Supporting Information

Electronic structure of small band gap oligomers

based on cyclopentadithiophenes and acceptor units

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**Detailed synthetic procedures**

**General methods.** $^1$H-NMR and $^{13}$C-NMR spectra were recorded in CDCl$_3$ on a 400 MHz NMR (Varian Mercury, 400 MHz for $^1$H-NMR and 100 MHz for $^{13}$C-NMR), chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). IR spectra were recorded on a Perkin Elmer 1600 FT-IR. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry has been performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Recycling GPC was performed on a LC system equipped with JAIGEL 2H and JAIGEL 2.5H columns and a UV-detector, using a preparative flow cell (path length 0.5 mm). The eluent was chloroform at 3.5 mL/min, the injection volume was 2 mL. **Materials.** Solvents were purchased from Biosolve and used without further purification, unless stated otherwise. THF was distilled over 4 Å molsieves, pyridine was dried over 4 Å molsieves before use. Chemicals were purchased from Acros or Aldrich and used without purification. 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (1) and 2,5-dibromo-3,4-dinitrothiophene (7) were prepared following literature procedures.$^{1,2}$ Oxygen and moisture-sensitive reactions were performed under an argon atmosphere.

**2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (2).** This product was obtained as a by-product in the synthesis of 2,6-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene, following a literature procedure. The title compound was separated from the main product by recycling GPC. $^1$H-NMR (400 MHz): $\delta$ 7.43 (m, 2H, Ar-H), 7.17 (m, 2H, Ar-H), 6.92, (m, 2H, Ar-H), 1.85 (m, 4H, -C$_2$H$_2$CH(C$_2$H$_5$)(C$_4$H$_9$)), 1.35 (s, 12H, -BO$_2$C$_2$(CH$_3$)$_4$), 0.85 (m, 18H, alkyl-H), 0.74 (m, 6H, -CH$_3$), 0.58 (m, 6H, -CH$_3$). $^{13}$C-NMR (100 MHz): $\delta$ 160.97, 144.07, 131.87, 83.97, 52.66, 43.20, 35.13, 33.80, 28.31,
27.43, 24.77, 22.77, 14.08, 10.57. MALDI-TOF-MS: m/z 527.21 (20%), 528.20 (100), 529.21 (35), 530.20 (15), 531.20 (5).

2-(Tributylstannyl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (3). Compound 1 (215 mg, 0.53 mmol) was dissolved in THF (2 mL). At -78 °C, n-Butyllithium (0.215 mL, 2.5 M, 0.54 mmol) was added and the mixture was stirred at -78 °C for 2 h. Tributyltin chloride (0.145 mL, 0.53 mmol) was added and the mixture was stirred for 16 h, while warming to room temperature. Diethyl ether (15 mL) was added and the mixture was washed with water (3×5 mL), dried with MgSO₄ and the solvent was evaporated. Yield: 369 mg (> 99%). ¹H-NMR (400 MHz): δ 7.05 (d, J = 4.8 Hz, 1H, Ar-H), 6.93-6.88 (m, 2H, Ar-H), 1.90-1.82 (m, 4H, -C₆H₂CH(C₂H₅)(C₄H₉)), 1.63-1.52 (m, 6H, -C₆H₂C₃H₇), 1.40-1.30 (m, 6H, -C₂H₅C₂H₅), 1.13-1.06 (m, 6p, -C₂H₄C₂H₅), 1.06-0.82 (m, 27H, alkyl-H), 0.75 (t, J = 6.7 Hz, 6H, -CH₃), 0.58 (t, J=7.6 Hz, 6H, -CH₃)

5,8-Dibromoquinoxaline (4). 2,3-Diamino-1,4-dibromobenzene (2.45 g, 0.39 mmol) was dissolved in ethanol (30 mL). Glyoxal (1.5 mL, 40 wt. % solution in water) and two drops of dry triethylamine were added. The mixture was stirred at room temperature overnight. The white crystals that had formed were filtered off and recrystallized from ethanol to give white needles. Yield: 0.76 g (76%). ¹H-NMR (400 MHz): δ 9.01 (s, 2H, Ar-H), 8.00 (s, 2H, Ar-H). ¹³C-NMR (100 MHz): δ 146.03, 141.56, 133.72, 123.97.

4,7-Dibromo-2,1,3-benzothiadiazole (5). 2,1,3-Benzothiadiazole (10.18 g, 79.3 mmol) was dissolved in aqueous HBr (48 wt. %, 100 mL). At 150 °C, bromine (12 mL, 233 mmol) was added slowly. This mixture was stirred at 150 °C for 2 h and reaction mixture was cooled to room temperature. The mixture was filtered over a Büchner funnel; solids were washed extensively with water. Solids were dissolved in diethyl ether (1 L) and the mixture was washed with water and saturated NaCl. The solvent was evaporated and the product was
recrystallized from methanol to give off-white needles. Yield: 17.18 g (78 %). $^1$H-NMR (400 MHz): $\delta$7.72 (s, 2H, Ar-$H$) $^{13}$C-NMR (100 MHz): $\delta$152.96, 132.31, 113.87.

4,7-Dibromo-2,1,3-benzoxadiazole (6). To a melt of 2,1,3-benzoxadiazole (8.46 g, 40.4 mmol) with iron dust (93 mg, 1.6 mmol), bromine (15.2 g, 95 mmol) was added dropwise. The mixture was stirred at 90 °C for 2 h and the mixture was poured into water. A solution of sodium bisulfite was added until no gas evolution was observed. Solids were filtered, impregnated on silica and purified by column chromatography on silica, using heptane as the eluent. The product was recrystallized from ethanol to give yellow crystals. Yield: 8.40 g (75 %). $^1$H-NMR (400 MHz): $\delta$7.51 (s, 2H, Ar-$H$). $^{13}$C-NMR (100 MHz): $\delta$149.38, 134.17, 108.70.

5,8-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)quinoxaline (Q). To a mixture of compound 2 (36 mg, 68 μmol), 5,8-dibromoquinoxaline (4) (8 mg, 28 μmol), Aliquat 336 (one drop) and degassed aqueous 2M K$_2$CO$_3$ (0.3 mL) in degassed toluene (3 mL), a few grains of tetrakis(triphenylphosphine)palladium were added. The mixture was stirred overnight at 120 °C. Heptane (10 mL) was added and the mixture was washed with water. The product was purified by column chromatography on silica, using ethyl acetate/heptane as the eluent. Yield: 10 mg (16%). $^1$H-NMR (400 MHz): $\delta$8.98 (s, 2H, Ar-$H$), 8.11 (s, 2H, Ar-$H$), 7.72 (s, 2H, Ar-$H$), 7.18 (m, 2H, Ar-$H$), 6.97 (m, 2H, Ar-$H$), 1.90 (m, 8H, -CH$_2$CH(C$_2$H$_5$)(C$_4$H$_9$)), 0.95 (m, 36H, alkyl-$H$), 0.76 (m, 12H, -CH$_3$), 0.64 (m, 12H, -CH$_3$). $^{13}$C-NMR (100 MHz): $\delta$157.85, 157.10, 142.81, 139.60, 137.36, 131.90, 126.28, 124.83, 122.33, 122.29, 121.50, 121.42, 53.48, 53.41, 43.25, 35.10, 35.07, 34.22, 29.68, 28.62, 28.56, 28.05, 27.41, 27.33, 22.79, 22.76, 22.68, 14.07, 10.72, 10.60. IR: $\nu_{\text{max}}$/cm$^{-1}$ 2955, 2921, 2870, 2855, 1731, 1661, 1567, 1504, 1458, 1428, 1406, 1377, 1321, 1275, 1078,
939, 891, 861, 828, 798, 725, 708, 658. MALDI-TOF-MS: m/z 930.65 (100 %), 931.65 (70), 932.65 (40), 933.65 (15), 934.65 (5).

**4,7-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)-2,1,3-benzothiadiazole (BT)**. This compound was prepared following the same procedure as for Q, using compound 2 (325 mg, 0.61 mmol) and 4.7-dibromo-2,1,3-benzothiadiazole (5) (90 mg, 0.30 mmol). Yield: 71 mg (25 %). $^1$H -NMR (400 MHz): $\delta$ 8.05 (m, 2H, Ar-H), 7.82 (m, 2H, Ar-H), 7.19 (m, 2H, Ar-H), 6.97 (m, 2H, Ar-H), 1.97 (m, 8H, -CH$_2$CH(C$_2$H$_5$)(C$_4$H$_9$)), 0.95 (m, 36H, alkyl-H), 0.75 (m, 12H, -CH$_3$), 0.63 (m, 12H, -CH$_3$). $^{13}$C-NMR: (100 MHz) $\delta$ 158.55, 158.29, 152.53, 139.04, 138.73, 136.97, 126.04, 125.23, 124.15, 53.72, 43.27, 43.16, 35.16, 35.13, 34.18, 29.70, 28.63, 28.53, 27.45, 27.33, 22.77, 14.12, 14.08, 14.04, 10.76, 10.63. IR: $\nu_{max}$/cm$^{-1}$ 2955, 2921, 2854, 1668, 1574, 1563, 1533, 1505, 1478, 1458, 1428, 1397, 1377, 1339, 1269, 1181, 1082, 885, 859, 826, 798, 708, 659. MALDI-TOF-MS: m/z 936.23 (100 %), 937.24 (70), 938.23 (45), 939.23 (20), 940.23 (5).

**4,7-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)-2,1,3-benzoxadiazole (BO)**. This compound was prepared following the same procedure as for Q, using compound 2 (32 mg, 61 $\mu$mol) and 4.7-dibromo-2,1,3-benzoxadiazole (6) (8 mg, 29 $\mu$mol). Yield: 20 mg (72 %). $^1$H -NMR (400 MHz): $\delta$ 8.05 (s, 2H, Ar-H), 7.53 (s, 2H, Ar-H), 7.22 (m, 2H, Ar-H), 6.98 (m, 2H, Ar-H), 1.96 (m, 8H, -CH$_2$CH(C$_2$H$_5$)(C$_4$H$_9$)), 0.90 (m, 36H, alkyl-H), 0.75 (m, 12H, -CH$_3$), 0.63 (m, 12H, -CH$_3$). $^{13}$C-NMR (100 MHz): $\delta$ 159.19, 158.95, 147.86, 138.61, 137.59, 136.57, 125.89, 124.46, 124.07, 122.48, 121.88, 53.88, 43.18, 43.14, 43.05, 35.17, 34.15, 28.61, 28.50, 27.43, 27.31, 22.75, 14.05, 13.95, 13.91, 10.74, 10.60. IR: $\nu_{max}$/cm$^{-1}$ 2956, 2921, 2855, 1668, 1591, 1531, 1459, 1425, 1407, 1378, 1326, 1261, 1188, 1113, 1079, 1015, 895, 873, 832, 799, 709, 661. MALDI-TOF-MS: m/z 920.46 (100 %), 921.46 (70), 922.46 (40), 923.45 (15).
2,5-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2-yl)-3,4-
dinitrothiophene (8). compound 3 (396 mg, 0.53 mmol) and 2,5-dibromo-3,4-
dinitrothiophene (7) were dissolved in THF (2 mL). Bis(triphenylphosphine)palladium(II) 
dichloride (9 mg, 13 μmol) was added and the mixture was stirred at 70 °C for 2 h. The 
solvent was evaporated and the crude product was purified by flash chromatography on silica, 
using ethyl acetate/heptane as the eluent. Yield: 234 mg (94 %). 1H-NMR (400 MHz): δ 7.24 
t, J = 1.8 Hz, 2H, Ar-H), 7.31 (d, J = 4.9 Hz, 2H, Ar-H), 6.98 (m, 2H, Ar-H), 1.99-1.86 (m, 
8H, -CH2CH(C2H5)(C4H9)), 1.44-1.31 (m, 4H, -CH2CH(C2H5)(C4H9)), 1.10-0.82 (m, 32H, alkyl-H), 0.80-0.73 (m, 12H, -CH3), 0.66-0.54 (m, 12H, -CH3). 13C-NMR (100 MHz): δ 
160.18, 158.41, 143.95, 135.78, 134.65, 127.87, 126.79, 126.08, 125.98, 122.50, 54.06, 43.10, 
35.16, 34.27, 34.16, 28.61, 28.57, 28.27, 27.38, 27.28, 26.76, 22.79, 22.71, 17.28, 14.09, 
14.04, 13.57, 10.63. IR: νmax/cm−1 2956, 2922, 2871, 2855, 1546, 1459, 1425, 1376, 1308, 
1181, 733, 709, 664. MALDI-TOF-MS: m/z 974.23 (100 %), 975.23 (65), 976.23 (40), 
977.22 (20), 978.22 (10).

2,5-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2-yl)-3,4-
diaminothiophene (9). compound 8 (234 mg, 0.24 mmol) and tin(II) chloride (650 mg, 2.9 
mmol) were dissolved in ethyl acetate (5 mL). The mixture was stirred at reflux for 2 h, 
cooled to room temperature and added to Na2CO3 (0.25 M, 20 mL). Dichloromethane (20 
ml) was added, the mixture was stirred vigorously and filtered over celite. Phases were 
separated and the organic phase was washed with water (3×30 mL), dried with MgSO4 and 
the solvent was evaporated. Yield: 220 mg (>99 %). 1H-NMR (400 MHz): δ 7.12 (d, J = 4.8 
Hz, 2H, Ar-H), 6.97-6.91 (m, 4H, Ar-H), 3.73 (s, 4H, -NH2), 1.95-1.82 (m, 8H, 
-CH2CH(C2H5)(C4H9)), 1.41-1.22 (m, 4H, -CH2CH(C2H5)(C4H9)), 1.14-0.83 (m, 32H, alkyl-
H), 0.83-0.71 (m, 12H, -CH3), 0.71-0.56 (m, 12H, -CH3). 13C-NMR (100 MHz): δ 158.03,
157.17, 136.77, 135.76, 134.93, 133.12, 124.27, 122.29, 119.28, 111.36, 53.64, 43.21, 35.07, 35.04, 34.22, 34.19, 28.68, 28.59, 27.82, 27.33, 22.81, 22.74, 14.09, 14.06, 10.71, 10.64. IR: ν_{max}/cm^{-1} 2956, 2922, 2871, 2855, 1613, 1457, 1377, 906, 732. MALDI-TOF-MS: m/z 914.37 (100 %), 915.37 (65), 916.36 (45), 917.36 (20), 918.36 (5).

5,7-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)thieno[3,4-b]pyrazine (TP-a). Compound 9 (110 mg, 0.12 mmol) was dissolved in ethanol (3 mL). Glyoxal (40 %, 0.1 mL) was added and the mixture was stirred at reflux for 2 h. The solvent was evaporated and the product was purified by flash chromatography on silica, using ethyl acetate/heptane and dichloromethane/heptane as the eluents. The product was further purified by recycling GPC. Yield: 59 mg (52 %). \(^1\)H-NMR (400 MHz): δ 8.47 (s, 2H, Ar-H), 7.43 (m, 2H, Ar-H), 7.18 (m, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 2.00-1.85 (m, 8H, -C\(_2\)H\(_2\)CH(C\(_2\)H\(_5\))(C\(_4\)H\(_9\))), 1.10-0.85 (m, 36H, alkyl-H), 0.80-0.58 (m, 24H, -C\(_3\)H\(_3\)). \(^{13}\)C-NMR (100 MHz): δ 158.10, 158.79, 143.70, 139.31, 139.02, 136.95, 133.74, 125.56, 125.21, 122.35, 119.44, 53.55, 43.31, 43.25, 43.16, 35.13, 34.18, 28.62, 28.55, 28.33, 27.42, 27.33, 22.82, 22.79, 22.75, 14.07, 10.73, 10.60, 10.57, 43.36. IR: ν_{max}/cm^{-1} 2955, 2919, 2867, 1509, 1457, 1406, 1377, 1179, 1113, 1020, 974, 891, 852, 797, 706. MALDI-TOF-MS: m/z 936.36 (100 %), 937.36 (70), 938.36 (45), 939.35 (20), 940.35 (5).

8,10-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)acenaphtho[1,2-e]thieno[3,4-b]pyrazine (TP-b). Compound 9 (110 mg, 0.12 mmol) and acenaphthenequinone (33 mg, 0.18 mmol) were dissolved in ethanol (3 mL) and the mixture was stirred at reflux for 16 h. The solvent was evaporated and the product was purified by flash chromatography on silica, using ethyl acetate/heptane and dichloromethane/heptane as the eluents. Yield: 66 mg (52 %). \(^1\)H-NMR (400 MHz): δ 8.41 (d, J = 6.9 Hz, 2H, Ar-H), 8.08 (d, J = 8.2 Hz, 2H, Ar-H), 7.85 (t, J = 7.4 Hz, 2H, Ar-H), 7.49 (s, 2H, Ar-H), 7.20 (s, 2H, Ar-
H), 6.98 (s, 2H, Ar-H), 2.04-1.87 (m, 8H, -CH2CH(C2H5)(C4H9)), 1.10-0.85 (m, 36H, alkyl-H), 0.82-0.60 (m, 24H, -CH3). 13C-NMR (100 MHz): δ 158.01, 157.60, 153.14, 139.48, 138.16, 137.64, 137.26, 134.59, 131.51, 130.04, 128.77, 128.44, 125.58, 124.94, 122.38, 121.08, 119.11, 53.49, 43.41, 43.30, 35.17, 34.26, 34.21, 29.70, 28.68, 28.62, 28.59, 27.41, 22.92, 22.88, 22.82, 22.69, 14.15, 14.12, 10.77, 10.70, 10.67. IR: νmax/cm−1 2955, 2919, 2870, 2854, 1458, 1418, 1377, 1282, 1214, 1176, 1115, 1078, 1033, 891, 823, 798, 769, 706. MALDI-TOF-MS: m/z 1060.45 (100 %), 1061.45 (75), 1062.45 (50), 1063.45 (25), 1064.45 (10).

4,6-Di(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2-yl)thieno[3,4-c][1,2,5]thiadiazole (TT). Compound 9 (89 mg, 0.10 mmol) was dissolved in pyridine (3 mL). N-thionylaniline (0.03 mL, 0.26 mmol) an chlorotrimethylsilane (0.03 mL, 0.23 mmol) were added and the mixture was stirred for 16 h at 80 °C. The solvent was evaporated and the mixture was purified by flash chromatography on silica, using ethyl acetate/heptane and dichloromethane/heptane as the eluents. The product was further purified by recycling GPC. Yield: 33 mg (36 %). 1H-NMR (400 MHz): δ 7.41 (t, J = 4.8 Hz, 2H, Ar-H), 7.18 (d, J = 4.8 Hz, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 1.98-1.85 (m, 8H, -CH2CH(C2H5)(C4H9)), 1.10-0.85 (m, 36H, alkyl-H), 0.79-0.58 (m, 24H, -CH3). 13C-NMR (100 MHz): δ 159.16, 158.18, 156.29, 137.50, 136.84, 135.11, 125.33, 122.41, 112.14, 53.67, 43.31, 43.20, 43.16, 35.17, 34.15, 28.62, 28.53, 27.39, 27.33, 22.80, 22.77, 14.07, 10.73, 10.61. IR: νmax/cm−1 2955, 2918, 2870, 2854, 1504, 1480, 1457, 1398, 1377, 1181, 829, 797, 706. MALDI-TOF-MS: m/z 942.19 (100 %), 943.19 (70), 944.19 (50), 945.19 (20), 946.18 (10).