Experimental

4-Octyloxybenzaldehyde:
A mixture of 1-bromooctane (43.5 g, 0.22 mol), 4-hydroxybenzaldehyde (25 g, 0.20 mol), potassium carbonate (69 g, 0.5 mol) and butanone (500 cm^3) was heated under reflux for 24 hours. The cooled solution was filtered and the filtrate evaporated down under reduced pressure. The crude product was then distilled off to yield 39.2 g (67.6 %) of the desired product. Boiling point /°C: 142-144 @ 0.6 mbar, Purity: >99 % (GC), ^{1}H NMR ($CDCl_3$) δ_H: 0.88 (3H, d), 1.29-1.45 (10H, m), 1.80 (2H, quint), 4.03 (2H, t), 6.98 (2H, d, *J*=8.5), 7.81 (2H, d, *J*=8.5), 9.86 (1H, s), IR ν_{max} /cm^{-1}: 3042, 2926, 2855, 1694, 1602, 1577, 1509, 1467, 1311, 1259, 1159, 1019, 832, 651, 618, 514, MS *m/z*: 234(M^+), 222, 123, 110(M100), 77, 71.

2-(4-Octyloxyphenyl)benzothiazole:
A solution of 4-octyloxybenzaldehyde (30 g, 0.128 mol), 2-aminothiophenol (16 g, 0.128 mol) and dimethylsulfoxide (200 cm^3) was heated at 80 °C for 24 hours. The cooled solution was added to water and extracted into dichloromethane (3 x 75 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate evaporated down under reduced pressure. The solid residue was recrystallised from ethanol to give 32.4g (74.6 %) of the desired product. Melting point /°C: 77-78, Purity: >99 % (GC), ^{1}H NMR ($CDCl_3$) δ_H: 0.91 (3H, d), 1.29-1.45 (10H, m), 1.81 (2H, quint), 4.03 (2H, t), 6.99 (2H, d, *J*=8.5), 7.34-7.36 (1H, m), 7.44-7.47 (1H, m), 7.87 (1H, m), 8.00 (2H, d), 8.04 (1H, m), IR ν_{max} /cm^{-1}: 3041, 2920, 2851, 2360, 1606, 1521, 1473, 1259, 1172, 965, 833, 753, 668, MS *m/z*: 339(M^+), 227(M100), 198, 108, 69.

6-Bromo-2-(4-octyloxyphenyl)benzothiazole:
Bromine (14.1 g, 0.088 mol) was added dropwise to a solution of 2-(4-octyloxy-phenyl)benzothiazole (**61**) (25 g, 0.073 mol) and dilute acetic acid (1,000 cm^3). The reaction mixture was then heated for a further 6 h. The cooled reaction mixture was then added to aqueous sodium metabisulphite solution (200 cm^3). The product was extracted using diethyl ether (3 x 200 cm^3). The combined organic layers are washed with concentrated sodium carbonate solution (2 x 200 cm^3) and then with water (2 x 100 cm^3), dried ($MgSO_4$), filtered and then evaporated down under partially reduced pressure The product was purified by column chromatography [silica gel, dichloromethane:hexane 2:1] followed by recrystallisation from ethanol to yield 12.3 g (39.9 %) of the desired product. Melting point /°C: 114-115, Purity: >99 % (GC), ^{1}H NMR ($CDCl_3$) δ_H: 0.89 (3H, d), 1.29-1.45 (10H, m), 1.81 (2H, quint), 4.03 (2H, t), 6.98 (2H, d, *J*=8.5), 7.56 (1H, dd, *J*=8.5 and *J*=1.9), 7.86 (1H, d, *J*=8.5), 7.98 (2H, d, *J*=8.5), 8.01 (1H, d, *J*=1.9), IR ν_{max} /cm^{-1}: 3045, 2919, 2851, 1605, 1520, 1465, 1301, 1261, 1222, 1175, 1045, 998, 834, 817, 694, 561, MS *m/z*: 421(M^+), 419(M^+), 307(M100), 278, 107, 63.

2-[(S)-3,7-Dimethyloct-6-enyl]thiophene:
n-Butyllithium in hexanes (62 cm^3, 2.5M , 0.155 mol) was added slowly to a solution of thiophene (12.6 g, 0.15 mol) in THF (150 cm^3) at -78 °C. The solution was stirred for 1 h at -78 °C, *S*-(+)-citronellyl bromide (35 g, 0.16 mol) was added slowly and the temperature raised to RT after completion of the addition. HCl_{aq} (20%, 100 cm^3) and water (100 cm^3) were added and the product extracted into diethyl ether (2 x 100 cm^3). The ethereal extracts were dried ($MgSO_4$) and concentrated to a pale brown oil. The product was purified by distillation to yield 17.61 g (54 %) of the desired product. Boiling point /°C: 107-109 @ 0.5 mbar, Purity: >99 % (GC), ^{1}H NMR ($CDCl_3$) δ_H: 0.92 (3H, d, *J*=6.5), 1.13-1.22 (1H, m), 1.30-1.37 (1H, m), 1.53-1.60 (2H, m), 1.64 (3H, s), 1.68 (3H, s), 1.83-1.87 (1H, m), 1.95-2.06 (2H, m), 2.74-2.82 (2H, m), 5.07-5.11 (1H, m), 6.75 (1H, dd), 6.89 (1H, dd), 7.07 (1H, dd), IR ν_{max}/cm^{-1} : 2959, 1555, 1450, 1366, 1258, 1073. 796, 655, MS(m/z): 223(M^+), 137, 110, 97(M100), 69.

5-Tributylstannyl-2-[(S)-3,7-dimethyloct-6-enyl]thiophene:
n-Butyllithium in hexanes (41.2 cm^3, 2.5M , 0.1 mol) was added slowly to a solution of 2-[(*S*)-3,7-dimethyloct-6-enyl]thiophene (17.6 g, 0.08 mol) in THF (100 cm^3) at -78 °C. The solution was stirred for 1 h at -78 °C, tri-*n*-butyltin chloride (39 g, 0.12 mol) was added slowly and the temperature raised to RT after completion of the addition. HCl_{aq} (20%, 100 cm^3) and water (100 cm^3) were added and the product extracted into diethyl ether (2 x 100 cm^3). The ethereal extracts were dried ($MgSO_4$) and concentrated to a pale brown oil. The product was purified by distillation to yield 21 g (51 %) of the desired product. Boiling point /°C: 205-208 @ 0.5 mbar, Purity: >99% (GC), ^{1}H NMR ($CDCl_3$) δ_H: 0.85 (9H, t), 0.95 (3H, d), 1.05-1.10 (12H, m), 1.13-1.30 (2H, m), 1.42-1.48 (6H, m), 1.53-1.60 (2H,

m), 1.64 (3H, s), 1.68 (3H, s), 1.83-1.87 (1H, m), 1.95-2.06 (2H, m), 2.74-2.82 (2H, m), 5.09 (1H, t), 6.89 (1H, d), 6.99 (1H, d), IR ν_{max}/cm^{-1}: 2957, 2852, 1453, 1376, 1073. 795, 655, MS (m/z): 512(M^+), 455(M100), 399, 341, 217, 79, 69.

2-{5-[(S)-3,7-Dimethyloct-6-enyl]thiophen-2-yl}-5-(4-octyloxyphenyl)benzothiazole (Compound 1):

A mixture of 6-bromo-2-(4-octyloxyphenyl)benzothiazole (1.7 g, 0.0041 mol) 5-tributylstannyl-2-[(*S*)-3,7-dimethyloct-6-enyl]thiophene (2.29 g, 0.0045 mol) and *tetrakis*(triphenylphosphine)palladium (0) (0.23 g, 2.03×10^{-4} mol) in DMF (75 cm^3) was heated at 90 °C for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution (100 cm^3) to destroy the tin side products. DCM (2×200 cm^3) was added and the combined organic layers were washed with brine (4×200 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography [silica gel, ethyl acetate: hexane, 10 %: 90 %] to yield a white solid (1.31 g, 58 %), which was further purified by preparative HPLC and recrystallisation from a DCM and ethanol solvent mixture. Purity: 99.9% (HPLC), ^{1}H NMR ($CDCl_3$) δ_H: 0.89 (3H, t), 0.96 (3H, d), 1.16-1.40 (10H, m), 1.48 (2H, quint), 1.56 (2H, quint), 1.62 (3H, s), 1.69 (3H, s), 1.70-1.76 (1H, m), 1.82 (2H, quint), 1.94-2.07 (2H, m), 2.76-2.88 (2H, m), 4.03 (2H, t), 5.11 (1H, t), 6.76 (1H, d, *J*=3.6), 6.98 (2H, d, *J*=8.7), 7.18 (1H, d, *J*=3.6), 7.67 (1H, dd, *J*=8.7 and *J*=1.7), 7.97 (2H, d, *J*=8.7), 8.00-8.02 (2H, m), IR ν_{max} /cm^{-1}: 3045, 2919, 2851, 1605, 1520, 1465, 1301, 1261, 1222, 1175, 1045, 998, 834, 817, 694, 561, MS (m/z): 559 (M^+, M100), 474, 434, 322, 293.

Instrumentation:

The structures of intermediates and final products were confirmed by proton (^{1}H) nuclear magnetic resonance (NMR) spectroscopy (JOEL Lambda 400 spectrometer), infra-red (IR) spectroscopy (Perkin-Elmer Paragon 1000 Fourier Transform-Infrared (FT-IR) spectrometer) and mass spectrometry (MS) (GC/MS QP5050A Schimadzu with electron impact (EI)). Reaction progress and product purity was checked using a Varian CP 3380 capillary gas chromatograph fitted with a 10 m CP-SIL 5CB (0.12 μm, 0.25 mm) capillary column. All of the final products were more than 99.5% pure by GC. Transition temperatures were determined using a Nikon E400 polarising light microscope together with a Linkam 350 heating stage and control unit. The analysis of transition temperatures and enthalpies was carried out by a Perkin-Elmer DSC-7 differential scanning calorimeter and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the reported value of the transition temperatures. Purity of the final compound (compound **1**) was confirmed by analytical HPLC (Gilson) equipped with a Luna 5 microns reverse phase C18 column (250 × 4.60 mm)