

SUPPORTING INFORMATION

Synthesis, monolayer formation, characterization and nanometer-scale photolithographic patterning of conjugated oligomers bearing terminal thioacetates

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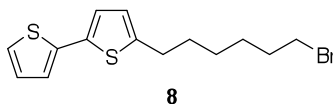
INSTRUMENTATION

Microwave irradiation was performed using a Biotage Smith Creator synthesiser. NMR spectra were run on a Bruker AC-250 spectrometer, operating at 250 MHz for ¹H, 62 MHz for ¹³C, a Bruker AMX2-400 spectrometer, operating at 400 MHz for ¹H and 101 MHz for ¹³C, and a Bruker DRX-500 Ultrashield spectrometer, operating at 500 MHz for ¹H, and 126 MHz for ¹³C in CDCl₃. All chemical shifts are reported in parts per million. EI mass spectra were run on a VG Autospec spectrometer, and ES spectra were recorded on a Waters LCT spectrometer. UV-Vis absorption spectra were obtained on a Cary-50 spectrometer and run in THF. IR spectra were run on a Perkin-Elmer RX 1 FT-IR spectrometer, fitted with a Sensir Technologies DuraSamplir II ATR attachment. C, H, N, and S elemental analyses

were performed on a Perkin Elmer Series 2 CHNS/O 2400 analyser. Br analyses were performed by titration. Melting points were obtained on a Sanyo-Gallencamp melting point apparatus, and are reported uncorrected.

SYNTHETIC PROTOCOLS

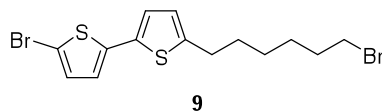
Synthesis of 5-(6-bromohexyl)-[2,2']-bithiophenyl **8**¹



A stirred solution of **7** (10 g, 60.15 mmol.) in dry THF (1 L) was cooled to -78 °C under N₂, and n-BuLi (24.1 mL, 1.0 eq., 2.5 M in hexanes) was added dropwise. The reaction was stirred at -78 °C for 1 h, then 1,6-dibromohexane (32.29 g, 2.2 eq.) was added rapidly in one portion. The mixture was stirred and allowed to warm to room temperature overnight. After addition of H₂O (50 mL), the THF was removed *in vacuo*, and Et₂O (200 mL) was added. The organic phase was washed with brine (3 x 50 mL) and H₂O (3 x 50 mL), dried over MgSO₄, and the solvent removed *in vacuo*. Excess 1,6-dibromohexane was distilled off (98-104 °C at 6 mmHg), and the crude green solid was purified *via* column chromatography (petroleum ether 40-60 °C to 98:2 petroleum ether 40-60 °C: EtOAc), yielding the title compound as a white-yellow solid (6.575 g, 48 %). Mpt. = 44-46 °C. R_f = 0.51 (98:2 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 7.20 (dd, 1H, ³J = 5.0 Hz, ⁴J = 1.2 Hz), 7.16 (dd, 1H, ³J = 3.7 Hz, ⁴J = 1.2 Hz), 7.05 (d, 1H, ³J = 3.7 Hz), 7.04 (dd, 1H, ³J = 5.2 Hz, 3.7 Hz), 6.71 (d, 1H, ³J = 3.7 Hz), 3.41 (t, 2H, ³J = 7.0 Hz), 2.80 (t, 2H, ³J = 7.0 Hz), 1.87 (p, 2H, ³J = 7.0 Hz), 1.71 (p, 2H, ³J = 7.0 Hz), 1.56-1.31 (m, 4H). ¹³C NMR δ = 144.99, 138.00, 135.00, 127.80, 124.95, 123.89, 123.51, 123.15, 34.01, 32.78, 31.47, 30.11, 28.25, 28.00. MS (EI⁺) m/z = 328 ([M]⁺, 95 %). HRMS (EI⁺) = 327.995186, C₁₄H₁₇BrS₂ requires 327.995505. IR (film, cm⁻¹) = 3106, 3068, 2932, 2854, 1518, 1462, 1427, 1352, 1259, 1233,

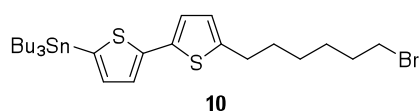
1203, 1079, 1046, 886, 838, 797, 726, 693, 642. Elemental Anal. = 50.85 % C, 5.19 % H, 24.32 % Br, 19.75 % S, C₁₄H₁₇BrS₂ requires 51.06 % C, 5.20 % H, 24.26 % Br, 19.47 % S.

Synthesis of 5-bromo-5'-(6-bromohexyl)-[2,2']-bithiophenyl **9**



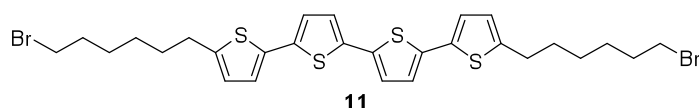
A stirred solution of **8** (1 g, 3.04 mmol) in DMF (5 mL) was cooled to 0 °C in the absence of light. To this solution, NBS (649 mg, 1.2 eq.) in DMF (5 mL) was added *via* syringe in the absence of light. The mixture was stirred overnight, and allowed to warm to room temperature. The reaction was poured into H₂O (100 mL), and extracted with Et₂O (3 x 30 mL). The organic phase was washed with brine (6 x 30 mL), and the aqueous washings were washed with a further 30 ml of Et₂O. The combined organic layers were dried over MgSO₄, and the solvent removed *in vacuo*. The light brown crude solid obtained was purified *via* column chromatography (98:2 petroleum ether 40-60 °C: EtOAc), yielding the title compound as a light yellow solid (1.216 g, 98 %). Mpt. = 62-63 °C. R_f = 0.73 (98:2 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 6.95 (d, 1H, ³J = 3.6 Hz), 6.93 (d, 1H, ³J = 3.6 Hz), 6.84 (d, 1H, ³J = 3.6 Hz), 6.68 (d, 1H, ³J = 3.6 Hz), 3.42 (t, 2H, ³J = 7.0 Hz), 2.79 (t, 2H, ³J = 7.3 Hz), 1.88 (p, 2H, ³J = 7.0 Hz), 1.70 (p, 2H, ³J = 7.3 Hz), 1.58-1.30 (m, 4H). ¹³C NMR δ = 145.46, 139.53, 133.89, 130.62, 125.03, 123.77, 123.08, 110.24, 34.03, 32.81, 31.42, 30.11, 28.31, 28.02. MS (EI⁺) m/z = 406 ([M]⁺, 23 %). HRMS (EI⁺) = 405.905970, C₁₄H₁₆Br₂S₂ requires 405.906016. IR (solid, cm⁻¹) = 2932, 2854, 1520, 1463, 1427, 1283, 1240, 1194, 1059, 1027, 996, 868, 801, 788, 732, 639. Elemental Anal. = 40.81 % C, 3.95 % H, 39.14 % Br, 15.89 % S, C₁₄H₁₆Br₂S₂ requires 41.19 % C, 3.95 % H, 39.15 % Br, 15.71 % S.

Synthesis of 5'-(6-bromohexyl)-5-tributylstannyl-[2,2']-bithiophenyl **10**



A stirred solution of **8** (1.069 g, 3.25 mmol) in dry THF (30 mL) was cooled to -78 °C under N₂ and n-BuLi (1.36 mL, 1.05 eq., 2.5 M in hexanes) was added dropwise. The mixture was stirred at -78 °C for 45 min, before Bu₃SnCl (1.16 g, 1.1 eq.) was added dropwise and the reaction was allowed to warm to room temperature overnight. To the mixture H₂O (10 mL) was added, and extracted with Et₂O (3 x 30 mL). The combined organic extractions were washed with brine (3 x 10 mL), dried over MgSO₄, and the solvent removed *in vacuo*. The crude brown oil was filtered through a short plug of neutral Al₂O₃ (98:2 petroleum ether 40-60 °C: EtOAc) yielding the title compound as orange oil, which was used immediately (1.562 g, 78 %). R_f=0.49 (petroleum ether 40-60 °C, Al₂O₃). ¹H NMR δ = 7.21 (d, 1H, ³J = 3.3 Hz), 7.04 (d, 1H, ³J = 3.3 Hz), 6.97 (d, 1H, ³J = 3.6 Hz), 6.66 (d, 1H, ³J = 3.6 Hz), 3.41 (t, 2H, ³J = 7.0 Hz), 2.79 (t, 2H, ³J = 7.3 Hz), 1.87 (p, 2H, ³J = 6.7 Hz), 1.73-1.20 (m, 20H), 1.16-0.85 (m, 13H). ¹³C NMR δ = 144.42, 143.27, 136.02, 135.85, 135.26, 124.82, 124.28, 123.08, 33.79, 32.71, 31.37, 30.03, 29.32, 28.98, 28.15, 27.91, 27.44, 27.28, 13.75, 13.68, 10.89, 8.79. MS (EI⁺) = 618 ([M]⁺, 21%). HRMS (EI⁺) = 618.100654, C₂₆H₄₃BrS₂Sn requires 618.101155.

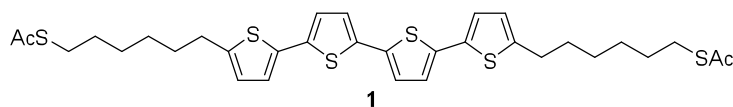
Synthesis of 5,5'''-bis-(6-bromohexyl)-[2,2';5',2''; 5'',2''']-quaterthiophene **11**



To **9** (204 mg, 0.5 mmol.) and **10** (370 mg, 1.2 eq.) was added 20 mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and Pd(PPh₃)₄ (29 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 24 h. Once cool, the solvent was removed *in vacuo*, and the black solid residue was stirred in MeOH (30 mL) for 1 h. The solid was filtered off and loaded into a soxhlet extractor, before

being washed repeatedly with MeOH, then THF. The THF washings were evaporated to dryness *in vacuo*, yielding the title compound as an orange/brown solid (141 mg, 43 %). Mpt. = 175-176 °C. ^1H NMR δ = 7.04 (d, 2H, ^3J = 3.7 Hz), 6.99 (d, 2H, ^3J = 3.7 Hz), 6.98 (d, 2H, ^3J = 3.7 Hz), 6.69 (d, 2H, ^3J = 3.7 Hz), 3.42 (t, 4H, ^3J = 7.0 Hz), 2.81 (t, 4H, ^3J = 7.3 Hz), 1.87 (p, 4H, ^3J = 7.0 Hz), 1.70 (p, 4H, ^3J = 7.3 Hz), 1.59-1.35 (m, 8H). ^{13}C NMR δ = 145.2, 136.7, 135.4, 134.6, 125.0, 124.1, 123.7, 123.4, 33.9, 32.7, 31.4, 30.1, 28.2, 27.9. MS (EI^+) m/z = 654 ($[\text{M}]^+$, 44 %), 656 ($[\text{M}+2]^+$, 100 %). HRMS (EI^+) = 653.975757, $\text{C}_{28}\text{H}_{32}\text{Br}_2\text{S}_4$ requires 653.975361. IR (solid, cm^{-1}) = 3072, 2934, 2850, 1714, 1627, 1597, 1512, 1463, 1441, 1426, 1369, 1288, 1277, 1236, 1215, 1194, 1064, 1026, 987, 962, 900, 866, 846, 798, 784, 768, 730, 661, 641. UV-Vis. λ_{max} = 400 nm. Elemental Anal. = 51.92 % C, 4.84 % H, 24.65 % Br, 19.45 % S %, $\text{C}_{28}\text{H}_{32}\text{Br}_2\text{S}_4$ requires 51.22 % C, 4.91 % H, 24.34 % Br, 19.53 % S.

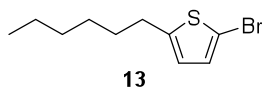
Synthesis of thioacetic acid *S*-{6-[5'''-(6-acetylsulfanylhexyl)-[2,2':5',2'':5'',2''']-quaterthiophen-5-yl]-hexyl}ester **1**



To a stirred solution of **11** (125 mg, 0.19 mmol.) in dry THF (10 mL), KSAc (87 mg, 4.0 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as an orange/brown powder (71 mg, 58%). Mpt. = 147.3-148.4 °C. ^1H NMR δ = 7.03 (d, 2H, ^3J = 3.7 Hz), 6.98 (d, 2H, ^3J = 3.9 Hz), 6.97 (d, 2H, ^3J = 3.9 Hz), 6.67 (d, 2H, ^3J = 3.7 Hz), 2.86 (t, 4H, ^3J = 7.1 Hz), 2.78 (t, 4H, ^3J = 7.6 Hz), 2.32 (s, 6H), 1.73-1.20 (m, 16H). ^{13}C NMR δ = 145.30, 136.70, 135.39, 134.56, 124.95, 124.03, 123.61, 123.40, 31.37, 30.64, 30.08, 29.71, 29.40, 29.08, 28.50,

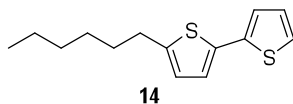
28.17. MS (EI^+) m/z = 646 ($[\text{M}]^+$, 43%), 648 ($[\text{M}+2]^+$, 14%). HRMS (EI^+) = 646.119172, $\text{C}_{32}\text{H}_{38}\text{S}_6\text{O}_2$ requires 646.119612. IR (solid, cm^{-1}) = 2921, 2852, 1687, 1645, 1514, 1441, 1353, 1260, 1178, 1135, 1048, 954, 876, 844, 790, 766, 625. UV-Vis. λ_{max} = 408 nm.

Synthesis of 2-bromo-5-hexylthiophene **13**



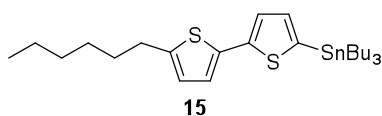
A stirred solution of **12** (3 g, 17.85 mmol) in DMF (5 mL) was cooled to 0 °C in the absence of light. To this, NBS (3.81 g, 1.2 eq.) in DMF (10 mL) was added *via* syringe in the absence of light. The mixture was allowed to warm to room temperature overnight with stirring, and then poured into H_2O (150 mL). The aqueous layer was then extracted with Et_2O (3 x 30 mL), and the combined organic layers washed with brine (6 x 30 mL). The combined aqueous washings were washed with a further 30 mL of Et_2O . The combined organic layers were dried over MgSO_4 , and the solvent removed *in vacuo*. The resulting orange/red oil was purified *via* column chromatography (petroleum ether 40-60 °C) yielding the title compound as clear oil (4.319 g, 98 %). R_f = 0.88 (petroleum ether 40-60 °C). ^1H NMR δ = 6.83 (d, 1H, 3J = 3.7 Hz), 6.52 (d, 1H, 3J = 3.7 Hz), 2.74 (t, 2H, 3J = 7.3 Hz), 1.70-1.52 (m, 2H), 1.43-1.21 (m, 6H), 0.88 (t, 3H, 3J = 6.4 Hz). ^{13}C NMR δ = 147.66, 129.37, 124.32, 108.53, 31.51, 31.41, 30.33, 28.64, 22.54, 14.06. MS (EI^+) m/z = 246 ($[\text{M}]^+$, 34 %). HRMS (EI^+) = 246.008992, $\text{C}_{10}\text{H}_{15}\text{BrS}$ requires 246.007784. IR (oil, cm^{-1}) = 2954, 2926, 2854, 1541, 1446, 1377, 1214, 1046, 960, 788, 758, 725, 668, 628, 606. Elemental Anal. = 48.38 % C, 6.39 % H, 32.48 % Br, 12.96 % S %, $\text{C}_{10}\text{H}_{15}\text{BrS}$ requires 48.59 % C, 6.12 % H, 32.32 % Br, 12.97 % S.

Synthesis of 5-hexyl-[2,2']-bithiophenyl **14**²



To a stirred suspension of **13** (2 g, 8.10 mmol.) and Pd(dppf)Cl₂ (661 mg, 10 mol.%) in dry Et₂O (40 mL), cooled to 0 °C under Ar, was added thiophen-2-yl magnesium bromide (12.15 mL, 1.5 eq., 1 M in THF) dropwise. The mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with saturated aq.NH₄Cl solution (20 mL), and then poured into hexane (40 mL). Added to this was Et₂O (200 mL), and the organic layer was washed with H₂O (3 x 80 mL). The organic layer was dried over MgSO₄ and the solvent removed *in vacuo*. The resulting dark red/brown oil was purified *via* column chromatography (petroleum ether 40-60 °C), yielding the title compound as clear oil, which turned pale green on standing (1.911 g, 94 %). R_f = 0.64 (petroleum ether 40-60 °C). ¹H NMR δ = 7.17 (dd, 1H, ³J = 3.3 Hz, ⁴J = 1.2 Hz), 7.10 (dd, 1H, ³J = 3.7 Hz, ⁴J = 1.2 Hz), 7.00 (d, 1H, ³J = 3.3 Hz), 6.99 (dd, 1H, ³J = 3.7 Hz, 3.3 Hz), 6.68 (d, 1H, ³J = 3.3 Hz), 2.79 (t, 2H, ³J = 7.7 Hz), 1.68 (p, 2H, ³J = 6.7 Hz), 1.44–1.25 (m, 6H), 0.89 (t, 3H, ³J = 6.7 Hz). ¹³C NMR δ = 145.39, 137.98, 134.74, 127.66, 124.68, 123.69, 123.38, 122.97, 31.58, 30.16, 28.76, 22.58, 14.09. MS (EI⁺) m/z = 250 ([M⁺], 64%). HRMS (EI⁺) = 250.083858, C₁₄H₁₈S₂ requires 250.084994. IR (oil, cm⁻¹) = 3069, 2954, 2926, 2853, 1518, 1466, 1426, 1377, 1205, 1079, 1046, 887, 837, 816, 794, 756, 687, 601.

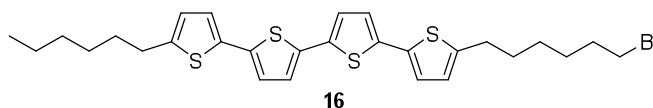
Synthesis of 5-tributylstannyl-5'-hexyl-[2,2']-bithiophenyl **15**



A stirred solution of **14** (1.986 g, 7.94 mmol.) in dry THF (30 mL) was cooled to -78 °C under N₂, and n-BuLi (3.492 mL, 1.1 eq., 2.5 M in hexanes) was added dropwise. The reaction was stirred at -78 °C for 1 h, and then Bu₃SnCl (2.84 g, 1.1 eq.) was added dropwise. The reaction was stirred overnight, and allowed to warm to room temperature. To the mixture H₂O (10 mL) was added, and then was extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with brine (3 x 10 mL), dried over MgSO₄, and the

solvent removed *in vacuo*. The crude brown oil was purified *via* filtration through a short plug of neutral Al₂O₃ (petroleum ether 40-60 °C), yielding the title compound as clear oil (4.212 g, 98 %), which was used immediately. *R*_f = 0.82 (petroleum ether 40-60 °C, Al₂O₃). ¹H NMR δ = 7.22 (d, 1H, ³J = 3.3 Hz), 7.04 (d, 1H, ³J = 3.3 Hz), 6.98 (d, 1H, ³J = 3.4 Hz), 6.68 (d, 1H, ³J = 3.4 Hz), 2.79 (t, 2H, ³J = 7.3 Hz), 1.74-1.24 (m, 22H), 1.18-0.77 (m, 16H). ¹³C NMR δ = 144.94, 136.01, 127.66, 124.66, 124.21, 123.68, 123.37, 123.06, 122.96, 31.61, 30.18, 29.31, 28.98, 28.79, 27.46, 27.30, 22.62, 14.12, 13.70, 10.86, 8.77. MS (EI⁺) *m/z* = 540 ([M]⁺, 22 %). HRMS (EI⁺) = 540.192989, C₂₆H₄₄S₂Sn requires 540.190644.

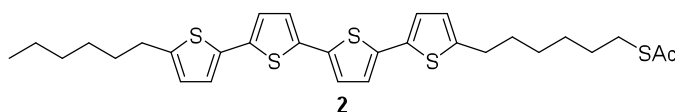
Synthesis of 5'''-(6-bromohexyl)-5-hexyl [2,2';5',2'';5'',2''']-quaterthiophene **16**



To **9** (689 mg, 1.69 mmol.) and **15** (1 g, 1.1 eq.) was added 30 mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and Pd(PPh₃)₄ (98 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 24 h. Once cool, the solvent was removed *in vacuo*, and the black solid residue was stirred in MeOH (30mL) for 1 h under Ar. The solid was filtered off and loaded into a soxhlet extractor, before being washed repeatedly with MeOH, then THF under Ar. The THF washings were evaporated to dryness *in vacuo*, yielding the title compound as an orange solid (314 mg, 32 %) which was stored in a flame-dried flask under Ar. Mpt. = 139.6-141.2 °C. ¹H NMR δ = 7.03 (2H, ³J = 3.7 Hz), 6.99 (d, 2H, ³J = 3.7 Hz), 6.97 (d, 2H, ³J = 3.7 Hz), 6.68 (d, 2H, ³J = 3.7 Hz), 3.41 (t, 2H, ³J = 6.8 Hz), 2.79 (t, 4H, ³J = 7.0 Hz), 1.88 (p, 2H, ³J = 6.8 Hz), 1.74-1.26 (m, 16H), 0.89 (t, 3H, ³J = 6.6 Hz). ¹³C NMR δ = 145.70, 145.16, 136.81, 136.65, 135.47, 135.34, 134.64, 134.47, 125.01, 124.86, 124.05, 124.03, 123.65, 123.58, 123.41,

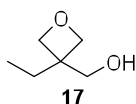
33.87, 32.68, 31.59, 31.36, 30.23, 30.06, 29.74, 28.79, 28.16, 27.90, 22.60, 14.11. MS (EI^+) $m/z = 576$ ($[\text{M}]^+$, 28 %), 578 ($[\text{M}+2]^+$, 35 %). HRMS (EI^+) = 576.063564, $\text{C}_{28}\text{H}_{33}\text{BrS}_4$ requires 576.064850. IR (solid, cm^{-1}) = 2956, 2922, 2854, 1708, 1621, 1556, 1514, 1440, 1367, 1340, 1286, 1262, 1238, 1193, 1113, 1066, 1035, 958, 844, 790, 724, 645. UV-Vis. $\lambda_{\text{max}} = 400$ nm.

Synthesis of thioacetic acid S-[6-(5'''-hexyl-[2,2';5',2'';5'',2''']-quaterthiophen-5-yl)-hexyl] ester **2**



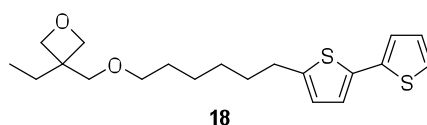
To a stirred solution of **16** (100 mg, 0.17 mmol.) in dry THF (10 mL), KSAc (19 mg, 1.2 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as an orange/brown powder (72 mg, 74%). Mpt. = 145.6-146.4 °C. ^1H NMR $\delta = 7.03$ (d, 2H, $^3J = 3.6$ Hz), 6.98 (d, 2H, $^3J = 3.9$ Hz), 6.97 (d, 2H, $^3J = 3.9$ Hz), 6.68 (d, 2H, $^3J = 3.6$ Hz), 2.87 (t, 2H, $^3J = 7.3$ Hz), 2.79 (t, 4H, $^3J = 7.3$ Hz), 2.33 (s, 3H), 1.77-1.25 (m, 16H), 0.89 (t, 3H, $^3J = 7.6$ Hz). ^{13}C NMR $\delta = 145.68, 145.29, 136.68, 135.42, 132.60, 124.95, 124.02, 123.57, 123.39, 31.94, 31.56, 30.64, 30.21, 30.08, 29.71, 29.40, 29.08, 28.76, 28.49, 22.57, 14.07$. MS (EI^+) $m/z = 572$ ($[\text{M}]^+$, 100 %), 574 ($[\text{M}+2]^+$, 48 %). HRMS (EI^+) = 572.135798, $\text{C}_{30}\text{H}_{36}\text{S}_5\text{O}$ requires 572.136975. IR (solid, cm^{-1}) = 2956, 2922, 2853, 1691, 1625, 1560, 1514, 1441, 1352, 1260, 1096, 1019, 958, 844, 791, 628. UV-Vis. $\lambda_{\text{max}} = 409$ nm.

Synthesis of (3-ethyl-3-oxetan-3-yl)-methanol **17**³



To a 100 mL round-bottom flask fitted with thermometer, condenser, distillation head and receiver, trimethylolpropane (13.56 g, 100 mmol), Et₂CO₃ (12.25 g, 100 mmol), KOH (20 mg) and EtOH (1 mL) were added. The mixture was heated at reflux, until the pot temperature was less than 105 °C, when the first fraction was distilled off (80-86 °C, 760 mmHg). The pot was heated further until its temperature reached 145 °C, when the pressure was reduced. The pot was then heated further until 185 °C, which was accompanied with large volumes of CO₂ evolution, and a further fraction distilled over (150-160 °C, 20 mmHg). The fraction collected at reduced pressure, along with the pot residue was fractionally distilled through a vigreux column, yielding the title compound as clear viscous oil (6.465 g, 56 %). Bpt. = 116-118 °C @ 15 mmHg, R_f = 0.09 (4:1 petroleum ether 40-60 °C: EtOAc, KMnO₄ stain). ¹H NMR δ = 4.47 (d, 2H, ²J = 6.3 Hz), 4.42 (d, 2H, ²J = 6.3 Hz), 3.78 (s, 2H), 1.79 (br. s, 1H), 1.74 (q, 2H, ³J = 7.5 Hz), 0.90 (t, 3H, ³J = 7.5 Hz). ¹³C NMR δ = 78.12, 65.53, 44.44, 26.30, 8.31. MS (EI⁺) m/z = 117 ([M]⁺, 2 %). HRMS (EI⁺) = 117.091697, C₆H₁₂O₂ requires 117.091555. IR (liquid, cm⁻¹) = 3374, 2961, 2874, 1460, 1381, 1267, 1146, 1047, 1028, 966, 823, 783.

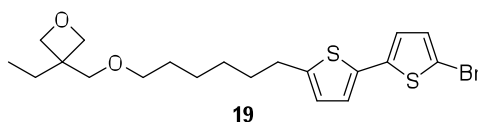
Synthesis of 3-(6-[2,2']-bithiophenyl-5-yl-hexyloxymethyl)-3-ethyloxetane **18**



A 100 mL round-bottom flask was charged with **8** (1 g, 3.04 mmol) in hexane (20 mL), **17** (387 mg, 1.1 eq.), Bu₄NBr (98 mg, 10 mol.%), and 50 % aq.KOH (20 mL). The biphasic mixture was heated at reflux with rapid stirring for 4 h. Once cooled to room temperature, the reaction was diluted with hexane (20 mL) and H₂O (20 mL), and the aqueous phase extracted with hexane (3 x 20 mL). The combined organic layers were dried over MgSO₄ and the solvent removed *in vacuo*. The crude oil was purified *via* column chromatography (4:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as a clear viscous oil

(869 mg, 78 %). R_f = 0.67 (4:1 petroleum ether 40-60 °C: EtOAc). ^1H NMR δ = 7.16 (dd, 1H, 3J = 5.2 Hz, 4J = 1.2 Hz), 7.09 (dd, 1H, 3J = 3.6 Hz, 4J = 1.2 Hz), 7.00 (d, 1H, 3J = 3.7 Hz), 6.99 (dd, 1H, 3J = 5.2 Hz, 3.6 Hz), 6.67 (d, 1H, 3J = 3.7 Hz), 4.45 (d, 2H, 2J = 5.8 Hz), 4.38 (d, 2H, 2J = 5.8 Hz), 3.52 (s, 2H), 3.45 (t, 2H, 3J = 6.4 Hz), 2.79 (t, 2H, 3J = 7.3 Hz), 1.79-1.52 (m, 6H), 1.45-1.34 (m, 4H), 0.88 (t, 3H, 3J = 7.6 Hz). ^{13}C NMR δ = 145.1, 137.9, 134.8, 127.66, 124.74, 123.73, 123.37, 122.99, 78.63, 73.42, 71.51, 43.42, 31.52, 30.07, 29.43, 28.82, 26.76, 25.90, 8.21. MS (EI^+) m/z = 364 ($[\text{M}]^+$, 69 %). HRMS (EI^+) = 364.154737, $\text{C}_{20}\text{H}_{28}\text{S}_2\text{O}_2$ requires 364.153074. IR (liquid, cm^{-1}) = 2931, 2857, 1518, 1458, 1373, 1239, 1205, 1113, 1046, 978, 908, 837, 796, 755, 729, 690, 647.

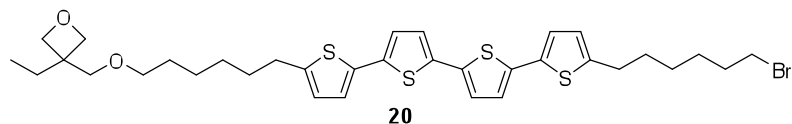
Synthesis of 3-[6-(5'-bromo-[2,2']-bithiophenyl-5-yl)-hexyloxymethyl]-3-ethyloxetane **19**



A stirred solution of **18** (100 mg, 0.275 mmol) in DMF (5 mL) was cooled to 0 °C in the absence of light. To the solution, NBS (59 mg, 1.2 eq.) in DMF (5 mL) was added *via* syringe, in the absence of light. The mixture was stirred overnight, and allowed to warm to room temperature. The mixture was then poured into H_2O (100 mL), and extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (6 x 30 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude oil was purified *via* column chromatography (4:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as yellow oil (100 mg, 82 %). R_f = 0.69 (3:1 petroleum ether 40-60 °C: EtOAc). ^1H NMR δ = 6.94 (d, 1H, 3J = 3.6 Hz), 6.91 (d, 1H, 3J = 3.6 Hz), 6.83 (d, 1H, 3J = 3.6 Hz), 6.66 (d, 1H, 3J = 3.6 Hz), 4.45 (d, 2H, 2J = 5.8 Hz), 4.38 (d, 2H, 2J = 5.8 Hz), 3.52 (s, 2H), 3.45 (t, 2H, 3J = 6.4 Hz), 2.78 (t, 2H, 3J = 7.3 Hz), 1.79-1.53 (m, 6H), 1.39 (p, 4H, 3J = 3.7 Hz), 0.88 (t, 3H, 3J = 7.6 Hz). ^{13}C NMR δ = 145.64, 139.46, 133.75, 130.48, 124.85, 123.66, 122.98, 110.09, 78.49, 73.42, 71.46, 60.33, 43.40, 31.50, 30.07, 29.46, 28.85, 26.80, 25.93, 8.26. MS (EI^+)

$m/z = 442$ ($[M]^+$, 10 %) . HRMS (EI^+) = 442.064671, $C_{20}H_{27}BrS_2O_2$ requires 442.063585. IR (liquid, cm^{-1}) = 2930, 2856, 1518, 1458, 1418, 1371, 1113, 970, 870, 825, 787, 730, 611.

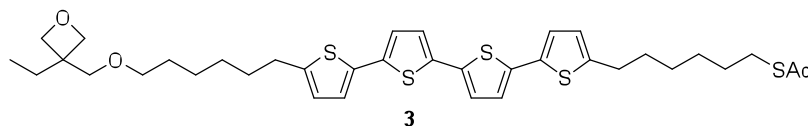
Synthesis of 3-{6-[5'''-(6-bromohexyl)-[2,2';5',2'':5'',2''']-quaterthiophen-5-yl]-hexyloxymethyl}-3-ethyloxetane **20**



To **19** (500 mg, 1.13 mmol.) and **10** (834 mg, 1.2 eq.) was added 30 mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and $Pd(PPh_3)_4$ (65 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 24 h. Once cool, the solvent was removed *in vacuo*, and the black solid residue was stirred in MeOH (30 mL) for 1 h under Ar. The solid was filtered off and loaded into a soxhlet extractor, before being washed repeatedly with MeOH, then THF under Ar. The THF washings were evaporated to dryness *in vacuo*, yielding the title compound as an orange solid (235 mg, 30%) which was stored in a flame-dried flask under Ar. Mpt. = 144.2-145.3 °C. 1H NMR δ = 7.03 (d, 2H, $^3J = 3.6$ Hz), 6.99 (d, 2H, $^3J = 3.6$ Hz), 6.98 (d, 2H, $^3J = 3.6$ Hz), 6.68 (d, 2H, $^3J = 3.6$ Hz), 4.45 (d, 2H, $^2J = 5.6$ Hz), 4.38 (d, 2H, $^2J = 5.6$ Hz), 3.52 (s, 2H), 3.45 (t, 2H, $^3J = 6.4$ Hz), 3.41 (t, 2H, $^3J = 6.9$ Hz), 2.80 (t, 4H, $^3J = 7.4$ Hz), 1.87 (p, 2H, $^3J = 6.4$ Hz), 1.78-1.65 (m, 4H), 1.64-1.23 (m, 12H), 0.88 (t, 3H, $^3J = 7.4$ Hz). ^{13}C NMR δ = 145.46, 145.16, 136.74, 136.67, 135.43, 135.37, 134.61, 134.52, 125.00, 124.92, 124.04, 123.63, 123.60, 123.40, 78.62, 73.45, 71.52, 43.45, 33.85, 32.66, 31.52, 31.34, 30.12, 30.04, 29.45, 28.84, 28.14, 27.88, 26.78, 25.92, 8.22. MS (EI^+) m/z = 690 ($[M]^+$, 82%), 692 ($[M+2]^+$, 100%). HRMS (EI^+) = 690.132748, $C_{34}H_{43}BrS_4O_2$ requires 690.132929. IR (solid, cm^{-1}) =

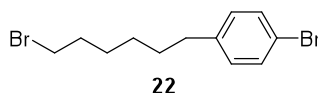
3063, 2924, 2855, 1619, 1514, 1463, 1443, 1372, 1261, 1237, 1218, 1194, 1112, 1067, 979, 899, 844, 788, 724, 642, 607. UV-Vis. λ_{max} = 403 nm.

Synthesis of thioacetic acid S-(6-{5'''-[6-(3-ethyloxetan-3-ylmethoxy)-hexyl]-[2,2':5',2'':5'',2''']-quaterthiophen-5-yl}-hexyl) ester **3**



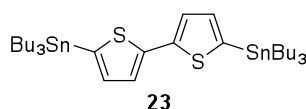
To a stirred solution of **20** (100 mg, 0.15 mmol.) in dry THF (10 mL) KSAc (20 mg, 1.2 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as an orange/brown powder (64 mg, 64%). Mpt. = 104.4-105.8 °C. ^1H NMR δ = 7.02 (d, 2H, 3J = 3.7 Hz), 6.98 (d, 2H, 3J = 3.3 Hz), 6.96 (d, 2H, 3J = 3.3 Hz), 6.67 (d, 2H, 3J = 3.7 Hz), 4.45 (d, 2H, 2J = 5.8 Hz), 4.38 (d, 2H, 2J = 5.8 Hz), 3.52 (s, 2H), 3.45 (t, 2H, 3J = 6.1 Hz), 2.87 (t, 2H, 3J = 7.0 Hz), 2.78 (t, 4H, 3J = 7.6 Hz), 2.32 (s, 3H), 1.79-1.52 (m, 10H), 1.42-1.25 (m, 8H), 0.88 (t, 3H, 3J = 7.6 Hz). ^{13}C NMR δ = 145.46, 136.74, 135.42, 134.57, 124.93, 124.03, 123.60, 123.40, 78.60, 73.50, 71.53, 43.47, 31.50, 31.36, 30.61, 30.12, 29.53, 29.45, 29.40, 29.07, 28.84, 28.49, 26.79, 25.91, 23.84, 8.20. MS (ES^+) m/z = 685 ($[\text{M}-\text{H}]^+$, 100 %), 709 ($[\text{M}+\text{Na}]^+$, 10 %). HRMS (EI^+) = 709.1927, Calc. Mass = 709.1948 ($[\text{M}+\text{Na}]^+$), Found. IR (solid, cm^{-1}) = 2955, 2880, 1723, 1692, 1458, 1441, 1366, 1341, 1187, 1112, 1066, 1034, 922, 845, 790, 622. UV-Vis. λ_{max} = 404 nm.

Synthesis of 1-bromo-4-(6-bromohexyl)-benzene **22**⁴



A stirred solution of **21** (5 g, 21.19 mmol) in dry THF (43 mL) was cooled to -78 °C under N₂, and n-BuLi (10.1 mL, 1.0 eq., 2.1 M in hexanes) was added dropwise. The solution was stirred at -78 °C for 30 min, and then 1,6-dibromohexane (10.34 g, 2.0 eq.) was added in one portion. The solution was stirred at -78 °C for 2 h, and then allowed to warm to room temperature, and Et₂O (40 mL) was added. The organic phase was washed with H₂O (2 x 50 mL), dried over MgSO₄, and the solvent removed *in vacuo*. The excess 1,6-dibromohexane was distilled off (98-102 °C @ 6 mmHg), and the residue purified *via* column chromatography (petroleum ether 40-60 °C to 9:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as clear oil (2.933 g, 43 %). R_f = 0.48 (petroleum ether 40-60 °C). ¹H NMR δ = 7.39 (d, 2H, ³J = 8.2 Hz), 7.04 (d, 2H, ³J = 8.2 Hz), 3.40 (t, 2H, ³J = 4.9 Hz), 2.56 (t, 2H, ³J = 7.3 Hz), 1.85 (p, 2H, ³J = 4.9 Hz), 1.67-1.25 (m, 6H). ¹³C NMR δ = 141.06, 131.31, 130.15, 119.13, 35.17, 33.87, 32.67, 31.05, 28.23, 27.95. MS (EI⁺) m/z = 318 ([M]⁺, 33 %), 320 ([M+2]⁺, 57 %). HRMS (EI⁺) = 317.962103, C₁₂H₁₆Br₂ requires 317.961873. IR (liquid, cm⁻¹) = 2929, 2855, 1487, 1462, 1403, 1252, 1072, 1010, 830, 798, 756, 726, 643, 634, 601. Elemental Anal. = 46.15 % C, 5.42 % H, 47.20 % Br, C₁₂H₁₆Br₂ requires 45.03 % C, 5.04 % H, 49.93 % Br.

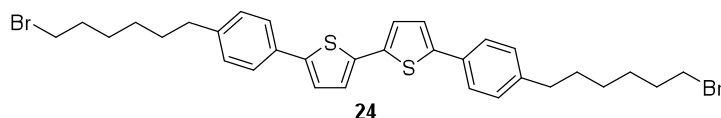
Synthesis of 5,5'-bis-tributylstannyl-[2,2']-bithiophenyl **23**⁵



A stirred solution of **7** (2 g, 12.03 mmol.) in dry THF (50 mL) was cooled to -78 °C under N₂, and n-BuLi (15.79 mL, 2.1 eq., 2.5 M in hexanes) was added dropwise. The reaction mixture was allowed to stir at -78 °C for 1 h, and then Bu₃SnCl (7.54 mL, 2.2 eq.) was added dropwise. The reaction was allowed to warm to room temperature overnight with stirring. To the mixture, H₂O (50 mL) was added, and then was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with brine (3 x 20 mL) and then dried over MgSO₄,

and the solvent removed *in vacuo*. The crude brown oil was purified *via* filtration through a small plug of neutral alumina (petroleum ether 40-60 °C), yielding the title compound as clear oil (6.127 g, 69 %), which was used immediately. $R_f = 0.75$ (petroleum ether 40-60 °C, alumina). ^1H NMR δ = 7.29 (d, 2H, $^3J = 3.4$ Hz), 7.06 (d, 2H, $^3J = 3.4$ Hz), 1.62-1.53 (m, 12H), 1.35 (sex., 12H, $^3J = 8.2$ Hz), 1.11 (t, 12H, $^3J = 8.2$ Hz), 0.90 (t, 18H, $^3J = 8.2$ Hz). ^{13}C NMR δ = 136.05, 127.74, 124.96, 124.33, 123.93, 123.75, 123.43, 29.44, 29.28, 29.13, 28.95, 27.82, 27.41, 27.25, 27.01, 13.72, 11.25, 11.13, 10.87, 8.75, 6.37. MS (EI^+) m/z = 746 ($[\text{M}]^+$, 26%). HRMS (EI^+) = 746.200777, $\text{C}_{32}\text{H}_{58}\text{S}_2\text{Sn}_2$ requires 746.202394.

Synthesis of 5,5'-bis-[4-(6-bromohexyl)-phenyl]-[2,2']-bithiophenyl **24**

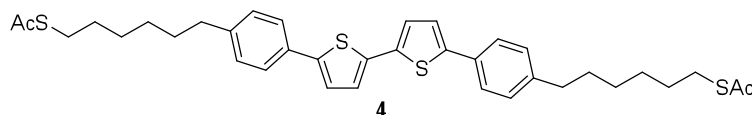


To **23** (745 mg, 1.1 mmol.) and **22** (750 mg, 2.1 eq.) was added 30 mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and $\text{Pd}(\text{PPh}_3)_4$ (64 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 24 h. Once cool, the solvent was removed *in vacuo*, and the black solid residue was stirred in MeOH (30 mL) for 1 h. The solid was filtered off and loaded into a soxhlet extractor, before being washed repeatedly with MeOH, then THF. The THF washings were evaporated to dryness *in vacuo*, yielding the title compound as a yellow solid (290 mg, 41 %). Mpt. = 221.4-223.9 °C. ^1H NMR δ = 7.52 (d, 4H, $^3J = 8.2$ Hz), 7.20-7.18 (m, 6H), 7.15 (d, 2H, $^3J = 3.6$ Hz), 3.41 (t, 4H, 7.0 Hz), 2.63 (t, 4H, $^3J = 7.3$ Hz), 1.87 (p, 4H, $^3J = 7.0$ Hz), 1.71-1.37 (m, 12H). ^{13}C NMR δ = 143.18, 142.22, 136.33, 131.62, 125.56, 124.32, 123.32, 35.49, 33.93, 32.72, 31.12, 28.35, 28.01. MS (EI^+) m/z = 642 ($[\text{M}]^+$, 9 %), 644 ($[\text{M}+2]^+$, 19 %). HRMS (EI^+) = 642.060801, $\text{C}_{32}\text{H}_{36}\text{Br}_2\text{S}_2$ requires 642.062517. IR (solid, cm^{-1}) = 3022, 2925,

2852, 1532, 1498, 1447, 1414, 1259, 1235, 1071, 1018, 960, 870, 818, 793, 726, 695, 646.

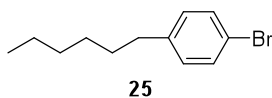
UV-Vis. λ_{max} = 372 nm.

Synthesis of thioacetic acid S-[6-(4-{5'-[4-(6-acetylsulfanylhexyl)-phenyl]-[2,2']-bithiophenyl-5-yl}-phenyl)-hexyl] ester **4**



To a stirred solution of **24** (66 mg, 0.10 mmol.) in dry THF (10 mL) KSAc (47 mg, 4.0 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude yellow/brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as a dark yellow powder (39 mg, 60%). Mpt. = 202.3-204.1 °C. ^1H NMR δ = 7.52 (d, 4H, 3J = 8.0 Hz), 7.20-7.18 (m, 6H), 7.14 (d, 2H, 3J = 3.7 Hz), 2.86 (t, 4H, 3J = 7.4 Hz), 2.61 (t, 4H, 3J = 7.6 Hz), 2.32 (s, 6H), 1.70-1.20 (m, 16H). ^{13}C NMR δ = 189.77, 143.21, 142.33, 136.33, 131.60, 128.95, 125.56, 124.31, 123.31, 35.54, 31.17, 30.65, 29.44, 29.12, 28.72, 28.65. MS (EI^+) m/z = 634 ($[\text{M}]^+$, 72%), 636 ($[\text{M}+2]^+$, 36%). HRMS (EI^+) = 634.207414, $\text{C}_{36}\text{H}_{42}\text{O}_2\text{S}_4$ requires 634.206768. IR (solid, cm^{-1}) = 3020, 2921, 2851, 1687, 1596, 1531, 1498, 1446, 1413, 1352, 1317, 1261, 1237, 1131, 1106, 1072, 1012, 951, 870, 819, 793, 755, 688, 626. UV-Vis. λ_{max} = 379 nm.

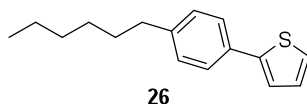
Synthesis of 1-bromo-4-hexylbenzene **25**



A stirred solution of **21** (5 g, 21.19 mmol.) in THF (43 mL) was cooled to -78 °C under N_2 , and n-BuLi (10.1 mL, 1.0 eq., 2.1 M in hexanes) was added dropwise. The reaction mixture was allowed to stir at -78 °C for 30 min, and then 1-bromohexane (7 g, 2.0 eq.) was added.

The reaction was allowed to stir at -78 °C for 2 h, and then warmed to room temperature. The mixture was diluted with Et₂O (40 mL) and washed with H₂O (2 x 50 mL). The organic layer was dried over MgSO₄, and the solvent removed *in vacuo*. Excess 1-bromohexane was distilled off (28-30 °C @ 6 mmHg), and the residue purified *via* column chromatography (petroleum ether 40-60 °C), yielding the title compound as clear oil (2.459 g, 48 %). R_f = 0.59 (petroleum ether 40-60 °C). ¹H NMR δ = 7.68 (d, 2H, ³J = 8.2 Hz), 7.44 (d, 2H, ³J = 8.2 Hz), 2.87 (t, 2H, ³J = 7.0 Hz), 1.64 (m, 2H), 1.39-1.22 (m, 6H), 0.88 (t, 3H, ³J = 6.6 Hz). ¹³C NMR δ = 141.85, 131.26, 130.18, 119.26, 35.38, 31.70, 31.32, 28.89, 22.62, 14.11. MS (EI⁺) m/z = 240 ([M]⁺, 60 %), 242 ([M+2]⁺, 58 %). HRMS (EI⁺) = 240.051444, C₁₂H₁₇Br requires 240.051362. IR (liquid, cm⁻¹) = 2946, 2925, 2855, 1486, 1461, 1401, 1376, 1117, 1072, 1007, 803, 723, 698, 663, 633. Elemental Anal. = 59.63 % C, 7.30 % H, 33.13 % Br, C₁₂H₁₇Br requires 59.76 % C, 7.11 % H, 33.13 % Br.

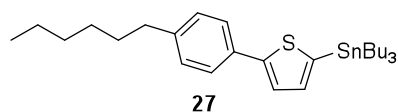
Synthesis of 2-(4-hexylphenyl)-thiophene 26



To a flame dried microwave tube **25** (1 g, 4.15 mmol.), 2-(tributylstannyl)-thiophene (1.703 g, 1.1 eq.), and Pd(PPh₃)₄ (240 mg, 5 mol.%) was added. Dry PhMe (4 mL), previously degassed with 3 x freeze/thaw/pump cycles (Ar) was added, ensuring that all traces of solids were washed below the solvent level. The reaction mixture was bubbled with Ar for 20 min, and then heated at 170 °C with microwave irradiation for 2 h. The reaction tube was allowed to cool to room temperature and filtered through Celite, before the solvent was removed *in vacuo*. The crude oil was purified *via* column chromatography (petroleum ether 40-60 °C), yielding the title compound as clear oil (1.011 g, 99 %). R_f = 0.37 (petroleum ether 40-60 °C). ¹H NMR δ = 7.42 (d, 2H, ³J = 8.0 Hz), 7.16 (dd, 1H, ³J = 3.3 Hz, ⁴J = 0.7 Hz), 7.11 (dd, 1H, ³J = 5.1 Hz, ⁴J = 0.7 Hz), 7.07 (d, 2H, ³J = 8.0 Hz), 6.94 (dd, 1H, ³J = 3.3 Hz, 5.1 Hz),

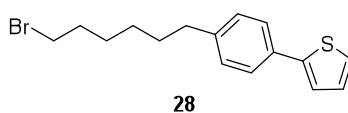
2.51 (t, 2H, $^3J = 7.6$ Hz), 1.55 (p, 2H, $^3J = 7.6$ Hz), 1.33-1.17 (m, 6H), 0.84 (t, 3H, $^3J = 7.1$ Hz). ^{13}C NMR $\delta = 144.69, 142.43, 131.94, 128.97, 127.96, 124.26, 122.61, 35.74, 31.47, 28.39, 26.86, 17.36, 13.69$. MS (EI^+) $m/z = 244$ ($[\text{M}]^+$, 19 %). HRMS (EI^+) = 244.128816, $\text{C}_{16}\text{H}_{20}\text{S}$ requires 244.128573. IR (liquid, cm^{-1}) = 2955, 2924, 2853, 1536, 1502, 1489, 1463, 1414, 1377, 1293, 1256, 1211, 1184, 1152, 1075, 1049, 1020, 959, 875, 850, 811, 756, 690.

Synthesis of tributyl-[5-(4-hexylphenyl)-thiophen-2-yl]-stannane **27**



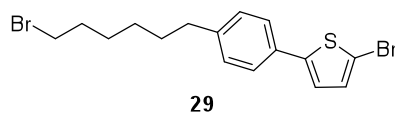
A stirred solution of **26** (750 mg, 3.07 mmol.) in dry THF (30 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ under N_2 , and $n\text{-BuLi}$ (1.47 mL, 1.05 eq., 2.2 M in hexanes) was added dropwise. The reaction was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 1 h, and Bu_3SnCl (1.20 g, 1.2 eq.) was added dropwise. The mixture was allowed to warm to room temperature overnight, with stirring. The reaction was then poured into H_2O (30 mL), and extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (3 x 10 mL), dried over MgSO_4 , and the solvent removed *in vacuo*. The crude oil was filtered through a short plug of neutral alumina (petroleum ether $40\text{-}60\text{ }^{\circ}\text{C}$), yielding the title compound as clear oil (1.622 g, 99 %), which was used immediately. $R_f = 0.73$ (petroleum ether $40\text{-}60\text{ }^{\circ}\text{C}$, alumina). ^1H NMR $\delta = 7.53$ (d, 2H, $^3J = 8.2$ Hz), 7.39 (d, 1H, $^3J = 3.3$ Hz), 7.17 (d, 2H, $^3J = 8.2$ Hz), 7.12 (d, 1H, $^3J = 3.3$ Hz), 2.60 (t, $^3J = 7.3$ Hz), 1.71-0.77 (m, 38H). ^{13}C NMR $\delta = 150.22, 142.02, 136.34, 136.10, 132.10, 128.81, 125.84, 123.79, 29.30, 28.99, 27.85, 27.43, 27.27, 26.94, 13.66, 13.61, 10.85, 8.77$. MS (EI^+) $m/z = 534$ ($[\text{M}]^+$, 12 %). HRMS (EI^+) = 534.235314, $\text{C}_{28}\text{H}_{46}\text{SSn}$ requires 534.234223.

Synthesis of 2-[4-(6-bromohexyl)-phenyl]-thiophene **28**



To a flame dried microwave tube **22** (500 mg, 1.56 mmol.), 2-(tributylstannyl)-thiophene (700 mg, 1.2 eq.), and Pd(PPh₃)₄ (90 mg, 5 mol.%) was added. Dry PhMe (4 mL), previously degassed with 3 x freeze/thaw/pump cycles (Ar) was added, ensuring that all traces of solids were washed below the solvent level. The reaction mixture was bubbled with Ar for 20 min, and then heated at 170 °C with microwave irradiation for 2 h. The reaction tube was allowed to cool to room temperature and filtered through Celite, before the solvent was removed *in vacuo*. The crude oil was purified *via* column chromatography (petroleum ether 40-60 °C to 9:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as clear oil, which solidified to a white/green solid on standing (372 mg, 74 %). *R*_f = 0.12 (petroleum ether 40-60 °C). ¹H NMR δ = 7.39 (d, 2H, ³J = 8.2 Hz), 7.14 (dd, 1H, ³J = 3.5 Hz, ⁴J = 1.2 Hz), 7.11 (dd, 1H, ³J = 3.5 Hz, ⁴J = 1.2 Hz), 7.04 (d, 2H, ³J = 7.9 Hz), 6.93 (dd, 1H, ³J = 3.5 Hz), 3.27 (t, 2H, ³J = 6.7 Hz), 2.48 (t, 2H, ³J = 7.6 Hz), 1.72 (p, 2H, ³J = 6.7 Hz), 1.58-1.14 (m, 6H). ¹³C NMR δ = 144.55, 142.01, 131.99, 128.92, 127.96, 125.91, 124.32, 122.63, 35.47, 33.94, 32.76, 31.30, 28.50, 17.52. MS (EI⁺) *m/z* = 322 ([M]⁺, 35 %), 324 ([M+2]⁺, 36 %). HRMS (EI⁺) = 322.040021, C₁₆H₁₉BrS requires 322.039084. IR (solid, cm⁻¹) = 3018, 2928, 2853, 1536, 1501, 1462, 1432, 1414, 1351, 1288, 1257, 1210, 1185, 1122, 1079, 1050, 1019, 959, 850, 810, 692, 637.

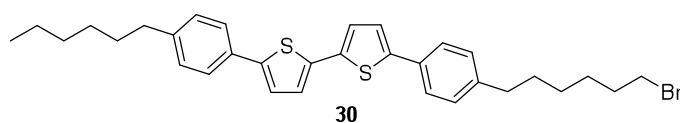
Synthesis of 2-bromo-5-[4-(6-bromohexyl)-phenyl]-thiophene **29**



A stirred solution of **28** (531 mg, 1.64 mmol.) in DMF (5 mL) was cooled to 0 °C in the absence of light. To this, NBS (351 mg, 1.2 eq.) in DMF (5 mL) was added dropwise *via* syringe, also in the absence of light. The reaction mixture was allowed to warm to room temperature overnight, before being poured into H₂O (100 mL) and extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with brine (6 x 30 mL), and the

combined aqueous layers were re-extracted with a further 30 mL of Et₂O. The organic phases were combined, dried over MgSO₄ and the solvent removed *in vacuo*. The crude product was purified *via* column chromatography (97.5:2.5 petroleum ether 40-60 °C: EtOAc), yielding the title compound as a white solid (628 mg, 95 %). Mpt. = 53.7-55.3 °C. R_f = 0.39 (97.5:2.5 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 7.44 (d, 2H, ³J = 8.2 Hz), 7.19 (d, 2H, ³J = 8.2 Hz), 7.02 (s, 2H), 3.41 (t, 2H, ³J = 7.0 Hz), 2.63 (t, 2H, ³J = 7.3 Hz), 1.87 (p, 2H, ³J = 7.0 Hz), 1.74-1.56 (m, 2H), 1.55-1.21 (m, 4H). ¹³C NMR δ = 142.54, 131.22, 130.77, 129.02, 125.59, 122.76, 110.81, 107.41, 35.47, 33.93, 32.71, 31.10, 28.34, 28.01. MS (EI⁺) m/z = 400 ([M]⁺, 50 %), 402 ([M+2]⁺, 82 %). HRMS (EI⁺) = 399.950048, C₁₆H₁₈Br₂S requires 399.949595. IR (film, cm⁻¹) = 2929, 2854, 1505, 1464, 1434, 1246, 1207, 1126, 1063, 978, 942, 832, 793, 740, 674, 647.

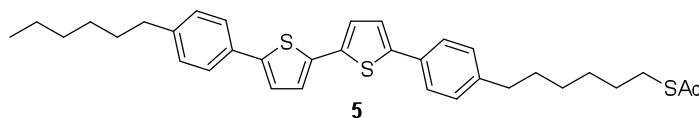
Synthesis of 5'-[4-(6-bromohexyl)-phenyl]-5-(4-hexylphenyl)-[2,2']-bithiophenyl **30**



To **29** (500 mg, 1.24 mmol.) and **27** (794 mg, 1.2 eq.) was added 30 mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and Pd(PPh₃)₄ (72 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 24 h. Once cool, the solvent was removed *in vacuo*, and the black solid residue was stirred in MeOH (30 mL) for 1 h under Ar. The solid was filtered off and loaded into a soxhlet extractor, before being washed repeatedly with MeOH, then THF, also under Ar. The THF washings were evaporated to dryness *in vacuo*, yielding the title compound as a yellow solid (271 mg, 39 %), which was stored in a flame-dried flask under Ar. Mpt. = 198.7-202.1 °C. ¹H NMR δ = 7.52 (d, 4H, ³J = 7.9 Hz), 7.23-7.12 (m, 8H), 3.41 (t, 2H, ³J = 6.7 Hz), 2.63 (t,

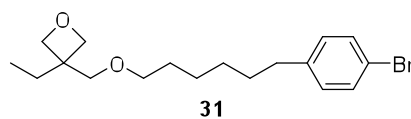
4H, $^3J = 7.6$ Hz), 1.87 (p, 2H, $^3J = 6.7$ Hz), 1.70-0.78 (m, 17H). ^{13}C NMR $\delta = 128.99$, 125.59, 125.54, 124.34, 124.33, 123.34, 123.30, 35.51, 33.94, 32.74, 31.14, 28.36, 28.03. MS (EI^+) $m/z = 564$ ($[\text{M}]^+$, 8 %), 566 ($[\text{M}+2]^+$, 9 %). HRMS (EI^+) = 564.152068, $\text{C}_{32}\text{H}_{37}\text{BrS}_2$ requires 564.152006. IR (solid, cm^{-1}) = 3021, 2923, 2852, 1676, 1596, 1531, 1498, 1446, 1414, 1376, 1317, 1259, 1205, 1073, 960, 870, 794, 754. UV-Vis. $\lambda_{\text{max}} = 378$ nm. Elemental Anal. = 68.05 % C, 6.40 % H, 13.94 % Br, 11.63 % S, $\text{C}_{32}\text{H}_{37}\text{BrS}_2$ requires 67.94 % C, 6.59 % H, 14.13 % Br, 11.34 % S.

Synthesis of thioacetic acid S-(6-{4-[5'-(4-hexylphenyl)-[2,2']-bithiophenyl-5-yl]-phenyl}-hexyl) ester **5**



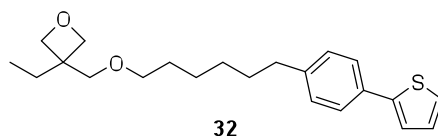
To a stirred solution of **30** (100 mg, 0.18 mmol.) in dry THF (10 mL) KSAc (40 mg, 2.0 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude yellow/brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as a dark yellow powder (75 mg, 74%). Mpt. = 178.1-180.5 °C. ^1H NMR $\delta = 7.51$ (d, 4H, $^3J = 8.1$ Hz), 7.20-7.16 (m, 6H), 7.14 (d, 2H, $^3J = 3.7$ Hz), 2.87 (t, 2H, $^3J = 7.3$ Hz), 2.62 (t, 4H, $^3J = 7.1$ Hz), 2.33 (s, 3H), 1.65-1.25 (m, 16H), 0.94 (t, 3H, $^3J = 7.3$ Hz). ^{13}C NMR $\delta = 196.01$, 143.19, 142.33, 136.35, 131.61, 128.98, 125.56, 124.32, 123.31, 35.56, 31.75, 31.38, 31.18, 30.66, 29.73, 29.45, 29.13, 29.00, 28.75, 28.66, 28.32, 22.64, 14.13. MS (EI^+) $m/z = 560$ ($[\text{M}]^+$, 54 %). HRMS (EI^+) = 560.221380, $\text{C}_{34}\text{H}_{40}\text{OS}_3$ requires 560.224132. IR (solid, cm^{-1}) = 2922, 2852, 1690, 1531, 1498, 1446, 1414, 1352, 1318, 1261, 1104, 1073, 1017, 951, 870, 794, 755, 688, 626. UV-Vis. $\lambda_{\text{max}} = 380$ nm.

Synthesis of 3-[6-(4-bromophenyl)-hexyloxymethyl]-3-ethyloxetane **31**



To a mixture of aqueous NaOH (20 mL, 50 % w/v) and tetrabutylammonium bromide (101 mg, 10 mol.%), a solution of **22** (1 g, 3.13 mmol.) and **17** (399 mg, 1.1 eq.) in hexane (20 mL) was added. The reaction mixture was heated at reflux for 2 h, and then allowed to cool to room temperature. The reaction was diluted with hexane (20 mL) and H₂O (20 mL), and the organic layer separated, dried over MgSO₄, and the solvent removed *in vacuo*. The crude oil was purified *via* column chromatography (4:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as clear oil (522 mg, 47%). $R_f = 0.53$ (4:1 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 7.38 (d, 2H, ³J = 8.2 Hz), 7.04 (d, 2H, ³J = 8.2 Hz), 4.34 (d, 2H, ²J = 5.8 Hz), 4.37 (d, 2H, ²J = 5.8 Hz), 3.51 (s, 2H), 3.43 (t, 2H, ³J = 6.4 Hz), 2.55 (t, 2H, ³J = 7.3 Hz), 1.73 (q, 2H, ³J = 7.3 Hz), 1.66-1.50 (m, 4H), 1.42-1.31 (m, 4H), 0.87 (t, 3H, ³J = 7.3 Hz). ¹³C NMR δ = 141.67, 131.26, 130.16, 119.29, 78.61, 73.39, 71.52, 43.41, 35.27, 31.24, 29.45, 28.94, 26.76, 26.00, 8.22. MS (EI⁺) m/z = 354 ([M]⁺, 14 %), 356 ([M+2]⁺, 13 %). HRMS (EI⁺) = 354.119327, C₁₈H₂₇BrO₂ requires 354.119441. IR (liquid, cm⁻¹) = 2929, 2858, 1488, 1459, 1404, 1375, 1272, 1114, 1072, 1011, 979, 828, 798, 729, 633, 604. Elemental Anal. = 61.15 % C, 8.20 % H, 22.28 % Br, C₁₈H₂₇BrO₂ requires 60.85 % C, 7.66 % H, 22.49 % Br.

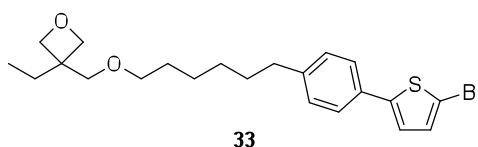
Synthesis of 3-ethyl-3-[6-(4-thiophen-2-yl-phenyl)-hexyloxymethyl]-oxetane **32**



To **31** (305 mg, 1.41 mmol.) and 2-(tributylstannyl)-thiophene (385 mg, 1.2 eq.) was added 10mL dry PhMe, previously degassed with 3 x freeze/thaw/pump cycles (Ar). The mixture

was stirred under Ar until dissolution of the starting materials was observed, then bubbled with Ar for 20 min. The mixture was then heated to reflux, and Pd(PPh₃)₄ (46 mg, 5 mol.%) in dry, degassed PhMe (5 mL) was added *via* cannula. The reaction mixture was stirred at reflux under Ar for 18 h. Once cool, the reaction mixture was filtered through Celite, and the solvent removed *in vacuo*. The crude oil was purified *via* column chromatography (4:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as clear oil (266 mg, 86 %). *R*_f = 0.68 (3:1 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 7.52 (d, 2H, ³J = 8.2 Hz), 7.27 (dd, 1H, ³J = 3.7 Hz, ⁴J = 1.2 Hz), 7.24 (dd, 1H, ³J = 3.7 Hz, ⁴J = 1.2 Hz), 7.18 (d, 2H, ³J = 8.2 Hz) 7.07 (dd, 1H, ³J = 5 Hz, 3.7 Hz), 4.45 (d, 2H, ²J = 5.8 Hz), 4.38 (d, 2H, ²J = 5.8 Hz), 3.52 (s, 2H), 3.44 (t, 2H, ³J = 6.4 Hz), 2.62 (t, 2H, ³J = 7.6 Hz), 1.74 (q, 2H, ³J = 7.3 Hz), 1.68-1.51 (m, 4H), 1.43-1.32 (m, 4H), 0.88 (t, 3H, ³J = 7.3 Hz). ¹³C NMR δ = 144.55, 142.19, 131.89, 128.88, 127.89, 125.85, 124.25, 122.55, 78.57, 73.39, 71.53, 60.35, 43.40, 35.54, 31.31, 29.03, 28.21, 26.77, 26.03, 21.00, 17.40, 14.18, 13.59, 8.20. MS (EI⁺) *m/z* = 358 ([M]⁺, 74 %), 359 ([M+1]⁺, 18 %). HRMS (EI⁺) = 358.196175, C₂₂H₃₀O₂S requires 358.196652. IR (oil, cm⁻¹) = 2928, 2856, 1536, 1502, 1459, 1433, 1414, 1375, 1288, 1210, 1114, 1050, 979, 850, 814, 692, 635, 600.

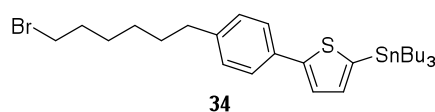
Synthesis of 3-{6-[4-(5-bromothiophen-2-yl)-phenyl]-hexyloxymethyl}-3-ethyloxetane **33**



A stirred solution of **32** (150 mg, 0.42 mmol.) in DMF (5 mL) was cooled to 0 °C in the absence of light. To this, NBS (89 mg, 1.2 eq.) in DMF (5 mL) was added dropwise *via* syringe, also in the absence of light. The reaction mixture was allowed to warm to room temperature overnight, before being poured in to H₂O (100 mL), and extracted with Et₂O (3 x 30 mL). The combined organic phases were washed with brine (6 x 30 mL), and the aqueous

layers combined and re-extracted with a further 30 mL of Et₂O. The combined organic layers were dried over MgSO₄, and the solvent removed *in vacuo*. The crude yellow product was purified *via* column chromatography (4:1 petroleum ether 40-60 °C: EtOAc), yielding the title compound as clear oil that solidified to a white solid on standing (159 mg, 87 %). Mpt. = 51.6-52.0 °C. R_f = 0.52 (4:1 petroleum ether 40-60 °C: EtOAc). ¹H NMR δ = 7.42 (d, 2H, ³J = 8.2 Hz), 7.18 (d, 2H, ³J = 8.2 Hz), 7.01 (s, 2H), 4.45 (d, 2H, ²J = 5.8 Hz), 4.38 (d, 2H, ²J = 5.8 Hz), 3.52 (s, 2H), 3.44 (t, 2H, ³J = 6.4 Hz), 2.61 (t, 2H, ³J = 7.3 Hz), 1.74 (q, 2H, ³J = 7.3 Hz), 1.67-1.52 (m, 4H), 1.43-1.32 (m, 4H), 0.88 (t, 3H, ³J = 7.3 Hz). ¹³C NMR δ = 146.06, 142.77, 131.14, 130.76, 129.03, 125.55, 122.73, 110.76, 78.61, 73.41, 71.55, 43.43, 35.58, 31.29, 29.48, 29.05, 26.78, 26.05, 8.24. MS (EI⁺) m/z = 436 ([M]⁺, 79 %), 438 ([M+2]⁺, 84 %). HRMS (EI⁺) = 436.108543, C₂₂H₂₉BrO₂S requires 436.107163. IR (powder, cm⁻¹) = 2960, 2923, 2852, 2797, 1504, 1464, 1433, 1363, 1273, 1244, 1210, 1110, 1063, 1016, 972, 940, 904, 830, 790, 747, 723, 674, 635, 617. Elemental Anal. = 60.14 % C, 6.68 % H, 18.36 % Br, 7.36 % S, C₂₂H₂₉BrO₂S requires 60.41 % C, 6.68 % H, 18.27 % Br, 7.33 % S.

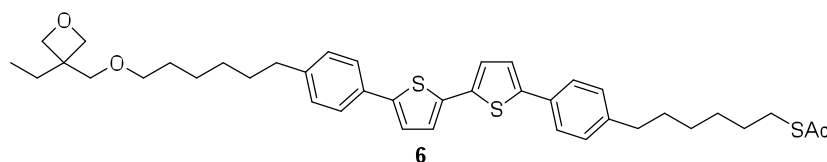
Synthesis of {5-[4-(6-bromohexyl)-phenyl]-thiophen-2-yl}-tributylstannane **34**



A stirred solution of **28** (420 mg, 1.30 mmol.) in dry THF (30 mL) was cooled to -78 °C under N₂, and n-BuLi (0.62 mL, 1.05 eq. 2.2 M in hexanes) was added dropwise. The reaction was allowed to stir for 1 h at -78 °C, before Bu₃SnCl (508 mg, 1.2 eq.) was added dropwise, and the reaction mixture allowed to room temperature overnight with stirring. The mixture was poured into H₂O (30 mL) and extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with brine (3 x 10 mL), dried over MgSO₄, and the solvent removed *in vacuo*. The crude product was filtered through a short plug of neutral alumina

NMR δ = 143.22, 142.44, 136.31, 131.58, 128.95, 125.55, 124.31, 123.31, 78.62, 73.41, 71.55, 43.42, 35.56, 35.47, 33.91, 32.70, 31.30, 31.11, 29.46, 29.04, 28.33, 28.00, 26.76, 26.02, 8.20. MS (EI^+) m/z = 678 ($[\text{M}]^+$, 11 %), 680 ($[\text{M}+2]^+$, 12 %). HRMS (EI^+) = 678.217997, $\text{C}_{38}\text{H}_{47}\text{BrO}_2\text{S}_2$ requires 678.220086. IR (solid, cm^{-1}) = 2924, 2853, 1676, 1597, 1532, 1498, 1446, 1414, 1372, 1260, 1097, 1017, 979, 870, 793, 727, 692, 648. UV-Vis. λ_{max} = 373 nm.

Synthesis of thioacetic acid S-{6-[4-(5'-{4-[6-(3-ethyloxetan-3-ylmethoxy)-hexyl]-phenyl]-[2,2']-bithiophenyl-5-yl)-phenyl]-hexyl} ester **6**



To a stirred solution of **35** (100 mg, 0.15 mmol.) in dry THF (10 mL) KSAc (20 mg, 1.2 eq.) was added. The mixture was heated at reflux overnight. Once cool, the solvent was removed *in vacuo*, and CHCl_3 (50 mL) was added. The organic phase was washed with H_2O (3 x 10 mL), dried over MgSO_4 and the solvent removed *in vacuo*. The crude yellow/brown residue was recrystallised (1:1 PhMe: hexane), yielding the title compound as a yellow powder (85 mg, 84%). Mpt. = 193.6-194.1 °C. ^1H NMR δ = 7.52 (d, 4H, 3J = 8.0 Hz), 7.20-7.18 (m, 6H), 7.14 (d, 2H, 3J = 3.7 Hz), 4.45 (d, 2H, 2J = 5.9 Hz), 4.38 (d, 2H, 2J = 5.9 Hz), 3.52 (s, 2H), 3.45 (t, 2H, 3J = 6.4 Hz), 2.86 (t, 2H, 3J = 7.4 Hz), 2.62 (t, 4H, 3J = 7.3 Hz), 2.32 (s, 3H), 1.76 (q, 2H, 3J = 7.6 Hz), 1.69-1.31 (m, 16H), 0.88 (t, 3H, 3J = 7.6 Hz). ^{13}C NMR δ = 143.21, 142.45, 136.32, 131.59, 128.97, 125.55, 124.31, 123.30, 78.64, 73.43, 71.58, 43.44, 35.55, 31.31, 31.17, 30.65, 29.44, 29.12, 28.73, 26.78, 26.05, 8.22. MS (EI^+) m/z = 674 ($[\text{M}]^+$, 87%), 676 ($[\text{M}+2]^+$, 37%). HRMS (EI^+) = 674.290844, $\text{C}_{40}\text{H}_{50}\text{O}_3\text{S}_3$ requires 674.292211. IR (solid, cm^{-1}) = 2923, 2852, 1690, 1597, 1532, 1498, 1446, 1413, 1353, 1317, 1261, 1237, 1110, 978, 959, 870, 822, 793, 727, 665, 626. UV-Vis. λ_{max} = 379 nm.

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