

## Experimental

All commercially available starting materials, reagents and solvents were used as supplied, or otherwise stated, and were obtained from Aldrich, Strem Chem. Inc., Acros or Lancaster Synthesis. Tetrahydrofuran and diethylether were dried over sodium wire and distilled over sodium wire and benzophenone indicator prior to use. All reactions were carried out using a dry nitrogen atmosphere unless water was present as solvent or reagent and the temperatures were measured internally. Reactions involving the methacrylate group were always doped with BHT, to prevent polymerisation of the methacrylate group. Mass spectra were recorded using a Gas Chromatography/Mass Spectrometer (GC/MS)-QP5050A Shimadzu with Electron Impact (EI) at a source temperature of 200 °C. IR spectra were recorded using a Perkin-Elmer Paragon 1000 Fourier Transform-Infrared (FT-IR) spectrometer. <sup>1</sup>H NMR spectra were recorded using a JEOL Lambda 400 spectrometer and an internal standard of tetramethylsilane (TMS) was used. GC was carried out using a Chromopack CP3800 gas chromatograph equipped with a 10 m CP-SIL 5CB column. Analytical High Pressure Liquid Chromatography (HPLC) using a Gilson 233 XL instrument with a Luna 5 microns reverse phase C18 column (250 × 4.60 mm), using acetonitrile as the mobile phase. Purification of intermediates and final products was mainly accomplished by gravity column chromatography<sup>1</sup>, using silica gel (40-63 microns, 60 Å) obtained from Fluorochem. The melting point and liquid crystal transition temperatures of the solids prepared were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarising microscope. The transition temperatures of all of the final products were confirmed using a Perkin-Elmer DSC-7 and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the reported value of the transition temperatures. The purity of all final compounds was checked by elemental analysis using a Fisons EA 1108 CHN analyzer.

### 2-(4-Octyloxyphenyl)thiophene (2)

A mixture of 1-bromo-4-octyloxybenzene (**1**) (10.0 g, 0.0351 mol), 2-(tributylstannyl)thiophene (14.4 g, 0.0386 mol) and *tetrakis*(triphenylphosphine)-palladium (0) (1.22 g, 1.05 × 10<sup>-3</sup> mol) in DMF (200 cm<sup>3</sup>) 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<sup>3</sup>) to destroy the tin side products. Hexane (2 × 200 cm<sup>3</sup>) was added and the combined organic layers were washed with brine (2 × 200 cm<sup>3</sup>), water (200 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. Catalyst residues were removed by passing the crude product through 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<sup>3</sup>) to yield a light blue crystalline solid (5.00 g, 49.5 %). Melting point /°C: 68-70. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 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<sub>max</sub> /cm<sup>-1</sup>: 3069, 2955, 2922, 2855, 1606, 1572, 1501, 1474, 1289, 1252, 1180, 1114, 1075, 1025, 854, 813. MS *m/z* (EI): 288 (M<sup>+</sup>), 256, 216, 176 (M100), 147, 115, 89, 77, 69. Combustion analysis: Expected: C 74.95%, H 8.39%, S 11.12% Obtained: C 75.37%, H 8.99%, S 10.02%.

### 2-[(4-Octyloxyphenyl)-5-tributylstannyl]thiophene (3)

A solution of *n*-BuLi in hexanes (30.7 cm<sup>3</sup>, 2.5M, 0.0767 mol) was added slowly to a solution of 2-(4-octyloxyphenyl)thiophene (**2**) (17.0 g, 0.0590 mol) in THF (dry, 200 cm<sup>3</sup>) at -78 °C. After stirring for 1 h at -78 °C, tri-*n*-butyltin chloride (30.7 g, 0.0944 mol) was added slowly and the temperature of the reaction mixture was allowed to reach RT after completion of the addition. The reaction mixture was stirred overnight. Water (100 cm<sup>3</sup>) was added and the product extracted into diethyl ether (2 × 200 cm<sup>3</sup>). The combined ethereal extracts were dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to yield a pale brown oil. The product was not purified further (28.4 g, 90.2 %). Purity: 90 % (GC). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 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<sub>max</sub> /cm<sup>-1</sup>: 3100, 3054, 2951, 2922, 2854, 1599, 1569, 1500, 1476, 1279, 1252, 1181, 1117, 1025, 930, 850, 811. MS *m/z* (EI): 578 (M<sup>+</sup>), 518, 465, 288, 176, 145, 115 (M100), 71, 57, 41.

### 1-Bromo-4-hexylbenzene (5)

A solution of 1-bromohexane (20.0 g, 0.1212 mol) in diethyl ether (30 cm<sup>3</sup>) was added to a stirred suspension of magnesium turnings (2.91 g, 0.1212 mol) in diethyl ether (30 cm<sup>3</sup>) at such a rate that the reaction mixture maintained self-refluxing. After the addition was complete, the mixture was further refluxed for 30 mins. The resulting Grignard reagent was transferred to an addition funnel and added dropwise into a mixture containing 1,4-dibromobenzene (**4**) (28.61 g, 0.1212 mol), PdCl<sub>2</sub>(dppf) (0.89 g, 0.0012 mol) and diethyl ether (60 cm<sup>3</sup>). The resulting mixture was refluxed overnight and then poured into water. The catalyst residue was filtered off over hyflo supercel and the filtrate was

Supplementary material (ESI) for Journal of Materials Chemistry  
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extracted with diethyl ether ( $2 \times 200 \text{ cm}^3$ ). The combined ethereal extracts were washed with water ( $100 \text{ cm}^3$ ), dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. The crude product was purified by kugelrohr distillation to yield a colourless oil (14.3 g, 49 %). Boiling Point / $^\circ\text{C}$ : 140 @ 0.5 mmHg. Purity: 95 % (GC).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 0.88 (3H, t), 1.26-1.31 (6H, m), 1.57 (2H, quint), 2.55 (2H, t), 7.04 (2H, d,  $J=8.4 \text{ Hz}$ ), 7.38 (2H, d,  $J=8.4 \text{ Hz}$ ), IR  $\nu_{\text{max}}$  / $\text{cm}^{-1}$ : 3033, 2954, 2927, 2854, 1592, 1510, 1120, 1080, 851, 820. MS  $m/z$  (EI): 242, 240 ( $\text{M}^+$ ), 213, 199, 171 (M100), 158, 105, 91, 63.

2-(4-Hexylphenyl)thiophene (6)

A mixture of 1-bromo-4-hexylbenzene (5) (14.0 g, 0.0581 mol), 2-(tributylstannyl)thiophene (23.8 g, 0.0639 mol) and *tetrakis*(triphenylphosphine)-palladium (0) (2.01 g,  $1.74 \times 10^{-3}$  mol) in DMF ( $150 \text{ cm}^3$ ) was heated at  $90^\circ\text{C}$  for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution ( $100 \text{ cm}^3$ ) to destroy the tin side products. Hexane ( $2 \times 200 \text{ cm}^3$ ) was added and the combined organic layers were washed with brine ( $3 \times 200 \text{ cm}^3$ ), dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography [silica gel, DCM: hexane, 20%: 80 %] to yield a blue oil which partly crystallised out overnight (7.10 g, 50 %). Melting point / $^\circ\text{C}$ : 28. Purity: 95 % (GC).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 0.88 (3H, t), 1.24-1.40 (6H, m), 1.62 (2H, quint), 2.61 (2H, t), 7.05 (1H, dd,  $J=3.4, 5.0 \text{ Hz}$ ), 7.17 (2H, d,  $J=8.1 \text{ Hz}$ ), 7.23 (1H, dd,  $J=1.1, 5.1 \text{ Hz}$ ), 7.26 (1H, dd,  $J=1.1, 3.6 \text{ Hz}$ ), 7.51 (2H, d,  $J=8.1 \text{ Hz}$ ), IR  $\nu_{\text{max}}$  / $\text{cm}^{-1}$ : 3108, 3074, 3022, 2956, 2928, 2856, 1566, 1502, 1465, 1433, 1258, 1120, 1080, 1050, 851, 811, 692., MS  $m/z$  (EI): 244 ( $\text{M}^+$ ), 231, 186, 173 (M100), 153, 128, 115, 86, 63.

5-[(4-Hexylphenyl)-2-tributylstannyl]thiophene (7)

A solution of *n*-BuLi in hexanes ( $7.76 \text{ cm}^3$ , 2.5M, 0.0194 mol) was added slowly to a solution of 2-(4-hexylphenyl)thiophene (6) (3.85 g, 0.0149 mol) in THF (dry,  $50 \text{ cm}^3$ ) at  $-78^\circ\text{C}$ . After stirring for 1 h at  $-78^\circ\text{C}$ , tri-*n*-butyltin chloride (7.77 g, 0.0239 mol) was added slowly and the temperature was allowed to reach RT after completion of the addition. The reaction mixture was stirred overnight. Water ( $100 \text{ cm}^3$ ) was added and the product extracted into diethyl ether ( $2 \times 200 \text{ cm}^3$ ). The combined ethereal extracts were dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure to yield a pale yellow oil. The product was not purified further (8.00 g, 98 %). Purity: 90 % (GC).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 0.87-0.95 (12H, m), 1.13 (6H, t), 1.26-1.41 (12H, m), 1.56-1.68 (8H, m), 2.61 (2H, t), 7.12 (1H, d,  $J=3.4 \text{ Hz}$ ), 7.16 (2H, d,  $J=8.2 \text{ Hz}$ ), 7.37 (1H, d,  $J=3.4 \text{ Hz}$ ), 7.52 (2H, d,  $J=8.2 \text{ Hz}$ ). IR  $\nu_{\text{max}}$  / $\text{cm}^{-1}$ : 3064, 3024, 2957, 2930, 2871, 2854, 1533, 1499, 1466, 1073, 1021, 928, 800. MS  $m/z$  (EI): 533 ( $\text{M}^+$ ), 474 (M100), 421, 363, 291, 211, 175, 173, 129, 85, 71.

2-Bromo-7-iodo-9,9-dipropylfluorene (9)

A 50 % aqueous solution of NaOH ( $60 \text{ cm}^3$ ) was added to a mixture of 2-bromo-7-iodofluorene (8) (8.00 g, 0.0216 mol) and TBAB (0.35 g, 0.0011 mol) in toluene ( $50 \text{ cm}^3$ ). 1-Bromopropane ( $6.10 \text{ g}$ , 0.0496 mol) in toluene ( $10 \text{ cm}^3$ ) was then added dropwise at RT and the reaction mixture was stirred vigorously overnight at  $60^\circ\text{C}$ . The reaction mixture was cooled to RT and water was added ( $200 \text{ cm}^3$ ). Toluene ( $300 \text{ cm}^3$ ) was added and the resultant organic layer washed with water ( $200 \text{ cm}^3$ ), dried ( $\text{MgSO}_4$ ), 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 pale yellow crystalline solid (6.00 g, 61.2 %). Melting point / $^\circ\text{C}$ : 136-139. Purity: >99 % (GC).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 0.59-0.69 (10H, m), 1.90-1.94 (4H, m), 7.44 (1H, d,  $J=7.6 \text{ Hz}$ ), 7.47-7.49 (2H, m), 7.55 (1H, d,  $J=7.9 \text{ Hz}$ ), 7.66 (1H, dd,  $J=1.7, 8.2 \text{ Hz}$ ), 7.70 (1H, d,  $J=1.7 \text{ Hz}$ ), IR  $\nu_{\text{max}}$  / $\text{cm}^{-1}$ : 3054, 2954, 2923, 2875, 2851, 1598, 1559, 1456, 1415, 1132, 1059, 1003, 881, 811, 752, 723, MS  $m/z$  (EI): 456, 454 ( $\text{M}^+$ , M100), 411, 371, 332, 286, 189, 176, 163, 150, 88, 81, 63. Combustion analysis: Expected: C 50.14%, H 4.43%. Obtained: C 50.07%, H 4.32%

2-Bromo-7-[5-(4-octyloxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (10)

A mixture of 2-bromo-7-iodo-9,9-dipropylfluorene (9) (9.80 g, 0.0215 mol), 5-[(4-octyloxyphenyl)-2-tributylstannyl]thiophene (3) (11.5 g, 0.0215 mol) and *tetrakis*(triphenylphosphine)palladium (0) (0.75 g,  $6.46 \times 10^{-4}$  mol) in DMF ( $100 \text{ cm}^3$ ) was heated at  $90^\circ\text{C}$  for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution ( $100 \text{ cm}^3$ ) to destroy the tin side products. DCM ( $2 \times 200 \text{ cm}^3$ ) was added and the combined organic layers were washed with brine ( $4 \times 200 \text{ cm}^3$ ), water ( $200 \text{ cm}^3$ ), dried ( $\text{MgSO}_4$ ), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography [silica gel, DCM: hexane, 20 %: 80 %] to yield a yellow powder (6.47 g, 49 %). Melting point / $^\circ\text{C}$ : 129-131.  $^1\text{H}$  NMR

(CDCl<sub>3</sub>) δ<sub>H</sub>: 0.65-0.74 (10H, m), 0.89 (3H, t), 1.25-1.40 (8H, m), 1.47 (2H, quint), 1.80 (2H, quint), 1.92-2.01 (4H, m), 4.00 (2H, t), 6.92 (2H, d, J=8.7 Hz), 7.20 (1H, d, J=3.7 Hz), 7.33 (1H, d, J=3.7 Hz), 7.44 (1H, d, J=1.7 Hz), 7.45 (1H, dd, J=1.7, 8.4 Hz), 7.53 (1H, overlapping d), 7.56 (2H, d, J=8.7 Hz), 7.60 (1H, dd, J=1.7, 7.9 Hz), 7.65 (2H, d, J=7.9 Hz), IR ν<sub>max</sub>/cm<sup>-1</sup>: 3055, 2926, 2864, 2852, 1602, 1545, 1502, 1465, 1283, 1254, 1179, 1037, 885, 871, 829, 800, MS m/z (MALDI): 616, 614 (M<sup>+</sup>).

2-{5-[4-(Hexyl)phenyl]thien-2-yl}-7-{5-[4-(octyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene (**11**)

A mixture of 2-bromo-7-[5-(4-octyloxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**10**) (2.80 g, 0.0046 mol), 5-[(4-hexylphenyl)-2-tributylstannyl]thiophene (**7**) (3.15 g, 0.0059 mol) and *tetrakis*(triphenylphosphine)palladium (0) (0.26 g, 2.27 × 10<sup>-4</sup> mol) in toluene (100 cm<sup>3</sup>) was heated under reflux for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution (100 cm<sup>3</sup>) to destroy the tin side products. Toluene (200 cm<sup>3</sup>) was added and the resultant solution washed with brine (2 × 200 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography [silica gel, DCM: hexane, 20 %: 80 %] to yield a green powder (2.50 g, 70.6 %). Transition temp. /°C: T<sub>g</sub> 25 Cr 149 N 163 I <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 0.67-0.78 (10H, m), 0.90 (6H, t), 1.26-1.40 (14H, m), 1.48 (2H, quint), 1.64 (2H, quint), 1.81 (2H, quint), 2.00-2.04 (4H, m), 2.63 (2H, t), 3.99 (2H, t), 6.92 (2H, d, J=8.7 Hz), 7.20 (1H, d, J=3.7 Hz), 7.21 (2H, d, J=8.7 Hz), 7.28 (1H, d, J=3.7 Hz), 7.33 (1H, d, J=3.7 Hz), 7.35 (1H, d, J=3.7 Hz), 7.57 (4H, d, J=8.7 Hz), 7.57 (2H, overlapping d), 7.60 (1H, dd, J=1.7, 7.9 Hz), 7.62 (1H, dd, J=1.7, 7.9 Hz), 7.67 (2H, d, J=7.8 Hz), IR ν<sub>max</sub>/cm<sup>-1</sup>: 3100, 3055, 2953, 2926, 2853, 1605, 1546, 1511, 1473, 1390, 1283, 1252, 1178, 1112, 1035, 874, 829, 800, MS m/z (MALDI): 779 (M<sup>+</sup>). Combustion analysis: Expected: C 81.70%, H 8.02%, S 8.23% Obtained: C 81.44%, H 8.10%, S 7.92%

2-[5-(4-Hydroxyphenyl)thien-2-yl]-7-{5-[4-(hexyl)phenyl]thien-2-yl}-9,9-dipropylfluorene (**12**)

Boron tribromide (0.45 cm<sup>3</sup>, 0.0047 mol) in DCM (10 cm<sup>3</sup>) was added dropwise to a cooled (0 °C) stirred solution of 2-{5-[4-(hexyl)phenyl]thien-2-yl}-7-{5-[4-(octyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene (**11**) (2.45 g, 3.15 × 10<sup>-3</sup> mol) in chloroform (60 cm<sup>3</sup>). The reaction mixture was stirred at RT overnight, then poured onto an ice/water mixture (200 g) and stirred for 30 mins. The product was extracted into ethyl acetate (2 × 200 cm<sup>3</sup>). The combined organic layers were washed with water (2 × 100 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude product was recrystallised from ethyl acetate to yield a green powder (1.80 g, 85.7 %). Melting point /°C: 162. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 0.68-0.78 (10H, m), 0.90 (3H, t), 1.26-1.38 (6H, m), 1.64 (2H, quint), 2.00-2.04 (4H, m), 2.63 (2H, t), 4.94 (1H, s, -OH), 6.88 (2H, d, J=8.7 Hz), 7.20 (1H, d, J=3.7 Hz), 7.21 (2H, d, J=8.7 Hz), 7.28 (1H, d, J=3.7 Hz), 7.33 (1H, d, J=3.7 Hz), 7.35 (1H, d, J=3.7 Hz), 7.57 (4H, d, J=8.7 Hz), 7.57 (2H, overlapping d), 7.61 (1H, dd, J=1.7, 7.9 Hz), 7.63 (1H, dd, J=1.7, 7.9 Hz), 7.68 (2H, d, J=7.8 Hz), IR ν<sub>max</sub>/cm<sup>-1</sup>: 3100-3500, 3100, 3054, 2954, 2925, 2852, 1654, 1609, 1542, 1511, 1474, 1375, 1235, 1173, 1105, 885, 832, 799, MS m/z (EI): 666 (M<sup>+</sup>, M100), 594, 523, 510, 300, 262, 188, 159, 133, 115, 81, 69. Combustion analysis: Expected: C 81.03%, H 6.95%, S 9.62% Obtained: C 80.86%, H 7.10%, S 9.32%

2-{5-[4-(Hexyl)phenyl]thien-2-yl}-7-{5-[4-(6-methacryloyloxyhexyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene (**monomer 1**)

A mixture of 2-[5-(4-hydroxyphenyl)thien-2-yl]-7-{5-[4-(hexyl)phenyl]thien-2-yl}-9,9-dipropylfluorene (**12**) (0.80 g, 0.0012 mol) and potassium carbonate (0.50 g, 0.0036 mol) in butanone (60 cm<sup>3</sup>) was heated under reflux for 24 h. Then ((6-methacroyloxy)hexyl)bromide (0.36 g, 1.44 × 10<sup>-3</sup> mol) and BHT (spatula tip) were added to the resulting potassium salt and refluxed for a further 6 h. The reaction mixture was cooled to RT, water (50 cm<sup>3</sup>) was added and the product extracted into DCM (2 × 100 cm<sup>3</sup>). The combined organic layers were washed with water (2 × 100 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), 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 green glassy solid (0.65 g, 65 %). Transition temp. /°C: T<sub>g</sub> 14 Cr - N 124 I. Purity: 100 % (HPLC). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub>: 0.66-0.78 (10H, m), 0.90 (3H, t), 1.26-1.38 (6H, m), 1.45-1.57 (4H, m), 1.64 (2H, quint), 1.73 (2H, quint), 1.83 (2H, quint), 1.95 (3H, s), 2.00-2.04 (4H, m), 2.63 (2H, t), 4.00 (2H, t), 4.17 (2H, t), 5.55 (1H, s), 6.11 (1H, s), 6.92 (2H, d, J=8.7 Hz), 7.20 (1H, d, J=3.7 Hz), 7.21 (2H, d, J=8.7 Hz), 7.28 (1H, d, J=3.7 Hz), 7.33 (1H, d, J=3.7 Hz), 7.35 (1H, d, J=3.7 Hz), 7.57 (4H, d, J=8.7 Hz), 7.57 (2H, overlapping d), 7.60 (1H, dd, J=1.7, 7.9 Hz), 7.62 (1H, dd, J=1.7, 7.9 Hz), 7.67 (2H, d, J=7.8 Hz), IR ν<sub>max</sub>/cm<sup>-1</sup>: 3073, 2954, 2868, 1732, 1640, 1606, 1572, 1499, 1473, 1289, 1254, 1179, 1166, 1112, 1064, 984, 934, 836, 798, MS m/z (MALDI): 835 (M<sup>+</sup>).

Co-polymer 1

A solution of 7-[4-(6-methacryloyloxyhexyloxy)benzoyloxy]coumarin (**monomer 2**)<sup>14,16</sup> (0.10 g,  $2.22 \times 10^{-4}$  mol), 2-{5-[4-(hexyl)phenyl]thien-2-yl}-7-{5-[4-(6-methacryloyloxyhexyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene (**monomer 1**) (0.046 g,  $5.55 \times 10^{-5}$  mol) and AIBN (1.46 mg,  $8.89 \times 10^{-6}$  mol) in THF (dry, 5 cm<sup>3</sup>) was refluxed for 5 days. The reaction mixture was cooled to RT and purified by several solution-precipitation cycles using THF (minimum amount) to dissolve and methanol (500 cm<sup>3</sup>) to precipitate. A green powder was obtained (0.10 g, 68.5 %). GPC analysis yielded  $M_n = 12047$ ,  $M_w = 18063$  and  $M_w/M_n = 1.489$  and DSC analysis gave a  $T_g$  at 69 °C. The ratio of the two monomers present in the co-polymer was determined by integration of the appropriate <sup>1</sup>H NMR signals and was approximately 1:4, **monomer 1:monomer 2** respectively.

The absorbance of the monomers **1** and **2** and **copolymer 1** was measured using a Unicam 5625 UV-vis spectrophotometer. 1 mM of the compound was dissolved in 5 cm<sup>3</sup> of an electrolytic solution of 0.1M tetrabutylammonium hexafluorophosphate in dichloromethane for the cyclic voltammetry measurement. The solution was placed in a standard three-electrode electrochemical cell. A glassy carbon electrode was used as the working electrode. Silver/silver chloride (3M NaCl and saturated AgCl)) and a platinum wire formed the reference and counter electrodes respectively. The electrolyte was recrystallized twice before use and oxygen contamination was avoided by purging the solution with dry Argon before each measurement. The measured potentials were corrected to an internal ferrocene reference added at the end of each measurement. A typical scan rate of 20 mV s<sup>-1</sup> was used. Two scans were performed to check the repeatability.

#### Device preparation and evaluation

The polarised light-emitting device were made by spin coating the **co-polymer 1** from a 0.5 wt % solution in cyclopentanone onto either a PSS/PEDOT/InSnO substrate for EL or quartz for PL. The film was baked at 110 °C for 15 minutes, cooled slowly to room temperature and then dried under hard vacuum for several hours to remove solvent. The film was then irradiated with polarised light from the HeCd laser using a total fluence of 5 J cm<sup>-2</sup>. Photopatterning was achieved by irradiating through a mask, turning the sample by 90 degrees and irradiating the unexposed regions through the same mask. The green light-emitting material **RM 1** was subsequently deposited, baked at 110 °C and cooled at 5 °C per minute to room temperature. A fluence of 500 J cm<sup>-2</sup> was used. The red emitting mixture, of composition specified above, was processed similarly. The film was crosslinked by UV irradiation using a HeCd laser at 325 nm. For the EL device a hole-blocking layer (6 nm) of commercially available (H. W. Sands) 3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole (TAZ) was deposited on top of the crosslinked emission layer by vapour deposition using a vacuum of 10<sup>-6</sup> mbar or better. Layers of lithium fluoride (1 nm) and aluminium (80 nm) were sequentially deposited in the same chamber as a combined cathode. EL was measured using a Labview controlled, Agilent E3631A DC power supply with Minolta LS100 luminance meter and Avaspec2048 fibre spectrometer. PL was measured with the samples mounted in a chamber filled with dry nitrogen using a photodiode array (Ocean Optics S2000) with a spectral range from 200 nm to 850 nm and a resolution of 2 nm.

