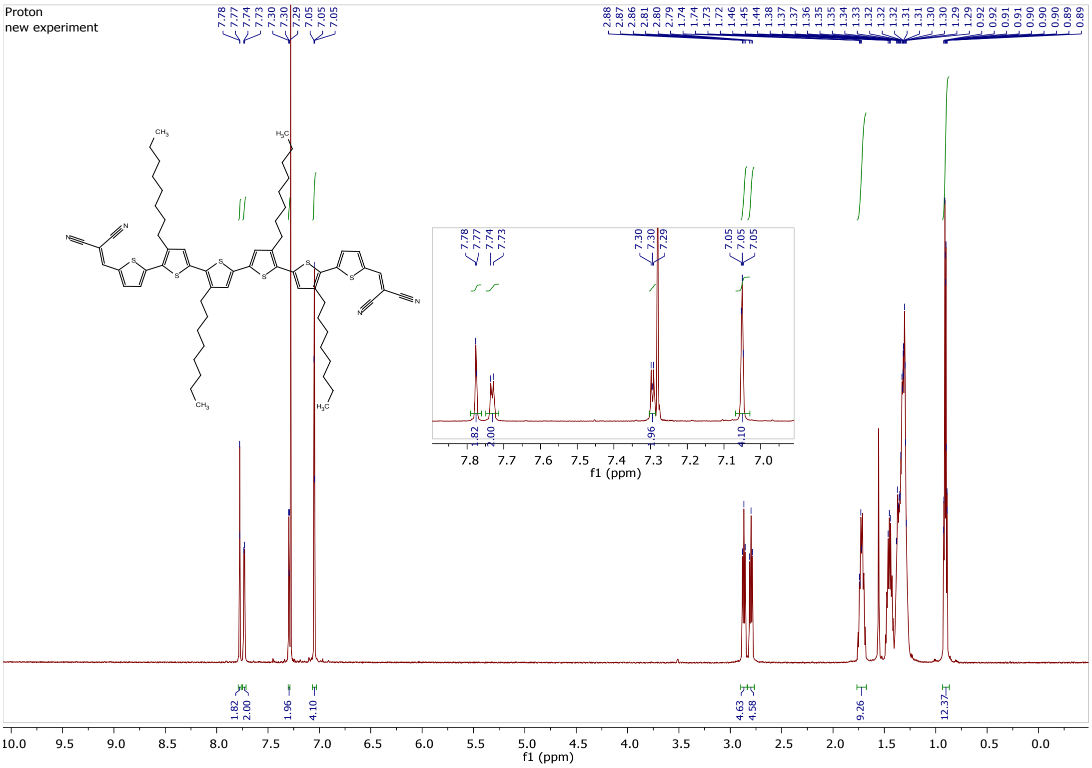


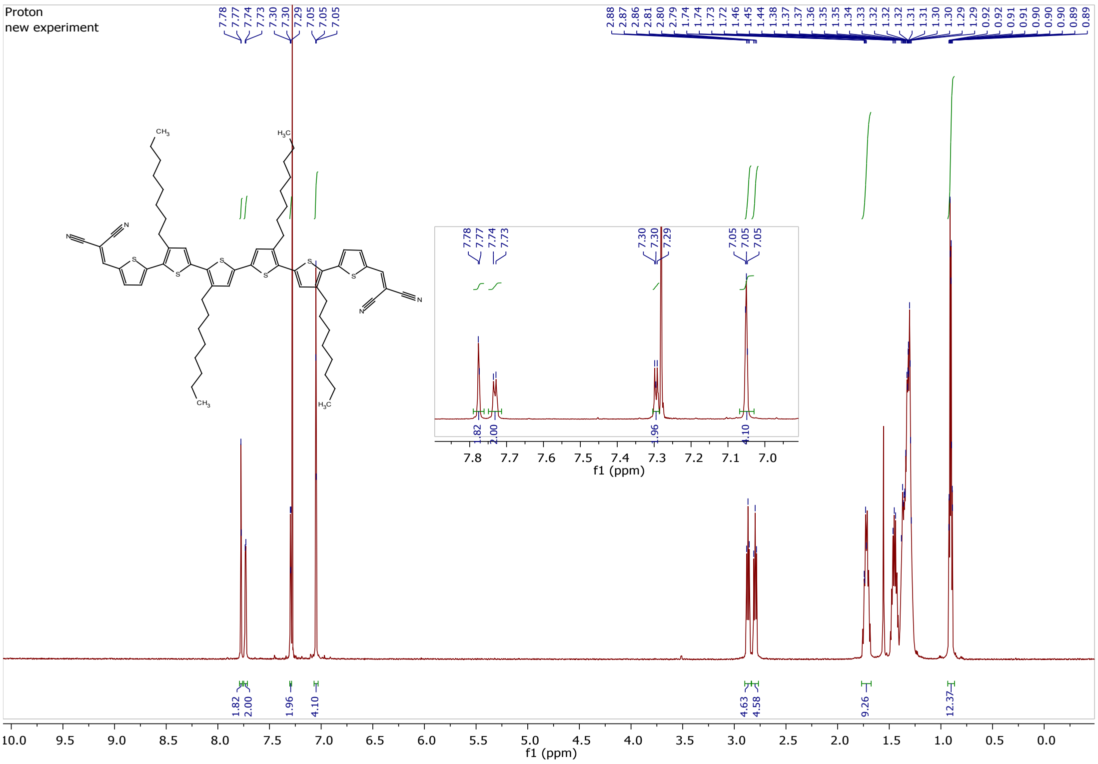
S3.13 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T^6)**



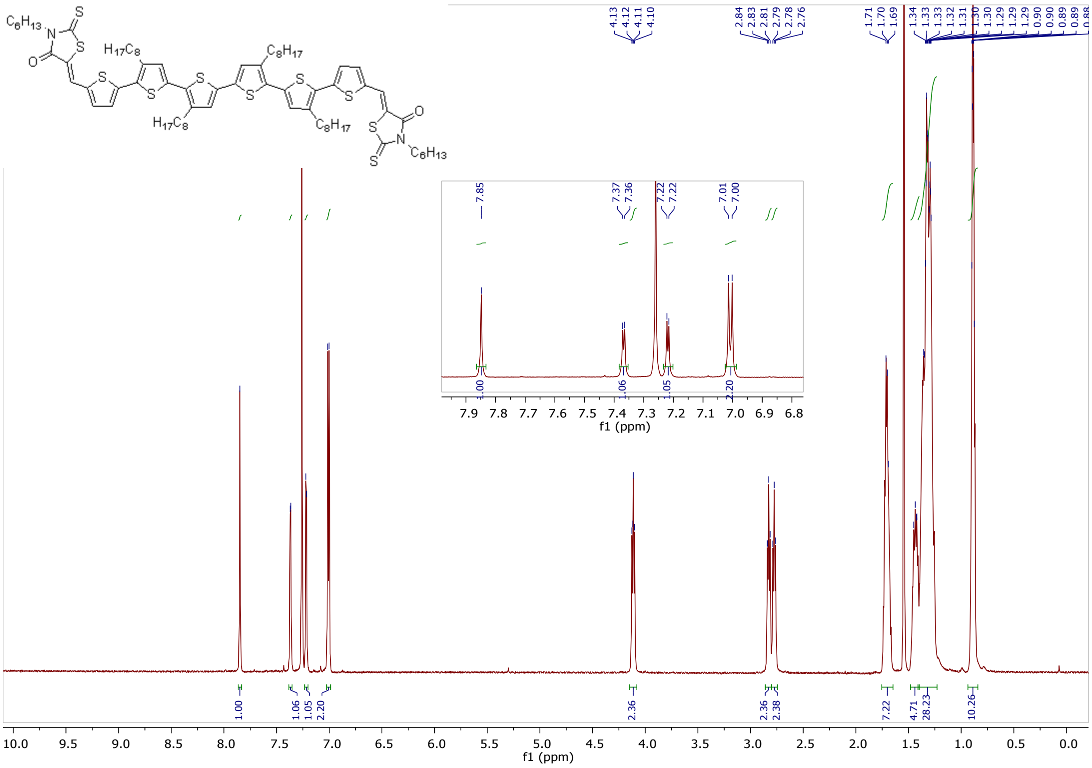


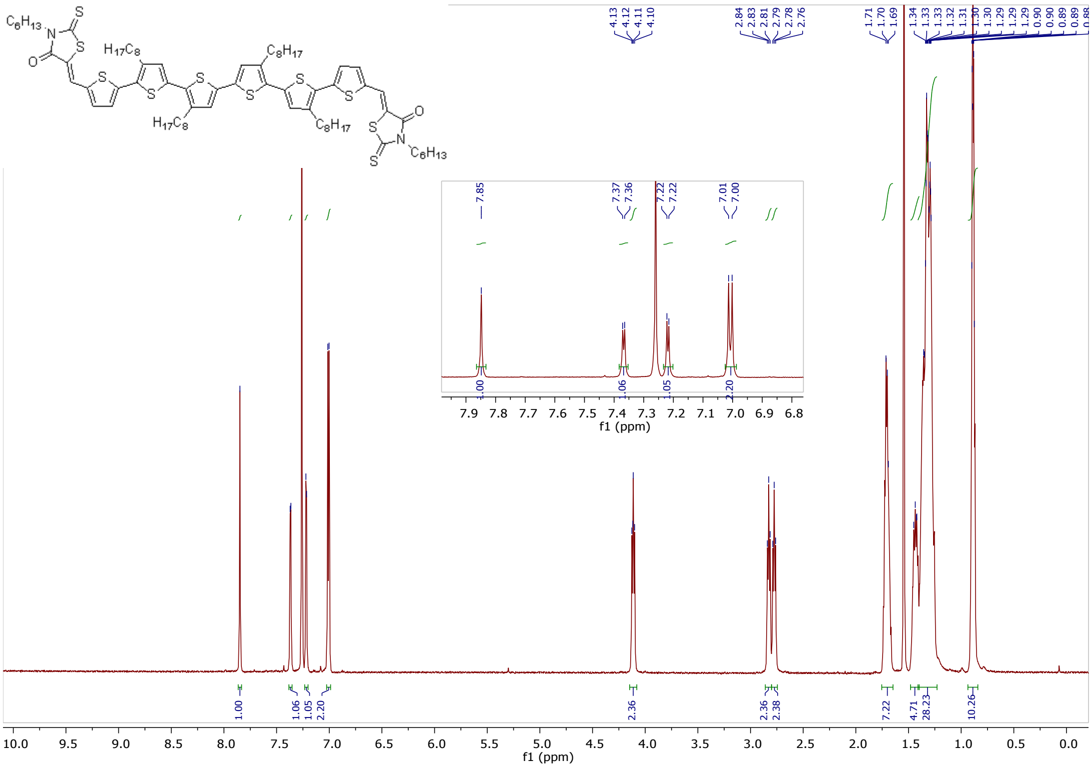
S3.14 *2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^8)**



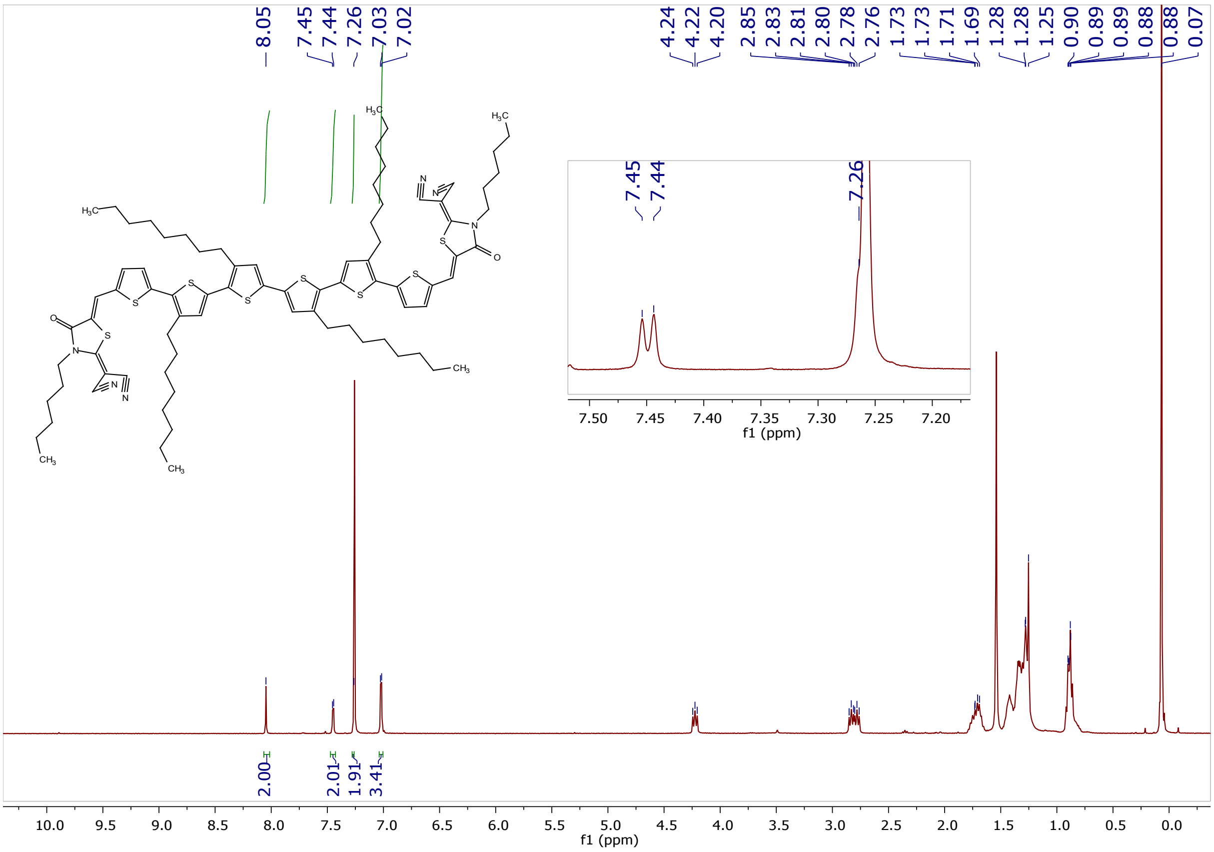


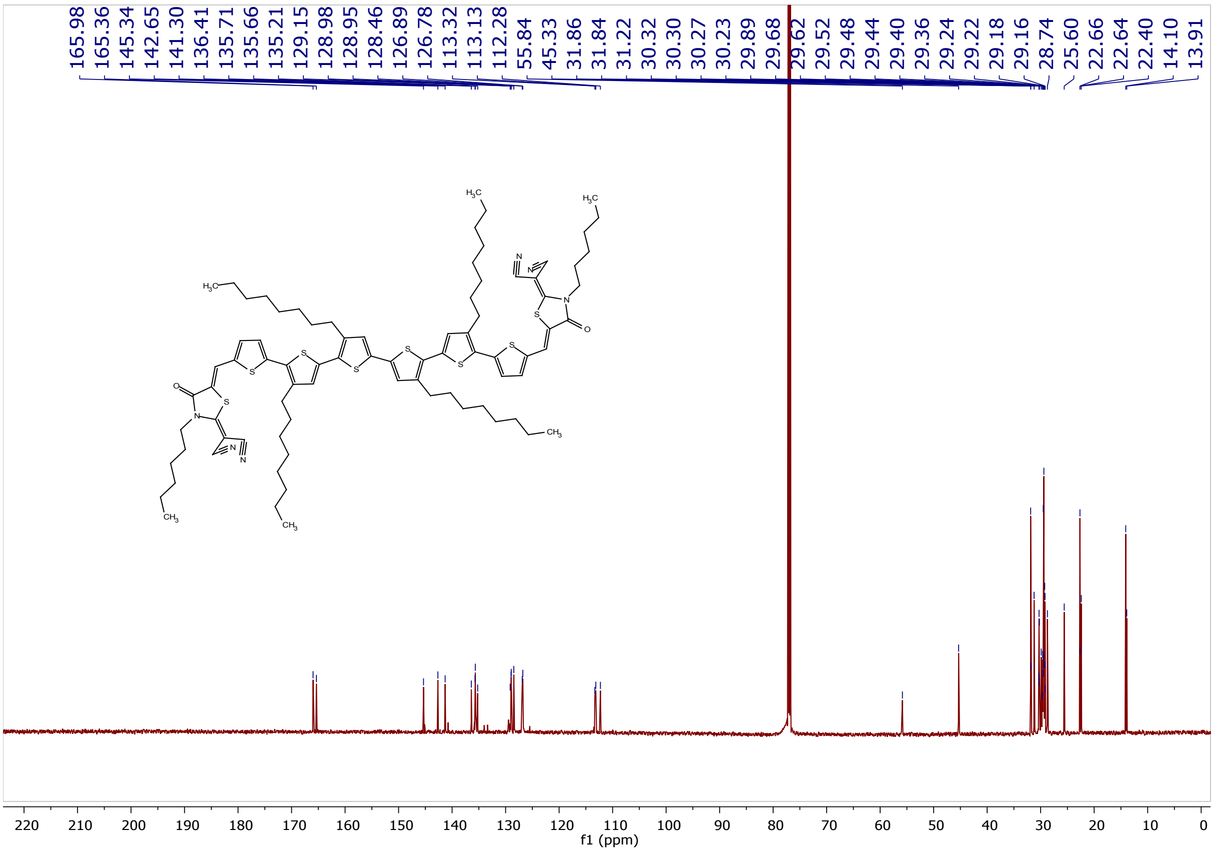
S3.15 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T^8)**





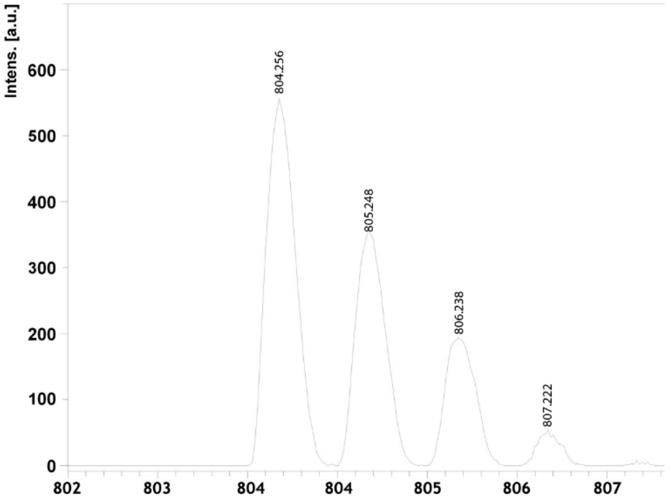
S3.16 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T^8)**



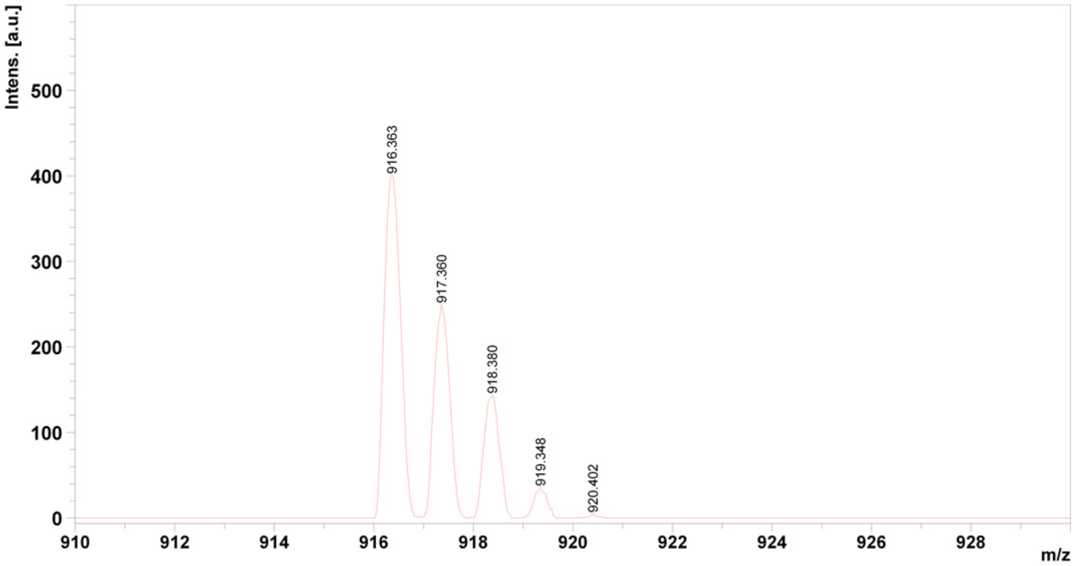


S4 MALDI spectra for the Oligothiophene material series

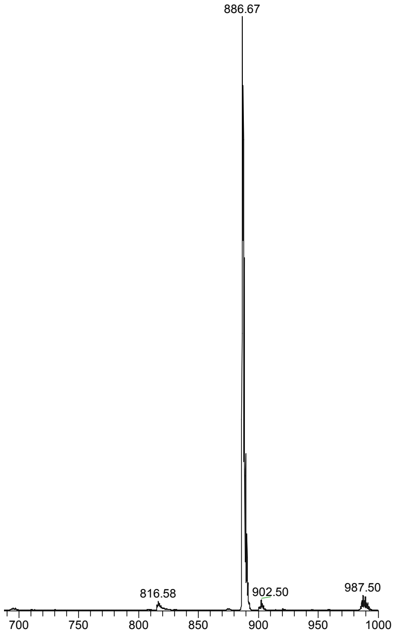
S4.1 *3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3a)**



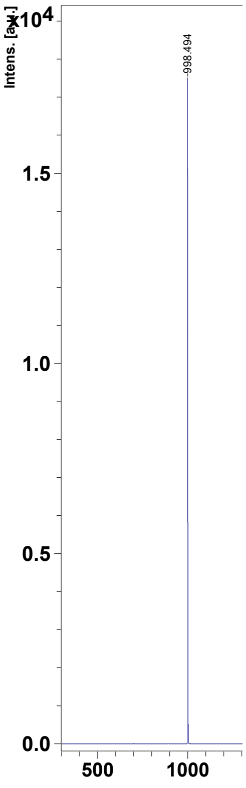
S4.2 *3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde* **(3b)**



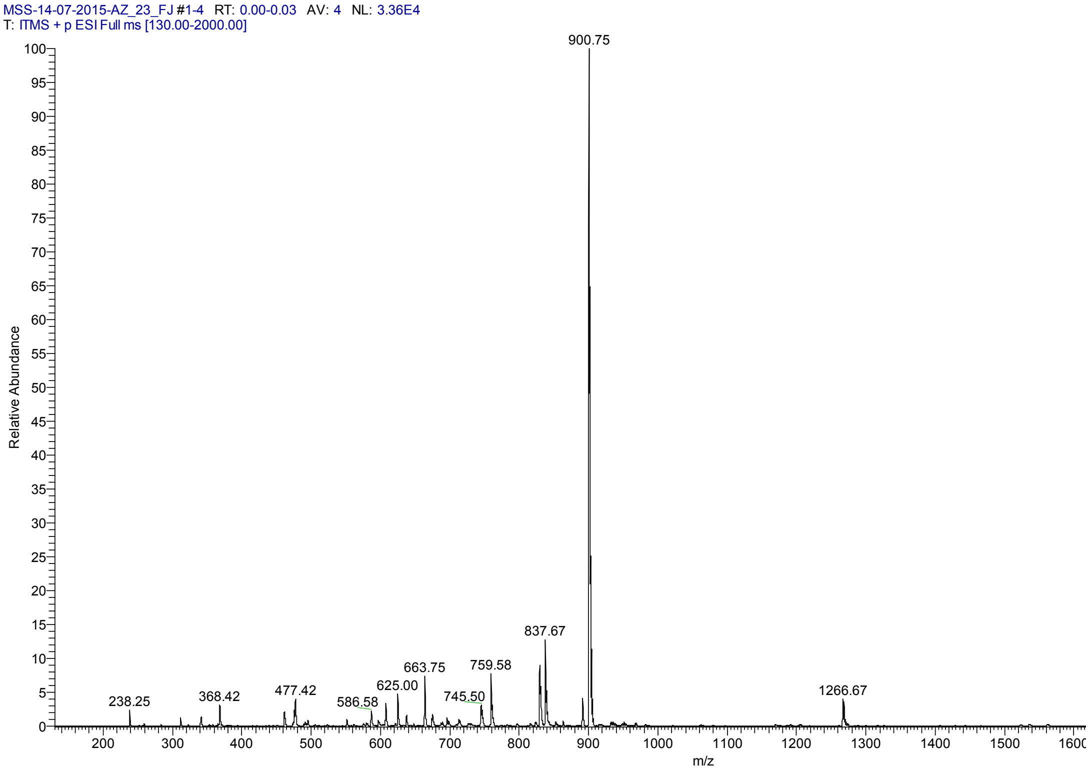
S4.3 *3',3'',4''',4''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(4a)**



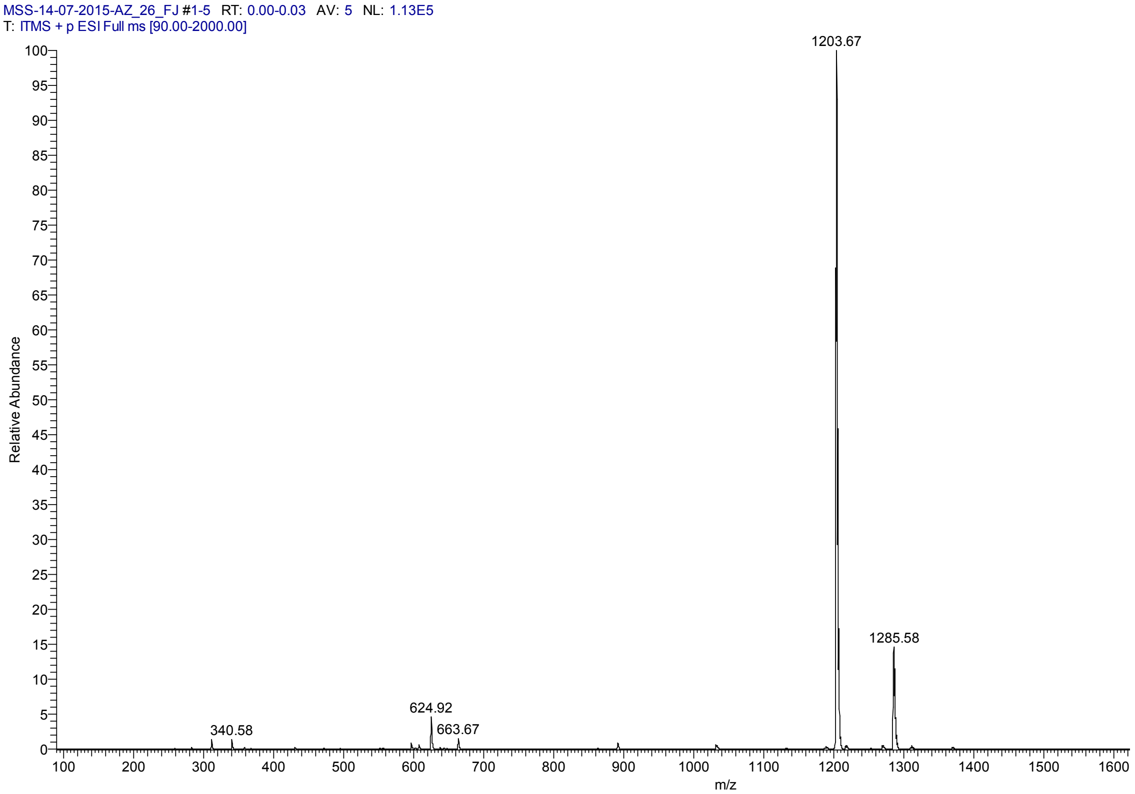
S4.4 *3',3'',4''',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene]-5,5'''''-dicarbaldehyde* **(4b)**



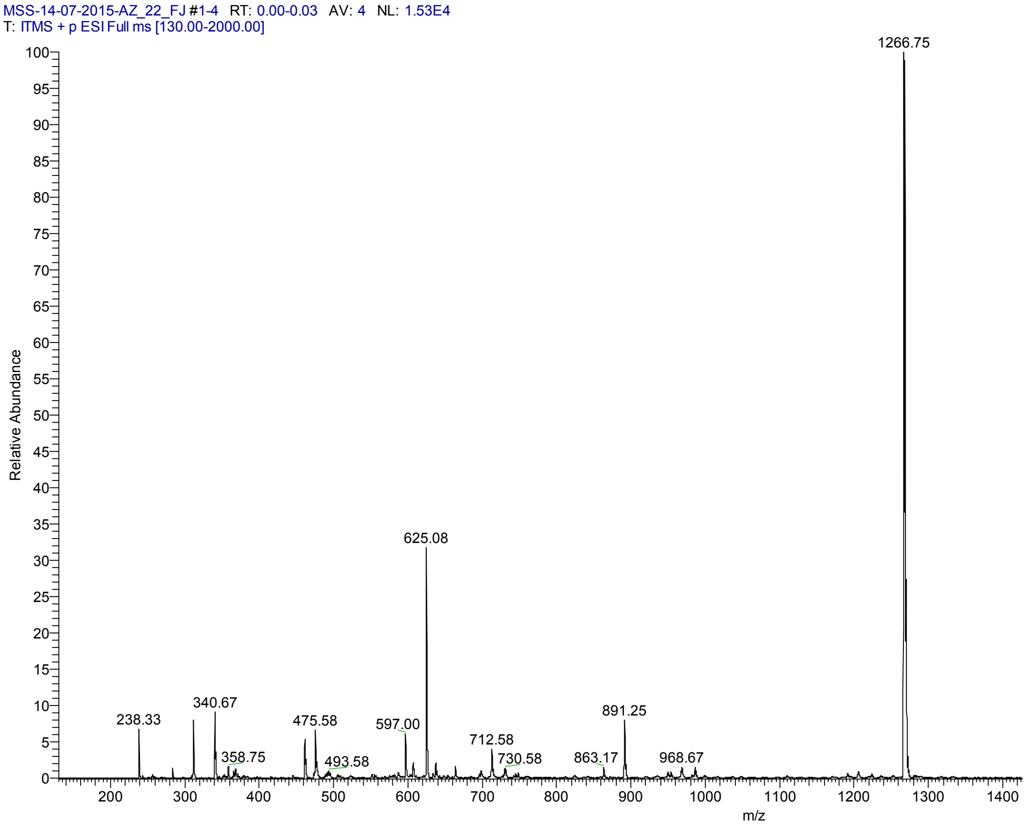
S4.5 *2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T^{6})**



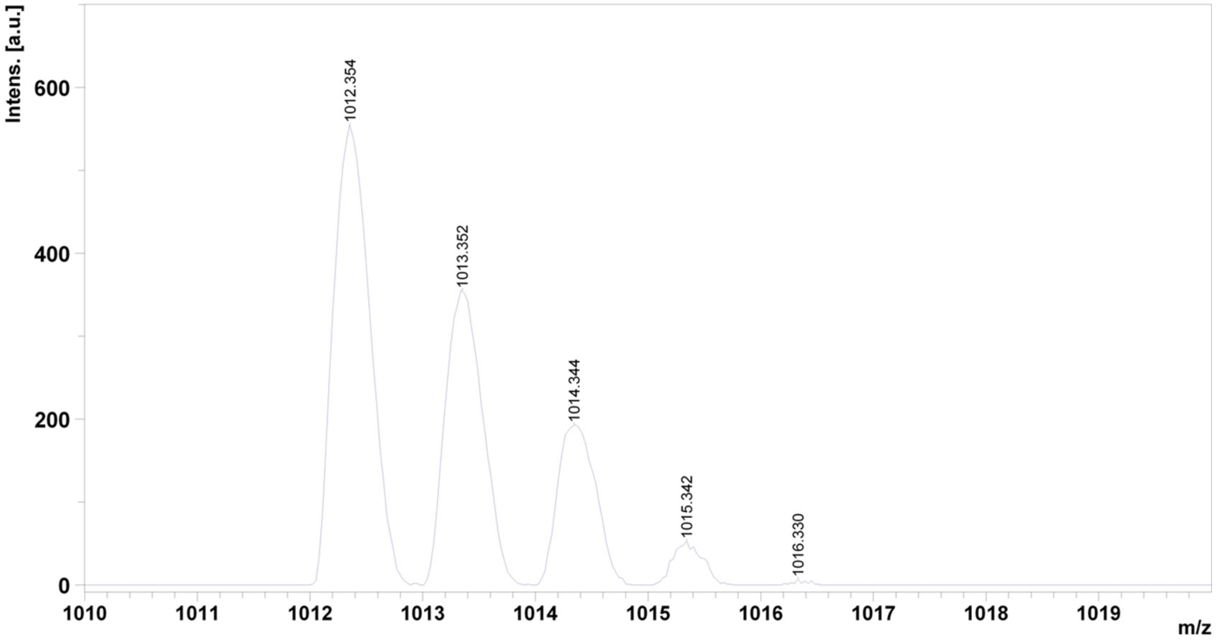
S4.6 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR5T^{6})**



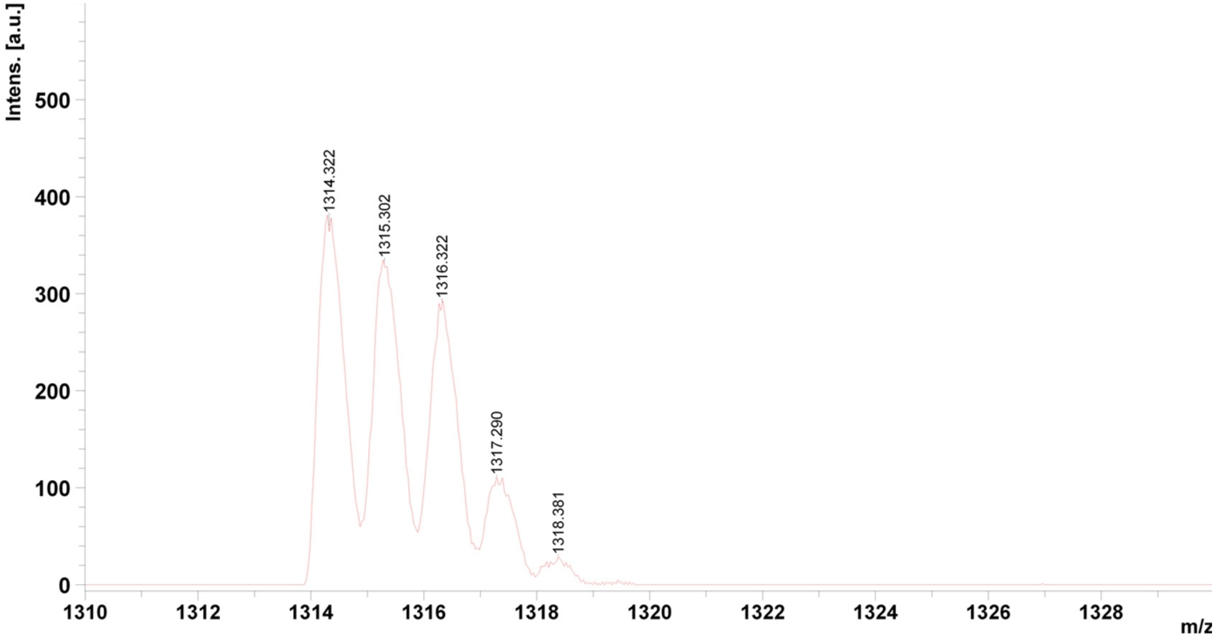
S4.7 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T⁶)**



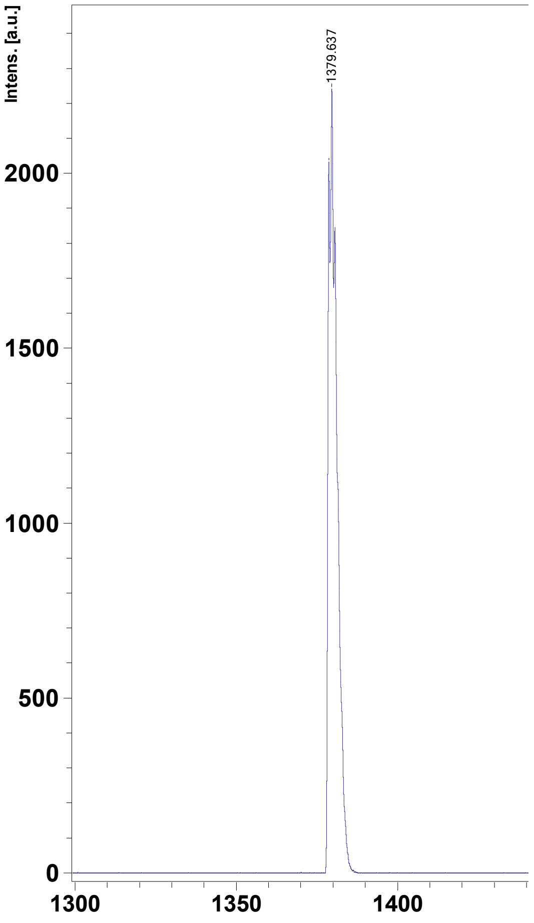
S4.8 *2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN5T⁸)**



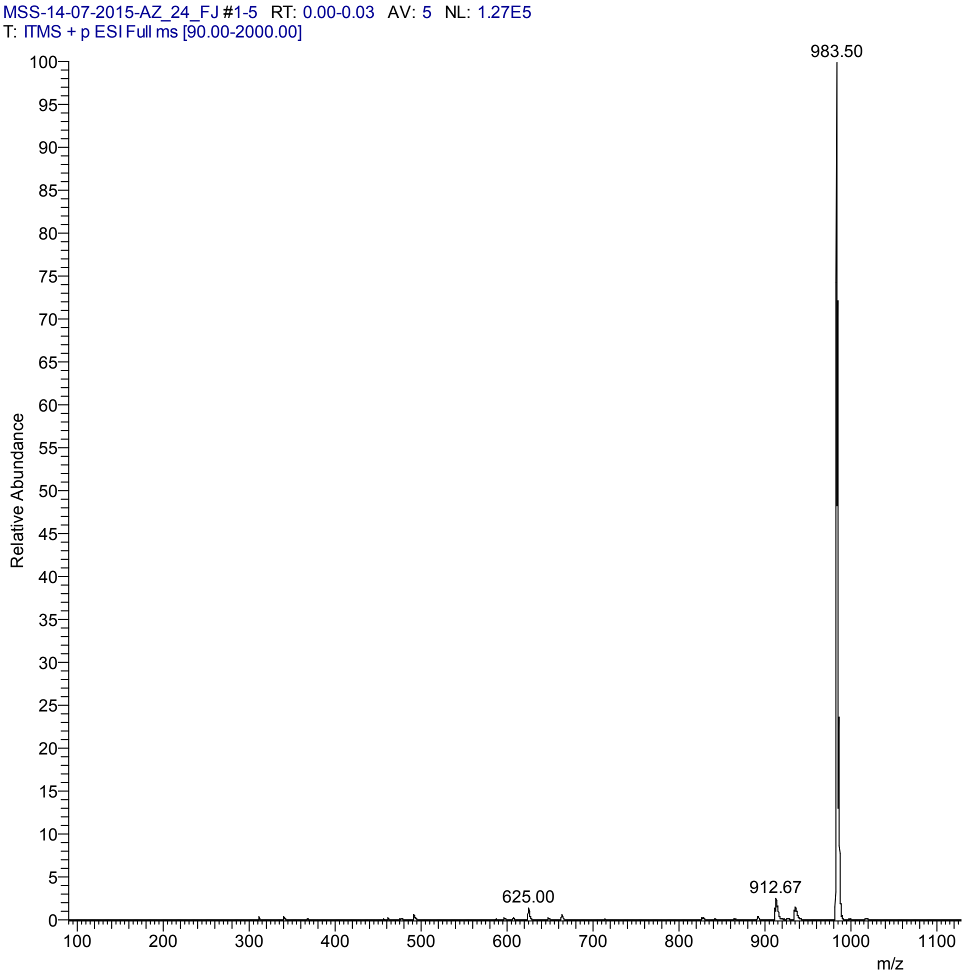
S4.9 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* (HR5T^{8})



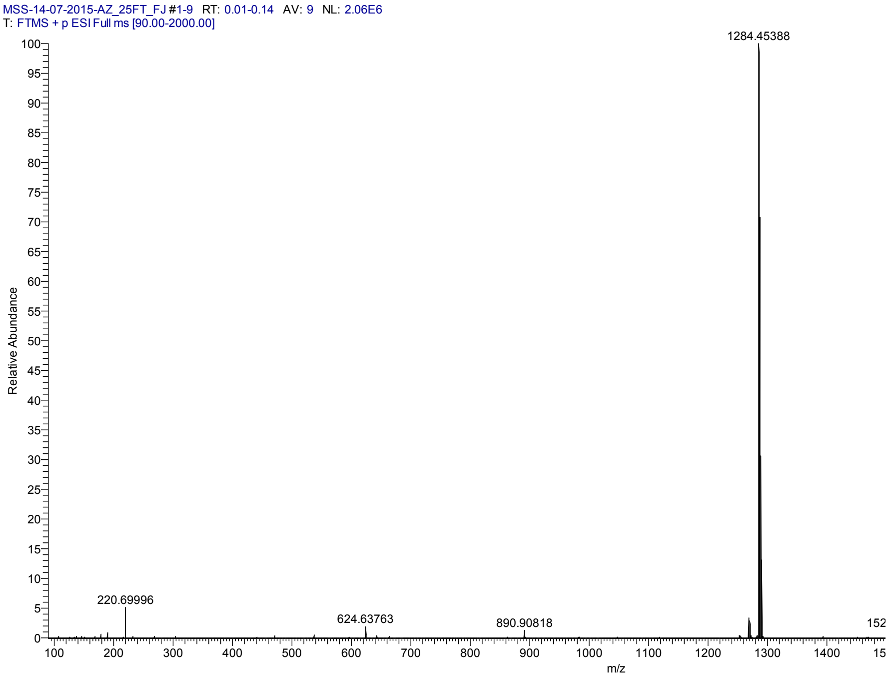
S4.10 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR5T^{8})**



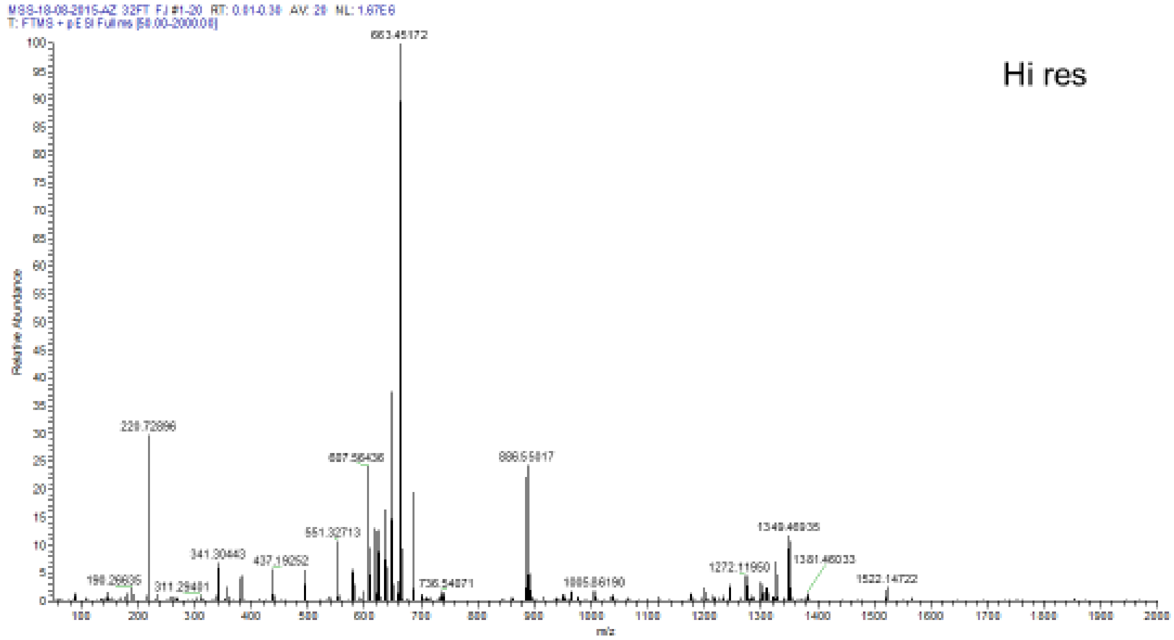
S4.11 *2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^6)**



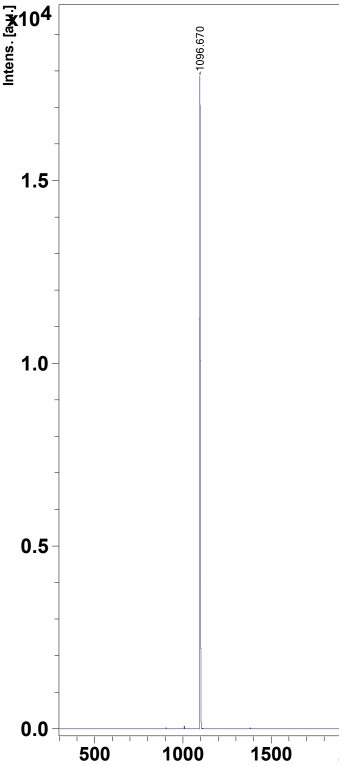
S4.12 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T^6)**



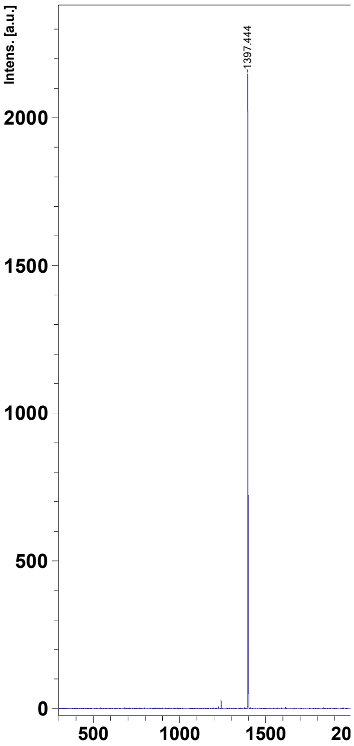
S4.13 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T^{6})**



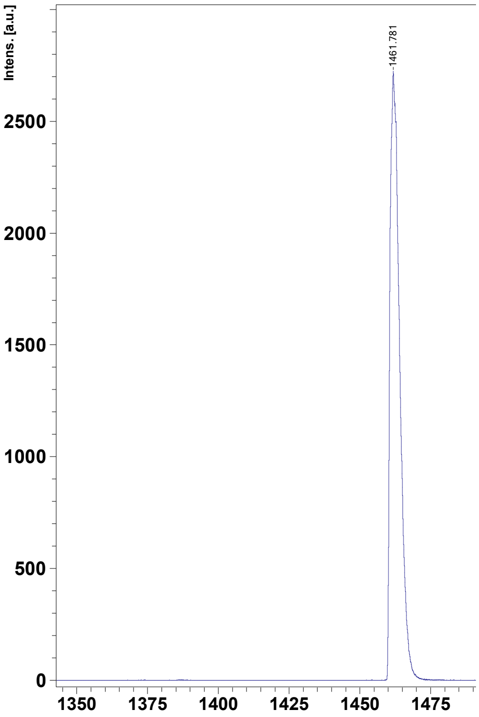
S4.14 *2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile* **(MN6T^{8})**



S4.15 *(5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)* **(HR6T[8])**



S4.16 *2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile* **(CHR6T[8])**



S5 Thermogravimetric Analysis

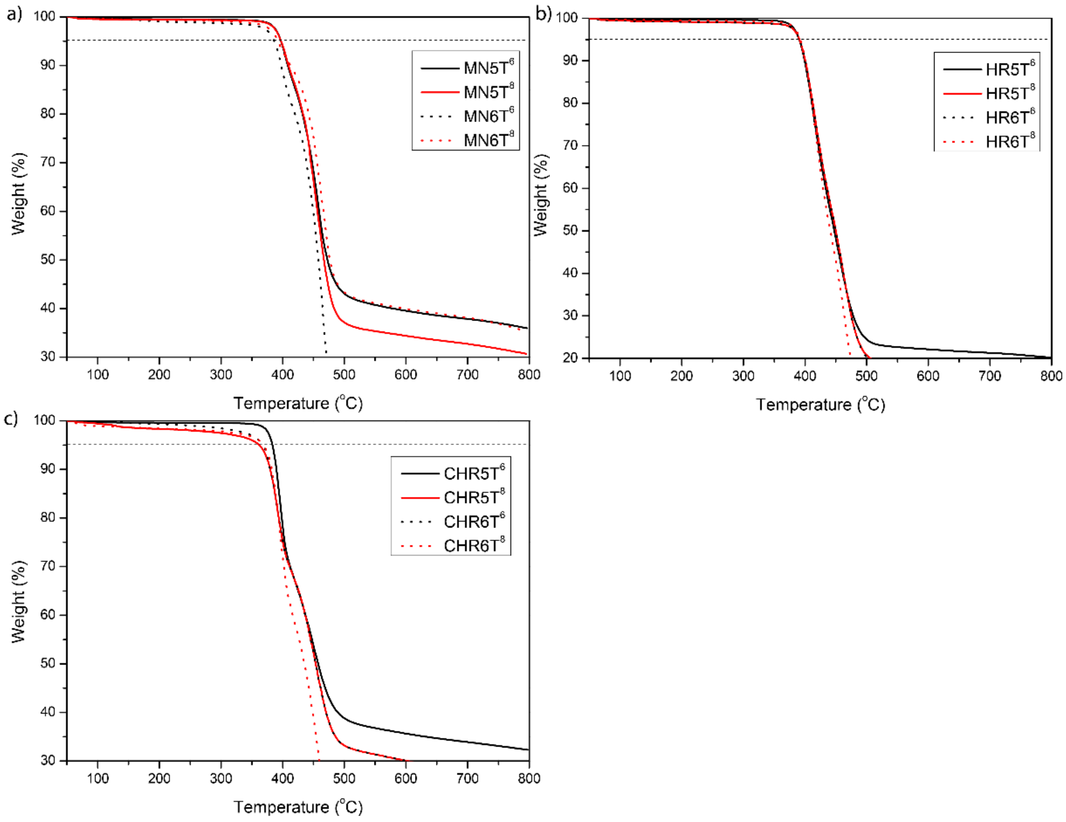


Figure S5.1. TGA thermograms of our oligothiophene materials with a) **MN-**, b) **HR-** and c) **CHR-** end-group acceptors.

Table S1. Thermal decomposition temperatures for our oligothiophene materials.

Oligothiophene	**T$_{Decomp}$ (5% weight) ^{0}C**
MN5T^6	*395*
MN5T^8	*395*
MN6T^6	*383*
MN6T^8	*389*
HR5T^6	*388*
HR5T^8	*389*
HR6T^6	*388*
HR6T^8	*391*
CHR5T^6	*381*
CHR5T^8	*351*
CHR6T^6	*363*
CHR6T^8	*361*

S6 DSC thermograms for the Oligothiophene material series

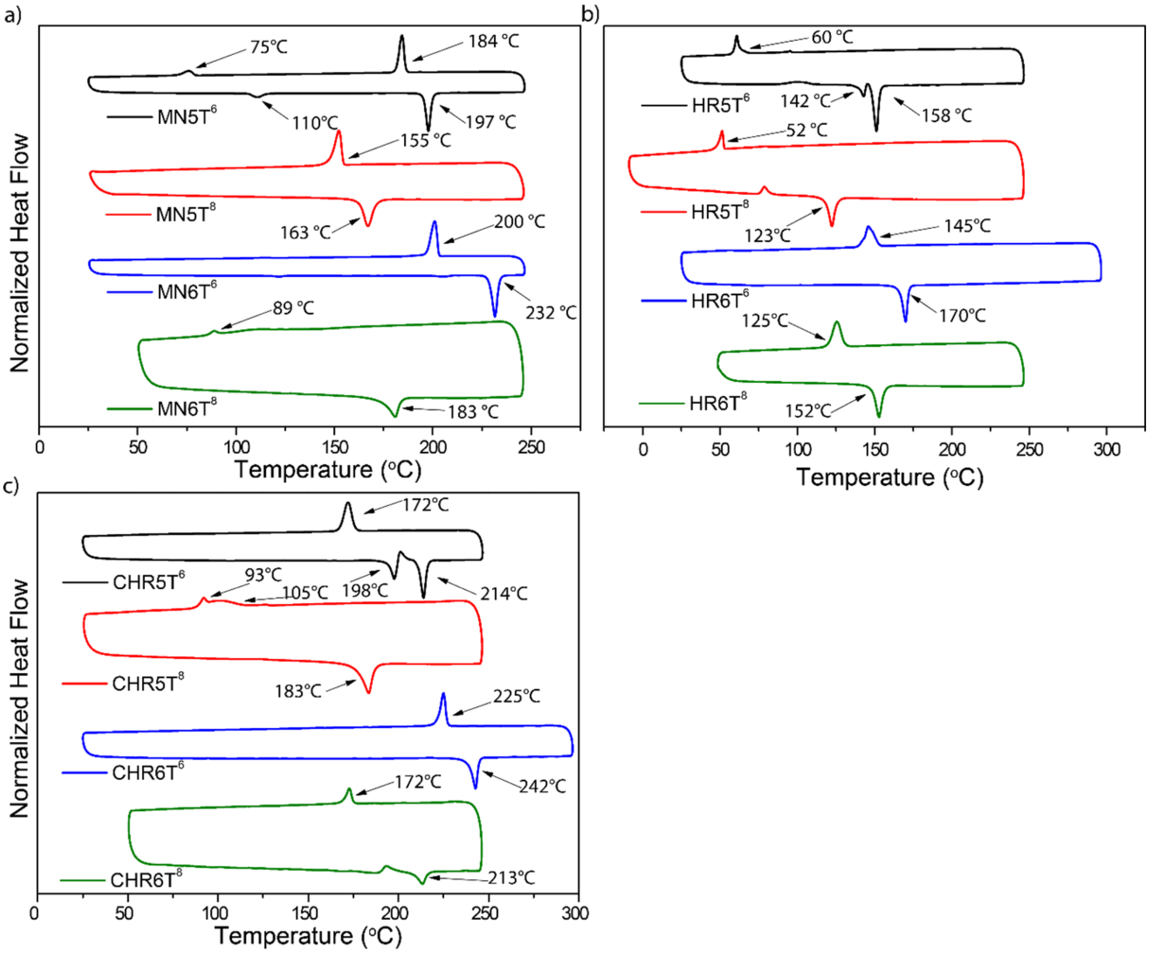


Figure S6.1. Normalized DSC thermograms for our oligothiophene materials with a) **MN-**, b) **HR-** and c) **CHR-** end-group acceptors with labelled phase transition temperatures

Table S2. Melting point temperatures for our oligothiophene materials

Oligothiophene	Melting Point
MN5T^6	197
MN5T^8	163
MN6T^6	232
MN6T^8	183
HR5T^6	158
HR5T^8	130
HR6T^6	170
HR6T^8	152
CHR5T^6	214
CHR5T^8	183
CHR6T^6	242
CHR6T^8	213

For the polarized optical microscope images, A Linkham TMS 94 variable temperature stage was mounted on an Olympus BH2 fluorescence microscope. Samples were mounted using standard glass microscope slides with a cover slip and located in the microscope focus. A high resolution Luminera Infinity 4-11C 10.7 megapixel CCD camera was mounted on the microscope for image capture using the transmission light source of the microscope.

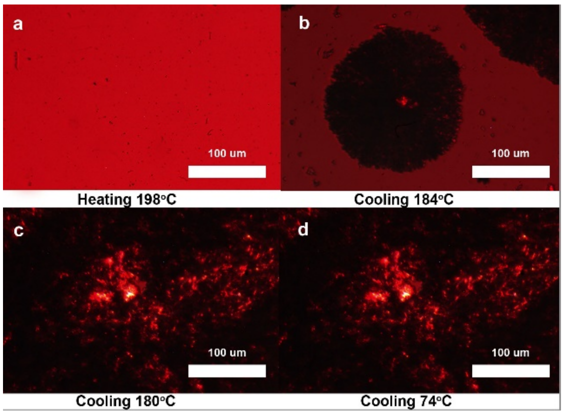


Figure S6.2. Selected POM images for **MN5T^6**, heating and cooling cycle

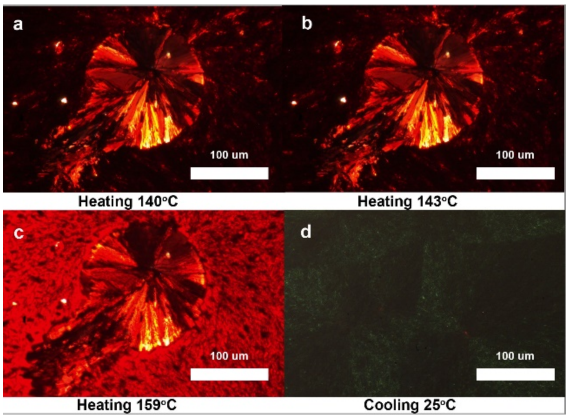


Figure S6.3. Selected POM images for **HR5T^6**, heating and cooling cycle

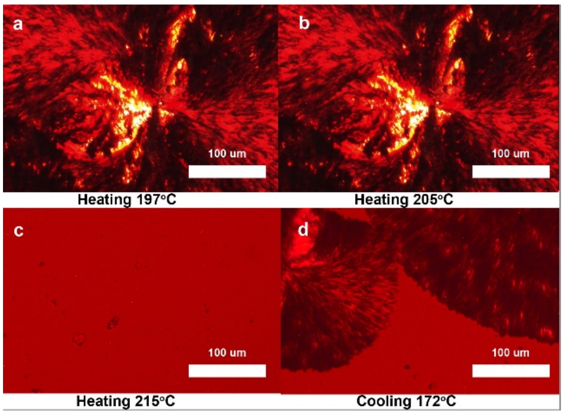


Figure S6.4. Selected POM images for **CHR5T^6**, heating and cooling cycle

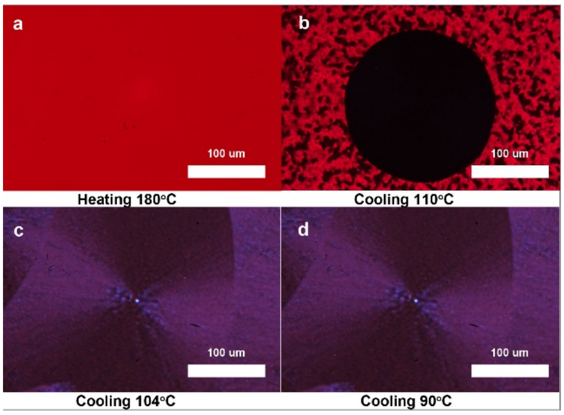


Figure S6.5. Selected POM images for **CHR5T^8**, heating and cooling cycle

S7 UV-vis absorption spectra

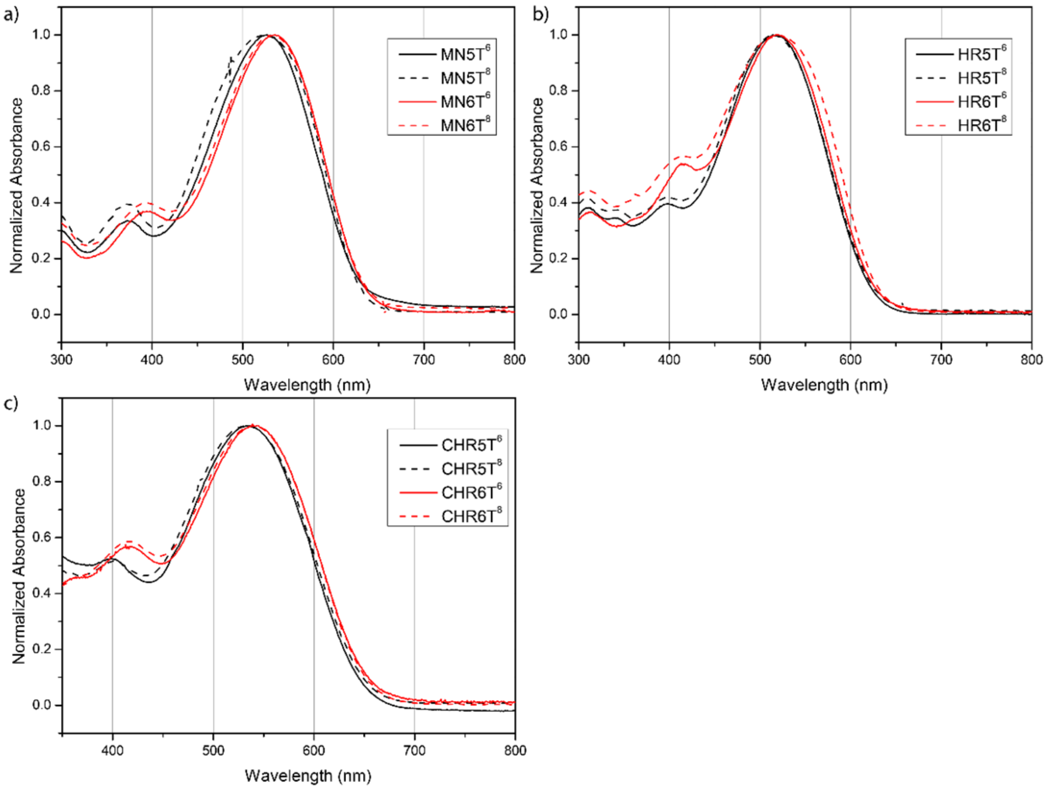


Figure S7.1: Normalized UV-vis absorption spectra of our oligothiophene materials with a) **MN-**, b) **HR-** and c) **CHR-** end-group acceptors, in chloroform solutions.

S8 Cyclic Voltammograms for the Oligothiophene material series

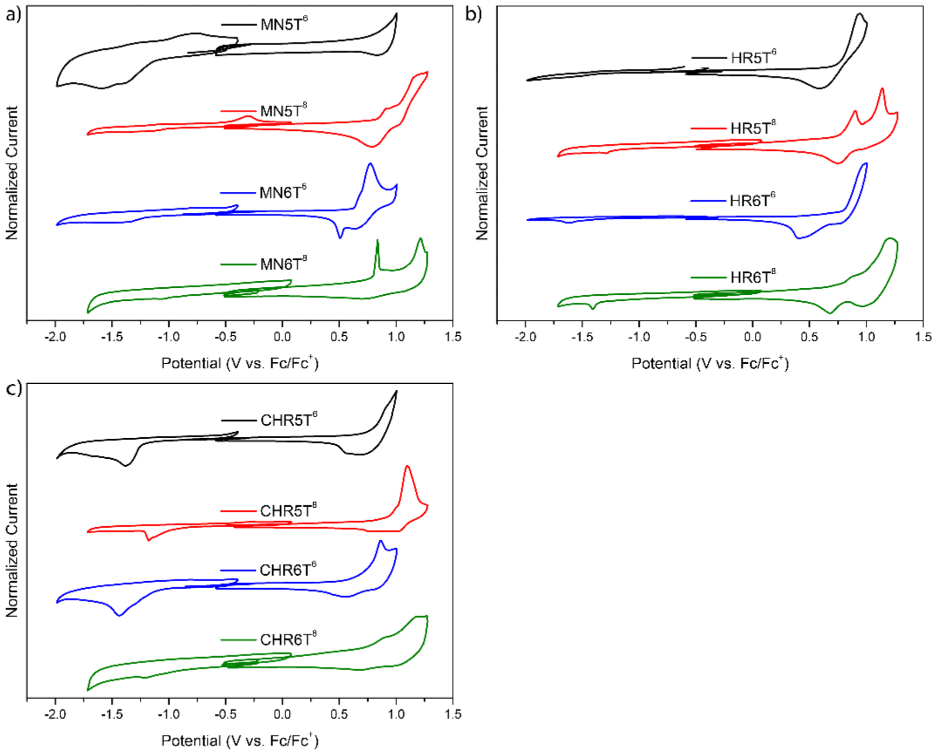


Figure S8.1: Normalized thin film cyclic voltammograms of our oligothiophene materials with a) **MN-**, b) **HR-** and c) **CHR-** end-group acceptors.

S9 Device Performance Parameters

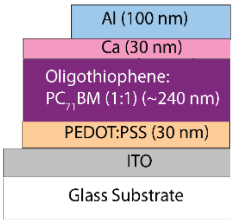


Figure S9.1: Schematic of OPV device architecture

Table S3. Oligothiophene device data for non-optimized processing conditions

Annealing Conditions	Active Layer (1:1 Donor: $PC_{71}BM$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
As-cast	**MN5T^{6}**	0.90	2.3	30	0.6
	MN5T^{8}	0.92	2.8	31	0.8
	MN6T^{6}	0.84	0.8	24	0.2
	MN6T^{8}	0.86	1.2	27	0.3
SVA (THF, 20 sec)	**MN5T^{6}**	0.84	1.8	38	0.6
	MN5T^{8}	0.82	1.4	44	0.5
	MN6T^{6}	0.78	1.7	32	0.4
	MN6T^{8}	0.84	2.1	36	0.6
As-cast	**HR5T^{6}**	1.00	3.3	29	1.0
	HR5T^{8}	0.98	3.9	31	1.2
	HR6T^{6}	0.92	3.4	49	1.5
	HR6T^{8}	0.92	3.8	46	1.6
Thermal Annealing (120°C, 10 min)	**HR5T^{6}**	0.60	3.3	47	0.9
	HR5T^{8}	0.58	3.0	44	0.8
	HR6T^{6}	0.82	2.3	52	1.0
	HR6T^{8}	0.82	1.1	59	0.5
As-cast	**CHR5T^{6}**	1.00	5.0	48	2.4
	CHR5T^{8}	0.98	6.5	46	2.6
	CHR6T^{6}	0.92	4.9	36	1.6
	CHR6T^{8}	0.90	4.7	33	1.4
SVA (THF, 20 sec)	**CHR5T^{6}**	0.96	5.6	42	2.3
	CHR5T^{8}	0.92	4.8	48	2.1
	CHR6T^{6}	0.90	3.2	29	1.0
	CHR6T^{8}	0.88	3.9	31	1.1

S10 SCLC charge mobility measurements

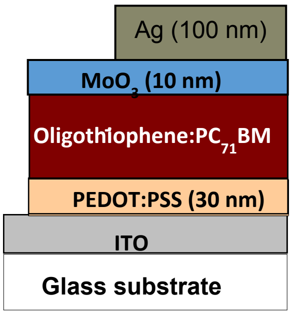


Figure S10.1: Schematic of OPV device architecture

Table S4. Oligothiophene SCLC mobility measurements on annealed films

Active Layer	Hole Mobility
MN5T^6	**1.7x10^{-4}**
MN5T^8	**2.3 x 10^{-4}**
MN6T^6	**4.5 x 10^{-5}**
MN6T^8	**2.5 x 10^{-5}**
HR5T^6	**3.1 x 10^{-4}**
HR5T^8	**4.2 x 10^{-4}**
HR6T^6	**8.3 x 10^{-4}**
HR6T^8	**1.1 x 10^{-3}**
CHR5T^6	**1.3 x 10^{-3}**
CHR5T^8	**9.8 x 10^{-4}**
CHR6T^6	**5.8 x 10^{-4}**
CHR6T^8	**4.5 x 10^{-4}**

S11 GIWAXS linecuts and scattering pattern data

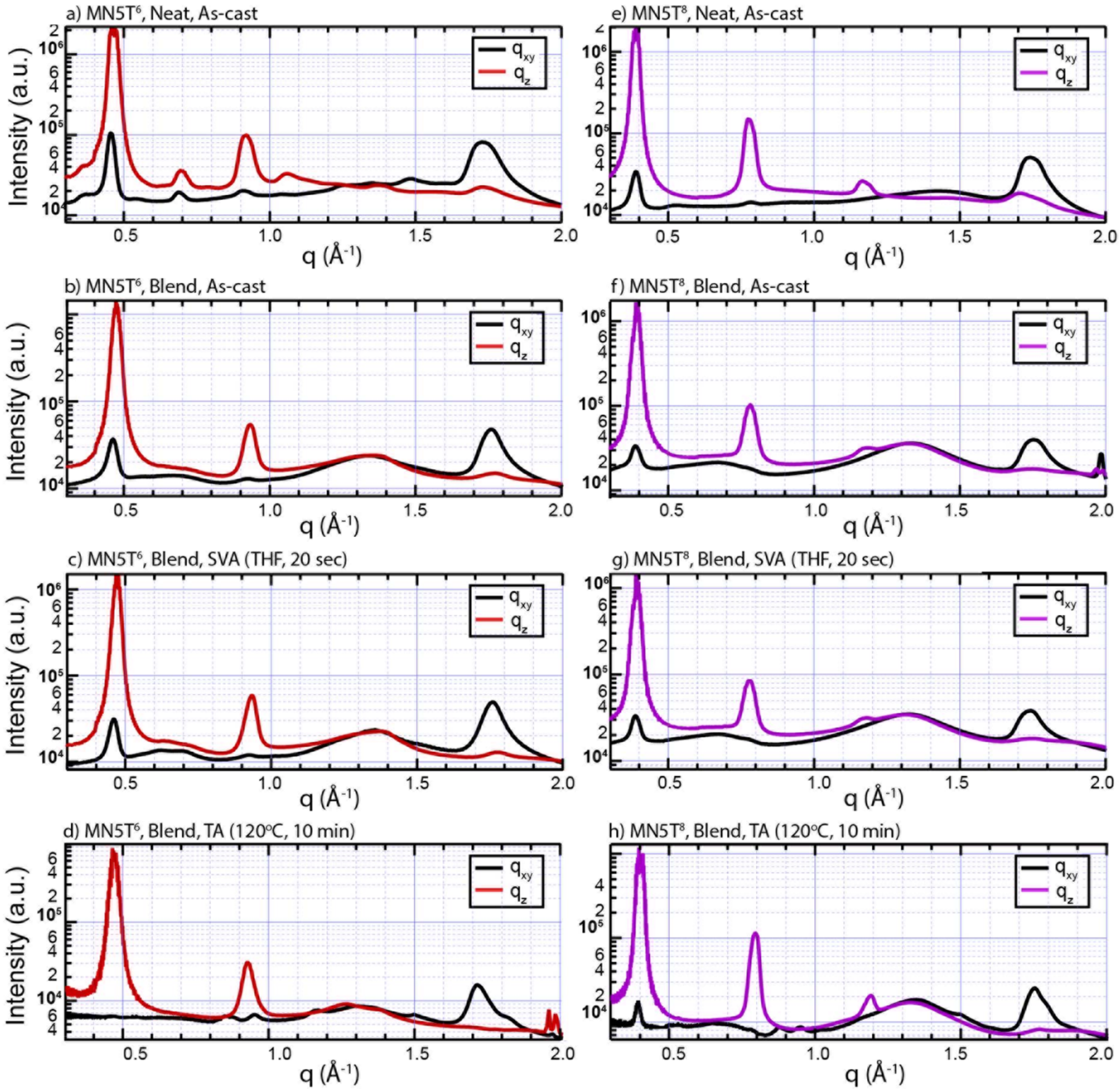


Figure S11.1 Linecuts of the GIWAXS scattering patterns for the **MN5T^6** (a-d) and **MN5T^8** (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S5. MN5T^X scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
MN5T^6	Neat, As-Cast	19.1	1.36	0.36	**MN5T^8**	Neat, As-Cast	24.7	1.62	0.36
	Blend, As-Cast	22.3	1.33	0.36		Blend, As-Cast	24.1	1.61	0.36
	Blend, SVA (THF)	24.2	1.33	0.36		Blend, SVA (THF)	24.6	1.60	0.36
	Blend, TA	22.1	1.36	0.37		Blend, TA	25.6	1.59	0.36

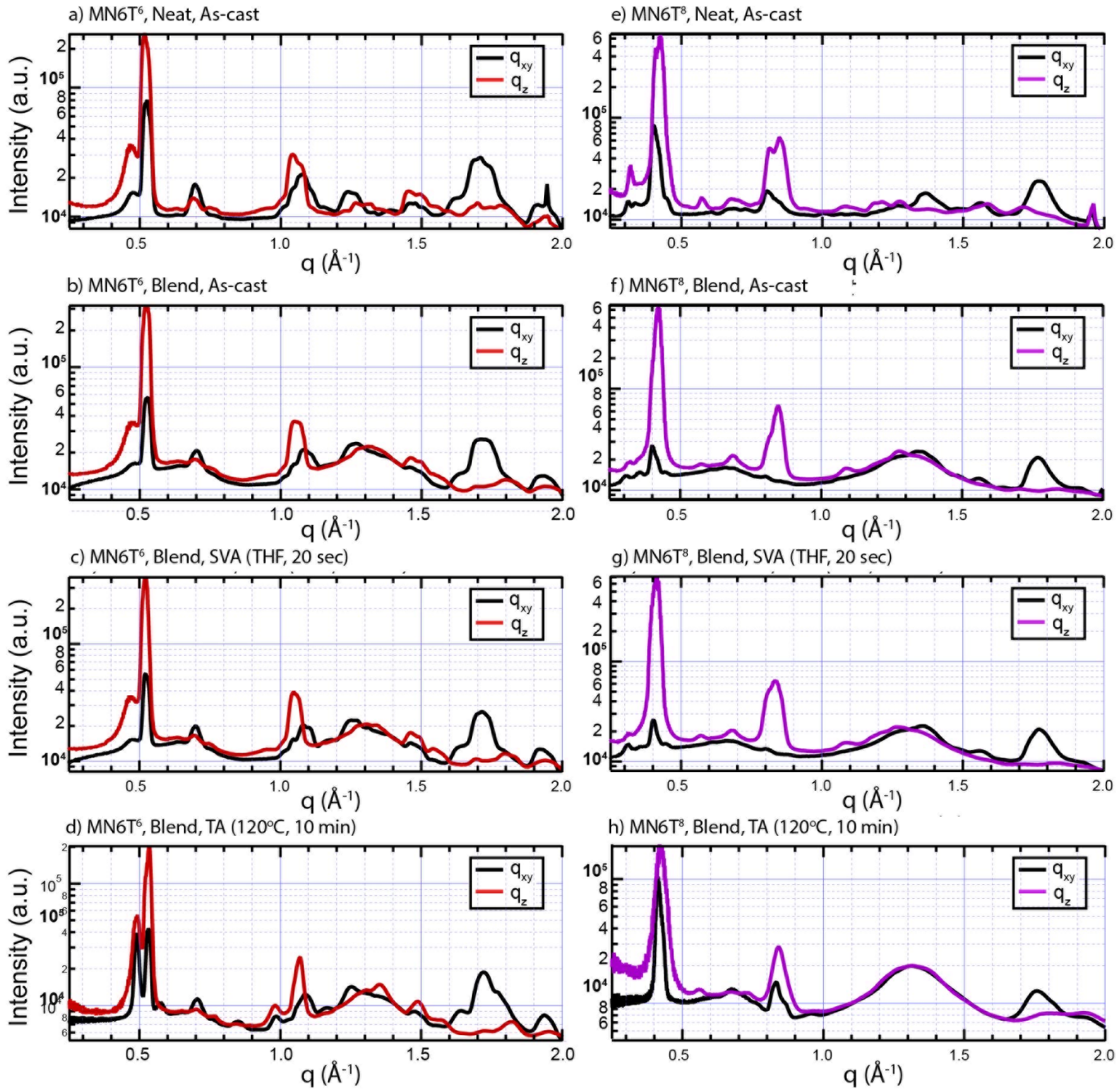


Figure S11.2 Linecuts of the GIWAXS scattering patterns for the **MN6T^6** (a-d) and **MN6T^8** (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S6. MN6T^X -functionalized oligothiophene scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
MN6T^6	Neat, As-Cast	23.2	1.21	0.37	**MN6T^8**	Neat, As-Cast	27.9	1.47	0.35
	Blend, As-Cast	24.6	1.20	0.37		Blend, As-Cast	26.0	1.48	0.36
	Blend, SVA (THF)	30.2	1.18	0.37		Blend, SVA (THF)	26.5	1.53	0.36
	Blend, TA	30.9	1.12	0.37		Blend, TA	17.8	1.49	0.36

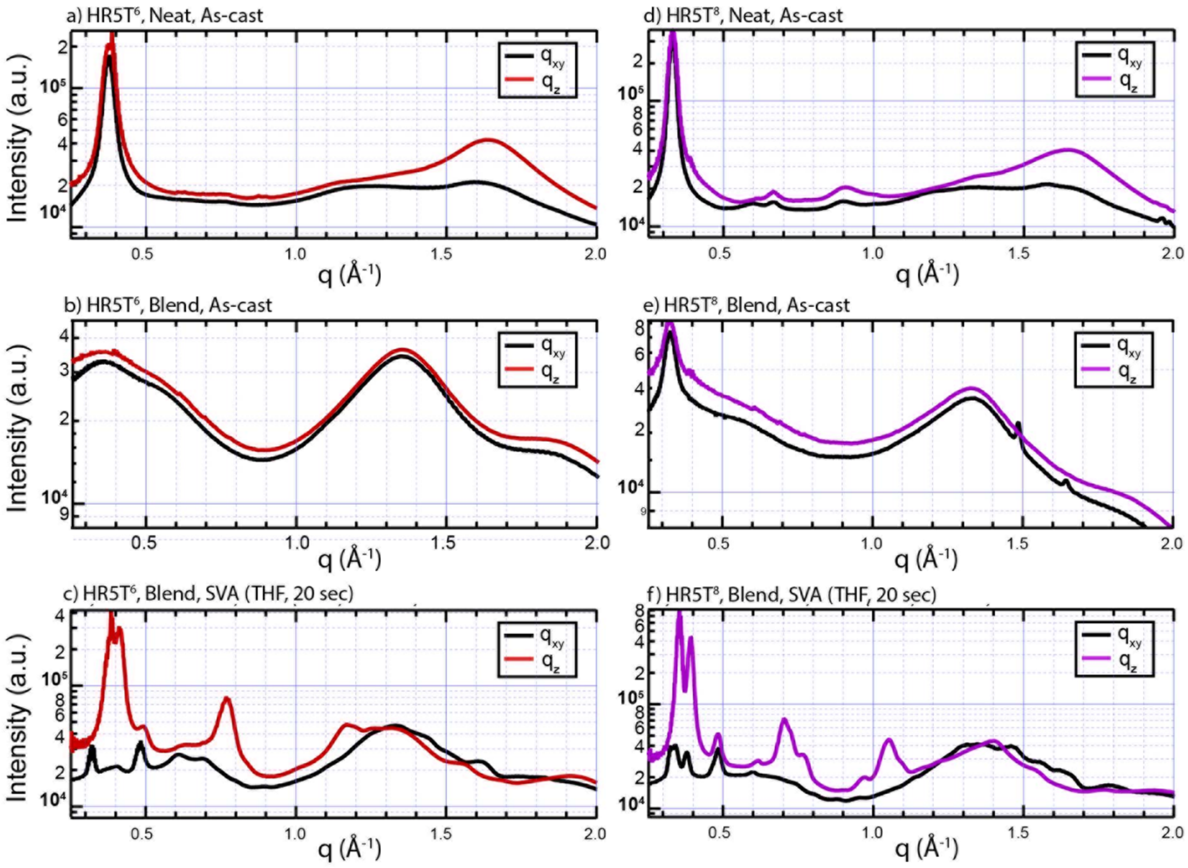


Figure S11.3 Linecuts of the GIWAXS scattering patterns for the **HR5T^6** (a-c) and **HR5T^8** (d-f) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S7. HR5T^X scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
HR5T^6	Neat, As-Cast	14.5	1.66	0.38	**HR5T^8**	Neat, As-Cast	21.8	1.91	0.38
	Blend, As-Cast	1.17	1.70	N/A		Blend, As-Cast	11.4	1.96	N/A
	Blend, SVA (THF)	27.1	1.64	0.38		Blend, SVA (THF)	36.1	1.78	0.38

	a (Å)	***b*** (Å)	***c*** (Å)	α (°)	β (°)	γ (°)		***a*** (Å)	***b*** (Å)	***c*** (Å)	α (°)	β (°)	γ (°)
HR5T^6 Blend, SVA (THF)	16.4	3.7	39.6	86.6	90	89.5	**HR5T^8 Blend, SVA (THF)**	18.3	3.8	37.7	79.8	90	90

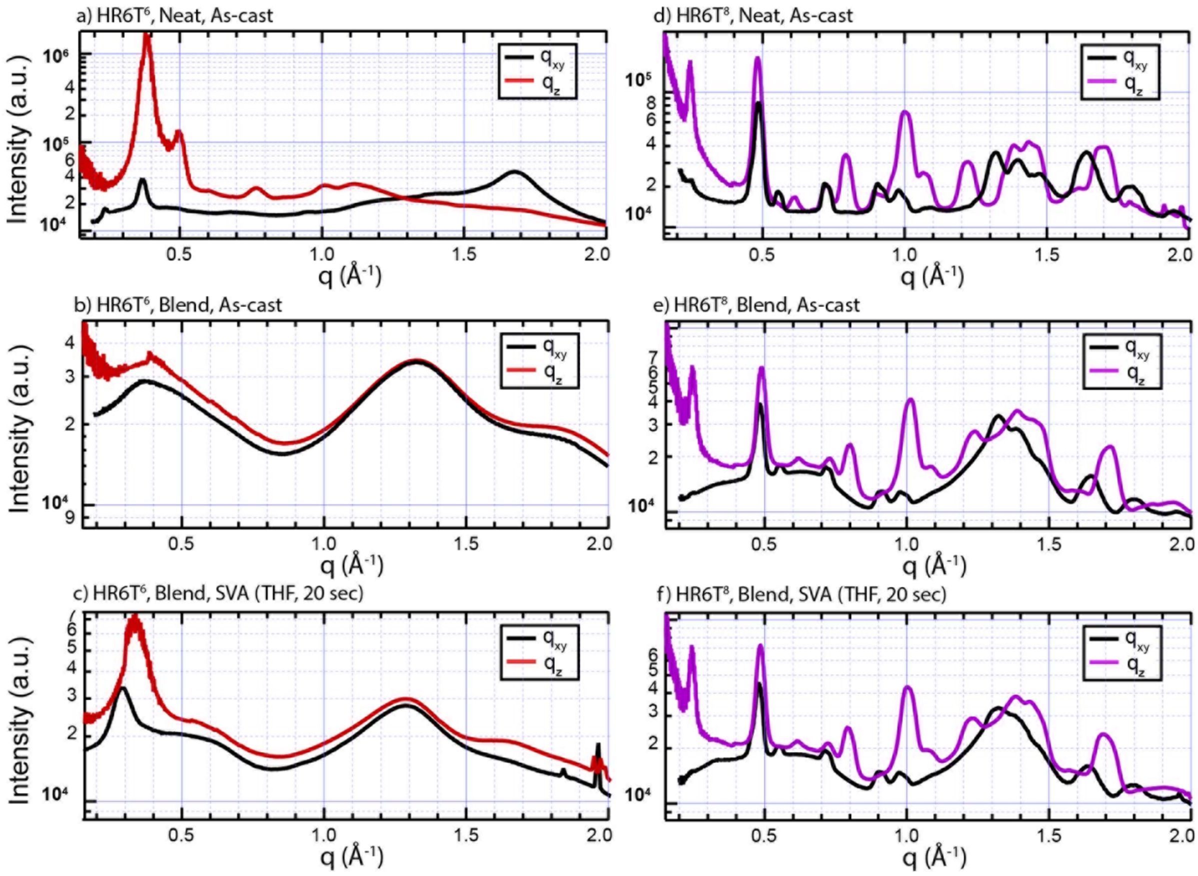


Figure S11.4 Linecuts of the GIWAXS scattering patterns for the **HR6T^6** (a-c) and **HR6T^8** (d-f) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S8. HR6T^X scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
HR6T^6	Neat, As-Cast	18.7	1.63	0.37	**HR6T^8**	Neat, As-Cast	23.6	1.31	0.38
	Blend, As-Cast	3.28	1.59	N/A		Blend, As-Cast	21.1	1.29	0.37
	Blend, SVA (THF)	8.2	1.52	0.38		Blend, SVA (THF)	21.6	1.30	0.37

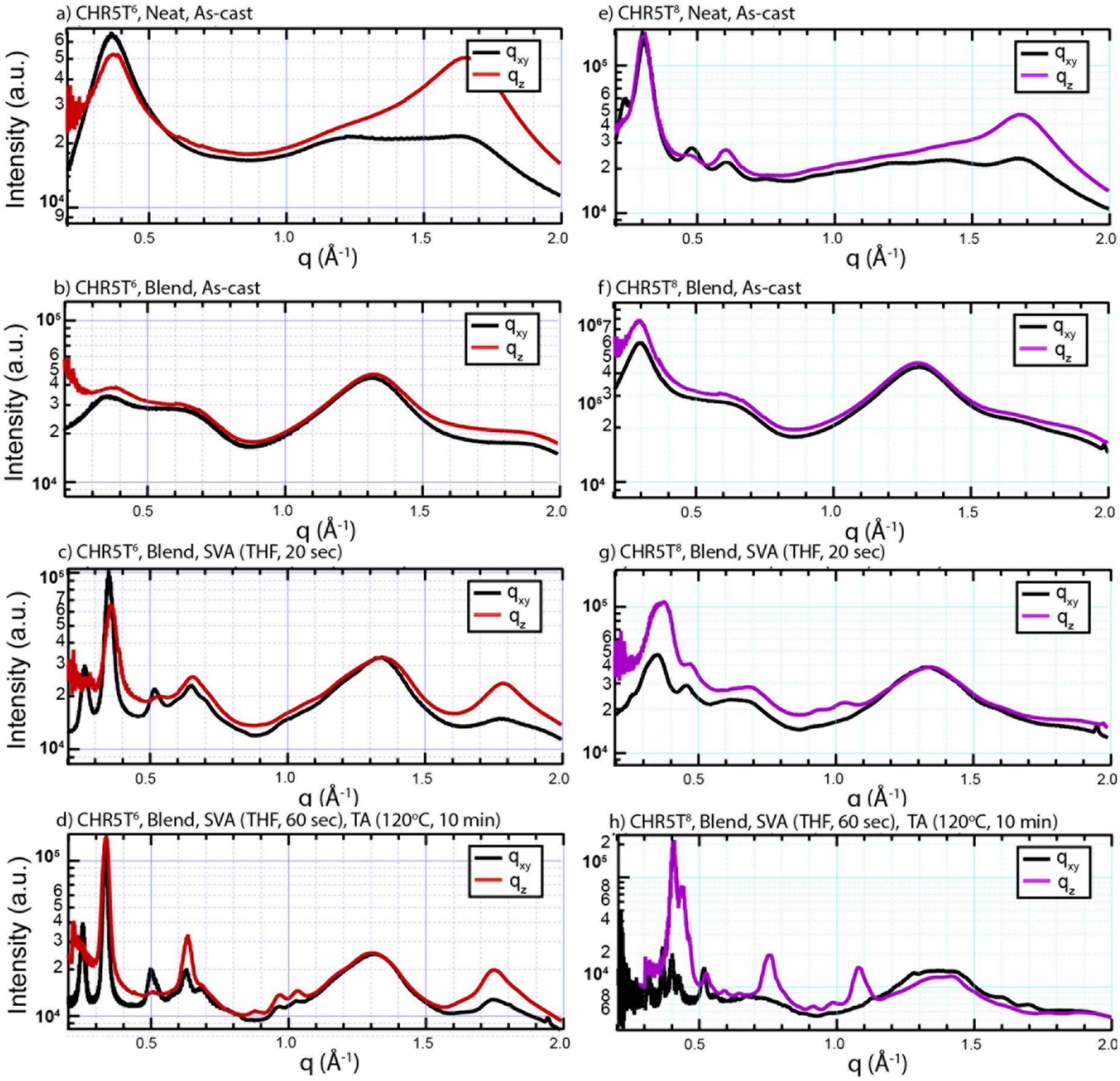


Figure S11.5 Linecuts of the GIWAXS scattering patterns for the **CHR5T^6** (a-d) and **CHR5T^8** (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S9. CHR5T^X scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
CHR5T^6	Neat, As-Cast	10.25	1.72	0.38	**CHR5T^8**	Neat, As-Cast	12.8	1.87	0.36
	Blend, As-Cast	3.12	1.72	N/A		Blend, As-Cast	8.0	1.87	N/A
	Blend, SVA (THF)	22.9	1.81	0.36		Blend, SVA (THF)	10.3	1.81	N/A
	Blend, SVA/ TA	37.8	1.87	0.36		Blend, SVA/TA	32.3	1.75	N/A

		a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
	CHR5T^8 Blend,	17.8	3.5	39.1	71.4	89.7	90

	SVA/TA	

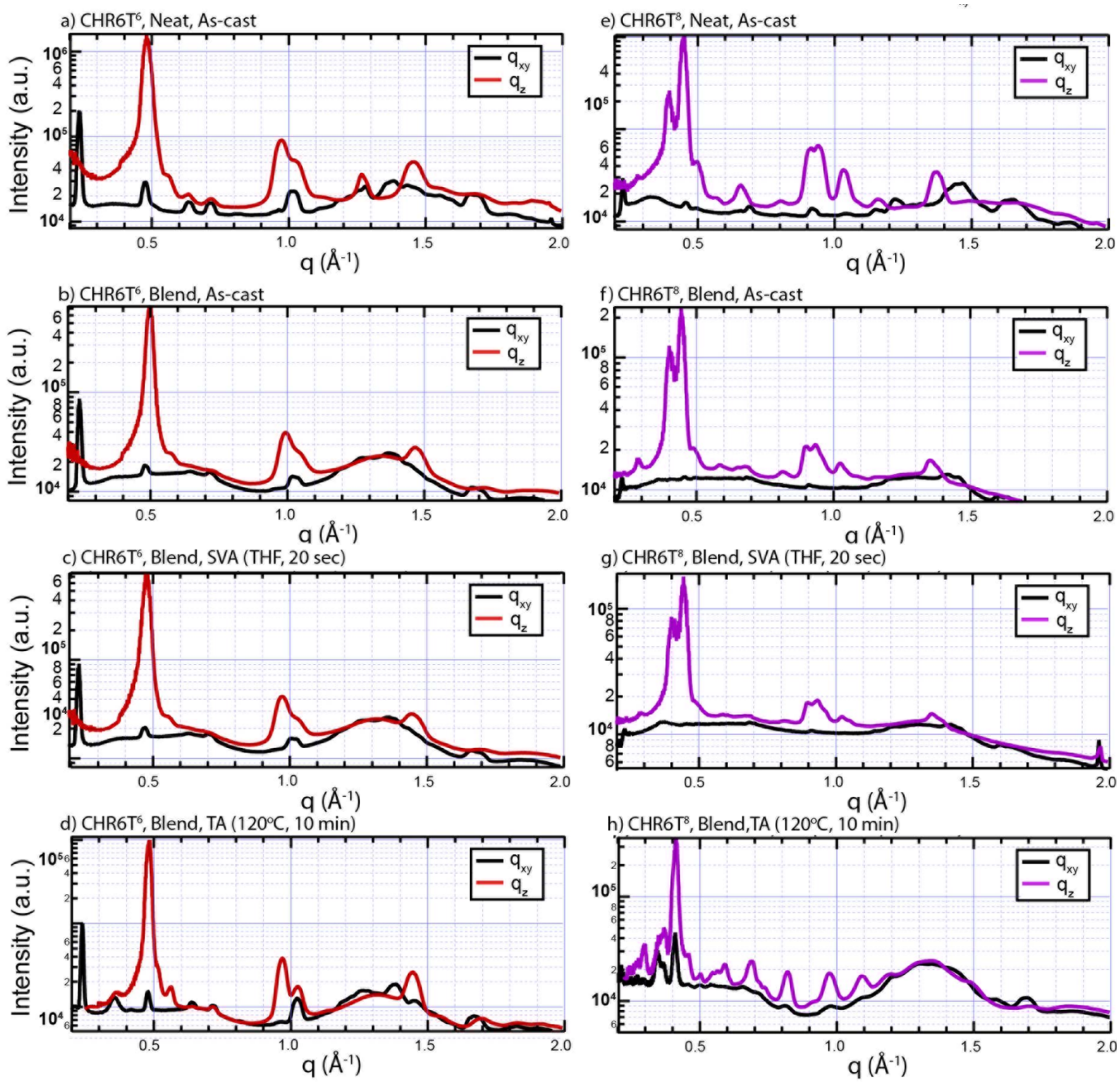


Figure S11.6 Linecuts of the GIWAXS scattering patterns for the **CHR6T^{6}** (a-d) and **CHR6T^{8}** (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table S10. CHR6T^{X} scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
CHR6T^{6}	Neat, As-Cast	21.1	1.28	0.37	**CHR6T^{8}**	Neat, As-Cast	30.3	1.37	0.38
	Blend, As-Cast	25.4	1.28	0.37		Blend, As-Cast	28.1	1.40	
	Blend, SVA (THF)	22.1	1.28	0.37		Blend, SVA (THF)	27.0	1.41	0.38
	Blend, TA	35.0	1.30	0.37		Blend, TA	36.2	1.53	0.37

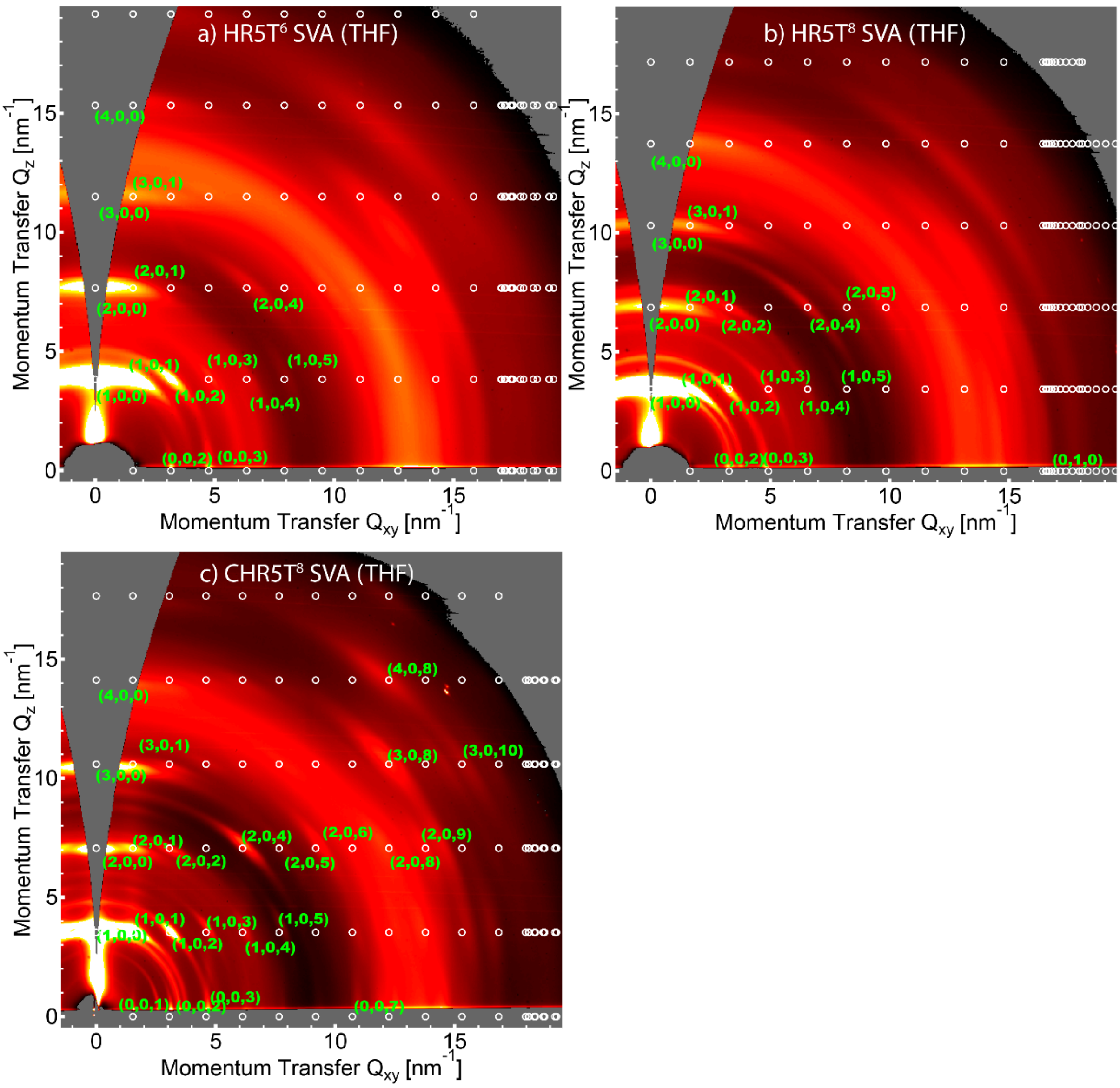


Figure S11.7 Overlay of calculated lattices points (white circles) onto experimental GIWAXS patterns of a) HR5T⁶, b) HR5T⁸ and c) CHR5T⁸. Unit cell parameters are given earlier.

S12 Atomic Force Microscopy

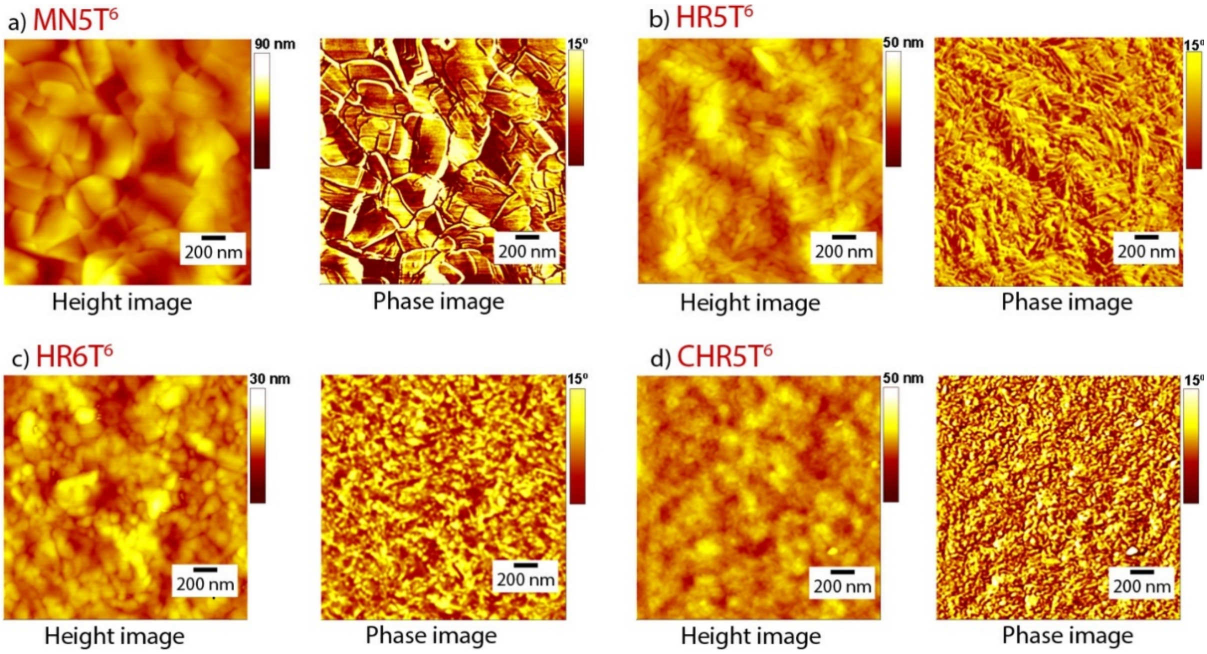


Figure S12.1 AFM images showing the surface topography of the annealed blend films of a) **MN5T^6**, b) **HR5T^6**, c) **HR6T^6** and d) **CHR5T^6**. Annealing conditions and film blend composition are identical to those that give the best OPV device performance.

S13 Crystallography

Table S10. Crystal data for MN5T[8]

Identification code	shelx	
Empirical formula	C60 H76 N4 S5	
Formula weight	1013.54	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.8510(10) Å	α= 86.18(3)°.
	b = 18.549(4) Å	β= 87.84(3)°.
	c = 31.923(6) Å	γ = 88.58(3)°.
Volume	2863.3(10) Å^3	
Z	2	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.243 mm^{-1}	
F(000)	1088	
Crystal size	0.04 x 0.03 x 0.005 mm^3	
Theta range for data collection	1.279 to 25.000°.	
Index ranges	-5<=h<=5, -22<=k<=22, -37<=l<=37	
Reflections collected	35134	
Independent reflections	9109 [R(int) = 0.1755]	
Completeness to theta = 25.000°	90.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9109 / 660 / 612	
Goodness-of-fit on F^2	1.686	
Final R indices [I>2sigma(I)]	R1 = 0.2094, wR2 = 0.5018	
R indices (all data)	R1 = 0.3094, wR2 = 0.5381	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.515 and -0.715 e.Å^{-3}	

S14 References

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