Supporting Information for: Conjugation-length dependence of regioregular oligo(3-alkyl thienylene-vinylene)s demonstrates polyene-like behaviour with weak electron-electron correlations.

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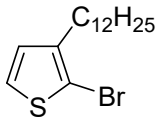
Contents

1/ Synthesis

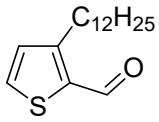
All solvents and chemicals for synthesis were purchased from Sigma-Aldrich, VWR, Fischer Scientific or Fluorochem and were used as received. NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer. GPC was carried out on an Agilent 1260 LC system with two Agilent PLgel MIXED-B columns, running in chlorobenzene at 80 °C and calibrated against narrow weight polystyrene standards. MALDI-TOF mass spectrometry was carried out by the ESPRC National Mass Spectrometry Service using an UltrafleXtreme (MALDI-ToF). DSC thermos-analysis was carried out on a TA Instruments DSC Q20 with a TA Instruments Refrigerated Cooling System 40, and melting points refer to the peak maximum. UV−vis absorption spectra were measured using a Shimadzu UV-1800 UV−vis spectrophotometer.

2-Bromo-3-dodecylthiophene



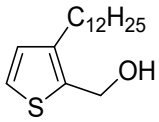
To a solution of 3-dodecylthiophene (50.006 g, 198 mmol) in DMF (300 mL) at 0 °C N-bromosuccinimide (35.253 g, 198 mmol) was slowly added. The reaction was stirred in the absence of light at room temperature for 24 h. The reaction mixture was diluted with hexane (300 mL) and washed with water (5 x 200 mL) and brine (200 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield an orange oil (64.954 g, 196 mmol, 99 %). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (d, J = 5.6 Hz, 1H), 6.80 (d, J = 5.6 Hz, 1H), 2.56 (t, J = 7.6 Hz, 2H), 1.57 (m, 2H), 1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.99, 128.24, 125.12, 108.78, 31.94, 29.74, 29.69, 29.68, 29.66, 29.59, 29.43, 29.40, 29.37, 29.23, 22.71, 14.14.

3-Dodecylthiophene-2-carboxaldehyde



Under an atmosphere of argon, isopropylmagnesium chloride lithium chloride complex solution (166 mL, 1.3 M in THF, 215.5 mmol) was added to a solution of 2-bromo-3-dodecylthiophene (64.905 g, 195.9 mmol) in THF (180 mL) at 0 °C. The solution was warmed to room temperature and stirred for 2 h. N,N-dimethylformamide (31 mL, 391.7 mmol) was added and the reaction stirred for 1 h. The reaction mixture was quenched with 1M aqueous HCl (500 mL) and extracted with Et_2O (300 mL). The organic layer was washed with water (2 x 250 mL) and brine (250 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield an orange oil (56.648 g, 202 mmol, >100% yield attributed to residual DMF). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.04 (d, J = 1.2 Hz, 1H), 7.64 (dd, J = 4.8, 1.2 Hz, 1H), 7.01 (d, J = 4.8 Hz, 1H), 2.95 (t, J = 7.6, 2H), 1.66 (M, 2H), 1.25 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.28, 152.92, 137.65, 134.40, 130.69, 31.92, 31.46, 29.64, 29.63, 29.62, 29.52, 29.38, 29.35, 29.30, 28.52, 22.69, 14.13.

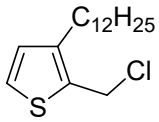
3-Dodecylthiophene-2-methanol



To a solution of 3-dodecylthiophene-2-carboxaldehyde (56.436 g, 201.2 mmol) in EtOH (250 mL) a solution of sodium borohydride (3.806 g, 100.6 mmol) in KOH (38 mL, 10 % w/w in H_2O) was added at room temperature. The reaction was stirred for 1 h, diluted with Et_2O (500 mL) and washed with water (3 x 500 mL) and brine (500 mL). The organic layer was dried

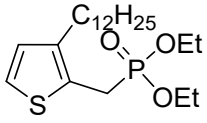
($MgSO_4$) and the solvent was removed *in vacuo* to yield a yellow oil (52.359 g, 185.3 mmol, 92 %). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (d, J = 5.2 Hz, 1H), 6.88 (d, J = 5.2 Hz, 1H), 4.76 (s, 2H), 2.60 (t, J = 7.8 Hz, 2H), 1.57 (m, 2H), 1.26 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.40, 136.53, 129.16, 123.90, 57.76, 31.93, 31.09, 29.67, 29.61, 29.50, 29.48, 29.36, 28.24, 22.71, 14.13. (29.67-29.61 overlapping peaks).

2-Chloromethyl-3-dodecylthiophene



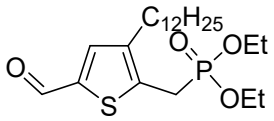
To a solution of 3-dodecylthiophene-2-methanol (52.332 g, 185.3 mmol) in DCM (240 mL) and triethylamine (60 mL) at 0 °C, thionyl chloride (17 mL, 231.6 mmol) was added dropwise. The reaction was stirred at 0 °C for 1 h before careful addition into saturated aqueous $NaHCO_3$ (300 mL). The resulting mixture was extracted with hexane (300 mL) and the organic phase washed with water (3 x 250 mL) and brine (250 mL). The organics were dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to yield an orange oil (56.808 g, 188.8 mmol, Q). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, J = 4.8 Hz, 1H), 6.86 (d, J = 4.8 Hz, 1H), 4.77 (s, 2H), 2.61 (t, J = 7.6 Hz, 2H), 1.61 (m, 2H), 1.26, (m, 18H), 0.89 (t, J = 6.8, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.54, 132.66, 129.03, 125.16, 38.68, 31.93, 30.59, 29.68, 29.65, 29.58, 29.47, 29.36, 28.24, 22.71, 14.13. (29.68-29.36 overlapping peaks).

(3-Dodecyl-thiophen-2-ylmethyl)-phosphonic acid diethyl ester



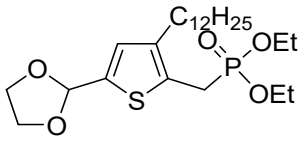
2-Chloromethyl-3-dodecylthiophene (56.742 g, 188.6 mmol) and triethyl phosphite (130 mL, 754.2 mmol) were refluxed for 5 h. After this time residual triethyl phosphite was removed by vacuum distillation. Upon cooling, a dark brown oil was obtained (81.124 g, 201.5 mmol, >100% due to some residual triethyl phosphite). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11 (dd, J = 5.2, 2.8 Hz, 1H), 6.84 (d, J = 5.2 Hz, 1H), 4.09 (m, 6H), 3.32 (d, J = 20.8 Hz, 2H), 2.54 (m, 2H), 1.56 (m, 2H), 1.25 (m, 22H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.80 (d, J_{C-P} = 9.5 Hz), 128.53 (d, J_{C-P} = 3.5 Hz), 125.69 (d, J_{C-P} = 11.3 Hz), 123.17 (d, J_{C-P} = 4.2 Hz), 63.66 (d, J_{C-P} = 5.8 Hz), 62.34 (d, J_{C-P} = 6.8 Hz), 31.92, 30.51, 29.67, 29.63, 29.57, 29.35, 28.34, 26.99, 25.56, 22.69, 16.43 (d, J_{C-P} = 6.0 Hz), 16.18 (d, J_{C-P} = 6.7 Hz), 14.12.

(3-Dodecyl-5-formyl-thiophen-2-ylmethyl)-phosphonic acid diethyl ester



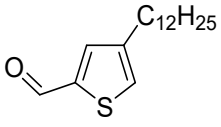
To a solution of crude (3-dodecyl-thiophen-2-ylmethyl)-phosphonic acid diethyl ester (28.651 g, 71.2 mmol) and dichloromethyl methyl ether (9 g, 78.3 mmol) in DCM (300 mL) at 0 °C titanium tetrachloride (32 mL, 291.8 mmol) was added dropwise. The reaction was stirred at 0 °C for 2 h, diluted with hexane (300 mL) and washed with saturated aqueous $NaHCO_3$ (2 x 150 mL) and brine (2 x150 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield an oil (29.752 g, 69.1 mmol, 97 %). NMR data agrees with that previously reported[1]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.79 (s, 1H), 7.53 (s, 1H), 4.10 (m, 6H), 3.36 (d, J = 22 Hz, 2H), 2.58 (m, 2H), 1.59 (m, 2H), 1.25 (m, 22H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.56, 142.66 (d, J_{C-P} = 8.9 Hz), 141.13 (d, J_{C-P} = 3.5 Hz), 138.14 (d, J_{C-P} = 11.6 Hz), 137.68 (d, J_{C-P} = 3.6 Hz), 62.65 (d, J_{C-P} = 6.8 Hz), 31.91, 31.58, 30.16, 29.64, 29.62, 29.56, 29.47, 29.42, 29.34, 28.20, 22.68, 16.42 (d, J_{C-P} = 6.0 Hz), 14.11.

(3-Dodecyl-5-(1,3-Dioxaolan-2-yl)-thiophen-2-ylmethyl)-phosphonic acid diethyl ester



(3-Dodecyl-5-formyl-thiophen-2-ylmethyl)-phosphonic acid diethyl ester (29.752 g, 69.1 mmol), ethylene glycol (8.578 g, 138.2 mmol) and p-toluenesulphonic acid monohydrate (394 mg, 2.1 mmol) were refluxed in toluene (300 mL) using Dean-Stark apparatus for 20 h. The reaction mixture was cooled and washed with saturated aqueous $NaHCO_3$ (200 ml) and the organic layer dried ($MgSO_4$). The solvent was removed *in vacuo* to yield an oil (27.012 g, 56.9 mmol, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.90 (s, 1H), 6.00 (s, 1H), 4.06 (m, 10H), 3.28 (d, J = 20.8 Hz, 2H), 2.49 (m, 2H), 1.53 (m, 2H), 1.25 (m, 22H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.51 (d, J_{C-P} = 9.5 Hz), 139.05 (d, J_{C-P} = 4.2 Hz), 127.68 (d, J_{C-P} = 3.6 Hz), 127.05 (d, J_{C-P} = 11.4 Hz), 100.35, , 65.16, 62.37 (d, J_{C-P} = 6.8 Hz), 31.93, 30.38, 29.67, 29.64, 29.60, 29.55, 29.36, 28.42, 27.19, 25.75, 22.70, 16.44 (d, J_{C-P} = 6.0 Hz), 14.13.

3-Dodecylthiophene-5-carboxaldehyde



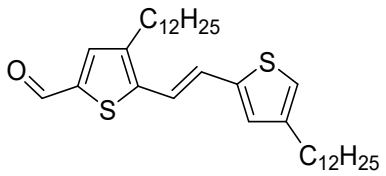
Under an atmosphere of argon, 3-dodecylthiophene (1.11 mL, 4.0 mmol) was added dropwise to 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex solution (3.1 mL, 1 M in THF/toluene, 4.8 mmol) at 0° C. The solution was warmed to room temperature and stirred for 3 h. N,N-dimethylformamide (3.1 mL, 40 mmol) was added, followed by THF (7 mL) and stirred for 1 h. The reaction mixture was poured into 1 M aqueous HCl (100 mL) and extracted with Et_2O (3 x 50 mL). The organics were washed with water (2 x 100 mL), brine

(100 mL) and dried over $MgSO_4$. The crude product was purified by column chromatography over silica (eluent: petroleum ether/EtO_2 9:1) yielding a yellow oil (664 mg, 2.7 mmol, 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.88 (d, *J* = 1.2 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.37 (br .s, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.63 (m, 2H), 1.35-2.20 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H).^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.99, 144.78, 143.60, 137.13, 130.41, 31.92, 30.41, 30.15, 29.67, 29.64, 29.56, 29.40, 29.36, 29.17, 22.70, 14.13. (29.67-29.64 overlapping peaks).

General Procedure for Synthesis of Formylated Oligomers (chain length n) via HWE Reaction

To a solution of formylated oligomer (chain length n-1) in THF (0.1 M), (3-dodecyl-5-(1,3-dioxaolan-2-yl)-thiophen-2-ylmethyl)-phosphonic acid diethyl ester (1 eq) and tBuOK (2 eq.) was added under an atmosphere of argon. After 1 hour of stirring at room temperature, aqueous 2M H_2SO_4 (ca. 3 eq.) was added, and the reaction was stirred for a further hour. The reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with hexane. The organic layer was washed three times with water, once with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product purified by column chromatography (hexane/Et_2O 9:1).

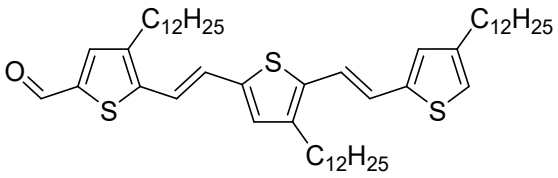
Formylated PTV Dimer



Isolated as an orange solid. Yield = quantitative. ^{1}H NMR (400 MHz, Chloroform-d) δ 9.80 (s, 1H), 7.50 (s, 1H), 7.18 (d, *J* = 15.7 Hz, 2H), 6.97 (d, *J*= 15.7 Hz, 2H), 6.97 (s, 1H), 6.86 (s, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.62 (m, 4H), 1.35-1.1 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.44, 146.47, 144.27, 141.75, 141.34, 139.38, 138.83, 129.23, 125.53, 120.68, 118.22, 31.94, 30.61, 30.39, 29.67, 29.60, 29.56,

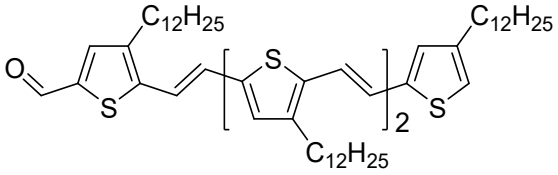
29.47, 29.42, 29.37, 29.29, 29.23, 28.25, 22.71, 14.13. (Not all C atoms observed due to overlapping peaks).

Formylated PTV Trimer



Isolated as a deep red solid. Yield = 32 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1H), 7.50 (s, 1H), 7.13 (d, *J* = 15.6 Hz, 1H), 6.97 (s, 2H), 6.94 (d, *J* = 15.6 Hz, 1H), 6.89 (m, 2H), 6.79 (s, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.65-1.55 (m, 16H), 1.35-1.10 (m, 48H), 0.88 (m, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.40, 146.57, 144.05, 142.23, 142.10, 141.87, 139.40, 138.87, 138.65, 137.07, 131.33, 127.57, 125.23, 122.06, 119.36, 119.01, 118.44, 31.94, 30.75, 30.62, 30.45, 30.39, 29.69, 29.67, 29.61, 29.59, 29.48, 29.47, 29.44, 29.37, 29.31, 29.25, 28.29, 22.71, 14.14. (Not all C atoms observed due to overlapping peaks).

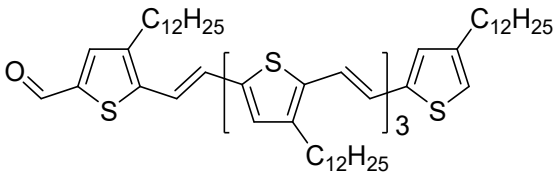
Formylated PTV Tetramer



Isolated as a purple solid. Yield = 21 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1H), 7.51 (s, 1H), 7.13 (d, *J* = 15.6 Hz, 1H), 6.93 (m, 7H), 6.78 (m, 2H), 2.65-2.55 (m, 8H), 1.75-1,65 (m, 8H), 1.4-1.1 (m, 64H), 0.88 (m, 12H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 181.43, 153.83, 151.40, 146.97, 146.40, 144.65, 142.94, 142.05, 141.73, 139.54, 139.36, 139.07, 136.86, 134.55, 131.35, 129.58, 128.67, 123.74, 121.36, 120.36, 119.61, 118.81, 112.99, 31.93, 29.70, 29.66,

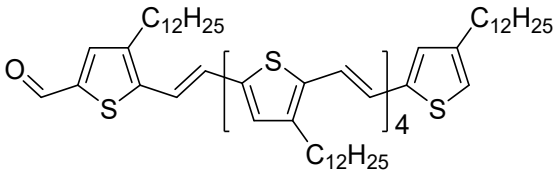
29.59, 29.53, 29.48, 29.44, 29.36, 29.24, 22.70, 14.13. (Not all C atoms observed due to overlapping peaks).

Formylated PTV Pentamer



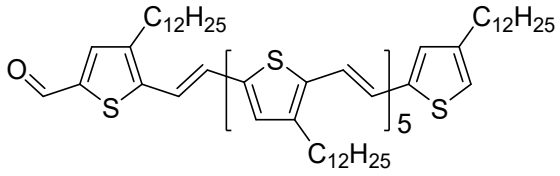
Isolated as a deep purple solid. Yield = 58 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1H), 7.50 (s, 1H), 7.13 (d, *J* = 15.5 Hz, 1H), 6.94 (m, 10H), 6.78 (m, 3H), 2.66-2.5 (m, 10H), 1.66-1.54 (m, 10H), 1.40-1.20 (m, 80H), 0.87 (m, 15H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 182.39, 146.56, 143.98, 142.50, 142.42, 142.30, 142.01, 139.93, 138.91, 138.87, 137.24, 135.87, 135.37, 131.40, 129.68, 127.19, 125.18, 119.54, 119.26, 118.96, 118.52, 31.94, 29.70, 29.62, 29.50, 29.45, 29.38, 29.33, 22.72, 14.14. (Not all C atoms observed due to overlapping peaks).

Formylated PTV Hexamer



Isolated as a deep purple solid. Yield = 51 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1H), 7.51 (s, 1H), 7.14 (d, *J* = 15.6 Hz, 1H), 6.93 (m, 12H), 6.77 (m, 3H), 2.68-2.52 (m, 12H), 1.66-1.52 (m, 12H), 1.40-1.20 (m, 96H), 0.87 (m, 18H). ^{13}C NMR could not be fully resolved due to low solubility and low relative intensity of quaternary carbons.

Formylated PTV Heptamer

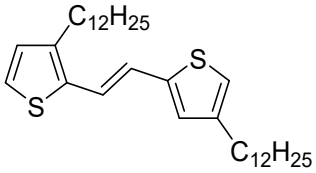


Isolated as a deep purple solid. Yield = 27 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1H), 7.51 (s, 1H), 7.14 (d, *J* = 15.6 Hz, 1H), 6.92 (m, 15H), 6.77 (m, 6H), 2.68-2.52 (m, 14H), 1.66-1.25 (m, 14H), 1.40-1.20 (m, 112H), 0.87 (m, 21H). ^{13}C NMR could not be fully resolved due to low solubility and low relative intensity of quaternary carbons.

General Procedure for Synthesis of Capped Oligomer (chain length n) via HWE Reaction

To a solution of formylated oligomer (chain length n-1) in THF (0.05 M), (3-dodecyl-thiophen-2-ylmethyl)-phosphonic acid diethyl ester (1 eq) and tBuOK (2 eq) was added under an atmosphere of argon. This was stirred at room temperature for 1 hour. The reaction mixture was diluted in hexane and washed three times with water, once with brine and the organic layer was dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was recrystallised to give the pure product.

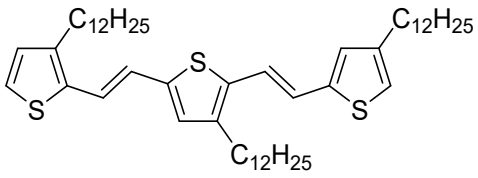
PTV Dimer



Recrystallised from acetone to give a pale yellow solid, yield = 64 %. M.pt. 38 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, *J* = 5.1 Hz, 1H), 7.01 (d, *J* = 15.8 Hz, 1H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.86 (d, *J* = 1.3 Hz, 1H), 6.83 (d, *J* = 5.1 Hz, 1H), 6.75 (d, *J* = 1.4 Hz, 1H), 2.64 (t, 2H), 2.55 (t, 2H), 1.58 (m, 4H), 1.26 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101

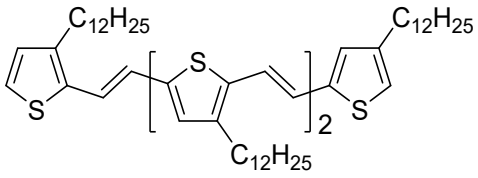
MHz): δ 143.87, 142.42, 140.94, 135.92, 129.78, 127.07, 122.71, 121.10, 119.54, 118.67, 31.94, 30.93, 30.47, 30.39, 29.68, 29.66, 29.61, 29.48, 29.37, 29.35, 29.32, 28.40, 22.71, 14.14. (31.94-14.14 overlapping peaks). HRMS (MALDI) *m/z* calcd. for $C_{34}H_{56}S_2$ 529.3823 [M^+]; found 529.3892.

PTV Trimer



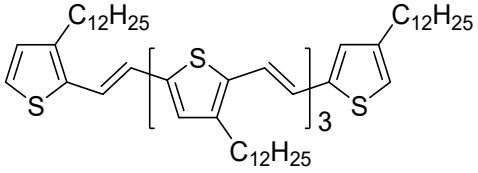
Recrystallised from acetone to give an orange solid, yield = 30 %. M. pt. 42 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 15.7 Hz, 1H), 6.99 (d, *J* = 15.7 Hz, 1H) 6.92 (d, *J* = 15.7 Hz, 1H), 6.90 (d, *J* = 15.7 Hz, 1H), 6.87 (s, 1H), 6.85 (d, *J* = 5.1 Hz, 1H), 6.76 (s, 2H), 2.61 (m, 6H), 1.60 (m, 6H), 1.27 (m, 48H), 0.89 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.95, 142.54, 141.87, 141.20, 139.92, 136.05, 134.97, 129.85, 129.06, 127.12, 122.95, 121.04, 120.87, 119.94, 119.33, 118.86, 31.95, 30.96, 30.79, 30.48, 30.40, 29.72, 29.68, 29.63, 29.51, 29.39, 29.34, 28.44, 28.34, 22.72, 14.15. (31.95-14.15 overlapping peaks). HRMS (MALDI) *m/z* calcd. for $C_{52}H_{84}S_3$ 804.5735 [M^+]; found 804.5717.

PTV Tetramer



Recrystallised from acetone to give a bright red solid, yield = 47 %. M. pt. 83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 15.6 Hz, 1H), 6.98 (d, *J* = 15.6 Hz, 1H), 6.95 – 6.83 (m, 6H), 6.76 (m, 3H), 2.60 (m, 8H), 1.59 (m, 8H), 1.26 (m, 64H), 0.88 (s, 12H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.97, 142.53, 142.18, 141.99, 141.27, 140.16, 140.03, 136.04, 135.17, 135.11, 129.87, 129.13, 127.14, 123.01, 121.07, 120.82, 120.76, 120.03, 119.69, 119.30, 118.89 (143.97-118.89 one overlapping peak), 31.94, 30.95, 30.79, 30.47, 30.39, 29.71, 29.67, 29.61, 29.50, 29.37, 29.33, 28.43, 28.35, 22.71, 14.14. (31.94-14.14 overlapping peaks). HRMS (MALDI) *m/z* calcd. for $C_{70}H_{112}S_4$ 1080.7647 [M^+]; found 1080.7612.

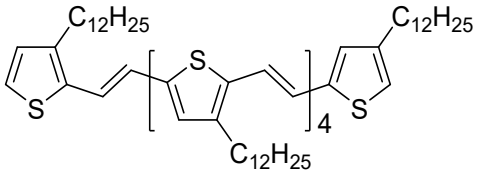
PTV Pentamer



Recrystallised from hexane to give a purple solid, yield = 38%. M. pt. 87 (first endotherm), 96 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 15.7 Hz, 1H), 6.99 (d, *J* = 15.7 Hz, 1H), 6.96 – 6.83 (m, 10H), 6.77 (s, 4H), 2.73 (m, 10H), 1.60 (m, 10H), 1.39 (m, 80H), 0.91 (m, 15H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.97, 142.54, 142.29, 142.23, 142.00, 141.28, 140.30, 140.23, 140.05, 136.05, 135.34, 135.22, 135.13, 129.86, 129.14, 127.14, 123.01, 121.09, 120.81, 120.72, 120.06, 119.78, 119.67, 119.30, 118.90 (143.97-118.90 overlapping peaks), 31.95, 30.96, 30.80, 30.48, 30.40, 29.87, 29.72, 29.68, 29.62, 29.51, 29.38,

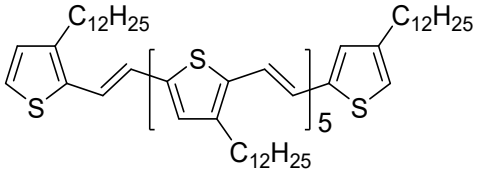
29.34, 28.45, 28.36, 22.72, 14.14. (31.94-14.14 overlapping peaks). MS (MALDI) *m/z* 1357.0 [M^+].

PTV Hexamer



Recrystallized from hexane to give a deep purple solid, yield = 38 %. M. pt. 101 (first endotherm), 108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.2 Hz, 1H), 7.03 (m, 12H), 6.77 (s, 5H), 2.61 (m, 12H), 1.59 (m, 12H), 1.42 (m, 96H), 0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.95, 142.51, 142.29, 142.25, 141.99, 141.27, 140.33, 140.27, 140.21, 140.01, 136.01, 135.34, 135.31, 135.19, 135.09, 129.86, 129.20, 129.14, 127.14, 123.01, 121.06, 120.78, 120.71, 120.04, 119.64, 119.26, 118.88 (143.95-118.88 overlapping peaks), 31.92, 30.94, 30.78, 30.45, 30.37, 29.69, 29.66, 29.60, 29.48, 29.36, 29.32, 28.41, 28.34, 28.30, 22.69, 14.12. (31.92-14.12 overlapping peaks). HRMS (MALDI) *m/z* 1633.1 [M^+].

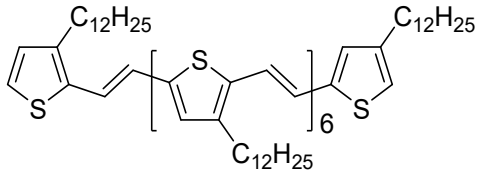
PTV Heptamer



Recrystallised from hexane to give a deep purple solid, yield = 57 %. M. pt. 109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.02 (m, 15H), 6.77 (m, 6H), 2.70 (m, 14H), 1.62 (m, 14H), 1.42 (m, 112H), 0.92 (m, 21H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.96, 142.30, 141.99, 141.28, 140.34, 140.02, 136.01, 135.35, 135.09, 129.86, 129.15, 127.14, 123.02, 121.06, 120.78, 120.05, 119.64, 119.27, 118.89 (143.96-118.89 overlapping peaks), 31.92,

30.94, 30.79, 30.45, 30.38, 29.70, 29.66, 29.60, 29.49, 29.36, 29.32, 28.42, 28.34, 22.70, 14.13. (31.92-14.13 overlapping peaks). MS (MALDI) *m/z* 1909.3 [M^+].

PTV Octamer



Recrystallised from hexane to give a deep purple solid, yield = 39 %. M. pt. 119 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 5.1 Hz, 1H), 7.02 (m, 16H), 6.77 (m, 7H), 2.61 (m, 16H), 1.61 (m, 16H), 1.28 (m, 128H), 0.93 (m, 24H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ143.96, 142.37, 142.30, 141.99, 141.28, 140.35, 136.01, 135.35, 135.08, 129.85, 129.22, 129.14, 127.14, 123.01, 121.06, 120.78, 120.05, 119.74, 119.27, 118.89 (143.96-118.89 overlapping peaks), 31.92, 30.94, 30.79, 30.45, 30.37, 29.70, 29.66, 29.60, 29.49, 29.36, 29.32, 28.42, 28.34, 22.69, 14.12. (31.92-14.13 overlapping peaks). HRMS (MALDI) *m/z* 2185.5 [M^+].

2/ Dilute solutions of nTV trimer show no evidence of aggregation

We measured the diffusion coefficient of the oligo(3-dodecyl(thienlyene-vinylene)) trimer in toluene solution using diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR). Figure S1a shows that the diffusion coefficient ($5.9 \times 10^{-6}\ cm^2 s^{-1}$) is independent of concentration (~200 μM-5 mM).

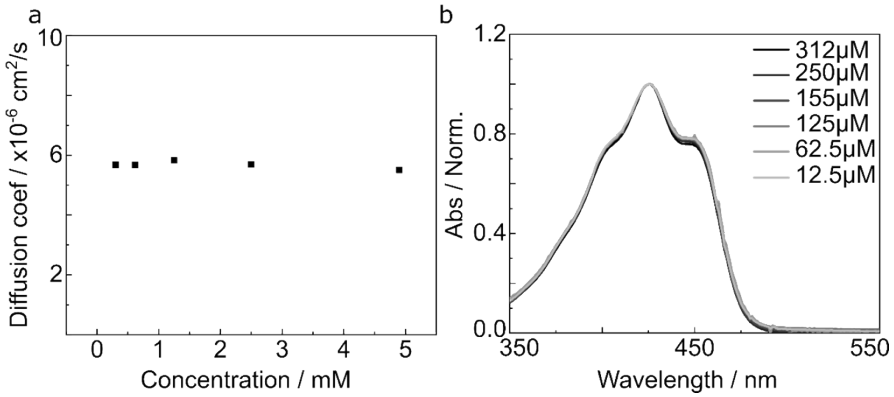


Figure S1: Ruling out aggregation in trimer samples with concentration dependent absorption. (a) Diffusion coefficient of trimer sampled over a large range of concentrations measured using DOSY NMR. The lack of change with concentration rules out large scale aggregation. (b) Ground state absorption of the trimer at several concentrations in toluene solution (1mm path length) within the range used in the measurements (Abs saturation 0.5 mM), showing no signs of aggregation.

The diffusion coefficient can be used to calculate the molecular weight of the species in solution using the methods discussed in Refs[2–4]. Therefore, DOSY NMR can be used as a sensitive test of molecular aggregation or diffusional interactions in solution. We find that the molecular weight calculated from the diffusion coefficient yields a value of ~1000 g/mol, similar to the expected value of a single, well solvated molecule. In addition, this value agrees with the molecular weight determined using gel permeation chromatography (1064 g/mol) and calculated via calibration with narrow dispersity polystyrene standards of known molecular weight Figure (S1a).

As the diffusion coefficient is constant across a range of concentrations (~200 μM – 5 mM), well above those used for the spectroscopic measurements in the main text, we conclude that

the nTV trimer does not aggregate in solution at the concentrations used in this work. We note that the absorption spectrum likewise shows no change with concentration (Figure S1b).

3/ Franck-Condon Modelling

We fit the absorption and fluorescence spectra in Figure 1 and 2 of the main text using a standard Franck Condon fitting procedure, outlined in Refs[5,6]. We assume that the electronic transition couples to a single effective vibrational mode. Using this assumption, the relative intensity of the vibronic replica follows a Poisson distribution, as described in Equations 1 (emission) and 2 (absorption):

$$I_{PL} = (n_x x)^3 \Sigma_m \left(e^{-s} \frac{S^m}{m!} e^{-\left(\frac{(x - (E_{0-0} - m\omega_{vib}))^2}{\sigma^2} \right)} \right) \quad (1)$$

$$I_{Abs} = (n_x x) \Sigma_m \left(e^{-s} \frac{S^m}{m!} e^{-\left(\frac{(x - (E_{0-0} + m\omega_{vib}))^2}{\sigma^2} \right)} \right) \quad (2)$$

Here I_{PL} (I_{Abs}) is the intensity of the relative emission (absorption) at energy x. n_x is the refractive index of the solvent at energy x, m is the quantum number of the vibronic replica and S is the Huang-Rhys factor, which is proportional to ΔQ^2, the square of the normal co-ordinate displacement between the ground- and excited-state potential energy surfaces. We use a Gaussian line shape function to account for inhomogeneous broadening which broadens all vibronic replica identically. For flexible chromophores in solution, this inhomogeneous broadening includes conformational and dynamic disorder of the molecule and surrounding solvent [5,7].

The spectra in Figures 1 and 3 are fitted using these functions and a Levenberg–Marquardt least squares fitting algorithm. The resulting Franck-Condon fits are shown for ground state absorption spectra below in Figure S2a, and fits to the photoluminescence spectra are shown in Figure 3 of the main text. To confirm accuracy of the fits we show the residual of these fits for the absorption spectra in Figure S2b and photoluminescence spectra in Figure S2c.

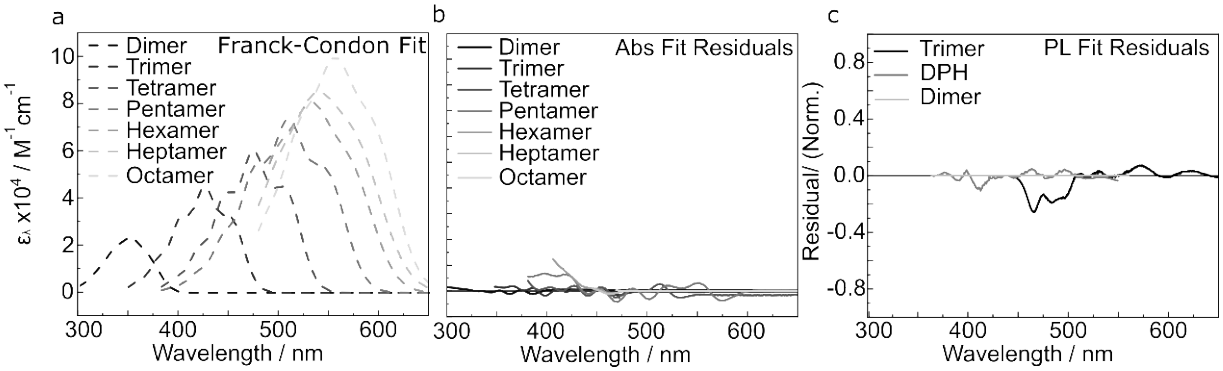


Figure S2: Franck-Condon fitting to the ground state absorption spectra of the nTV series. (a) Results of Franck Condon fitting to the ground state absorption spectra of the nTV series in toluene solution (OD of ~ 0.4-0.6, 1 mm path length). Parameters used for the fits are shown in Table 1 below. (b)/(c) Residuals of the fits shown in panel a (b), and in Figure 3 of the main text (c). For all fits to ground state absorption spectra the residual represents only measurement noise, other than a small divergence at the high energy edge of the measurement window. For the photoluminescence we find minimal residual for the 0-1 to 0-4 vibronic peaks, while the large negative residual represents the divergence discussed in the main text as due to Herzberg-Teller Coupling.

Table 1: Fitting parameters for the absorption spectra of nTVs (Figure 1/Figure S2).

Name	Extinction Coefficient ($M^{-1}cm^{-1}$)	Huang-Rhys Parameter	FWHM (meV)	Vibrational spacing (meV)	0-0 Peak Energy (eV)	fluorescence Quantum Yield (%)
Dimer	22240	1.53	228	180	3.35	3.6
Trimer	43100	1.41	174	176	2.75	10
Tetramer	55860	1.36	165	171	2.45	<0.1
Pentamer	69140	1.41	175	175	2.27	Unmeasurable
Hexamer	75380	1.46	190	162	2.17	Unmeasurable
Heptamer	81520	1.28	207	170	2.15	Unmeasurable
Octamer	97080	1.41	181	167	2.11	Unmeasurable

Table 2: Fitting parameters for the fluorescence spectra shown in Figure 3.

Name	Huang-Rhys Parameter	FWHM (meV)	Vibrational spacing (meV)	0-0 Peak Energy (eV)
Dimer	2.5	80	150	3.11
Trimer	1.4	139	170	2.59
Diphenyl-Hexatriene[8]	1.69	136	170	3.08

4/ Global Fitting of Fluorescence Up-conversion spectroscopy (FLUPS or time-resolved emission) data

In Figure 4 of the main text we present a global analysis of the FLUPS measurement yielding two spectral components. To carry out this analysis we first fit kinetics at the red and blue wavelength edges of the FLUPS spectra, as discussed and shown in the main text (Figure 4). After fitting the kinetics we then fit each probe wavelength with a combination of the two kinetic fits yielding an amplitude component for each term at each wavelength. Plotting the amplitudes of these components then results in the spectra associated with each state, and as such allows us to deconvolute the spectra into the two components, shown in Figure 4a of the main text. Throughout the fitting procedure all R^2 values associated with the fits are locked to a minimum of 0.99, otherwise the fit is considered unsuccessful. In Figure S3 we show the R^2 value for each fit as a function of wavelength.

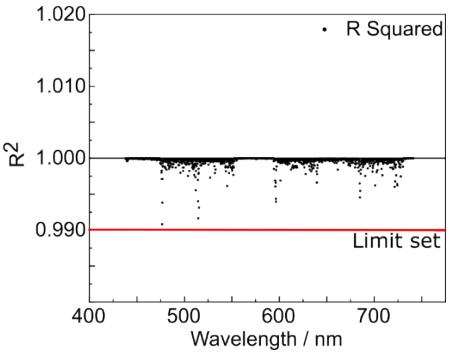


Figure S3: R value associated with the global fitting at each wavelength. Result of the global analysis was considered unsuccessful unless all fits have an R^2 value of 0.99 or more (labelled as a red line).

5/ Transient absorption Spectroscopy

In Figure S4 we show the full false colourmap of the transient absorption traces shown in the main text. We discuss the first 10 ps in the current publication, we will discuss the late time dynamics in a later publication.

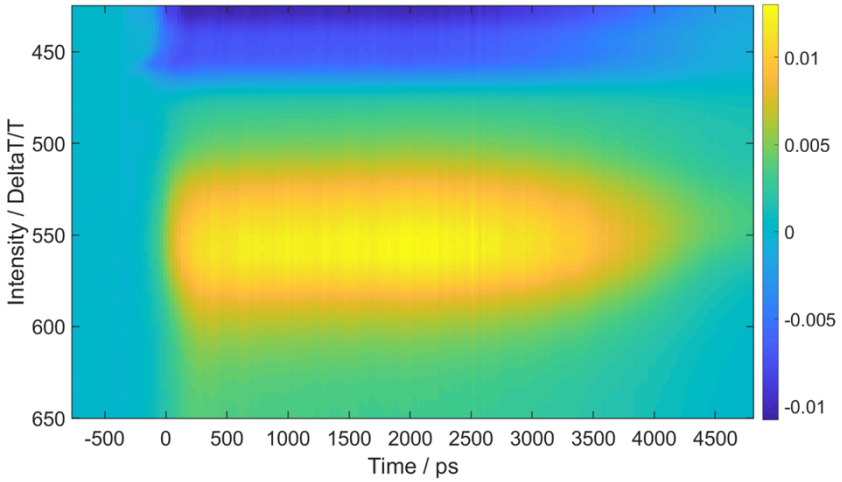


Figure S4: Transient absorption spectroscopy of the n = 3 nTV. Full false colour map of n = 3 nTV after 475 nm excitation in (OD ~ 0.3, 1 mm path length) toluene solution.

Table 3:

Oligomer	Theoretical Molecular Weight (g mol^{-1})	GPC Result, M_n (g mol^{-1})	GPC Result, M_w (g mol^{-1})	PDI
Dimer	529	807	822	1.02
Trimer	805	1036	1062	1.03
Tetramer	1082	1455	1488	1.02
Pentamer	1358	1846	1897	1.03
Hexamer	1635	2269	2340	1.04
Heptamer	1941	2666	2772	1.04
Octamer	2219	3093	3198	1.04

Molecular weight values obtained via GPC.

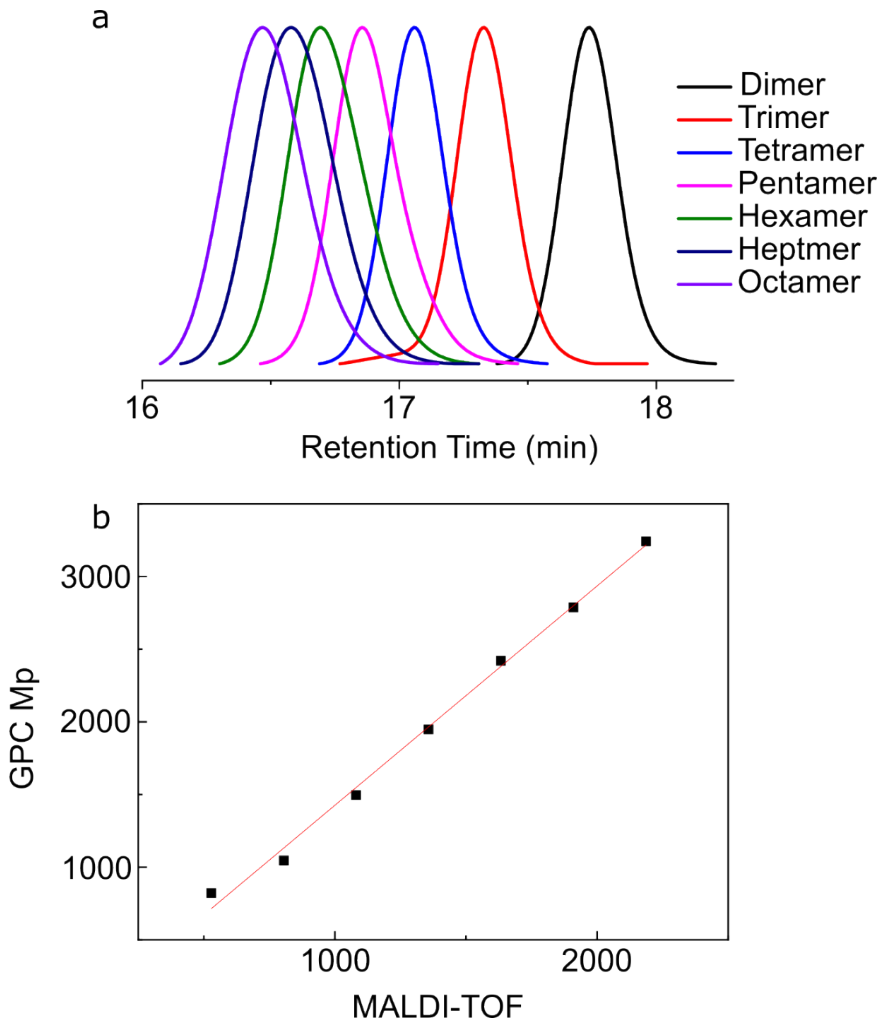
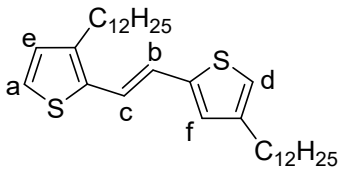


Figure S5. (a) GPC traces of the final oligomers with tabulated number and weight average mass versus polystyrene standards. (b) Oligomers obtained by GPC plot against mass values obtained by MALDI-TOF, a straight line of best fit (red) revealed a gradient and therefore a conversion factor of 1.51 between the two techniques.



c

Figure S6: NMR spectra of the purified dimer (top) with chemical shifts assigned and the the NMR spectrum of the crude dimer (bottom) with the proposed Z-isomer shifts labelled.

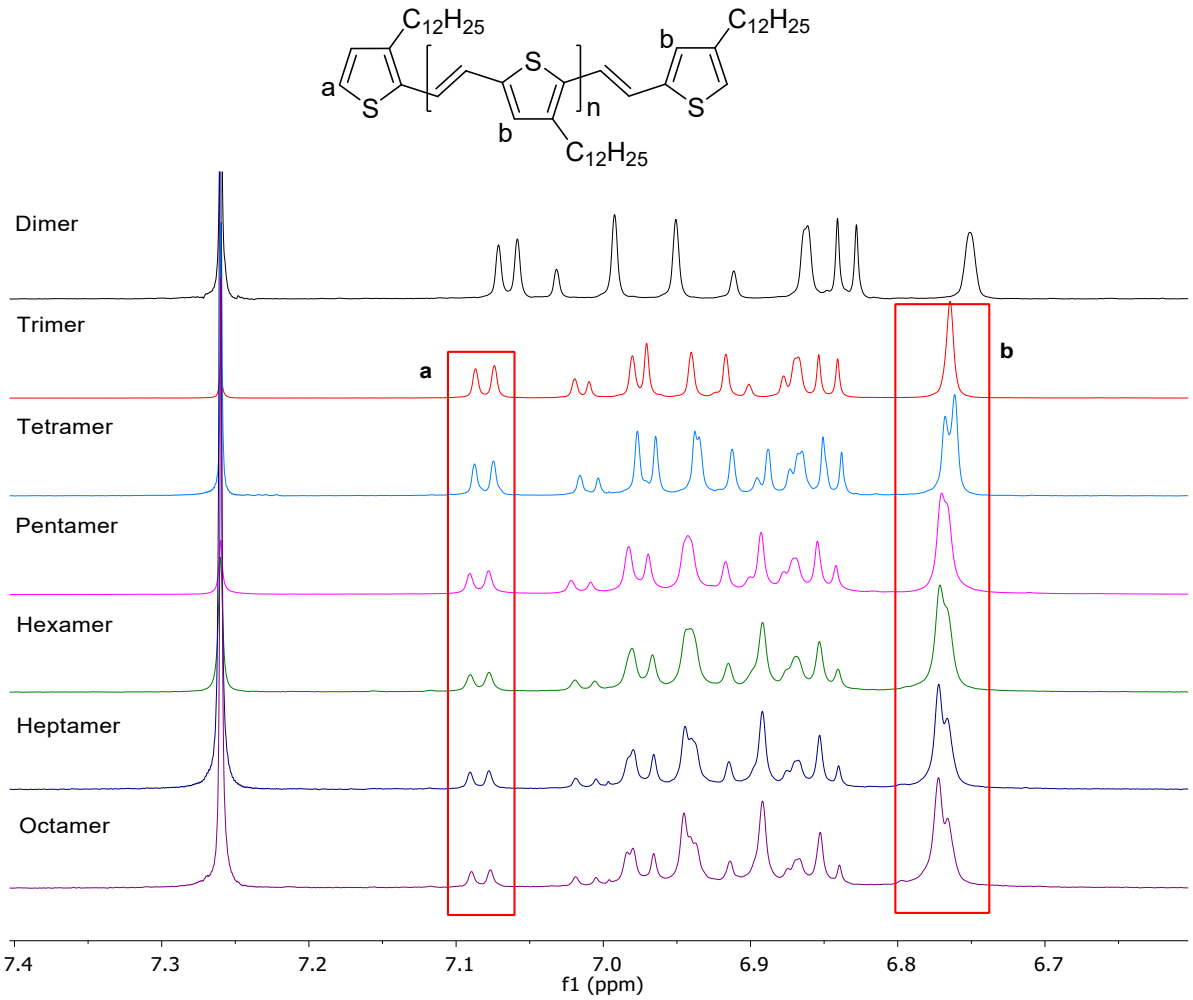


Figure S7: NMR spectra of the synthesised oligomers in the aromatic region. Here it can be seen that the chemical shifts relating to the protons labelled a and b are far enough removed from the rest of the peaks in the spectra to give accurate integrations.

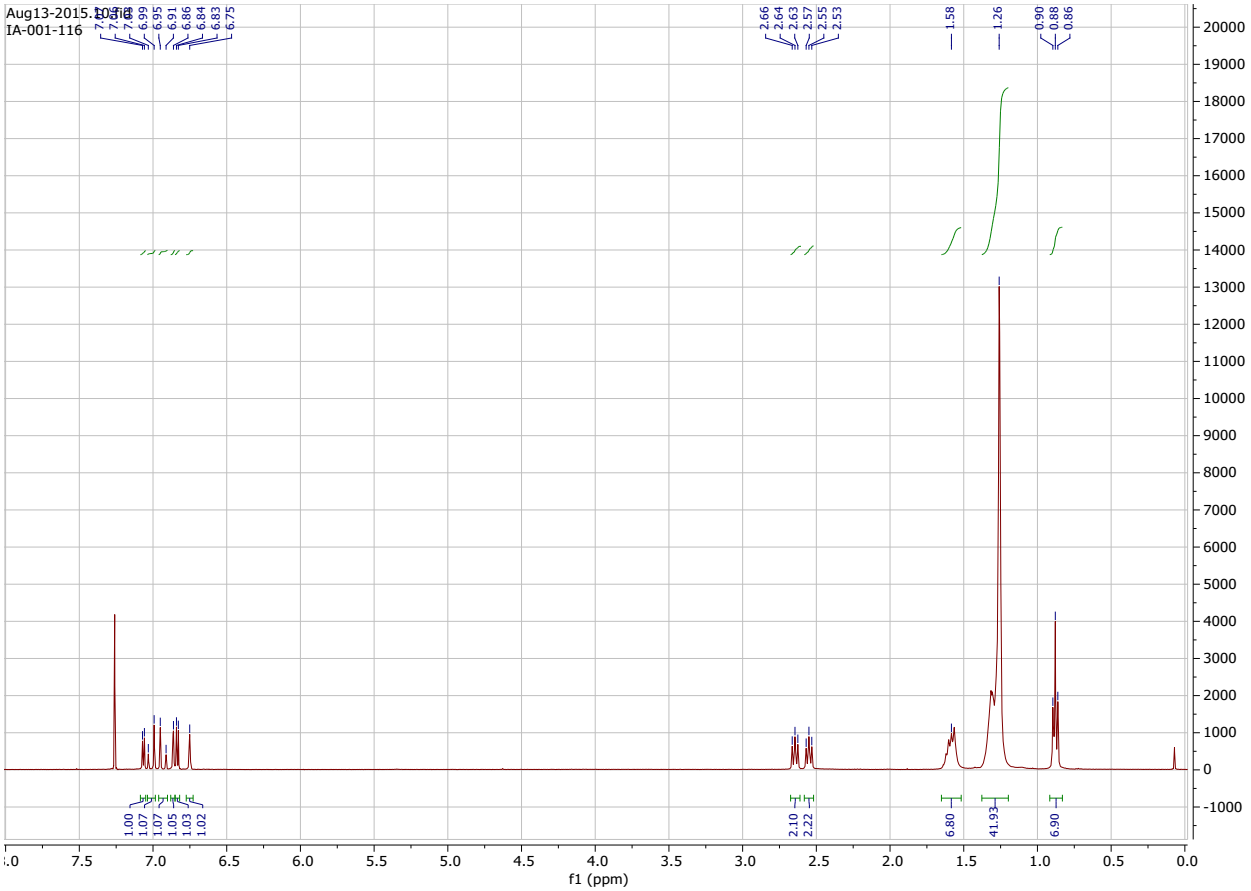


Figure S8. ^{1}H NMR of dimer

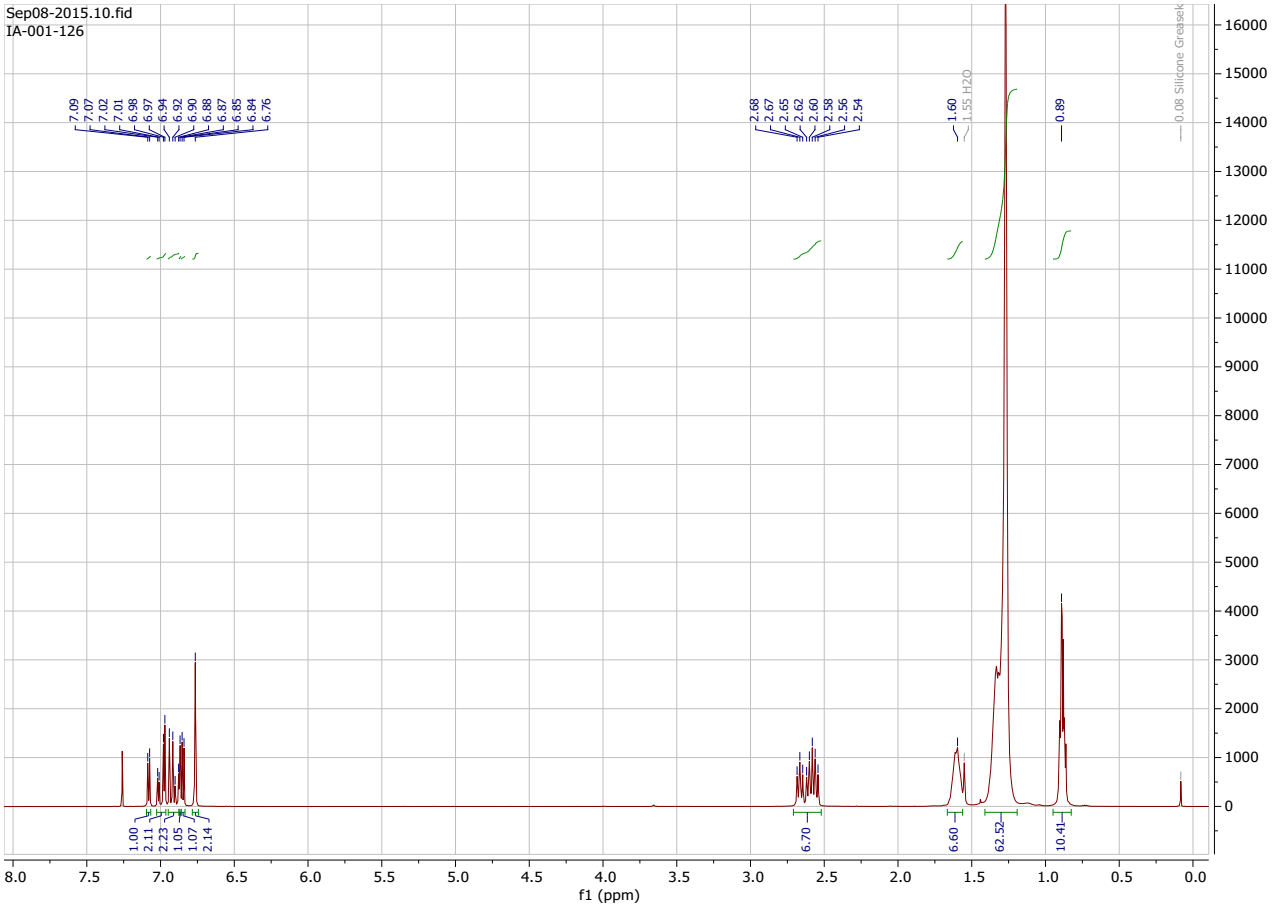


Figure S9. ^{1}H NMR of Trimer

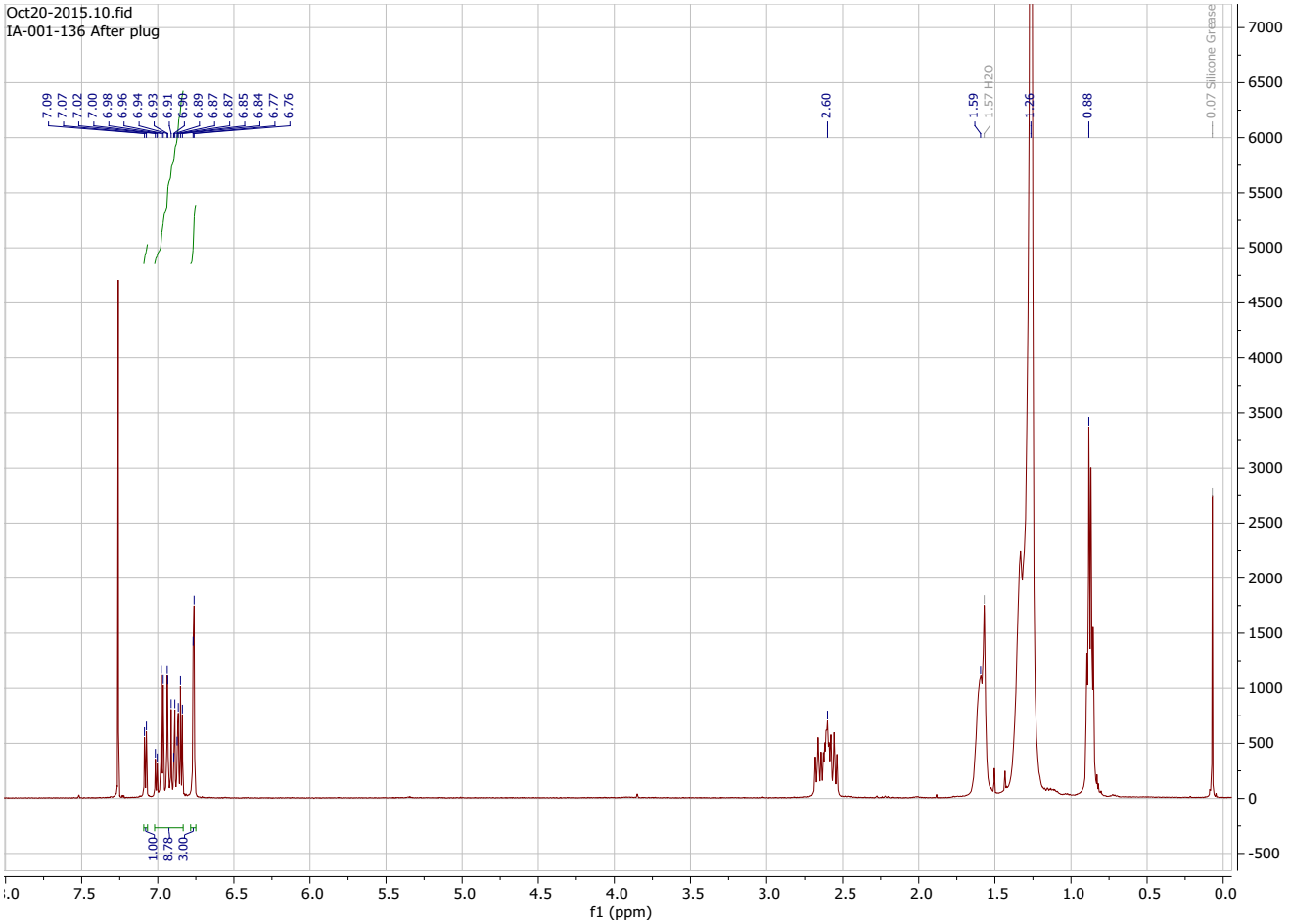


Figure S10. ^{1}H NMR of Tetramer

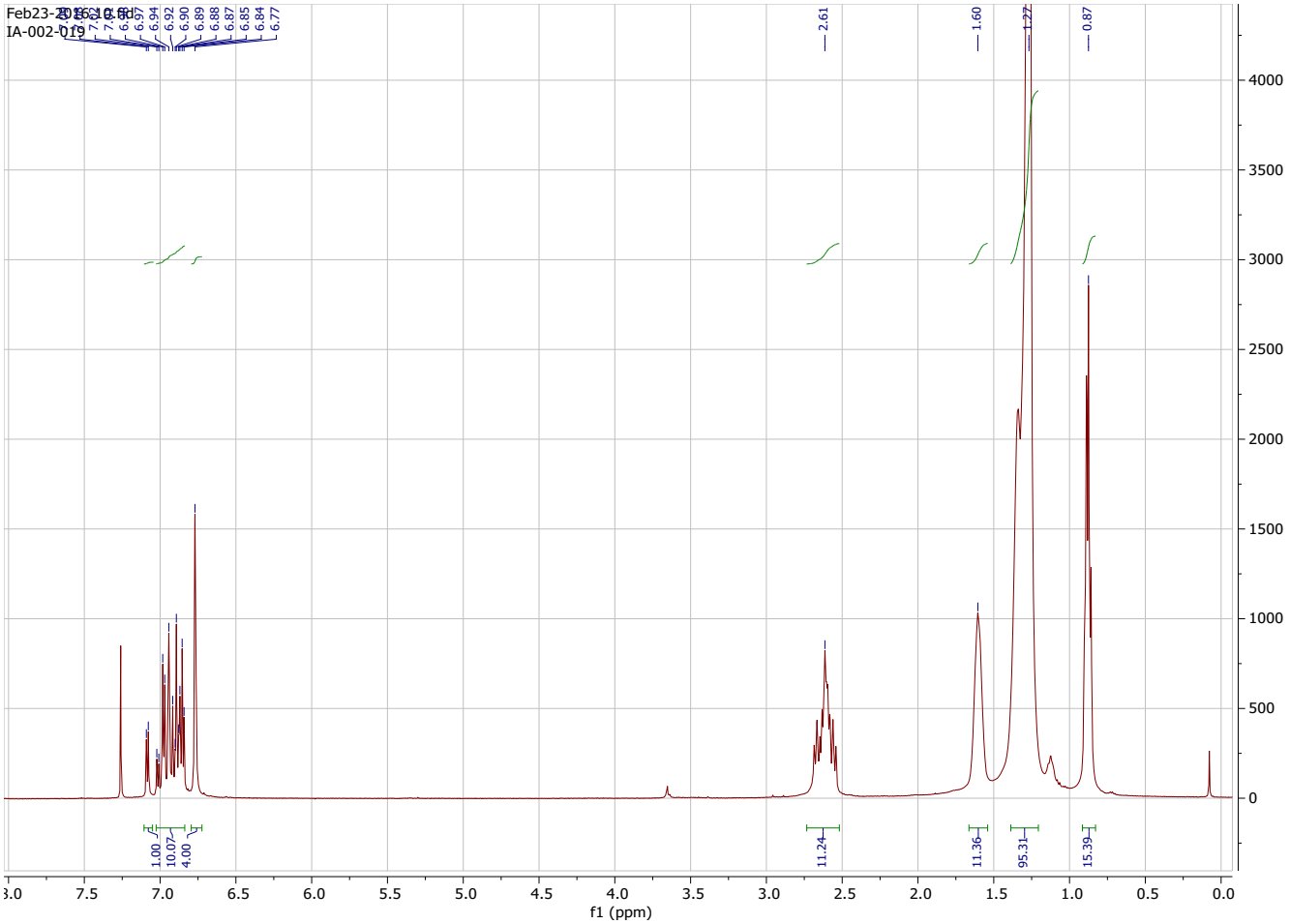


Figure S11. ^{1}H NMR of Pentamer

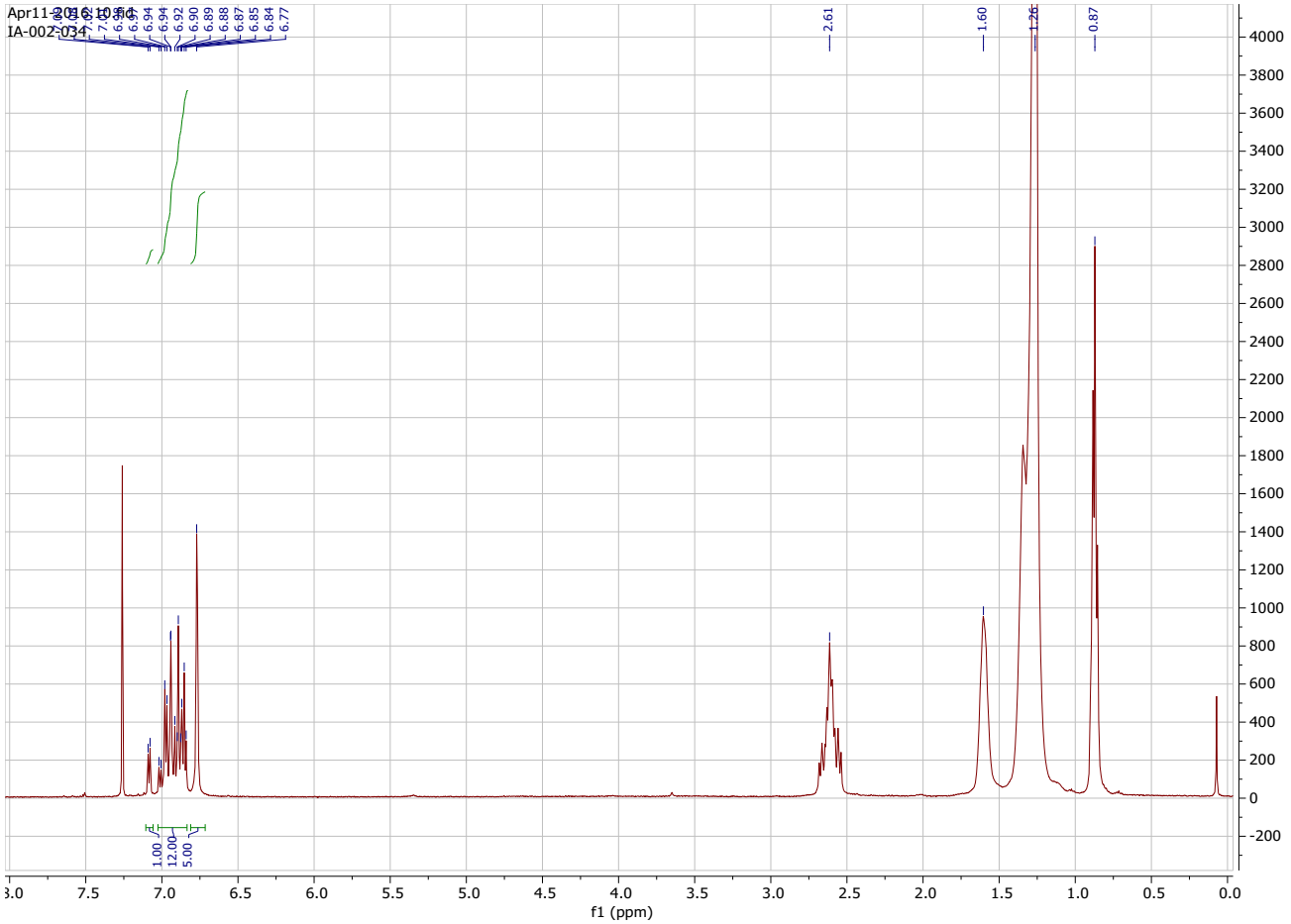


Figure S12. ^{1}H NMR of Hexamer

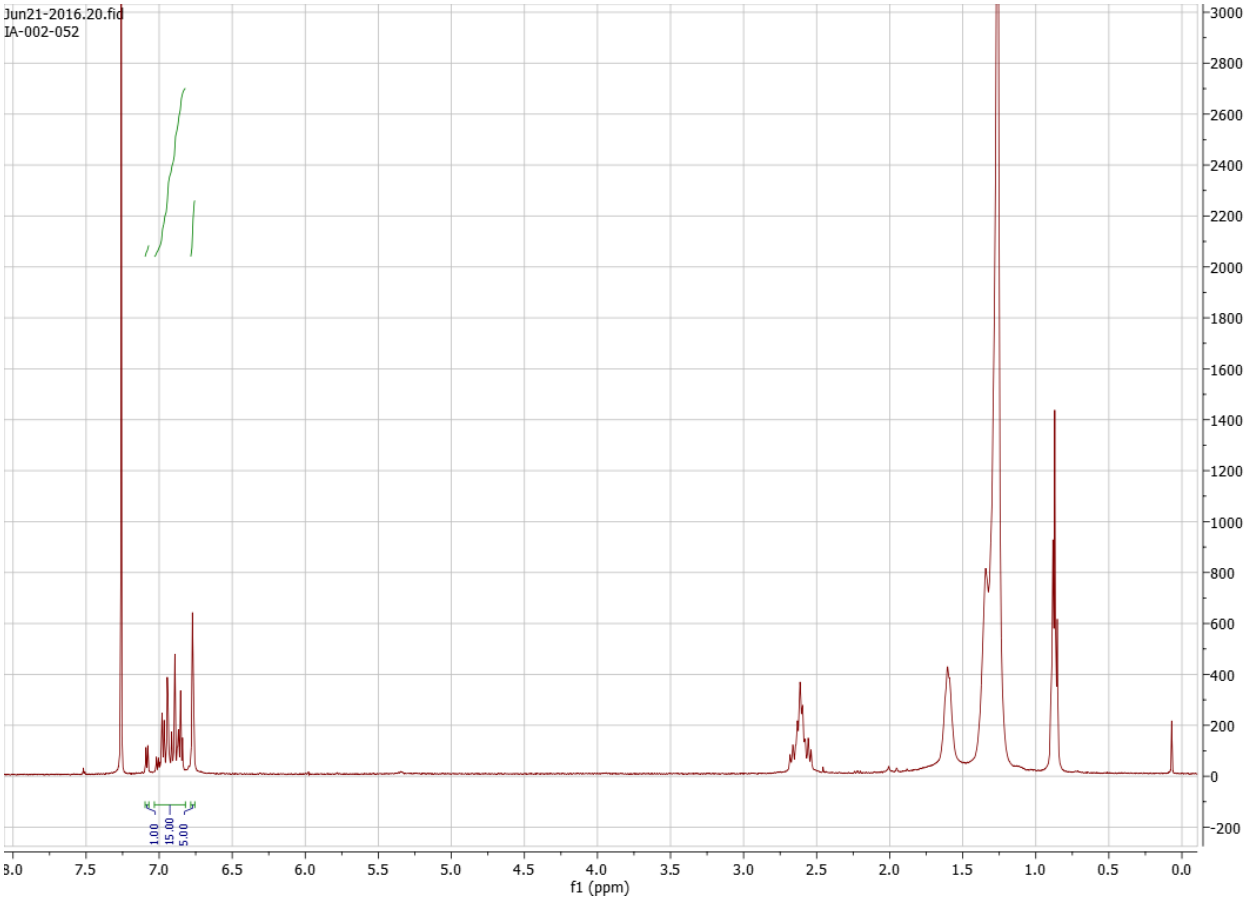


Figure S13. ^{1}H NMR of Heptamer

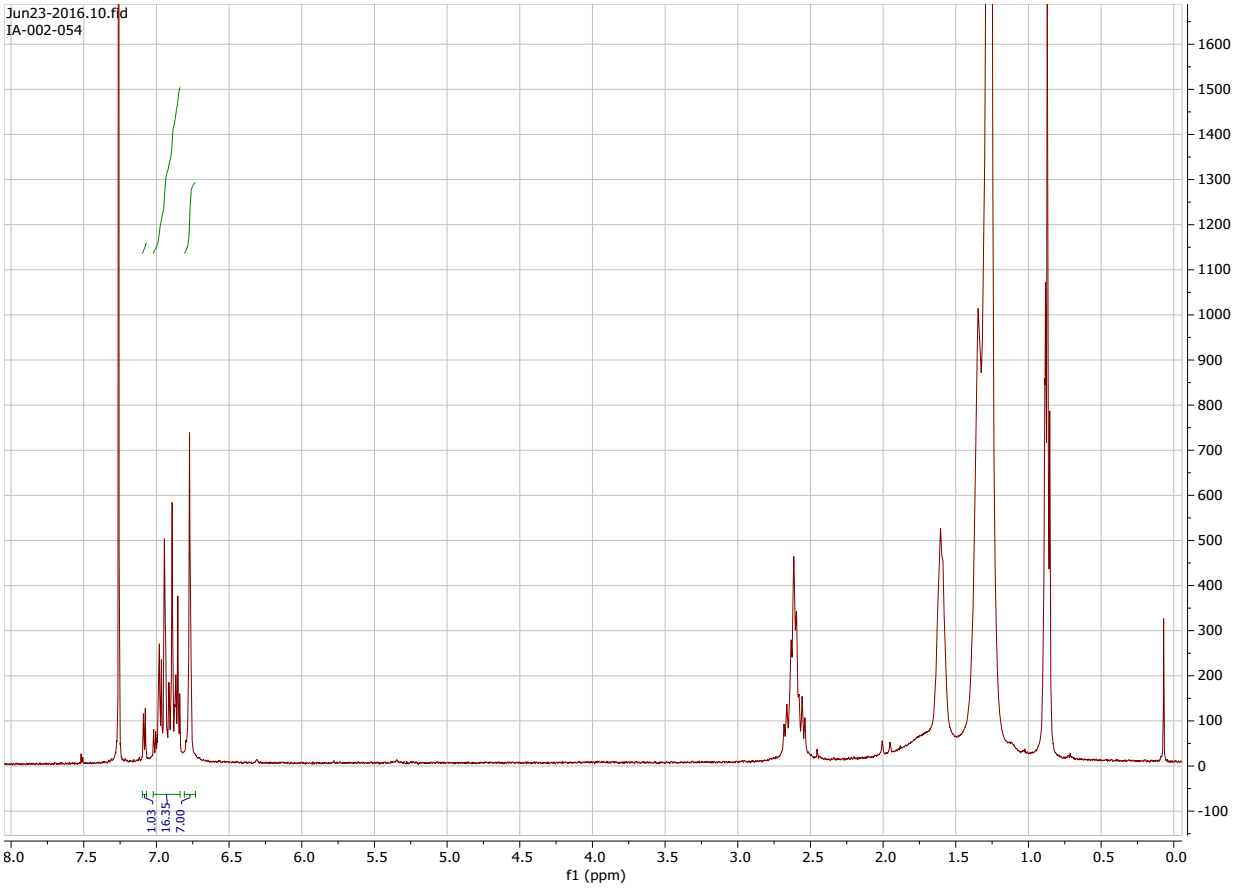


Figure S14. ^{1}H NMR of Octamer

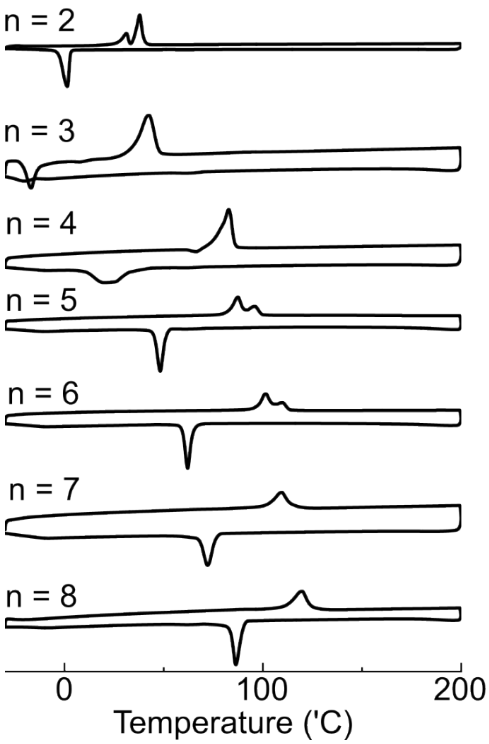


Figure S15. DSC plots (endotherm up), second cycle (10 °C/min).

6/ References

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