II. Experimental section

Materials Synthesis.

2-(4-Octyloxyphenyl)thiophene. A mixture of 1-bromo-4-octyloxybenzene (30.0 g, 0.105 mol), 2-(tributylstannyl)thiophene (41.0 g, 0.111 mol) and *tetrakis*(triphenylphosphine)-palladium (0) (3.5 g, 3.0×10^{-3} mol) in DMF (200 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. Hexane (2×200 cm^3) was added and the combined organic layers were washed with brine (2×200 cm^3), water (200 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Catalyst residues were removed by passing the crude product though a short column containing silica gel [DCM: hexane, 50 %: 50 %]. The product was recrystallised from ethanol, filtered and washed with cold ethanol (2×30 cm^3) to yield a light blue crystalline solid (18.2 g, 60.1 %). Purity (%): >99 (GC). Melting point /°C: 68-70. ^{1}H NMR ($CDCl_3$) δ_H: 0.89 (3H, t), 1.23-1.40 (8H, m), 1.46 (2H, quint), 1.70 (2H, quint), 3.97 (2H, t), 6.89 (2H, d, *J*=9.0 Hz), 7.04 (1H, dd, *J*=3.6, 5.00 Hz), 7.18 (1H, dd, *J*=1.1, 3.6 Hz), 7.20 (1H, dd, *J*=1.1, 5.3 Hz), 7.52 (2H, d, *J*=9.0 Hz). IR ν_{max} /cm^{-1}: 3069, 2955, 2922, 2855, 1606, 1572, 1501, 1474, 1289, 1252, 1180, 1114, 1075, 1025, 854, 813. MS *m/z* (EI): 288 (M^+), 256, 216, 176 (M100), 147, 115, 89, 77, 69. Combustion analysis: expected (%): C 74.95, H 8.39, S 11.12. Found (%): C 75.37, H 8.99, S 10.02.

2-[(4-Octyloxyphenyl)-5-tributylstannyl]thiophene. *n*-Butyllithium in hexanes (25.9 cm^3, 2.5M , 0.065 mol) was added slowly to a solution of 2-(4-octyloxyphenyl)thiophene (17.0 g, 0.059 mol) in THF (200 cm^3) at -78 °C. The solution was stirred for 1 h at -78 °C, tri-*n*-butyltin chloride (24.4 g, 0.075 mol) was added slowly and the temperature raised to RT after completion of the addition. Water (2 x 200 cm^3) was added and the product extracted into diethyl ether (2×200 cm^3). The ethereal extracts were dried ($MgSO_4$) and concentrated to a pale brown oil. The product was used to the next step without further purification. Purity: 90 % (GC). ^{1}H NMR ($CDCl_3$) δ_H: 0.86-0.94 (12H, m), 1.12 (6H, t), 1.26-1.48 (16H, m), 1.58 – 1.70 (8H, m), 4.00 (2H, t), 6.89 (2H, d, *J*=9.0 Hz), 7.13 (1H, d, *J*=3.4 Hz), 7.40 (1H, d, *J*=3.4 Hz), 7.54 (2H, d, *J*=9.0 Hz). IR ν_{max} /cm^{-1}: 3100, 3054, 2951, 2922, 2854, 1599, 1569, 1500, 1476, 1279, 1252, 1181, 1117, 1025, 930, 850, 811. MS *m/z* (EI): 578 (M^+), 518, 465, 288, 176, 145, 115 (M100), 71, 57, 41.

2,7-Dibromo-9,9-dioctylfluorene. A 50 % aqueous solution of NaOH (100 cm^3) was added to a mixture of 2,7-dibromofluorene (16.00 g, 0.0494 mol) and TBAB (0.35 g, 0.0049 mol) in toluene (100 cm^3). 1-Bromopropane (6.10 g, 0.0496 mol) in toluene (10 cm^3) was then added dropwise at room temperature and the reaction mixture was stirred vigorously under reflux overnight. The reaction mixture was cooled to room temperature and water was added (200 cm^3). Toluene (300 cm^3) was added and the resultant organic layer washed with water (200 cm^3), dried ($MgSO_4$), filtered and

concentrated under reduced pressure. The residue was purified by gravity column chromatography [silica gel, hexane, 100 %] and recrystallised from ethanol to yield a white crystalline solid (17.0 g, 62.7 %). Purity (%): >99 (GC). Melting point /°C: 54-56 . ^{1}H NMR ($CDCl_3$) δ_H: 0.58 (4H, quint), 0.83 (6H, t), 1.00-1.16 (16H, m), 1.21 (4H, sext), 1.88-1.93 (4H, m), 7.44-7.46 (4H, m), 7.51 (2H, d, *J*=7.6 Hz). IR ν_{max} /cm^{-1}: 3070, 2954, 2924, 2870, 2853, 1598, 1570, 1466, 1416, 1132, 1060, 1004, 955, 881, 811, 751, 723. MS *m/z* (EI): 550, 548, 546 (M^+, M100), 435, 356, 336, 323, 271, 258, 243, 218, 203, 189, 176, 163, 99, 85, 71. Combustion analysis: expected (%): C 63.51, H 7.35. Found (%): C 63.81, H 7.63.

2,7-bis(Thien-2-yl)-9,9-dioctylfluorene. A mixture of 2,7-dibromo-9,9-dioctylfluorene (10.0 g, 0.018 mol), 2-(tributylstannyl)thiophene (14.1 g, 0.038 mol) and *tetrakis*(triphenylphosphine)-palladium (0) (0.62 g, 5.4×10^{-4} mol) in DMF (100 cm^3) was heated at 90 °C for 24 h. Dichloromethane (200 cm^3) was added to the cooled reaction mixture and the resultant solution washed with HCl_{aq} (2×150 cm^3, 20%), water (2 x 100 cm^3), dried ($MgSO_4$) and concentrated onto silica gel for purification by column chromatography [silica gel, dichloromethane: hexane 1:1]. The compound was purified by recrystallisation from dichloromethane / ethanol to yield 7.3 g (73.2%) of the desired product. Melting point /°C: 75. ^{1}H NMR ($CDCl_3$) δ_H: 0.65 (4H, quint), 0.79 (6H, t), 1.00-1.23 (20H, m), 1.96-2.00 (4H, m), 7.10 (2H, dd, *J*=3.6, 5.1 Hz), 7.29 (2H, dd, *J*=1.2, 5.2 Hz), 7.38 (2H, dd, *J*=1.1, 3.6 Hz), 7.55 (2H, d, *J*=1.3 Hz), 7.60 (2H, dd, *J*=1.7, 7.9 Hz), 7.67 (2H, d, *J*=7.8 Hz). IR ν_{max}/cm^{-1}: 3060, 3000, 2956, 2922, 2857, 1600, 1570, 1512, 1471, 1376, 1266, 1207, 1051, 870, 853, 816, 748. MS (m/z): 554 (M^+), 498, 472, 343, 329 (M100), 310, 247, 160, 97, 85, 71.

2,7-bis(5-Bromothien-2-yl)-9,9-dioctyllfluorene. *N*-Bromosuccinimide (2.1 g, 0.012 mol freshly purified by recrystallisation from water) was added slowly to a stirred solution of 2,7-bis(thien-2-yl)-9,9-dioctylfluorene (2.3 g, 5.55×10^{-3} mol) in chloroform (25.0 cm^3) and glacial acetic acid (25.0 cm^3). The reaction mixture was heated under reflux for 1 h, then dichloromethane (100 cm^3) added to the cooled reaction mixture. The resultant mixture was washed with water (100 cm^3), HCl_{aq} (150 cm^3, 20%), saturated aqueous sodium sulphite solution (50 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the raw product purified by recrystallisation from an ethanol: dichloromethane mixture to yield 2.74 g (86%) of the desired product. Melting point /°C: 69. ^{1}H NMR ($CDCl_3$) δ_H: 0.65 (4H, quint), 0.78 (6H, t), 1.00-1.24 (20H, m), 1.95-2.00 (4H, m), 7.05 (2H, d, J=3.9 Hz), 7.11 (2H, d, J=3.9 Hz), 7.44 (2H, d, J=1.4 Hz), 7.49 (2H, dd, J=1.6, 7.8 Hz), 7.66 (2H, d, J=7.8 Hz). IR ν_{max}/cm^{-1}: 3066, 3000, 2955, 2920, 2856, 1470, 1441, 1290, 1204, 1063, 987, 878, 816, 788. MS (m/z): 714, 712, 710 (M^+), 500, 487, 422, 375, 356, 295, 239, 190, 112, 83, 71 (M100). Combustion analysis: expected (%): C 62.36, H 6.22, S 9.00. Found (%): C 62.10, H 6.44, S 8.74.

2,7-bis{5-[5-(4-Octyloxyphenyl)thiophen-2-yl]thiophen-2-yl}-9,9-dioctylfluorene 8. A mixture of 2-[(4-octyloxyphenyl)-5-tributylstannyl]thiophene (4.86 g, 8.4 x 10^{-3} mol), 2,7-bis(5-bromothiophen-2-yl)-9,9-dioctyllfluorene (1.5 g, 2.1 x 10^{-3}

mol) and tetrakis(triphenylphosphine)-palladium (0) (0.3 g, 2.5×10^{-4} mol) in DMF (50 cm^3) was heated at 90 °C for 24 h. Dichloromethane (150 cm^3) was added to the cooled reaction mixture and the resultant solution washed with HCl_{aq} (2×150 cm^3, 20%), water (100 cm^3), dried ($MgSO_4$) and concentrated onto silica gel for purification by column chromatography [silica gel, dichloromethane: hexane 1:1] to yield 1.85 g (80 %) of the desired product. Transition temp /°C: ^{1}H NMR ($CDCl_3$) δ_H: 0.65 (4H, quint), 0.78 (6H, t), 1.00-1.24 (20H, m), 1.95-2.00 (4H, m), 7.05 (2H, d, *J*=3.9 Hz), 7.11 (2H, d, *J*=3.9 Hz), 7.15 (4H, m), 7.44 (2H, d, *J*=1.4 Hz), 7.49 (2H, dd, *J*=1.6, 7.8 Hz), 7.66 (2H, d, *J*=7.8 Hz). IR ν_{max}/cm^{-1}: 3068, 2954, 2930, 2867, 1600, 1572, 1499, 1473, 1289, 1251, 1181, 1160, 1069, 834, 799. MS *m/z* (MALDI): 1128 (M^+).

2,7-bis{5-[5-(4-Hydroxyphenyl)thiophen-2-yl]thiophen-2-yl}-9,9-dioctylfluorene. Boron tribromide in dichloromethane (1.33 g, 5.32 x 10^{-3} mol) was added dropwise to a cooled (0 °C) stirred solution of 2,7-bis{5-[5-(4-octyloxyphenyl)thiophen-2-yl]thiophen-2-yl}-9,9-dioctylfluorene (1.50 g, 1.33 x 10^{-3} mol) in dichloromethane (100 cm^3). The reaction mixture was stirred at room temperature overnight, then poured onto an ice/water mixture (100 g) and stirred (30 min). The reaction mixture was extracted with ethyl acetate (2 x 100 cm^3) and the combined organic layers were washed with brine (2 x 50 cm^3) and dried ($MgSO_4$). After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, ethyl acetate: hexane 1:2] to yield 0.90 g (75 %) of the desired product. ^{1}H NMR ($CDCl_3$) δ_H: 0.69 (4H, quint), 0.77 (6H, t), 1.00-1.20 (20H, m), 1.99-2.03 (4H, m), 4.93 (2H, s, -OH), 6.86 (4H, d, *J*=8.7 Hz), 7.18 (2H, d, *J*=3.9 Hz), 7.13 (4H, m), 7.31 (2H, d, *J*=3.9 Hz), 7.53 (4H, d, *J*=8.7 Hz), 7.55 (2H, d, *J*=1.7 Hz), 7.58 (2H, dd, *J*=1.7, 7.8 Hz), 7.68 (2H, d, *J*=7.9 Hz). IR ν_{max} /cm^{-1}: 3100-3500, 2954, 2925, 2851, 1609, 1544, 1511, 1475, 1455, 1376, 1246, 1174, 1106, 883, 831, 799. MS *m/z* (MALDI): 903 (M^+).

2,7-bis[5-(5-{4-[10-(1-Vinylallyloxycarbonyl)decyloxy]phenyl]thiophen-2-yl]thiophen-2-yl}-9,9-dioctylfluorene 9. A mixture of 2,7-bis{5-[5-(4-hydroxyphenyl)thiophen-2-yl]thiophen-2-yl}-9,9-dioctylfluorene (0.5 g, 5.5 x 10^{-4} mol), 1,4-pentadien-3-yl 11-bromoundecanoate (0.54 g, 1.6 x 10^{-3} mol) and potassium carbonate (0.23 g, 1.6 x 10^{-3} mol) in DMF (40 cm^3) was heated (80 °C) overnight. The cooled reaction mixture was filtered and the filtrate concentrated under reduce pressure. The crude product was purified by column chromatography [silica gel, dichloromethane: hexane 2:1] followed by recrystallisation from ethanol/dichloromethane to yield 0.62 g (80 %) of the desired product. Transition temp. /°C: T_g 0 Cr 52 N 143 I. Purity: 100 % (HPLC). ^{1}H NMR ($CDCl_3$) δ_H: 0.70 (4H, quint), 0.78 (6H, t), 1.02-1.20 (20H, m), 1.28-1.40 (20H, m), 1.46 (4H, quint), 1.64 (4H, quint), 1.79 (4H, quint), 2.00-2.04 (4H, m), 2.34 (4H, t), 3.98 (4H, t), 5.23 (4H, dt), 5.30 (4H, dt), 5.72 (2H, tt), 5.80-5.88 (4H, m), 6.91 (4H, d, *J*=8.7 Hz), 7.12 (4H, m), 7.20 (2H, d, *J*=3.9 Hz), 7.34 (2H, d, *J*=3.9 Hz), 7.56 (4H, d, *J*=8.7 Hz), 7.58 (2H, d, *J*=1.5 Hz), 7.62 (2H, dd, *J*=1.5, 7.8 Hz), 7.67 (2H, d, *J*=7.9 Hz). IR ν_{max} /cm^{-1}:

3090, 3065, 2954, 2928, 2869, 1736, 1639, 1598, 1571, 1511, 1474, 1288, 1251, 1180, 1115, 1072, 988, 932, 834, 799. MS *m/z* (MALDI): 1404 (M^+).