Supporting Information

Effect of Extended Thiophene Segments in Small Band Gap Polymers with Thienopyrazine

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1. Synthesis

3',4'-Dinitroterthiophene (1). Compound 1 was synthesized according to literature procedure,\(^1\) giving 3.02 g of an orange solid (90% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.61 (dd, 2H, \(J = 5.1Hz, J = 1.1Hz\)), 7.55 (dd, 2H, \(J = 3.7Hz, J = 1.1Hz\)), 7.18 (dd, 2H, \(J = 5.1Hz, J = 3.7Hz\)). \(^{13}\)C-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 133.85, 131.27, 131.16, 128.42, 128.05. Anal. Calcd for C\(_{13}\)H\(_{10}\)N\(_2\)O\(_4\)S\(_3\): C, 44.06; H, 2.84; N, 7.90; O, 18.06; S, 27.14. Found: C, 42.54; H, 1.59; N, 8.25. MALDI-TOF MS (\(M_w = 337.95\)): m/z = 337.98 [M\(^+\)].

4,4''-dioctyl-3',4'-dinitro[2,2';5',2"]terthiophene (2). Compound 2 was synthesized according to literature procedure,\(^1\) giving 5.10 g of an orange solid (80% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, 2H, \(J = 1.4Hz\)), 7.18 (d, 2H, \(J = 1.0Hz\)), 2.62 (t, 4H, \(J = 7.7Hz\)), 1.63 (m, 4H), 1.29 (m, 20H), 0.89 (t, 6H, \(J = 7.0Hz\)). \(^{13}\)C-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 144.96, 135.56, 133.98, 132.27, 127.79, 126.02, 31.85, 30.35, 30.29, 29.35, 29.22, 22.66, 14.10. MALDI-TOF MS (\(M_w = 562.82\)): m/z = 562.29 [M\(^+\)].
5,5''-Dibromo-3',4'-dinitro[2,2';5',2'']terthiophene (3). To a solution of 1 (2.0 g, 5.9 mmol) in DMF (50 ml), N-bromosuccinimide (2.11 g, 11.9 mmol) is added. After stirring for 2 d at 50 °C, the product is precipitated in methanol (100 ml). Filtration, washing with methanol (3 × 50 ml) and subsequent drying afforded 2.22 g of 3 as an orange solid (76% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.30 (d, 2H, \(J = 4.1\)Hz), 7.15 (d, 2H, \(J = 4.0\)Hz). \(^{13}\)C-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 135.90, 132.95, 131.67, 131.19, 129.10, 119.62.

5,5''-Dibromo-4,4''-dioctyl-3',4'-dinitro[2,2';5',2'']terthiophene (4). Using compound 2 and an identical procedure to 3, 1.55 g of an orange solid was obtained (79% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.22 (s, 2H), 2.58 (t, 4H, \(J = 7.8\)Hz), 1.60 (m, 4H), 1.30 (m, 20H), 0.89 (t, 6H, \(J = 6.9\)Hz). \(^{13}\)C-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 143.87, 135.60, 133.19, 131.98, 127.41, 116.49, 31.84, 29.56, 29.47, 29.30, 29.19, 29.16, 22.65, 14.10. MALDI-TOF MS (\(M_w = 720.61\)): \(m/z = 719.99\) [M⁺].

2-(tributylstannyl)-4-dodecylthiophene (5). 3-Dodecylthiophene (2.0 g, 7.9 mmol) and tetramethylethlenediamine (TMEDA) (1.38 g, 11.9 mmol) were dissolved in THF (50 ml) and \(n\)-butyllithium (4.8 ml, 12.0 mmol) was added dropwise during 40 min at -78 °C. The reaction mixture was allowed to warm to room temperature and left to stir for 2.5 h. Tributyltinchloride (7.75 ml, 28.6 mmol) was added dropwise during 5 min at -78 °C. After stirring at room temperature for 1 h, the reaction mixture was quenched with water (100 ml) and extracted with ether (3 × 100 ml). The combined organic layers were dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Purification by kugelrohr destillation (160 °C, 5.0×10\(^{-2}\) mbar) gave 3.49 g of a slightly yellow oil (81% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.19 (s, 1H), 6.96 (s, 1H), 2.65 (t, 2H, \(J = 7.8\)Hz), 1.70-1.50 (m, 8H), 1.40-1.22 (m, 24H), 1.08 (t, 6H, \(J = 8.1\)Hz), 0.89 (t, 12H, \(J = 7.3\)Hz).

4,4'''-Didodecyl-3'',4'''-dinitro[2,2';5'',2''';5''',2'''']quinquethiophene (6). Stannane 5 (0.28 g, 0.5 mmol) was added to a solution of 3 (99 mg, 0.2 mmol) and
PdCl₂(PPh₃)₂ (7 mg, 0.01 mmol) in THF (10 ml). The reaction mixture was heated to reflux for 16 h, after which the solvent was evaporated. The crude product was purified by column chromatography on silica (CHCl₃/heptane, 1:1) resulting in 84 mg of red solid (50% yield).

¹H-NMR (400 MHz, CDCl₃): δ 7.46 (d, 2H, J = 4.0Hz), 7.17 (d, 2H, J = 4.0Hz), 7.13 (d, 2H, J = 1.2Hz), 6.92 (d, 2H, J = 0.8Hz), 2.59 (t, 4H, J = 7.7Hz), 1.63 (m, 4H), 1.35-1.22 (m, 4H), 0.88 (t, 6H, J = 7.0Hz).

¹³C-NMR (400 MHz, CDCl₃): δ 144.69, 143.96, 135.42, 135.10, 133.32, 132.02, 126.78, 126.09, 124.16, 121.18, 31.92, 30.44, 30.38, 29.65, 29.58, 29.44, 29.36, 29.27, 22.69, 14.12.

MALDI-TOF MS (Mᵪ = 839.28): m/z = 838.37 [M⁺].

₃',₄'''-Dioctyl-₃',₄'-dinitro[2,2';₅',₂'';₅'',₂''';₅'''';₂''''']quinquethiophene (7). Using 4 and an identical procedure to 6, 1.42 g of a red solid were obtained (94% yield).¹H-NMR (400 MHz, CDCl₃): δ 7.41 (dd, 2H, J = 5.1Hz, J = 1.1Hz), 7.22 (dd, 2H, J = 3.7Hz, J = 1.1Hz), 7.11 (dd, 2H, J = 5.1Hz, J = 3.7Hz), 2.77 (t, 4H, J = 7.8Hz), 1.65 (m, 4H), 1.40-1.20 (m, 36H), 0.88 (t, 6H, J = 6.9Hz).

¹³C-NMR (400 MHz, CDCl₃): δ 143.30, 140.83, 137.14, 134.25, 133.76, 133.38, 127.75, 127.21, 126.95, 125.67, 31.84, 30.47, 29.70, 29.45, 29.34, 29.21, 22.65, 14.11. MALDI-TOF MS (Mᵪ = 727.07): m/z = 726.12 [M⁺].

₅,₇-Bis(₄'-dodecyl-₂,₂'-dithien-₅-yl)-₂,₃-bis(₃,₅-dioctyloxyphenyl)thieno[₃,₄-b]pyrazine (8). Iron dust (0.51 g, 9.1 mmol) was added in one portion to a solution of 6 (0.62 g, 0.7 mmol) in acetic acid (50 ml) at 70 °C. After 2.5 h the reaction mixture was quenched with water (200 ml), extracted with ether (4 × 200 ml), washed with water (3 × 200 ml) and dried over Na₂SO₄. The crude product was dissolved in ethanol (50 ml) and heated to reflux, followed by addition of 1,2-bis(3,5-dioctyloxyphenyl)ethanedione (0.74 g, 1.0 mmol) in one portion. After 20 h the solvent was removed under reduced pressure and purification by column chromatography on silica (CHCl₃/heptane, 1:1) afforded 542 mg of a green sticky solid (50% yield).¹H-NMR (400 MHz, CDCl₃): δ 7.57 (d, 2H, J = 4.0Hz), 7.15 (d, 2H, J = 3.9Hz), 7.07 (s, 2H), 6.82 (s, 2H), 6.80 (d, 4H, J = 2.0Hz), 6.49 (t, 2H, J = 1.5Hz), 3.87 (t, 8H,
\(J = 6.3\text{Hz})\), 2.59 (t, 4H, \(J = 7.7\text{Hz}\)), 1.80-1.55 (m, 12H), 1.45-1.15 (m, 76H), 0.88 (m, 18H).

\(^{13}\text{C}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 159.87, 152.67, 144.28, 140.51, 138.86, 137.54, 136.95, 133.30, 125.34, 125.06, 124.58, 123.67, 119.28, 108.34, 103.60, 68.25, 31.92, 31.85, 30.56, 30.40, 29.69, 29.65, 29.63, 29.49, 29.37, 29.31, 29.17, 29.07, 22.69, 14.11. \text{MALDI-TOF MS} (M_w = 1466.39): m/z = 1465.96 [M^+].

5,7-Bis(3-octyl-2,2’-dithien-5-yl)-2,3-bis(3,5-dioctyloxyphenyl)thieno[3,4-b]pyrazine (9). Using quinquethiophene 7 and an identical procedure to 8, gave 1.14 g of a green solid (50% yield). \(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.48 (s, 2H), 7.32 (dd, 2H, \(J = 5.1\text{Hz}, J = 1.1\text{Hz}\)), 7.19 (dd, 2H, \(J = 3.6\text{Hz}, J = 1.1\text{Hz}\)), 7.08 (dd, 2H, \(J = 5.2\text{Hz}, J = 3.6\text{Hz}\)), 6.81 (d, 4H, \(J = 2.3\text{Hz}\)), 6.48 (t, 2H, \(J = 2.2\text{Hz}\)), 3.86 (t, 8H, \(J = 6.6\text{Hz}\)), 2.80 (t, 4H, \(J = 7.2\text{Hz}\)), 1.75-1.65 (m, 12H), 1.45-1.20 (m, 60H), 0.89 (t, 18H, \(J = 6.4\text{Hz}\)). \(^{13}\text{C}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 159.84, 152.49, 140.46, 139.71, 137.51, 136.26, 132.45, 132.31, 127.44, 127.36, 125.67, 125.30, 124.44, 108.29, 103.77, 68.23, 31.89, 31.84, 30.55, 29.58, 29.45, 29.36, 29.30, 29.16, 26.05, 22.69, 14.10. \text{MALDI-TOF MS} (M_w = 1354.17): m/z = 1352.84 [M^+].

5,7-Bis(5’-bromo-4’-dodecyl-2,2’-dithien-5-yl)-2,3-bis(3,5-dioctyloxyphenyl)thieno[3,4-b]pyrazine (10). \(N\)-bromosuccinimide (116 mg, 0.65 mmol) was added in 3 portions over 60 min. to a solution of 8 (454 mg, 0.31 mmol) in THF (50 ml) at 0 °C. After 5.5 h the solvent was removed under reduced pressure and purification by column chromatography on silica (CHCl\(_3\)/heptanes, 1:2) resulted in 484 mg of a green sticky solid (96%). \(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.53 (d, 2H, \(J = 3.7\text{Hz}\)), 7.10 (d, 2H, \(J = 3.7\text{Hz}\)), 6.91 (s, 2H), 6.79 (s,4H), 6.50 (m, 2H), 3.87 (t, 8H, \(J = 6.5\text{Hz}\)), 2.55 (t, 4H, \(J = 7.4\text{Hz}\)), 1.78-1.56 (m, 12H), 1.46-1.17 (m, 76H), 0.88 (m, 18H). \(^{13}\text{C}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 159.90, 152.82, 143.14, 140.40, 137.80, 137.63, 136.75, 133.66, 125.31, 124.54, 124.37, 123.81, 108.34, 108.01, 103.63, 68.28, 31.92, 31.85, 29.72, 29.68, 29.67, 29.65, 29.60, 29.43, 29.37, 29.36, 29.31, 29.28, 29.17, 26.08, 22.69, 14.11. \text{MALDI-TOF MS} (M_w = 1624.18): m/z = 1622.65 [M^+].
5,7-Bis(5’-bromo-3-octyl-2,2’-dithien-5-yl)-2,3-bis(3,5-dioctyloxyphenyl)thieno[3,4-b]pyrazine (11). N-bromosuccinimide (38 mg, 0.21 mmol) was dissolved in dimethylformamide (4 ml) and added dropwise during 5 min to a solution of 9 (143 mg, 0.11 mmol) in dimethylformamide (6 ml) at 0 °C. After 3 d extra N-bromosuccinimide (18 mg, 0.1 mmol) was added in a similar manner. After 3 h the reaction mixture was allowed to warm to room temperature and left to stir for 3 d. The mixture was poured out into water (200 ml), extracted with ether (3 × 100 ml), washed with water (3 × 100 ml), dried over Na₂SO₄ and concentrated under reduced pressure. Purification by column chromatography on silica (CH₂Cl₂/heptanes, 1:3) was repeated several times until 65 mg of 11 was obtained pure as a green solid (41% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.43 (s, 2H), 7.03 (d, 2H, J = 3.9 Hz), 6.92 (d, 2H, J = 3.8 Hz), 6.80 (br, 4H), 6.48 (br, 2H), 3.86 (t, 8H, J = 6.6 Hz), 2.75 (t, 4H, J = 7.7 Hz), 1.75–1.63 (m, 12H), 1.46–1.17 (m, 60H), 0.88 (m, 18H). ¹³C-NMR (400 MHz, CDCl₃): δ 159.85, 152.65, 140.32, 140.17, 137.78, 137.59, 132.85, 131.33, 130.28, 127.20, 125.81, 124.38, 111.90, 108.28, 103.79, 68.24, 31.91, 31.87, 31.83, 30.51, 29.68, 29.50, 29.41, 29.35, 29.29, 29.15, 26.05, 22.67, 14.10. MALDI-TOF MS (M₁) = 1511.96: m/z = 1510.55 [M+].

Polymer 12. A solution of 10 (57 mg, 0.04 mmol) in toluene (5 ml) was heated to 80 °C. Subsequently, Ni(cod)₂ (30 mg, 0.11 mmol) and bipyridine (18 mg, 0.12 mmol) were added in one portion. After 2.5 d a mixture of methanol/acetone/0.1 M HCl (1:1:1, 100 ml) was added and left to stir for 1 h. The polymer was extracted with CHCl₃ (200 ml) and stirred with an excess EDTA for 3 h. After washing with water (3 × 200 ml), the polymer was precipitated in methanol, filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane and CHCl₃ respectively. The polymer was obtained in 43 mg as a green solid (84% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.62 (br, 2H), 7.18 (br, 2H), 7.12 (br, 2H),
6.80 (br, 4H), 6.49 (br, 2H), 3.87 (m, 8H), 2.55 (br, 4H), 1.77-1.46 (m, 12H), 1.45-1.11 (m, 76H), 0.87 (m, 18H). GPC (ODCB at 80 °C): $M_w = 131$ kg/mol, PDI = 2.8.

**Polymer (13).** Using monomer 11 and an identical procedure to 12, afforded 50 mg of a green solid (64% yield). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (br, 2H), 7.20-7.02 (br, 4H), 6.82 (br, 4H), 6.49 (br, 2H), 3.87 (br, 8H), 2.82 (br, 4H), 1.84-1.49 (br, 12H), 1.48-1.05 (m, 60H), 0.86 (m, 18H). GPC (ODCB at 80 °C): $M_w = 230$ kg/mol, PDI = 3.1.

**Polymer (14).** Monomer 11 (104 mg, 0.064 mmol), 2,5-bis-thiopheneboronic acid pinacol ester (21.5 mg, 0.064 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.92 mg, 3.2 µmol) and Pd$_2$(dba)$_3$ (1.46 mg, 1.6 µmol) were dissolved in degassed THF (2 ml). The reaction mixture was heated to 70 °C, followed by the addition of a 2 M solution of K$_3$PO$_4$ in water (0.4 ml). After 3 days water was added and the polymer was extracted with CHCl$_3$. Ammonia (100 ml, 25% aq. sol.) was added and the mixture was heated to reflux for 3 h. After washing with water ($3 \times 100$ ml) the mixture was stirred for 16 h with an excess EDTA. The organic phase was washed with water ($3 \times 100$ ml) and the polymer was subsequently precipitated in methanol, filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane and CHCl$_3$ respectively. The polymer was obtained in 84 mg as a green solid (90% yield). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (br, 2H), 7.54 (br, endgroup), 7.32 (br, 2H), 7.17 (br, 2H), 7.14 (br, endgroup), 7.10 (br, endgroup), 7.08 (br, 2H), 6.92 (br, endgroup), 6.79 (br, 4H), 6.49 (br, 2H), 3.87 (br, 8H), 2.78 (br, 4H), 1.81-1.50 (br, 12H), 1.48-1.00 (br, 76H), 0.87 (m, 18H). GPC (ODCB at 80 °C): $M_w = 30$ kg/mol, PDI = 3.4.
2. GPC results

![GPC trace of the polymers measured (Refractive Index) at 80 °C in o-dichlorobenzene.](image)

**Figure S1.** GPC trace of the polymers measured (Refractive Index) at 80 °C in o-dichlorobenzene.

3. Optical absorption spectra of the monomers

![UV-Vis absorption spectra of compounds 6, 7, 8 and 9 in OBCB solution.](image)

**Figure S2.** UV-Vis absorption spectra of compounds 6, 7, 8 and 9 in OBCB solution.
4. Cyclic voltammetry

![Cyclic voltammograms](image)

**Figure S3.** Cyclic voltammograms (vs. Fc/Fc⁺) of 12 (top), 13 (middle) and 14 (bottom) recorded in ODCB at room temperature. The arrows indicate the onsets of the oxidation and reduction potentials.
5. AFM height images from polymer:[70]PCBM blends

Figure S4. AFM height images of [70]PCBM blended with 12 (left), 13 (middle), and 14 (right), all spin coated from ODCB in a polymer:PCBM ratio of 1:4 (by wt.).

6. Solar cells of 12 spin coated from different solvents

Figure S5. (a) J-V curves of solar cells of 12 with, [60]PCBM spin coated from CB (filled squares) or ODCB (filled circles), and [70]PCBM spin coated from CB (open triangles) or ODCB/CHCl₃ (1:4) (open circles) under 100 mW/cm² white light illumination. (b) Monochromatic EQEs of solar cells made with 12.
Figure S6. AFM height images of 12 blended with [60]PCBM spin coated from CB (left) or ODCB (2nd from left), and [70]PCBM spin coated from CB (2nd from right) or ODCB/CHCl₃ (1:4) (right). All blends were spin coated in a polymer:PCBM ratio of 1:4 (by wt.).

7. Solar cells of 13 & 14 spin coated from different solvents

Figure S7. (a) J-V curves of solar cells of 13:[60]PCBM spin coated from ODCB/CHCl₃ (open squares), 14:[60]PCBM spin coated from CB (filled circles) or CHCl₃ (open circles) under 100 mW/cm² white light illumination. (b) Monochromatic EQEs of solar cells made with 13 and 14.
Figure S8. AFM height images of 13:[60]PCBM (left), 14:[60]PCBM (middle), and 14:[60]PCBM (right), spin coated from ODCB/CHCl₃, CB and CHCl₃, respectively. All blends were spin coated in a polymer:PCBM ratio of 1:4 (by wt.).

8. Charge carrier mobilities

Figure S9. In Figures a, b and c semilogarithmic plots of the drain current $I_D$ versus gate voltage $V_G$ (left y-axis) and plot of $\sqrt{I_D}$ versus $V_G$ (right axis) from a bottom contact thin film transistors (TFT), consisting of either polymer 12 (a), 13 (c) or 14 (e) as semiconductor material, are depicted. Figures b, d and f show the transfer curves at different drain voltage, $V_D = -2$ V and -20 V. The temperature during measurement was fixed at 40 °C. The field-effect hole mobility $\mu$, calculated in the saturation regime (from the slope of the linear fit to the square-root of the $I_D$) at $V_D = -20$ V with $L = 10$ µm and $W = 2500$ µm, is $1.6 \times 10^{-4}$ cm²/Vs, $1.0 \times 10^{-3}$ cm²/Vs and $1.2 \times 10^{-5}$ cm²/Vs for 12, 13 and 14 respectively. The presence
of HH coupling and lower molecular weight probably explain the lower hole mobility for 12
and 14 compared to polymer 13. The $I_{on}/I_{off}$ ratio (when $V_G$ was scanned from -30 to +20 V)
for 12, 13 and 14 are $1.5 \times 10^6$, $3.0 \times 10^5$ and $2.3 \times 10^5$, correspondingly.