

Electronic Supplementary Information

Synthesis and properties of α,ω -phenyl-capped bithiophene derivatives

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General methods and materials

All the solvents purchased of Acros Chimica, Aldrich or Fluka were of p.a. quality. Dry DMF, diethyl ether and THF were obtained by distillation. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Toluene-4-sulfonic acid (S)-2-methylbutyl ester and 5,5'-Bis-trimethylstannanyl-[2,2']bithiophene were kindly provided by A.P.J. Spiering and M. Garcia respectively. BioBeads SX-3 Beads were obtained from Bio-Rad Laboratories. All other used chemicals are commercially available and were used without further purification.

Instrumentation:

¹H NMR and ¹³C NMR spectra were recorded at room temperature on a Varian Mercury 200, Varian Gemini 300 or Varian Mercury 400. ¹H and ¹³C chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) and multiplicities as singlet (s), doublet (d), triplet (t) and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with a Universal ATR Accessory for solids. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilizing an α -cyano-4-hydroxycinnamic acid matrix. GC-MS measurements were obtained with a Shimadzu GC/MS-QP5000 using a Zebron ZB-35 column with a Perkin Autosystem. Elemental analyses were carried out on a Perkin Elmer 2400. UV-vis and fluorescence spectra were performed on a Perkin Elmer Lambda 40 spectrophotometer and Perkin Elmer LS-50 B. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Differential Scanning Calorimeter Pyris 1 with Pyris 1 DSC Autosampler and Perkin Elmer CCA7 cooling element under nitrogen atmosphere with

heating and cooling rates of 10 or 20 °C/min. Samples of 2-4 mg were measured. Melting points were determined by DSC.

FETs

The FETs were prepared by spin coating a 1 wt.-% solution in toluene at a speed of 800 rpm for 8 seconds and then 2000 rpm for 20 seconds. Heavily doped silicon was used as the gate electrode, with a hexamethyldisilazane (HMDS) treated 200 nm thick layer of thermally oxidized SiO₂ as the gate-insulating layer. Gold was thermally evaporated and patterned to form interdigitated source and drain contacts. Channel length, L, was 10 μm and the channel width, W, 20 mm. Transistor measurements were performed at room temperature immediately after preparation using a HP 4156B semiconductor parameter analyzer in air and light.

TOF measurements

TOF mobilities were measured using 3.5 eV photon energies as obtained for a tripled Nd:YAG laser with 5 ns pulse width. TOF signals were recorded using a liquid crystal cell with 10 μm spacing between the electrodes. Bottom and top electrodes consisted of tin-doped indium oxide, covered with a thin, rubbed polyimide orientation layer. Rubbing direction of the bottom and top contact were parallel. The cells were filled in an inert atmosphere utilizing the capillary force acting on the material in its liquid crystalline phase. Temperature-dependent current transients were measured by first heating the cells to the isotropic phase followed by slow (<10 deg/min) cooling to the temperature of

interest. Processing and electrical characterization of the semiconductors was performed in ambient conditions.

Alignment experiments with polarized light microscopy

The cells used are commercially available from Linkam with a film thickness of 5 μm , anti-parallel rubbed polyimide alignment and a sample area of 9x9 mm. From the isotropic phase the cells were cooled with 1 $^{\circ}\text{C}/\text{min}$. From the different phases pictures were taken with a Jenaval polarization microscope with crossed polarizers equipped with a Linkam THMS 600 heating stage.

Synthesis

The compounds 5,5'-bis-trimethylstannanyl-[2,2']bithiophenyl (**22**) and 2-(4-bromophenyl)-ethanol (**14**) were synthesized according to literature procedures.

1-Bromo-4-undecyl-benzene (12)

n-Undecyl bromide (5.00 g, 21 mmol) was slowly added to Mg (0.62 g, 26 mmol) in dry THF (15 ml). The reaction was initiated with 1,2-dichloroethane (0.2 ml) and refluxed for 1 h. The Grignard reagent n-undecylmagnesium bromide solution was slowly added to a solution of 1,4-dibromobenzene (7.50 g, 32 mmol) in dry THF (20 ml) containing 1,3-bis[(diphenylphosphino)-propane]dichloronickel(II) ($\text{Ni}(\text{dppp})_2\text{Cl}_2$) (35 mg, 0.043 mmol) as a catalyst. After refluxing for 16 h, the reaction mixture was filtered over a short flash chromatography column using silica gel with hexane as eluent. After removal of the solvents the white crystals were purified with bulb-to-bulb distillation yielding 1-Bromo-

4-undecyl-benzene (3.9 g, 60%) as colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.96 (t, 3H, CH_3), 1.36 (m, 16H, CH_2), 1.65 (m, 2H, CH_2), 2.63 (t, 2H, PhCH_2), 7.13 (d, 2H, PhH), 7.48 (d, 2H, PhH) GC-MS (MW = 311.31) m/z = 310, 312.

1-Bromo-4-undec-10-enyl-benzene (13)

n-Undec-10-enyl bromide, (2.80 g, 12 mmol) was slowly added to Mg (0.35 g, 14.4 mmol) in dry THF (15 ml). The reaction was initiated with 1,2-dichloroethane (0.2 ml) and refluxed for 1 h. The Grignard reagent n-undec-10-enylmagnesium bromide solution was slowly added to a solution of 1,4-dibromobenzene (4.25 g, 18 mmol) in dry THF (ml) containing 1,3-bis[(diphenylphosphino)-propane]dichloronickel(II) ($\text{Ni}(\text{dppp})_2\text{Cl}_2$) (20 mg, 0.024 mmol) as a catalyst. After refluxing for 16 h, the reaction mixture was filtered over a short flash chromatography column using silica gel with hexane as eluent. After removal of the solvents the white crystals were purified with bulb-to-bulb distillation to yield 1-Bromo-4-undec-10-enyl-benzene (2.70 g, 73 %) as colorless oil. Part (11 %) of the terminal vinyl[#] groups was rearranged to internal vinyls^{*}. ^1H NMR (300 MHz, CDCl_3) δ 1.30 (m, 12H, CH_2), 1.57 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.57 (t, 2H, PhCH_2), 4.96[#] (m, 2H[#], $\text{CH}=\text{CH}_2$), 5.40^{*} (m, 4H^{*}, $\text{CH}_2=\text{CH}_2$), 5.82[#] (m, 1H[#], $\text{CH}=\text{CH}_2$), 7.06 (d, 2H, PhH), 7.38 (d, 2H, PhH) GC-MS (MW = 309.29) m/z = 308, 310.

Pentanoic acid 2-(4-bromo-phenyl)-ethyl ester (15)

Pentanoyl chloride (0.63 g, 5.22 mmol) was slowly added to a stirred solution of 2-(4-bromo-phenyl)-ethanol, **14** (1.00 g, 5.0 mmol) in dry diethyl ether under argon at reflux. After stirring overnight at reflux, the mixture was washed with a 1M NaOH solution, 1M

HCL solution, brine and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **15** (920 mg, 65 %) is obtained as a colorless oil. ¹H-NMR (200 MHz, CDCl₃), δ 0.96 (t, 3H, CH₃), 1.36 (m, 2H, CH₂), 1.61 (m, 2H, CH₂), 2.31 (t, 2H, CH₂), 2.93 (t, 2H, PhCH₂), 4.28 (t, 2H, OCH₂), 7.16 (d, 2H, PhH), 7.46 (d, 2H, PhH) GC-MS (MW = 285.18) *m/z* = 284, 286.

1-Bromo-4-(2-pentyloxy-ethyl)-benzene (16)

A solution of NaH (138 mg of a 60 % dispersion in mineral oil, 3.43 mol) in hexane (3 ml), was slowly added to a stirred solution of 2-(4-bromo-phenyl)-ethanol, **14** (1.13 g, 5.61 mmol) in dry DMF (5 ml) under argon at 0 °C. Subsequently 1-bromo-pentane (1.1 g, 7.3 mmol) was slowly added via syringe and was kept at 0 °C for 1 h. After stirring overnight under argon at room temperature, the mixture was poured into water and extracted with diethyl ether. The organic phase was washed with a saturated Na₂CO₃ solution, brine and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **16** (802 mg, 53 %) is obtained as a colorless oil. ¹H-NMR (300 MHz, CDCl₃), δ 0.98 (t, 3H, CH₃), 1.38 (m, 4H, CH₂), 1.62 (m, 2H, CH₂), 2.88 (t, 2H, PhCH₂), 3.46 (t, 2H, OCH₂), 3.66 (t, 2H, OCH₂), 7.18 (d, 2H, PhH), 7.45(d, 2H, PhH) GC-MS (MW = 271.20) *m/z* = 270, 272.

1-Bromo-4-[2-((S)-2-methyl-butoxy)-ethyl]-benzene (17)

A solution of KOH (420 mg, 7.5 mmol) in DMF (2 ml) and subsequently a solution of toluene-4-sulfonic acid (S)-2-methyl-butyl ester (1.82 g, 7.5 mmol) in dry DMF (1 ml) were slowly added to a stirred solution of 2-(4-bromo-phenyl)-ethanol, **14** (1.00 g, 5.0 mmol) in dry DMF (5 ml) under argon and was kept at 0 °C for 1 h. After stirring at overnight room temperature, the mixture was poured into water and extracted with diethyl ether. The organic phase was washed with a 6M HCl solution, brine and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **17** (530 mg, 39 %) is obtained as a colorless oil. ¹H-NMR (200 MHz, CDCl₃), δ 0.96 (m, 6H, CH₃), 1.36 (m, 2H, CH₂), 1.65 (m, 1H, CH), 2.93 (t, 2H, PhCH₂), 3.30 (m, 2H, OCH₂), 3.65 (t, 2H, OCH₂), 7.18 (d, 2H, PhH), 7.46 (d, 2H, PhH) GC-MS (MW = 271.20) *m/z* = 270, 272.

(S)-2-(4-bromophenyl)-1-methylethanol (18)

A solution of 12.92 (g) (54.78mmol) of *p*-dibromobenzene in 100 ml diethylether was cooled to -196°C with liquid N₂. A 22 ml solution (54.24) of *n*-Butyllithium (2.5 M hexanes) was slowly added. The reaction mixture was heated to -78°C, and a solution of 3.50 (g) (60.26mmol) (S)-propyleneoxide in diethylether was slowly added (exothermic reaction). The reaction mixture was stirred another 16 h at room temperature. The reaction mixture was quenched with a saturated NH₄Cl-solution. The water layer was extracted with diethylether (2x). Combined ether layers were dried over MgSO₄, filtered, and evaporated. After purification on SiO₂-column (eluens = DCM) **18** was obtained as a colorless oil. (9.25 g, 79%). ¹H-NMR (300 MHz, CDCl₃), δ 1.21 (d, 3H, CH₃), 1.69 (s, 1H, OH), 2.62 (d, 1H[#], CH₂, J = 7.42 Hz), 2.66 (d, 1H[#], CH₂ J = 7.69 Hz), 2.69 (d, 1H^{*},

CH_2 $J = 5.22$ Hz), 2.74 (d, 1H*, CH_2 $J = 5.22$ Hz), 3.97 (m, 1H, CH_3CH), 7.09 (d, 2H, PhH), 7.42 (d, 2H, PhH); ^{13}C -NMR (300 MHz, $CDCl_3$), δ 22.8, 44.9, 68.5, 120.2, 131.0, 131.4, 137.5; IR : ν (cm^{-1}) 710, 770, 849, 892, 1047, 1011, 1071, 1105, 1197, 1305, 1374, 1404, 1455, 1488, 2928, 2969, 3352 GC-MS (MW = 215.085) $m/z = 214, 216$.

[2-(4-Bromophenyl)-1-(S)-methyl]ethylpentanoate (19)

A solution of 1.80 g (8.356 mmol) **18** and 1.27 g (12.533 mmol) triethylamine in dry diethylether was heated to reflux. To this mixture a solution of pentanoylchloride (1.51 g, 12.53 mmol) in ether was slowly added. After 2 h refluxing the reaction mixture was cooled to room temperature and the white precipitate was removed by filtration. The remaining solution was washed with saturated $NaHCO_3$ -solution (2x) and with water (2x). The combined ether-layers were dried over $MgSO_4$, filtered, and evaporated. Further purification by column chromatography (SiO_2 , DCM: pentane 1:1) yielded 2.38 g (95%) of pure **19**. 1H -NMR (300 MHz, $CDCl_3$), δ 0.88 (t, 3H, CH_3), 1.21 (d, 3H, CH_3), 2.46 (m, 2H, CH_2CH_3), 1.52 (m, 2H, $CH_2CH_2CH_3$), 2.23 (t, 2H, $C=OCH_2$), 2.69 (d, 1H $PhCH_2$, $J = 6.04$ Hz), 2.74 (d, 1H $PhCH_2$, $J = 6.04$ Hz), 2.82 (d, 1H $PhCH_2$, $J = 7.14$ Hz), 2.87 (d, 1H $PhCH_2$, $J = 7.14$ Hz), 5.09 (m, 1H, $PhCH_2CH$), 7.06 (d, 2H, PhH, $J = 8.24$ Hz), 7.34 (d, 2H, PhH, $J = 8.24$ Hz); ^{13}C -NMR (300 MHz, $CDCl_3$), δ 13.6, 19.4, 22.0, 26.9, 34.2, 41.5, 70.6, 120.2, 131.0, 131.3, 136.6, 173.1; IR : ν (cm^{-1}) 796, 826, 951, 1012, 1057, 1071, 1091, 1108, 1133, 1174, 1253, 1378, 1458, 1489, 1729, 2872, 2933, 2959; GC-MS (MW = 299.202) $m/z = 298, 300$.

[2-(4-Bromophenyl)-1-(S)-methyl]ethoxypentane (20)

A solution of 1.89 g (8.77 mmol) **18** in dry DMF was cooled to -10°C in an ice bath. To the cooled mixture 0.225 g (9.39 mmol) NaH was added. After 10 min. a solution of 1.42 g (9.39 mmol) pentylbromide in DMF was slowly added. After 16 h stirring at room temperature the reaction mixture was quenched with water and the organics were dissolved in diisopropylether. The ether layer was washed with saturated NaHCO_3 -solution and with brine. The combined ether layers were dried over MgSO_4 , filtered, and evaporated. Further purification by column chromatography (SiO_2 , DCM: pentane 1:1) yielded 2.19 g (87.4%) of pure **20**. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ 0.94 (t, 3H, CH_2CH_3), 1.18 (d, 3H, CH_3), 1.32, (m, 4H, $(\text{CH}_2)_2\text{CH}_3$), 1.56 (m., 2H, OCH_2CH_2), 2.63 (d, 1H PhCH_2 , $J = 6.04\text{Hz}$), 2.68 (d, 1H PhCH_2 , $J = 6.04\text{Hz}$), 2.84 (d, 1H PhCH_2 , $J = 6.59\text{ Hz}$), 2.89 (d, 1H PhCH_2 , $J = 6.59\text{ Hz}$), (3.35 (double t, 1H, OCH_2), 3.52 (double t, 1H, OCH_2), 3.59 (m, 1H, CH), 7.14 (d, 2H, PhH , $J = 8.24\text{ Hz}$), 7.45 (d, 2H, PhH , $J = 8.24\text{ Hz}$); $^{13}\text{C-NMR}$ (300 MHz, CDCl_3), δ 13.9, 19.4, 22.4, 28.2, 29.6, 42.4, 68.7, 76.1, 119.7, 131.0, 131.1, 138.2; IR : ν (cm^{-1}) 795, 829, 1012, 1072, 1095, 1131, 1217, 1340, 1374, 1404, 1456, 1488, 2859, 2930, 2957; GC-MS (MW = 285.219) $m/z = 284, 286$.

[2-(4-Bromophenyl)-1-(S)-methyl]ethylbutylcarbamate (21)

To a solution of 1.71 g (7.96 mmol) **18** in dry chloroform 1.737 g (17.52 mmol) of butylisocyanate and three drops of tindibutylidilaureate were added. The solution was refluxed for 16 h. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO_2 , DCM:pentane 1:1) to yield **21** as a pure colorless oil (2.48 g, 99%); $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ 0.91 (t, 3H, CH_2CH_3), 1.18 (d, 3H, CH_3), 1.31 (m, 2H, CH_2CH_3), 1.43 (m, 2H, NCH_2CH_2), 2.68 (d, 2H, PhCH_2 , $J = 6.59\text{ Hz}$), 2.72

(d, 1H, PhCH₂, *J* = 6.32 Hz), 2.84 (d, 1H, PhCH₂, *J* = 6.32 Hz), 2.88 (d, 1H, PhCH₂, *J* = 6.32 Hz), 4.58 (s, 1H, NH), 4.98 (m, 1H, CH), 7.07 (d, 2H, PhH, *J* = 8.52 Hz), 7.39 (d, 2H, ArH, *J* = 8.52 Hz); ¹³C-NMR (300 MHz, CDCl₃), δ 13.6, 19.5, 19.7, 31.9, 40.5, 41.7, 70.9, 120.1, 131.0, 131.2, 136.6, 155.9; IR : ν (cm⁻¹) 776, 797, 831.3, 936, 1011, 1070, 1108, 1134, 1247, 1379, 1404, 1458, 1488, 1516, 1690, 2872, 2932, 2959, 3334; GC-MS (MW = 314.217) 313, 315.

5,5'-Bis-(4-octyl-phenyl)-[2,2']bithiophene (2)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene, **22** (369 mg, 0.75 mmol), 1-bromo-4-octyl-benzene **11**, (398 mg, 1.48 mmol) and tetrakis(triphenylphosphine)-palladium(0) (Pd(PPh₃)₄) (60 mg, 0.05 mmol) in dry and oxygen free DMF (5 ml) were stirred overnight under argon at room temperature. The reaction mixture was poured into water (50 ml) and extracted several times with dichloromethane. The organic phase was then washed with 6M HCl and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **2** (71 mg, 17 %) is obtained as an orange solid. ¹H-NMR (400 MHz, CDCl₃), δ 0.84 (t, 6H, CH₃), 1.30 (m, 20H, CH₂), 1.63 (m, 4H, CH₂), 2.60 (t, 4H, PhCH₂), 7.15 (d, 2H, TH), 7.18 (d, 2H, TH), 7.20 (d, 4H, PhH), 7.53 (d, 4H, PhH); ¹³C-NMR (300 MHz, CDCl₃), δ 14.0, 22.6, 29.1, 29.2, 29.4, 31.3, 31.8, 123.1, 124.2, 125.4, 128.9, 131.4, 136.2, 142.5, 143.1; MALDI-TOF MS (M = 542.90) *m/z* = 542.30 [M]⁺, IR (solid): ν (cm⁻¹) = 720, 792, 820, 831, 870, 961, 1015, 1076, 1127, 1447, 1468, 1498, 2849, 2919. Anal. Calc. for C₃₆H₄₂S₂: C 79.65, H 8.54, Found: C 79.24, H 8.58 %.

5,5'-Bis-[(4-undecyl)-phenyl]-[2,2']bithiophene (3)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene, **22** (250 mg, 0.51 mmol), 1-bromo-4-undecyl-benzene **12**, (350 mg, 1.12 mmol) and Pd(PPh₃)₄ (40 mg, 0.033 mmol) in dry and oxygen free DMF (5 ml) were stirred overnight under argon at 50 °C. The reaction mixture was precipitated in cold ethanol three times. **3** (250 mg, 78 %) is obtained pure via BioBeads SX-3 columnar chromatography with dichloromethane as eluent. ¹H-NMR (400 MHz, CDCl₃), δ 0.84 (t, 6H, CH₃), 1.30 (m, 32H, CH₂), 1.63 (m, 4H, CH₂), 2.66 (t, 4H, PhCH₂), 7.15 (d, 2H, TH), 7.18 (d, 2H, TH), 7.20 (d, 4H, PhH), 7.53 (d, 4H, PhH₂); ¹³C-NMR (300 MHz, CDCl₃), δ 14.0, 22.6, 29.2, 29.2, 29.4, 29.4, 29.5, 29.5, 31.3, 31.8, 35.5, 123.1, 124.2, 125.4, 128.8, 131.4, 136.2, 142.5, 143.1; IR (solid): ν (cm⁻¹) 719, 793, 829, 870, 1077, 1127, 1447, 1469, 1499, 1530, 1633, 1660, 2849, 2917, 2955, 3361; MALDI-TOF MS (M = 627.06) *m/z* = 626.24 [M]⁺. Anal. Calc. for C₄₂H₅₈S₂: C 80.45, H 9.32, Found: C 79.90, H 9.21 %.

5,5'-Bis-[(4-undec-10-enyl)-phenyl]-[2,2']bithiophene (4)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene **22** (492 mg, 1.0 mmol), 1-bromo-4-undec-10-enyl-benzene **13**, (773 mg, 2.5 mmol) and Pd(PPh₃)₄ (60 mg, 0.05 mol) in dry and oxygen free DMF (7 ml) were stirred overnight under argon at 50 °C. The reaction mixture was precipitated in cold ethanol until **4** (580 mg, 93 %) was obtained pure. Noted that part (11 %) of terminal vinyls[#] is rearranged to internal vinyls^{*}. ¹H NMR (300 MHz, CDCl₃) δ 1.30 (m, 24H, CH₂), 1.57 (m, 4H, CH₂), 2.05 (m, 4H, CH₂), 2.63 (t, 4H, PhH), 4.96[#] (m, 4H[#], CH=CH₂), 5.40^{*} (m, 8H^{*}, CH₂=CH₂), 5.82[#] (m, 2H[#], CH=CH₂), 7.14 (d, 2H, TH), 7.18 (d, 2H, TH), 7.19 (d, 2H, PhH), 7.53 (d, 2H, PhH); ¹³C-NMR (300 MHz, CDCl₃), δ 28.8, 29.0, 29.2, 29.2, 29.2, 31.3, 33.7, 35.5, 41.8, 114.0, 123.1, 124.2,

125.4, 128.8, 131.4, 136.2, 139.1, 142.6, 143.1; IR (solid): ν (cm^{-1}) 720, 793, 827, 870, 911, 991, 1467, 1498, 1642, 2849, 2918; MALDI-TOF MS ($M = 623.03$) $m/z = 622.30$ $[\text{M}]^+$; Anal. Calc. for $\text{C}_{42}\text{H}_{58}\text{S}_2$: C, 80.97; H, 8.74. Found: C 80.31, H 8.52 %.

5,5'-Bis-[(4-(2-pentanoyloxy-ethyl)-phenyl)-[2,2']bithiophene (5)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene, **22** (369 mg, 0.75 mmol), pentanoic acid 2-(4-bromo-phenyl)-ethyl ester, **15** (453 mg, 1.51 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.05 mmol) in dry and oxygen free DMF (5 ml) were stirred overnight under argon at room temperature. The reaction mixture was poured into water (50 ml) and extracted several times with dichloromethane. The organic phase was then washed with 6M HCl and water, dried over MgSO_4 , filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **5** (271 mg, 63 %) is obtained as a yellow solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3), δ 0.96 (t, 6H, CH_3), 1.36 (m, 4H, CH_2), 1.62 (m, 4H, CH_2), 2.35 (t, 4H, CH_2), 2.99 (t, 4H, PhCH_2), 4.36 (t, 4H, OCH_2), 7.18 (d, 2H, TH), 7.24 (d, 2H, TH), 7.28 (d, 4H, PhH), 7.57 (d, 4H, PhH); $^{13}\text{C-NMR}$ (300 MHz, CDCl_3), δ 13.6, 22.1, 26.9, 33.9, 34.7, 64.3, 123.5, 124.3, 129.4, 136.4, 137.4, 142.8, 173.7; MALDI-TOF MS ($M = 574.81$) $m/z = 574.44$ $[\text{M}]^+$; IR (solid): ν (cm^{-1}) 792, 833, 871, 1007, 1073, 1112, 1176, 1263, 1318, 1446, 1500, 1733, 2874, 2934, 2959; Anal. Calc. for $\text{C}_{34}\text{H}_{38}\text{O}_4\text{S}_2$: C 71.05, H 6.66, Found: C 70.72 H 6.71 %.

5,5'-Bis-[4-(2-pentyloxy-ethyl)-phenyl]-[2,2']bithiophene (6)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene, **22** (408 mg, 1.50 mmol), 1-bromo-4-(2-pentyloxy-ethyl)-benzene, **16** (383 mg, 0.78 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (60 mg,

0.05 mmol) in dry and oxygen free DMF (5 ml) were stirred overnight under argon at room temperature. The reaction mixture was poured into water (50 ml) and extracted several times with dichloromethane. The organic phase was then washed with 6M HCl and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **6** (120 mg, 29 %) is obtained as an orange solid. ¹H-NMR (300 MHz, CDCl₃), δ 0.97 (t, 6H, CH₃), 1.38 (m, 8H, CH₂), 1.62 (m, 4H, CH₂), 2.94 (t, 4H, PhCH₂), 3.49 (t, 4H, OCH₂), 3.69 (t, 4H, OCH₂), 7.18 (d, 2H, TH), 7.24 (d, 2H, TH), 7.28 (d, 4H, PhH), 7.57 (d, 4H, PhH); ¹³C-NMR (300 MHz, CDCl₃), δ 14.3, 22.8, 28.6, 29.6, 36.3, 71.4, 71.8, 123.7, 124.6, 125.8, 129.7, 132.3, 136.6, 139.1, 143.3; MALDI-TOF MS (M = 546.84) *m/z* = 546.51 [M]⁺; IR (solid): ν (cm⁻¹) 729, 792, 816, 833, 871, 1073, 1113, 1364, 1446, 1499, 1532, 2859, 2931, 2958; Anal. Calc. for C₃₄H₄₂O₂S₂: C 74.68, H 7.74, Found: C 74.67, H 7.74 %.

5,5'-Bis-{4-[2-((S)-2-methyl-butoxy)-ethyl]-phenyl}-[2,2']bithiophene (7)

A mixture of 5,5'-bis-trimethylstannanyl-[2,2']bithiophene, **22** (369 mg, 0.75 mmol), 1-bromo-4-[2-((S)-2-methyl-butoxy)-ethyl]-benzene, **17** (389 mg, 1.44 mmol) and Pd(PPh₃)₄ (60 mg, 0.05 mmol) in dry and oxygen free DMF (5 ml) were stirred overnight under argon at room temperature. The reaction mixture was poured into water (50 ml) and extracted several times with dichloromethane. The organic phase was then washed with 6M HCl and water, dried over MgSO₄, filtered and dried under reduced pressure. After purification by column chromatography on silica gel (hexane, chloroform), **7** (250 mg, 63 %) is obtained as an orange solid. ¹H-NMR (200 MHz, CDCl₃), δ 0.96 (m, 12H, CH₃), 1.36 (m, 4H, CH₂), 1.65 (m, 2H, CH), 2.93 (t, 4H, PhCH₂), 3.30 (m, 4H, OCH₂),

3.68 (t, 4H, OCH₂), 7.18 (d, 2H, TH), 7.24 (d, 2H, TH), 7.28 (d, 4H, PhH), 7.57 (d, 4H, PhH); ¹³C-NMR (300 MHz, CDCl₃), δ 11.2, 16.5, 26.2, 34.9, 36.0, 71.7, 76.3, 123.3, 124.2, 125.4, 129.4, 131.9, 136.3, 138.8, 143.0; MALDI-TOF MS (M = 546.84) *m/z* = 546.51 [M]⁺; IR (solid): ν (cm⁻¹) 727, 792, 816, 829, 871, 1106, 1367, 1377, 1446, 1499, 1531, 2857, 2875, 2934, 2962; Anal. Calc. for C₃₄H₄₂O₂S₂: C 74.68, H 7.74, Found: C 74.81, H 7.84 %.

5,5'-bis-[4-(2-pentanoyloxy-(S)-2-methylethyl)phenyl]-[2,2']-bithiophene (8)

In a schlenk of 10 ml, 1.46 g (4.88 mmol) of **19**, 0.96 g (1.95 mmol) of **22**, and 0.224 g (0.2 mmol) of Pd(PPh₃)₄, was dissolved in 2.5 ml of dry and oxygen free DMF. The mixture was stirred for 16h at 50°C. The reaction mixture was precipitated in cold ethanol. Further purification by column chromatography (SiO₂, DCM) yielded 0.871 g (74%) pure **8** as a yellow solid. ¹H-NMR (400 MHz, CDCl₃), δ 0.89 (t, 6H, CH₃), 1.25 (d, 6H, CH₃), 1.30 (m., 4H, CH₂CH₃), 1.56 (m, 4H, C=OCH₂CH₂), 2.26 (t, 4H, C=OCH₂), 2.77 (d, 2H, PhCH₂, *J* = 6.22 Hz), 2.80 (d, 2H, PhCH₂, *J* = 6.22 Hz), 2.91 (d, 2H, PhCH₂, *J* = 7.32 Hz), 2.94 (d, 2H, PhCH₂, *J* = 6.96 Hz), 5.16 (m, 2H, CH), 7.15 (d, 2H, TH, *J* = 3.66 Hz), 7.20 (d, 2H, PhCH₂, *J* = 3.73 Hz), 7.21 (d, 4H, PhH, *J* = 8.06 Hz), 7.53 (d, 4H, PhH, *J* = 8.42 Hz); ¹³C-NMR (100 MHz, CDCl₃), δ 14.0, 19.8, 22.4, 27.3, 34.6, 42.2, 71.2, 123.8, 124.6, 125.7, 130.2, 132.5, 136.7, 137.5, 143.2, 173.6; IR : ν (cm⁻¹) 731, 791, 855, 870, 950, 1053., 1110, 1135, 1182, 1269, 1378, 1415, 1446, 1498, 1723, 2873, 2934, 2958; MALDI-TOF MS (MW = 602.859) *m/z* = 602.30 [M]⁺; Anal. calc. for C₃₆H₄₂O₄S₂: C = 71.72 H = 6.97. Found: C 71.13, H 6.82 %

5,5'-bis-[4-(2-pentoxy-(S)-2-methylethyl)phenyl]-[2,2']-bithiophene (9)

In a schlenk of 10 ml, 1.430 g (5 mmol) of **20**, 0.984 g (2 mmol) of **22**, and 0.230 g (0.2 mmol) of Pd(PPh₃)₄, was dissolved in 2.5 ml of dry and oxygen free DMF. The mixture was stirred for 16h at 50°C. The reaction mixture was precipitated in cold ethanol. Further purification by column chromatography (SiO₂, DCM) yielded 0.392 g (35%) pure **9** as a yellow solid. ¹H-NMR (400 MHz, CDCl₃), δ 0.90 (t, 6H, CH₃), 1.16 (d, 6H, CH₃), 1.30 (m, 4H, (CH₂)₂CH₃), 1.55 (m, 4H, OCH₂CH₂), 2.64 (d, 2H, PhCH₂, J = 6.23 Hz), 2.67 (d, 2H, PhCH₂, J = 6.23 Hz), 2.89 (d, 2H, PhCH₂, J = 6.22 Hz), 2.93 (d, 2H, PhCH₂, J = 6.22 Hz), 3.36 (double t, 2H, OCH₂), 3.49 (double t, 2H, OCH₂), 3.61 (m, 2H, CH), 7.15 (d, 2H, TH, J = 4.03), 7.20 (d, 2H, TH, J = 4.03), 7.23 (d, 4H, PhH, J = 8.42), 7.53 (d, 4H, PhH, J = 8.42); ¹³C-NMR (100 MHz, CDCl₃), δ 14.3, 19.9, 22.8, 28.6, 30.1, 43.1, 69.1, 76.7, 123.6, 124.6, 125.6, 130.3, 132.1, 136.6, 139.2, 143.4; IR : ν (cm⁻¹) 725, 794.4, 852, 869, 924, 948, 998, 1014, 1057, 1105, 1210, 1338, 1373, 1447, 1459, 1498, 1532, 2857, 2931, 2960; MALDI-TOF MS (MW = 574.294) m/z = 574.40 [M]⁺; Anal. calc. for C₃₆H₄₆O₂S₂: C = 75.28 H = 8.07. Found: C 75.11, H 7.82 %

5,5'-bis-[4-(2-butylamidoyloxy-(S)-2-methylethyl)phenyl]-[2,2']-bithiophene (10)

In a schlenk tube of 10 ml, 1.460 g (4.65 mmol) of **21**, 0.914 g (1.86 mmol) of **22**, and 0.214 g (0.186 mmol) of Pd(PPh₃)₄, was dissolved in 2.5 ml of dry and oxygen free DMF. The mixture was stirred for 16h at 50°C. The reaction mixture was precipitated in cold ethanol. Further purification by column chromatography (SiO₂, DCM/MeOH 95:5) yielded 0.922 g (78%) pure **10** as a yellow solid. ¹H-NMR (400 MHz, CDCl₃), δ 0.87 (t, 6H, CH₃), 1.18 (d, 6H, CH₃), 1.28 (m, 4H, CH₂CH₃), 1.40 (m, 4H, NCH₂CH₂), 2.71 (d,

2H, PhCH₂, *J* = 6.59 Hz), 2.75 (d, 2H, PhCH₂, *J* = 6.22 Hz), 2.88 (d, 2H, PhCH₂, *J* = 6.23 Hz), 2.91 (d, 2H, PhCH₂, *J* = 6.23 Hz), 3.09 (m, 4H, NCH₂), 4.79 (t, 2H, NH), 4.98 (m, 2H, CH), 7.11 (d, 2H, TH, *J* = 3.66), 7.168 (d, 2H, TH, *J* = 3.66), 7.174 (d, 4H, PhH, *J* = 8.79), 7.48 (d, 4H, PhH, *J* = 8.06); ¹³C-NMR (300 MHz, CDCl₃ / CD₃OD 95:5), δ 13.2, 19.3, 19.5, 31.7, 40.3, 41.8, 71.1, 123.1, 124.0, 125.1, 129.7, 131.9, 136.2, 137.0, 142.7, 156.0; IR : ν (cm⁻¹) 791, 814, 870, 897, 946, 1015, 1057, 1118, 1131, 1218, 1270, 1379, 1415, 1446, 1498, 1543, 1684, 2863, 2931, 2960, 3323; MALDI-TOF MS (MW = 632.889) *m/z* = 632.20 [M]⁺; Anal. calc. for C₃₆H₄₄N₂O₄S₂: C = 68.32 H = 7.01 N = 4.43 Found: C 68.21, H 6.63, N 4.06%

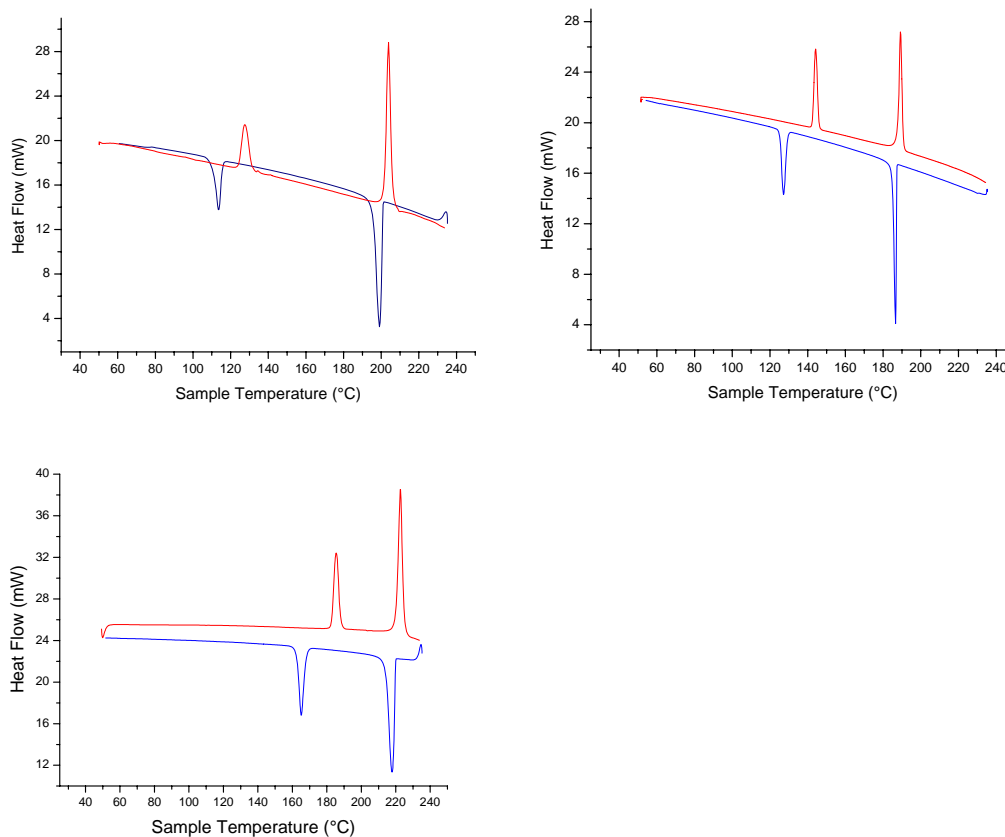
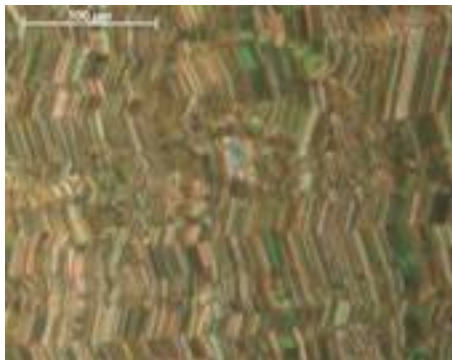
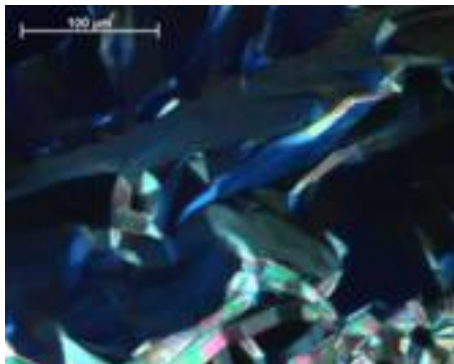


Fig. S1 DSC traces of **6** (top left), **7** (top right) and **5** (bottom left).

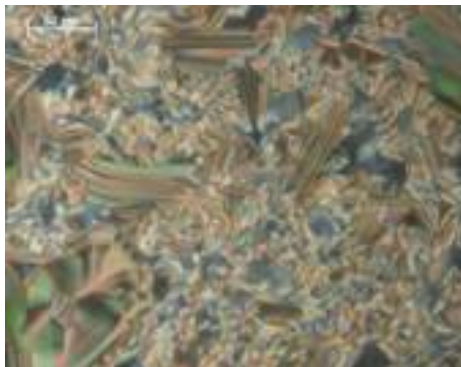
2 at 221 °C



5 at 216 °C



6 at 200 °C



7 at 190 °C

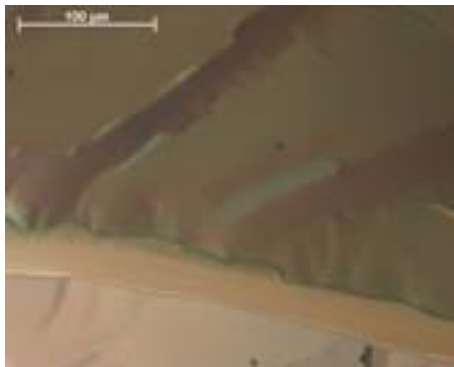
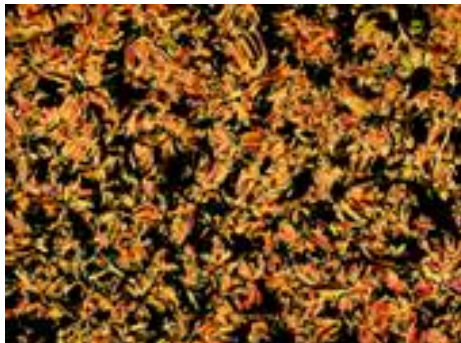


Fig. S2 Polarized optical micrographs of **2**, **5**, **6** and **7** on rubbed polyimide.

3 at 221 °C



5 at 220 °C



6 at 180 °C



7 at 190 °C



Fig. S3 Polarized optical micrographs of **3**, **5**, **6** and **7** on a glass substrate.

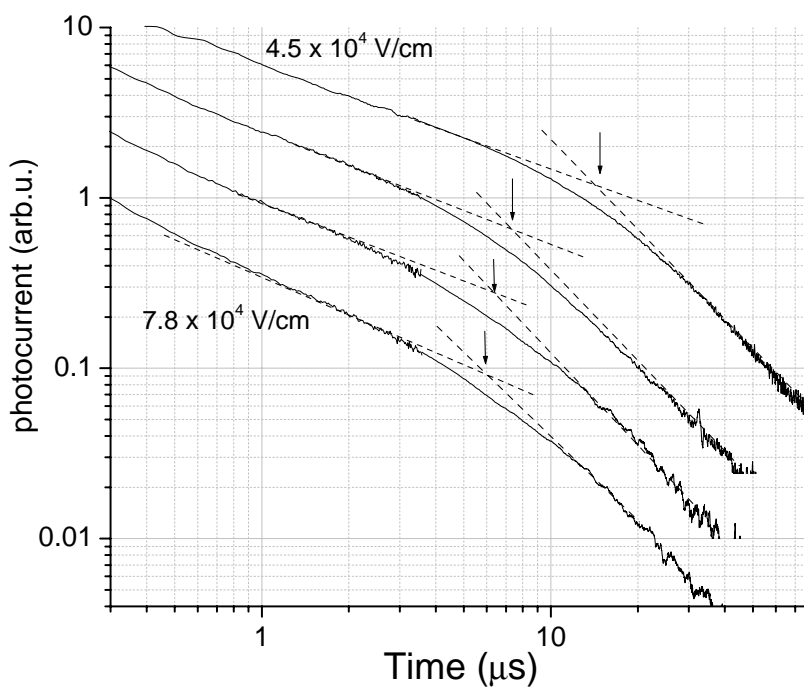


Fig. S4 Time-of Flight transients for holes recorded for **3** for different strengths of the electric field (E): 7.8, 6.7, 5.6 and 4.5 (10^4 V/cm) at $T = 353 \text{ K}$. The vertical arrows indicate estimates of the arrival time as determined by taking the intersection of the tangents to the traces in the for early and later time domain.

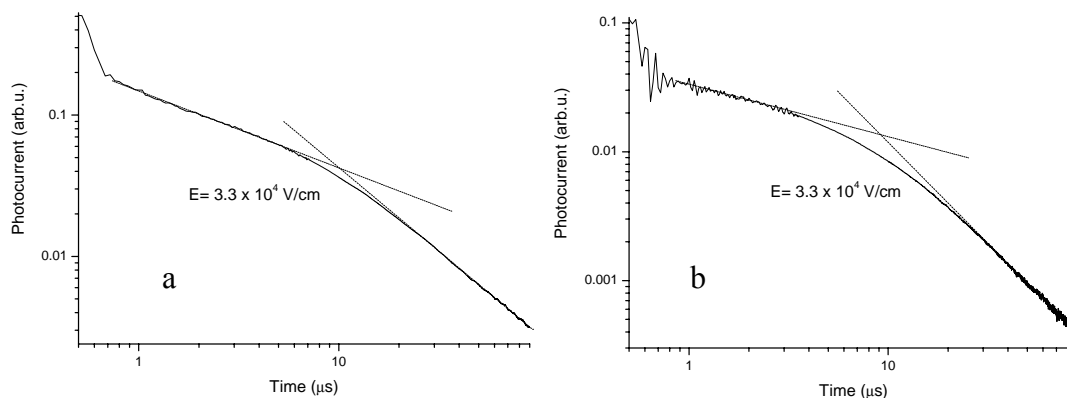


Fig. S5 Time-of Flight transients for **5** at 373 K for (a) holes and (b) electrons.

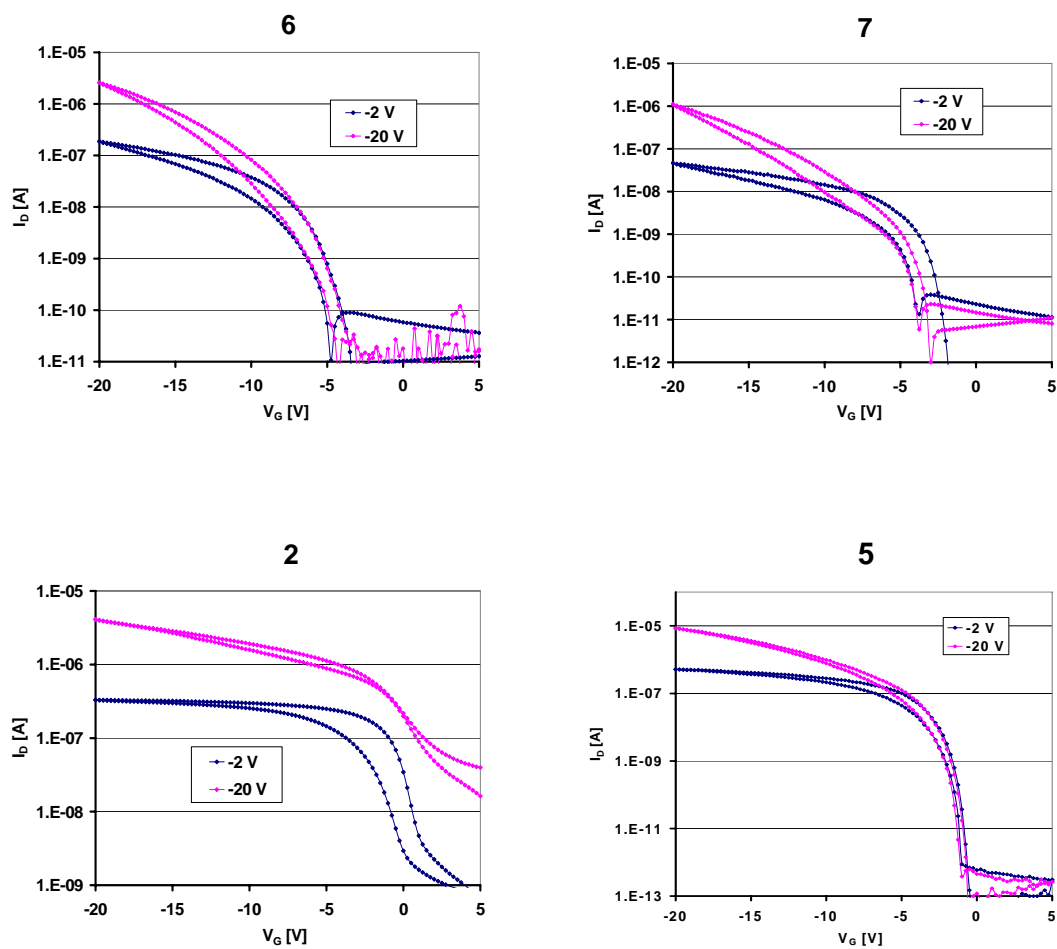


Fig. S6 Output characteristics (I_D - V_G -curves) of FETs based on 2, 5, 6 and 7.