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Supporting Information

Synthesis and photovoltaic performance of a series of small band gap polymers

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1. Synthetic procedures

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer.

Methyl-3,5-dioctyloxybenzoate (2a). A solution of methyl-3,5-dihydroxybenzoate **(1)** (5.04 g, 30.0 mmol), 1-iodooctane (17.90 g, 74.5 mmol), and K_2CO_3 (20.58 g, 148.9 mmol) in CH_3CN (150 ml) was prepared. The reaction mixture was refluxed for 16 h and subsequently quenched by addition of demineralized water (200 ml). The aqueous phase was extracted with CH_2Cl_2 (4× 100 ml). The combined organic layers were dried over Na_2SO_4 and the remaining solvent was evaporated. Purification by chromatography on silica gel (hexane:CH_2Cl_2) afforded 9.77 g of a white solid (83% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 2H, J = 2.2), 6.63 (t, 1H, J = 2.2Hz), 3.97 (t, 4H, J = 6.6 Hz), 3.90 (s, 3H), 1.77 (m, 4H), 1.44 (m, 4H), 1.39-1.23 (m, 16H), 0.89 (t, 6H, J = 6.6Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 167.04, 160.12, 131.70, 107.57, 106.58, 66.30, 52.25, 31.81, 29.33, 29.24, 26.01, 22.66, 14.11. Anal. Calcd for $C_{24}H_{40}O_3$: C, 76.55; H, 10.71; O, 12.75. Found: C, 73.68; H, 10.03. MALDI-TOF MS (M_w = 392.29): m/z = 392.35 [M^+].

Methyl-3,5-bis(2´-ethylhexyloxy)benzoate (2b). Procedure was identical to **(2a)**. 21.5 g of a colorless oil (92% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 2H, J = 2.5 Hz), 6.65 (t, 1H, J = 2.2 Hz), 3.90 (s, 3H), 3.87 (dd, 4H, J = 4.5 Hz, J = 1.5 Hz), 1.72 (m, 2H), 1.55-1.36 (m, 8H), 1.35-1.27 (m, 8H), 0.96-0.85 (m, 12 H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 167.03, 160.36, 131.70, 107.48, 106.48, 70.65, 52.18, 39.36, 30.48, 29.05, 23.82, 23.04, 14.09, 11.11. Anal. Calcd for $C_{24}H_{40}O_3$: C, 76.55; H, 10.71; O, 12.75. Found: C, 68.64; H, 9.96. GC-MS (M_w = 392.58): m/z = 392.40 [M^+].

1,2-Bis(3,5-dioctyloxyphenyl)ethanedione (3a). Compound **2a** (3.99 g, 10.2 mmol), dissolved in ether (40 ml) was added drop wise during 10 min. to sodium (0.48 g, 20.7 mmol) suspended in ether (40 ml). After stirring 16 h, the reaction mixture was cooled to -78 ^{o}C and $SOCl_2$ (3 ml, 41.4 mmol) was slowly added. The mixture was allowed to reach room temperature. After 8 h, the reaction was quenched by careful addition of ice/water (50 ml). The aqueous phase was extracted with ether (3× 50 ml). The combined organic layers were dried over Na_2SO_4 and the remaining solvent was evaporated. Purification by chromatography on silica gel (hexane:$CHCl_3$) resulted in 1.13 g of a yellow oil (31% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.03 (d, 4H, J = 2.6 Hz), 6.71 (t, 2H, J = 2.2 Hz), 3.95 (t, 8H, J = 6.6 Hz), 1.76 (m, 8H), 1.43 (m, 8H), 1.38-1.23 (m, 32H), 0.89 (t, 12H, J = 6.6 Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 194.43, 160.60, 134.58, 107.86, 68.46, 31.79, 29.21, 25.98, 22.65, 14.09. Anal. Calcd for $C_{46}H_{74}O_6$: C, 76.41; H, 10.32; O, 13.28. Found: C, 76.07; H, 10.33. MALDI-TOF MS (M_w = 722.55): m/z = 723.54 [M^+].

1,2-Bis[3,5-bis(2´-ethylhexyloxy)phenyl]ethanedione (3b). Procedure was identical to **(3a)** using **2b** instead of **2a**. 1.66 g of a yellow oil (37% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.05 (d, 4H, J = 2.2 Hz), 6.73 (t, 2H, J = 2.2 Hz), 3.86 (dd, 8H, J =

5.5 Hz, J = 2.2 Hz), 1.70 (m, 4H), 1.53-1.35 (m, 16H), 1.34-1.24 (m, 16H), 0.94-0.85 (m, 24H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 194.37, 160.82, 134.54, 107.82, 70.83, 39.35, 30.46, 29.05, 23.81, 23.01, 14.06, 11.09. Anal. Calcd for $C_{46}H_{74}O_6$: C, 76.41; H, 10.32; O, 13.28. Found: C, 73.74; H, 9.72. MALDI-TOF MS (M_w = 722.55): m/z = 723.61 [M^+].

2,5-Dibromo-3,4-dinitrothiophene (4). A mixture of concentrated H_2SO_4 (28 ml), fuming H_2SO_4 (44 ml), and fuming HNO_3 (23 ml) was cooled to 0 ^oC. To avoid temperatures above 20 ^oC, 2,5-dibromothiophene (25 g, 0.10 mol) was added drop wise. After 15 min. the mixture was poured out into ice. The precipitate was filtered and thoroughly washed with water. Recrystallization from MeOH (twice) afforded 10 g of the title compound (32% yield). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 123.96, 113.38. Anal. Calcd for $C_4Br_2N_2O_4S$: C, 14.47; Br, 48.15; N, 8.44; O, 19.28; S, 9.66. Found: C, 14.52; N, 7.99. MALDI-TOF MS (M_w = 331.79): m/z = 331.80 [M^-].

3',4'-Dinitroterthiophene (5). 2-Tributylstannylthiophene (7.6 g, 20.5 mmol) was added to a solution of **4** (3.3 g, 9.94 mmol) and $PdCl_2(PPh_3)_2$ (34.9 mg, 0.50 mmol) in toluene (40 ml). The reaction mixture was heated to 130 ^oC and left to stir for 16 h, after which the solvent was evaporated. Purification by chromatography on silica gel (solid deposition) (CH_2Cl_2/hexane, 1:9→1:1) gave 3.02 g of an orange solid (90% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 133.85, 131.27, 131.16, 128.42, 128.05. Anal. Calcd for $C_{13}H_{10}N_2O_4S_3$: 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^-].

3´,4´-Diaminoterthiophene (6). A solution of **5** (2.64 g, 7.80 mmol) and Sn (4.64 g, 39.1 mmol) in EtOH (60 ml) and HCl (120 ml) was prepared. After 1 h, no product

formation was observed, $SnCl_2$-H_2O (1.48 g, 7.82 mmol) was added. After 16 h the reaction mixture was treated with NaOH (until pH>10), extracted with CH_2Cl_2 (3× 100 ml) and precipitated in heptane/CH_2Cl_2, resulting in 1.50 g of a green solid (69% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, 2H, J = 4.9Hz, J = 1.5Hz), 7.09 (m, 4H), 3.73 (s, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 135.88, 133.53, 127.74, 124.00, 123.89, 110.05. Anal. Calcd for $C_{12}H_{10}N_2S_3$: C, 51.77; H, 3.62; N, 10.06; S, 34.55. Found: C, 51.42; H, 3.32; N, 9.90. MALDI-TOF MS (M_w = 278.00): m/z = 278.03 [M^+].

5,7-Di(2-thienyl)-2,3-bis(3,5-dioctyloxyphenyl)thieno[3,4-b]pyrazine (7a). A solution of **3a** (1.01 g, 1.40 mmol) and **6** (0.54 g, 1.94 mmol) in EtOH (40 ml) was prepared. The reaction mixture was refluxed for 3 days and then the solvent was evaporated. Purification by chromatography on silica gel (CH_2Cl_2/heptane, 1:2) gave 1.26 g of a purple solid (96% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, 2H, J = 5.0Hz, J = 1.1Hz), 7.38 (dd, 2H, J = 4.8 Hz, J = 1.1Hz), 7.14-7.10 (m, 2H), 6.74 (d, 4H, J = 2.2Hz), 6.47 (t, 2H, J = 2.2Hz), 3.83 (t, 8H, J = 6.6Hz), 1.71 (m, 8H), 1.40 (m, 8H), 1.37-1.23 (m, 32H), 0.89 (t, 12H, J = 7.0 Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.83, 152.85, 140.63, 137.37, 134.64, 127.31, 124.91, 126.61, 124.69, 108.41, 103.26, 68.23, 31.84, 29.34, 29.30, 29.10, 26.03, 22.68, 14.11. Anal. Calcd for $C_{59}H_{84}N_2O_4S_3$: C, 72.20; H, 8.63; N, 2.85, O, 6.52; S, 9.80. Found: C, 72.63; H, 8.34; N, 2.65. MALDI-TOF MS (M_w = 964.53): m/z = 964.44 [M^+].

5,7-Di(2-thienyl)-2,3-bis[3,5-bis(2´-ethylhexyloxy)phenyl]thieno[3,4-b]pyrazine (7b). The procedure was identical to **7a.** Starting from **3b** and **6**, 218 mg of a purple solid was obtained (78% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, 2H, J = 5.0Hz, J = 1.1Hz), 7.38 (dd, 2H, J = 4.8 Hz, J = 1.1Hz), 7.14-7.10 (m, 2H), 6.74 (d, 4H, J = 2.2Hz), 6.47 (t, 2H, J = 2.2Hz), 3.70 (d, 8H, J = 5.8Hz), 1.66 (m, 4H), 1.44-

1.26 (m, 32H), 0.89 (m, 24H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 160.07, 152.96, 140.48, 137.39, 134.67, 127.30, 126.54, 124.87, 124.67, 108.34, 103.26, 70.73, 39.16, 30.49, 29.00, 23.81, 23.07, 14.10, 11.03. Anal. Calcd for $C_{59}H_{84}N_2O_4S_3$: C, 72.20; H, 8.63; N, 2.85, O, 6.52; S, 9.80. Found: not determined. MALDI-TOF MS (M_w =964.53): m/z = 964.54 [M^+].

5,7-Bis(5-bromothien-2-yl)-2,3-bis(3,5-dioctyloxyphenyl)thieno[3,4-b]pyrazine (8a). NBS (0.475 g, 2.67 mmol) was added at 0 ^{o}C to a solution of **7a** (1.23 g, 1.31 mmol) in THF (40 ml). After 4 h the reaction mixture was allowed to slowly reach room temperature. After 16 h, demineralized water (50 ml) was added and the mixture was extracted with $CHCl_3$ (3× 75 ml). The organic phase was dried over Na_2SO_4 and the remaining solvent was evaporated. Purification by chromatography on silica gel (twice) (CH_2Cl_2/heptane, 1:4) afforded 0.92 g of **8a** as a purple solid (64% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (d, 2H, J = 4.0Hz), 7.05 (d, 2H, J = 4.0Hz), 6.74 (d, 4H, J = 2.2Hz), 6.49 (t, 2H, J = 2.2Hz), 3.85 (t, 8H, J = 6.5Hz), 1.72 (m, 8H), 1.41 (m, 8H), 1.37-1.25 (m, 32H), 0.89 (t, 12H, J = 7.0Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 159.89, 153.17, 140.22, 137.35, 135.93, 129.80, 124.15, 124.03, 114.69, 108.33, 103.64, 68.28, 31.84, 29.33, 29.30, 29.11, 26.03, 22.69, 14.11. Anal. Calcd for $C_{58}H_{78}Br_2N_2O_4S_3$: C, 62.02; H, 7.00; Br, 14.23; N, 2.49; O, 5.70; S, 8.56. Found: C, 61.78; H, 6.57; N, 2.20. MALDI-TOF MS (M_w = 1122.35): m/z = 1122.35 [M^+].

5,7-Bis(5-bromothien-2-yl)-2,3-bis[3,5-bis(2´-ethylhexyloxy)phenyl]thieno[3,4-b]pyrazine (8b). Procedure was identical to **8a**. Starting from **7b** and NBS, 113 mg of a purple solid (**8b**) was obtained (44% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (d, 2H, J = 4.0Hz), 7.05 (d, 2H, J = 4.0Hz), 6.74 (d, 4H, J = 2.2Hz), 6.49 (t, 2H, J = 2.2Hz), 3.71 (d, 8H, J = 5.8Hz), 1.66 (m, 4H), 1.44-1.26 (m, 32H), 0.89 (m, 24H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 160.15, 153.23, 140.11, 137.32, 135.96, 129.71,

124.11, 123.91, 114.71, 108.26, 103.66, 70.76, 39.20, 30.52, 29.02, 23.84, 23.08, 14.10, 11.07. Anal. Calcd for $C_{58}H_{78}Br_2N_2O_4S_3$: C, 62.02; H, 7.00; Br, 14.23; N, 2.49; O, 5.70; S, 8.56. Found: not determined. MALDI-TOF MS (M_w =1122.35): m/z = 1122.27 [M^+].

PTBOT. A solution of $Ni(cod)_2$ (80 mg, 0.29 mmol) and bypiridine (43 mg, 0.28 mmol) in toluene (3 ml) was heated to 80 ^oC. Subsequently, **8a** (103 mg, 0.09 mmol) was added in one portion. An additional amount of toluene (3 ml) was added to get all of the monomer in solution. After 20 hrs a mixture of MeOH/Acetone/0.1 M HCl (1:1:1, 100 ml) was added and was left to stir for 2 hrs. The polymer was extracted with $CHCl_3$ (2× 50 ml) to which EDTA (600 mg) was added. The mixture was left to stir for 20 h. The organic phase was washed with water (3× 100 ml) and concentrated. The polymer was precipitated in MeOH and filtered through a Soxhlet thimble. The polymer was fractionated by Soxhlet extraction using MeOH, hexane, CH_2Cl_2, $CHCl_3$ and ODCB respectively. The polymer was further purified by preparative SEC and gave 83 mg of a green solid (98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (br, 2H), 6.83-6.76 (m, 6H), 6.48 (br, 2H), 3.84 (br, 8H), 1.70 (br, 8H), 1.50-1.10 (m, 40H), 1.00-0.60 (m, 12H). GPC (ODCB at 80 ^oC): M_w = 50100 g/mol, M_n = 15200 g/mol, PDI = 3.3.

PTBEHT. Using monomer **7b** and a procedure identical to the synthesis of **PTBOT**, 92 mg of a green polymer was obtained (95% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58 (br, 2H), 6.90-6.75 (m, 6H), 6.51 (br, 2H), 3.62 (br, 8H), 1.75-1.10 (m, 36H), 1.00-0.70 (m, 24H). GPC (o-DCB at 80 ^oC): M_w = 157500 g/mol, M_n = 27400 g/mol, PDI = 5.8.

1,4-Dibromo-2,1,3-benzothiadiazole (10) Bromine (37.30 g, 233.4 mmol) was added drop wise during 1h to a solution of 2,1,3-benzothiadiazole **9** (9.95 g, 73.1 mmol) in

aqueous HBr (48%, 50 ml). An additional amount of aqueous HBr (30 ml) was added to commence stirring. The reaction mixture was refluxed for 2.5 h and subsequently filtrated (while hot). The filtrate was thoroughly washed with demineralized water and dissolved in ether (800 ml). The organic phase was washed with demineralized water (3× 200 ml), dried over Na_2SO_4 and the remaining solvent was evaporated. Recrystallization from MeOH afforded 16.56 g of white needles (77% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 2H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 152.94, 132.33, 113.90. Anal. Calcd for $C_6Br_2N_4O_4S$: C, 24.52; H, 0.69; Br, 54.36; N, 9.53: S, 10.91. Found: C, 24.42; H, 0.39; N, 9.20. GC-MS (M_w = 293.97): m/z = 293.90 [M^+].

1,4-Dibromo-5,6-dinitro-2,1,3-benzothiadiazole (11) A mixture of concentrated H_2SO_4 (100 ml) and fuming HNO_3 (100 ml) was cooled to 0 ^{o}C. To keep the temperature below 5 ^{o}C, compound **10** (5.22 g, 17.8 mol) was added in small portions. After stirring for 6 h at 0 ^{o}C, the reaction mixture was poured out into ice/water (300 ml). The precipitate was filtrated and washed with water. Purification by chromatography on silica gel (solid deposition) (EtOAc/heptane, 1:4) gave 1.83 g of **11** as a beige solid (27% yield). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 151.35, 144.93, 110.27. Anal. Calcd for $C_6Br_2N_4O_4S$: C, 18.77; Br, 41.62; N, 14.59; O, 16.67; S, 8.35. Found: C, 18.69; N, 14.10. MALDI-TOF MS (M_w = 383.80): m/z = 383.84 [M^-].

1,4-Di(2-thienyl)-5,6-dinitro-2,1,3-benzothiadiazole (12) To a solution of **11** (3.80 g, 9.90 mmol) and 2-tributylstannylthiophene (9.06 g, 24.3 mmol) in THF (150 ml), $Pd(PPh_3)_2Cl_2$ (338 mg, 0.48 mmol) was added. The reaction mixture was refluxed for 16 h, after which it was cooled to room temperature and concentrated to allow precipitation from hexane. After filtration and washing with hexane, recrystallization from toluene afforded 3.10 g of an orange solid (80% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, 2H, J = 5.1Hz, J = 0.7Hz), 7.52 (dd, 2H, J = 4.7Hz, J = 1.1Hz),

7.25 (m, 2H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 152.20, 141.86, 131.42, 130.98, 129.53, 128.00, 121.48. Anal. Calcd for $C_{14}H_{10}N_4S_3$: C, 43.07; H, 1.55; N, 14.35; O, 16.39; S, 24.64. Found: C, 43.67; H, 0.76; N, 13.57. MALDI-TOF MS (M_w = 389.95): m/z = 390.02 [M^-].

1,4-Di(2-thienyl)-5,6-diamino-2,1,3-benzothiadiazole (13). To a solution of **12** (502 mg, 1.29 mmol) in acetic acid (40 ml), of iron dust (878 mg, 15.72 mmol) was added. The reaction mixture was heated to 80 ^oC. After 5 h, demineralized water (100 ml) was added to the mixture and the product was extracted with ether (3× 100 ml). The ethereal phase was dried over Na_2SO_4 en the solvent was evaporated resulting in 416 mg of a brown solid (98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, 2H, J = 5.5Hz, J = 1.1Hz), 7.37 (dd, 2H, J = 3.3Hz, J = 1.1Hz), 7.26 (t, 2H, J = 4.7Hz), 4.39 (br, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 150.88, 139.27, 135.21, 128.50, 127.46, 127.19, 107.17. Anal. Calcd for $C_{14}H_{10}N_4S_3$: C, 50.89; H, 3.05; N, 16.95; S, 29.11. Found: C, 50.79; H, 2.65; N, 17.05. MALDI-TOF MS (M_w = 330.01): m/z = 330.05 [M^+].

4,7-Bis(5-bromothien-2-yl)-2,1,3-benzothiadiazole-5,6-diamine (14). In the dark, a solution of **13** (459 mg, 1.39 mmol) in THF (20 ml) was prepared. After cooling the mixture to 0 ^oC, NBS (497 mg, 2.80 mmol) was added in one portion. After 4 h, NBS (54 mg, 0.3 mmol) was added. After an additional 2 h, demineralized water (50 ml) was added to the reaction mixture. The product was extracted with $CHCl_3$ (4× 100 ml) and dried over Na_2SO_4. The remaining solvent was evaporated. Purification by chromatography on silica gel ($CHCl_3$) afforded 411 mg of **14** as a green solid (61% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.20 (d, 2H, J = 3.7Hz), 7.12 (d, 2H, J = 4.7Hz), 4.40 (br, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 150.40, 139.36, 136.85, 130.18, 128.92, 114.21, 106.60. Anal. Calcd for $C_{14}H_8Br_2N_4S_3$: C, 34.44; H, 1.65; Br,

32.73; N, 11.48; S, 19.70. Found: C, 34.57; H, 1.52; N, 10.91. MALDI-TOF MS (M_w = 487.83): m/z = 487.80 [M^+].

2,3,7,8-Tetrakis[3,5-bis(2´-ethylhexyloxy)phenyl]-5,6-bis(5-bromothien-2-yl) pyrazino[2,3-g]quinoxaline (15). Zinc dust (605 mg, 9.25 mmol) was added to a solution of **14** (198 mg, 0.41 mmol) in acetic acid (10 ml). The reaction mixture was heated to 70 ^oC. After 24 h, the mixture was cooled to room temperature; where after **3b** (610 mg, 0.84 mmol) was added. The reaction mixture was quenched, after stirring for 5 h at room temperature, by addition of demineralized water (50 ml). The product was extracted with $CHCl_3$ (3× 50 ml) and dried over Na_2SO_4. The remaining solvent was evaporated and purification by chromatography on silica gel (CH_2Cl_2/heptane, 1:4) resulted in 244 mg of a green solid (33% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.57 (d, 2H, J = 4.4Hz), 7.22 (d, 2H, J = 4.4Hz), 6.98 (d, 8H, J = 2.5Hz), 6.54 (t, 4H, J = 2.2Hz), 3.78 (d, 16H, J = 5.9Hz), 1.71-1.64 (m, 8H), 1.53-1.23 (m, 64H), 0.95-0.81 (m, 48H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 160.38, 152.55, 139.54, 136.38, 135.90, 134.88, 128.92, 126.90, 119.12, 108.48, 104.21, 70.79, 39.26, 30.54, 29.06, 23.87, 23.09, 14.12, 11.11. Anal. Calcd for $C_{106}H_{152}Br_2N_4O_8S_2$: C, 69.41; H, 8.35, Br, 8.71; N, 3.05; O, 6.98; S, 3.50. Found: C, 69.72; H, 7.38; N, 2.58. MALDI-TOF MS (M_w = 1834.35): m/z = 1834.68 [M^+].

2,3,7,8-Tetraoctyl-5,6-di(2-thienyl)pyrazino[2,3-g]quinoxaline (16) Zinc dust (229 mg, 3.50 mmol) was added to a solution of **13** (100 mg, 0.30 mmol) in acetic acid (6 ml). The reaction mixture was heated to 70 ^oC for 16 h, after which 9,10-octadecanedione (174 mg, 0.62 mmol) was added. After 24 h the reaction was quenched with demineralized water (50 ml) and treated with sat. Na_2CO_3 until the mixture was basic (pH=10). The product was extracted with CH_2Cl_2 (3× 50 ml) and dried over Na_2SO_4. The excess solvent was evaporated and purification by

chromatography on silica gel (CH_2Cl_2/heptane, 1:6→1:4) gave 170 mg of **16** as a red solid (71% yield) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, 2H, J = 3.7Hz, J = 1.1Hz), 7.63 (dd, 2H, J = 5.1Hz, J = 1.5Hz), 7.27 (t, 2H, J = 3.6Hz), 3.11 (t, 8H, J = 7.4Hz), 2.00 (m, 8H), 1.49-1.25 (m, 40H), 0.89 (t, 12H, J = 7.0Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 156.19, 136.30, 134.70, 133.44, 128.98, 127.88, 125.58, 35.16, 31.92, 29.64, 29.59, 29.27, 27.45, 22.71, 14.13. Anal. Calcd for $C_{50}H_{74}N_4S_2$: C, 75.51; H, 9.38; N, 7.04; S, 8.06. Found: C, 74.61; H, 9.39; N, 6.41. MALDI-TOF MS (M_w = 794.53): m/z = 794.51 [M^+].

2,3,7,8-Tetraoctyl-5,6-bis(5-bromothien-2-yl)pyrazino[2,3-g]quinoxaline (17) In the dark, a solution of **16** (153 mg, 0.19 mmol) in THF (10 ml) was prepared. After cooling the mixture to 0 ^{o}C, NBS (69 mg, 0.39 mmol) was added in one portion. After 2 h, extra NBS (13 mg, 0.07 mmol) was added. After 16 h, demineralized water (50 ml) was added to the reaction mixture. The product was extracted with $CHCl_3$ (3× 50 ml) and dried over Na_2SO_4. The remaining solvent was evaporated. Purification by chromatography on silica gel (CH_2Cl_2/heptane, 1:6) afforded 165 mg of **17** as a purple solid (90% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.48 (d, 2H, J = 4.0Hz), 7.18 (d, 2H, J = 4.4Hz), 3.11 (t, 8H, J = 7.7Hz), 2.00 (m, 8H), 1.53-1.25 (m, 40H), 0.90 (t, 12H, J = 7.0Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 156.37, 136.61, 135.85, 134.04, 128.57, 126.55, 118.08, 35.16, 31.91, 29.61, 29.59, 29.26, 27.70, 22.71, 14.14. $C_{50}H_{72}Br_2N_4S_2$: C, 63.01; H, 7.61; Br, 16.77; N, 5.88; S, 6.73. Found: C, 64.01; H, 7.77; N, 5.57. MALDI-TOF MS (M_w = 952.35): m/z = 952.37 [M^+].

PTBEHBQ. Using monomer **15**, and a procedure identical to the synthesis of **PTBOT**, 65 mg of a green solid (66% yield) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.72 (br, 2H), 7.58 (br, 2H), 7.09 (br, 4H), 6.49 (br, 2H), 3.72 (br, 16H),

1.56 (br, 8H), 1.31-1.18 (br, 64H), 0.78 (br, 48H). GPC (o-DCB at 80 ^{o}C): M_w = 54364 g/mol, M_n = 14618 g/mol, PDI = 3.7.

PTOBQ. Using monomer **17**, and a procedure identical to the synthesis of **PTBOT**, 58 mg of a blue solid (66% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.67 (br, 2H), 7.52 (br, 2H), 3.18 (br, 8H), 2.12 (br, 8H), 1.60-1.15 (m, 40H), 0.95-0.70 (m, 12H). GPC (o-DCB at 80 ^{o}C): M_w = 15716 g/mol, M_n = 4889 g/mol, PDI = 3.2.

2. Optical absorption spectra of the monomers

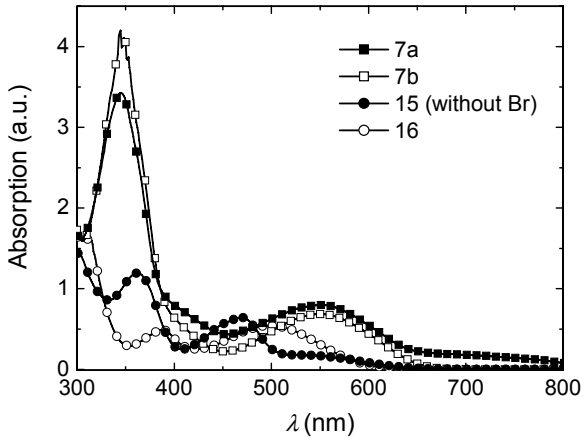

Figure S1. UV-Vis absorption spectra of monomers in OBCB solution

The optical absorption spectra of the monomers in solution (Figure S1) clearly reveal that the thienopyrazine in **7a** and **7b** unit causes an additional red shift of λ_{max} compared to the bisquinoxaline analogues **15** (without Br) and **16**. Both **7a** and **7b** show λ_{max} = 551 nm and λ_{onset} = 659 nm (E_g = 1.88 eV), while **16** exhibits a substantially blue shifted absorption spectrum. The electron donating character of the octyl side chains, directly attached to the electron accepting unit of **16**, decreases the acceptor strength of the bisquinoxaline and causes a widening of the optical gap (E_g). This results in a λ_{max} = 499 nm and λ_{onset} = 598 nm (2.07 eV) for monomer **16**. The absorption maximum of **15** (without Br) is even further blue shifted to λ_{max} = 469 nm.

Despite the absence of electron donating alkyl chains, a 30 nm shift of λ_{max} to shorter wavelengths is observed. Probably the bulky substituents cause a severe twist between the benzene and the thiophene rings, disrupting conjugation leading to an increase of the band gap.

3. Absorption vs. molecular weight and concentration for PTBOT

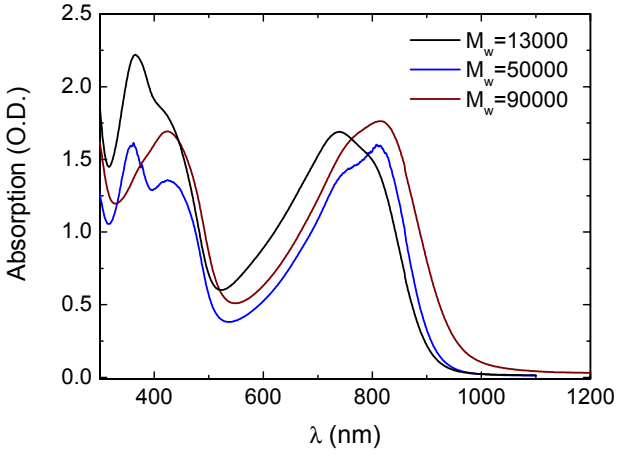

Figure S2. Optical absorption spectra of PTBOT for different molecular weights. The highest M_w polymer has the furthest red-shifted λ_{max}. In addition, the shoulder of the lowest M_w polymer becomes the dominant absorption peak at higher M_w material.

4. Cyclic voltammetry

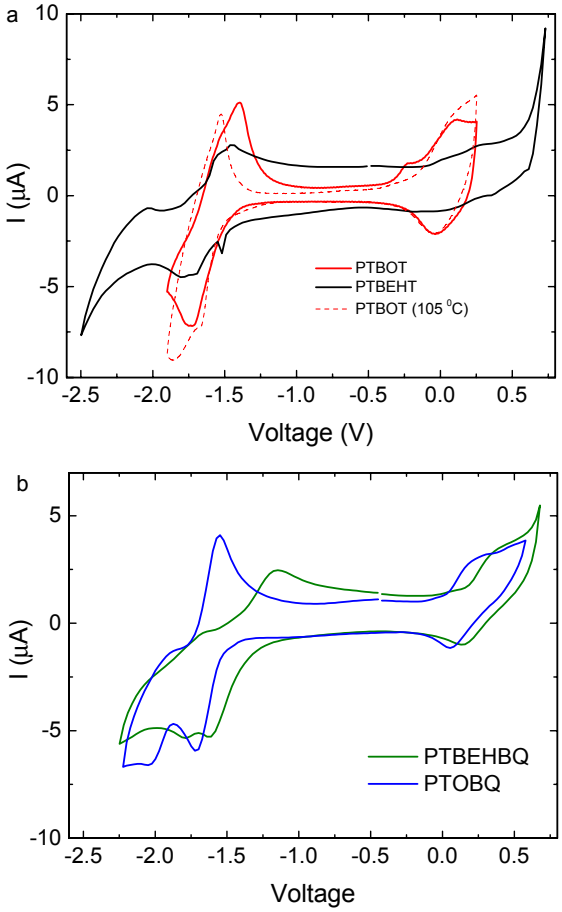

Figure S3. Cyclic voltammograms: (a) PTBOT (solid red line) and PTBEHT (black line) at room temperature, and PTBOT at 105 °C (dashed red line) (right). (b) PTOBQ (blue line) and PTBEHBQ (green line)

5. Morphology of the blends with [70]PCBM studied by AFM

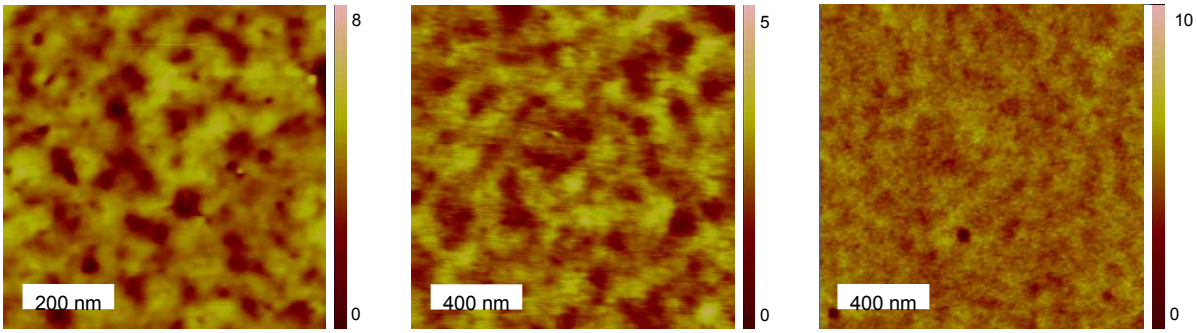

Figure S4. AFM height images of [70]PCBM blended with PTBOT:[70]PCBM (left), PTBEHT (middle), and PTOBQ (right), all spin coated from ODCB.