

**Supporting Information for**  
**Alternating Quinoxaline/Oligothiophene Copolymers**  
**Synthesis and Unexpected Absorption Properties**

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### *Experimental Section*

The UV-vis spectra were measured with a JASCO V-550 UV-Vis spectrophotometer. The emission spectra were recorded using a CARY Eclipse fluorescence spectrophotometer; the IR spectra using a JASCO FT/IR-4200 fourier transform spectrometer. The NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were measured on a Bruker ARX 400 (400 MHz) spectrometer using solutions in CDCl<sub>3</sub> (internally referenced to Me<sub>4</sub>Si); *J* values are given in Hz.

TLC was carried out on dry silica gel plates. For chromatography silica gel with a pore size 0.06-0.2 nm and aluminum oxide (pH 7.0±0.5) with a pore size 0.05-0.15 nm were used. Mass spectra were obtained on a Varian MAT 311A instrument with an electrospray ionization source (ESIMS). The microwave-promoted synthesis was carried out in a Discover (CEM) utilizing sealed reaction vials. The temperature inside the vial is monitored by an IR sensor; the pressure is monitored by the bowing of the septum of the vial by a hydraulic system. The polymerizations were performed under temperature control with a microwave power of 300 W.

All reactions were carried out under an argon atmosphere using the usual Schlenk techniques. All solvents were of reagent grade and used as received, unless otherwise specified. 4-Bromophenylboronic acid was purchased from Sigma-Aldrich, *o*-phenylenediamine, 2,3-diaminonaphthalene and 2-(tri-*n*-butylstannyl)thiophene were delivered by Acros. *n*-Octylboronic acid and *isopropyl* pinacolborate were supplied by Lancaster. 2,5-Bis(trimethylstannyl)thiophene [1], 5,5'-bis(trimethylstannyl)-2,2'-bithiophene [2], 3,6-dibromobenzene-1,2-diamine [3], octadecane-9,10-dione [4] and 1,2-bis(4'-octylbiphenyl-4-yl)-ethan-1,2-dione [5] were prepared according to literature procedures.

CV was carried out on drop-cast polymer films at room temperature in a glove-box. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, electrochemical grade, Aldrich), ca. 0.1 M in anhydrous acetonitrile (Aldrich). The working electrode (WE) as well as the counter electrode (CE) was a platinum foil. As a reference electrode (RE) a silver wire coated with AgCl was used. After each measurement the RE was calibrated with ferrocene ( $E^\circ = 400$  mV vs. NHE) and the potential axis was corrected to NHE (using  $-4.75$  eV for NHE) according to the difference of  $E^\circ$

(ferrocene) and the measured  $E_{1/2}$  (ferrocene). The onset for oxidation and reduction was determined as the point where the CV trace differed from the baseline by more than 1 mA relative to the baseline.

**5,8-Dibromo-2,3-bis(4'-octylbiphenyl-4-yl)quinoxaline (1a).** A mixture of 1,2-bis(4'-octylbiphenyl-4-yl)ethan-1,2-dione (442 mg, 7.5 mmol) and 3,6-dibromobenzene-1,2-diamine (199.4 mg, 7.5 mmol) in glacial acetic acid (30 ml) was heated for 12 h at 130 °C. The white precipitate was filtered off and washed with glacial acetic acid (100 ml). Recrystallization of the product from *n*-hexane gave a white powder in 83% yield (682 mg).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.83 (t,  $^3J = 6.61$  Hz, 6H, i), 1.25-1.18 (m, 20H, h-d), 1.70 (quintett,  $^3J = 6.61$  Hz, 4H, c), 2.59 (t,  $^3J = 7.62$  Hz, 4H, b), 7.21 (d,  $^3J = 8.13$  Hz, 4H, 1), 7.51 (d,  $^3J = 8.13$  Hz, 4H, 2), 7.58 (d,  $^3J = 8.13$  Hz, 4H, 3), 7.71 (d,  $^3J = 8.13$  Hz, 4H, 4), 7.87 (s, 2H, 5).  $^{13}\text{C-NMR}$  (100 MHz),  $\text{CDCl}_3$ ):  $\delta$  14.41, 22.88, 29.44, 29.59, 29.67, 32.07, 31.57, 35.79, 123.96, 136.65, 137.39, 139.53, 142.45, 143.25, 127.12, 127.22, 129.32, 131.02, 131.46, 159.94. IR: 3073, 3019 (C-H, arom.), 2905, 2854 (C-H, aliph.), 1595, 1506 (C=C, C=N), 1330, 1180, 1064, 982, 803. Mass (EI): calculation for  $\text{C}_{48}\text{H}_{52}\text{Br}_2\text{N}_2$  (M+H) $^+$ : 814.2 found 816. Elem. Anal. Calcd. for  $\text{C}_{48}\text{H}_{52}\text{Br}_2\text{N}_2$ : C 70.59, H 6.42, N 3.43. Found: C 70.84, H 5.88, N 3.34.

**5,8-Dibromo-2,3-dioctylquinoxaline (1b).** A mixture of octadecane-9,10-dione (772 mg, 0.0027 mmol) and 3,6-dibromobenzene-1,2-diamine (708.5 mg, 0.0027 mmol) in glacial acetic acid (30 ml) was heated for 12 h at 130 °C. The white precipitate was filtered off and washed with glacial acetic acid (50 ml). Recrystallization of the product from acetic acid afforded a white powder in 70% yield (778.9 mg).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.91 (t,  $^3J = 7.03$  Hz, 6H, i), 1.30-1.52 (m, 20H, h-d), 1.96 (quintett,  $J = 7.41$  Hz, 4H, c), 3.09 (t,  $^3J = 7.62$  Hz, 4H, b).  $^{13}\text{C-NMR}$  (100 MHz),  $\text{CDCl}_3$ ): 14.07, 22.65, 27.75, 29.24, 31.86, 34.74, 123.35, 131.92, 139.29, 158.24. IR: 2915, 2848, 1463, 1450, 1397, 1372, 1298, 1268, 1171, 1123, 1103, 934, 814, 728. Mass (EI): calculation for  $\text{C}_{18}\text{H}_{34}\text{O}_2$  (M+H) $^+$ : 510.12, found 512. Elem. Anal. Calcd. for  $\text{C}_{24}\text{H}_{36}\text{Br}_2\text{N}_2$ : C 56.28, H 7.07, N 5.47. Found: C 56.19, H 7.11, N 5.39.

**2,3-Bis(4'-octylbiphenyl-4-yl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (2a).**

**2,3-Bis(4'-octylbiphenyl-4-yl)-5,8-bis(thiophen-2-yl)quinoxaline (A) [6].** In a 250 ml three neck flask **1a** (1.72 g, 2.1 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (117.9 mg, 0.168 mmol) and KF (1.2 g, 21 mmol) were mixed, evacuated and the flask filled with argon. After addition of THF (50 ml) the mixture was heated to 80 °C. Then, 2-(tri-*n*-butylstannyl)thiophene (1.87 g, 5 mmol) was added *via* a syringe and the reaction mixture stirred for 24 h. The mixture was treated with  $\text{H}_2\text{O}$  (100 ml) and extracted with  $\text{CHCl}_3$  (3  $\times$  100 ml). The combined organic phases were dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. Purification by column chromatography (aluminium oxide, *n*-hexane/EtOAc 9/1 v/v) gave 1.65 g of an orange solid (yield: 80%).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0,9 (t,  $^3J = 7.12$  Hz, 6H), 1.39-1.30 (m, 20H), 1.70 (quintett,  $^3J = 7.62$  Hz, 4H), 2.68 (t,  $^3J = 7.62$  Hz, 4H), 7.22 (m, 2H), 7.29 (d,  $^3J = 8.13$  Hz, 4H), 7.55 (dd,  $^3J = 5.08$  Hz,  $^4J = 1.01$  Hz, 2H), 7.60 (d,  $^3J = 8.13$  Hz, 4H), 7.66 (d,  $^3J = 8.13$  Hz, 4H), 7.89 (d,  $^3J = 8.64$  Hz, 4H), 7.91 (dd,  $^3J = 5.08$  Hz,  $^4J = 1.01$  Hz, 2H), 8.16 (s, 2H).  $^{13}\text{C-NMR}$  (100 MHz),  $\text{CDCl}_3$ ):  $\delta$  14.07, 22.66, 29.26, 29.35, 29.48, 31.45, 31.89, 35.65, 126.44, 126.62, 126.73, 126.94, 127.04, 128.82, 128.91, 130.92, 131.33, 137.26, 137.33, 137.66, 138.85, 141.70, 142.60, 151.44. UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 398$ , 444 (sh), and 423 (sh) nm. Emission ( $\text{CHCl}_3$ ,  $\lambda_{\text{ex}} = 320$  nm):  $\lambda_{\text{max}} = 551$  nm. IR: 3023 (C-H, arom.), 2960, 2925, 2850 (C-H, aliph.), 1711, 1255, 962, 825, 807, 687, 607. Mass (EI): calculation for  $\text{C}_{56}\text{H}_{58}\text{N}_2\text{S}_2$  ( $\text{M}+\text{H}^+$ ): 822.4 found 822.3. Elem. Anal. Calcd. for  $\text{C}_{56}\text{H}_{58}\text{N}_2\text{S}_2$ : C 81.71, H 7.1, N 3.40, S 7.79. Found: C 82.52, H 7.05, N 3.34, S 7.55. TGA (Ar, 51.8% weight loss): 456 °C. DSC:  $T_c = 95^\circ\text{C}$ ,  $T_m = 166^\circ\text{C}$ .

**2,3-Bis(4'-octylbiphenyl-4-yl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (B) [7].** A solution of 2,3-bis(4'-octylbiphenyl-4-yl)-5,8-bis(thiophen-2-yl)quinoxaline (550 mg, 0.67 mmol) in acetic acid was protected from light and cooled to 0 °C. Then NBS (243.8 mg, 1.37 mmol) was added in small portions over 30 min. The solution was stirred for 3 h, the formed precipitate filtered off and washed with water. The solid was dissolved in  $\text{CHCl}_3$  (1-2 ml) and precipitated into *n*-hexane. The orange product was obtained in 85% yield (558 mg).

$^1\text{H-NMR}$  (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0,83 (t,  $^3J = 6.65$  Hz, 6H), 1.21-1.26 (m, 20H), 1.61 (quintett,  $^3J = 7.47$  Hz, 4H), 2.60 (t,  $^3J = 7.58$  Hz, 4H), 7.10 (d,  $^3J = 4.02$  Hz, 2H), 7.22 (d,  $^3J = 8.14$  Hz, 4H), 7.51 (d, 2H), 7.55 (d,  $^3J = 8.43$  Hz, 4H), 7.62 (d,  $^3J = 8.42$  Hz, 4H), 7.75 (d,  $^3J = 8.83$  Hz, 4H), 8.16 (s, 2H).  $^{13}\text{C-NMR}$  (100 MHz),  $\text{CDCl}_3$ ):  $\delta$  14.41, 22.89, 29.45, 29.57, 29.67, 31.56, 32.07, 35.79, 117.13, 125.61, 125.71, 126.76, 126.95, 128.93, 129.16, 130.62, 130.94, 136.68, 136.82, 137.52, 139.68, 141.91, 142.70, 151.92. UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 275$  (sh), 325, 404 (sh), and 459 (sh) nm. Emission ( $\text{CHCl}_3$ ,  $\lambda_{\text{ex}} = 330$  nm):  $\lambda_{\text{max}} = 558$  nm. IR: 2954, 2917, 2848, 1463, 1390, 1375, 1283, 1211, 1165, 1139, 1064, 1043, 965, 914, 838, 831, 734, 721. Mass (EI): calculation for  $\text{C}_{56}\text{H}_{58}\text{N}_2\text{S}_2$  ( $\text{M}+\text{H}^+$ ): 978.23 found 978.2. Elem. Anal. Calcd. for  $\text{C}_{56}\text{H}_{58}\text{Br}_2\text{N}_2\text{S}_2$ : C 68.56, H 5.75, N 2.86, S 6.54. Found: C 68.45, H 5.85, N 2.79, S 6.8.

### **2,3-Dioctyl-5,8-bis(5-bromothiophen-2-yl)quinoxaline (2b)**

**2,3-Dioctyl-5,8-bis(thiophen-2-yl)quinoxaline (A).** In a 250 ml three neck flask **1b** (700 mg, 1.37 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (96 mg, 0.128 mmol) and KF (792 mg, 14 mmol) were mixed, evacuated and the flask filled with argon. After the addition of dry THF (50 ml) the mixture was heated to 80 °C. Then 2-(tri-*n*-butylstannyl)thiophene (1.17 g, 1.37 mmol) was added *via* a syringe and the reaction mixture stirred for 24 h. The mixture was treated with  $\text{H}_2\text{O}$  (100 ml) and extracted with  $\text{CHCl}_3$  ( $3 \times 100$  ml). The combined organic phases were dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced

pressure. Purification by column chromatography (aluminium oxide, *n*-hexane/toluol 9/1 v/v) yielded 425 mg of an orange solid (yield: 60%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0,91 (t, <sup>3</sup>J = 7.12 Hz, 6H), 1.25-1.55 (m, 20H), 2.04 (quintett, <sup>3</sup>J = 7.62 Hz, 4H), 3.10 (t, <sup>3</sup>J = 7.62 Hz, 4H), 7.19 & 7.16 (m, 2H), 7.50 (d, <sup>3</sup>J = 5.08 Hz, 2H), 7.86 (d, <sup>3</sup>J = 4.31 Hz, 4H), 8.06 (s, 2H). <sup>13</sup>C-NMR (100 MHz), CDCl<sub>3</sub>): δ 14.01 22.69, 29.41, 29.26, 29.57, 29.59, 31.92, 34.95, 126.97, 126.11, 126.42, 128.29, 130.94, 137.29, 139.12, 155.45. UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 280, 315 (sh), and 425 (sh) nm. Emission (CHCl<sub>3</sub>, λ<sub>ex</sub> = 280 nm): λ<sub>max</sub> = 536 nm. IR: 2954, 2919, 2848, 2361, 1520, 1463, 1419, 1393, 1376, 1293, 1256, 1232, 1223, 1165, 1140, 1117, 1090, 1063, 921, 849, 840, 834, 828, 820, 746. Mass (EI): calculation for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>S<sub>2</sub> (M+H)<sup>+</sup>: 518.28 found 517.8. Elem. Anal. Calcd. for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>S<sub>2</sub>: C 74.08, H 8.16, N 5.40, S 12.36. Found: C 74.61, H 8.23, N 5.38, S 12.80.

**2,3-Dioctyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (B).** A solution of 2,3-dioctyl-5,8-bis(thiophen-2-yl)quinoxaline (549.7mg, 1.1 mmol) in DMF (250 ml) was protected from light and cooled to -20 °C. Then a solution of NBS (386.6 mg, 2.17 mmol) in DMF (50 ml) was slowly added. The mixture was stirred at -20 °C for 1 h, and then allowed to warm to room temperature. Stirring was continued for 5 h, and the mixture was poured into cold water (100 ml). The precipitate was filtered off, redissolved in CHCl<sub>3</sub> (2-3 ml) and precipitated into methanol. After filtration, a light orange product was obtained in 89% yield (602 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89 (t, <sup>3</sup>J = 6.68 Hz, 6H), 1.53-1.31 (m, 20H), 2.06 (quintett, <sup>3</sup>J = 7.52 Hz, 4H), 3.11 (t, <sup>3</sup>J = 7.51 Hz, 4H), 7.10 (d, <sup>3</sup>J = 4.05 Hz, 2H), 7.52 (d, <sup>3</sup>J = 4.01 Hz, 2H), 7.98 (s, 2H). <sup>13</sup>C-NMR (100 MHz), CDCl<sub>3</sub>): δ 14.11, 22.69, 28.03, 29.24, 29.60, 31.94, 32.05, 35.96, 116.75, 124.88, 125.06, 128.88, 130.24, 139.85, 155.90. UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 280, 315 (sh), and 425 (sh) nm. Emission (CHCl<sub>3</sub>, λ<sub>ex</sub> = 280 nm): λ<sub>max</sub> = 536 nm. IR: 2954, 2919, 2848, 2361, 1520, 1463, 1419, 1393, 1376, 1293, 1256, 1232, 1223, 1165, 1140, 1117, 1090, 1063, 921, 849, 840, 834, 828, 820, 746. Mass (EI): calculation for C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub> (M+H)<sup>+</sup>: 674.1 found 675.3. Elem. Anal. Calcd. for C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C 56.80, H 5.96, N 4.14, S 9.48. Found: C 56.85, H 6.13, N 4.05, S 8.81.

### Polymer Synthesis: 3a-series

**Copolymer based on 2,5-bis(trimethylstannyl)thiophene and 5,8-dibromo-2,3-bis(4'-octylbiphenyl-4-yl)quinoxaline (3a1).** In a 8 ml microwave vial 2,5-bis(trimethylstannyl)thiophene (50.2 mg, 0.12 mmol) and 5,8-dibromo-2,3-bis(4'-octylbiphenyl-4-yl)quinoxaline (**1a**) (117,7 mg, 0,12 mmol) were mixed. Subsequently, THF (5ml), KF (55.7 mg, 0.96 mmol) and PdCl<sub>2</sub>(PPH<sub>3</sub>)<sub>2</sub> (6.8 mg, 0.0096 mmol) were added and the mixture reacted at 110 °C for 13 min at a microwave power of 300 W. Afterwards the reaction mixture was poured into CHCl<sub>3</sub> (50 ml). The organic phase was separated and washed with H<sub>2</sub>O, saturated NaEDTA (3 × 50 ml) and saturated NaCl solution (2 × 50 ml) and then concentrated under reduced pressure. The alternating copolymer was precipitated into MeOH.

The raw polymer was washed/fractionated by Soxhlet extraction with ethyl acetate and CHCl<sub>3</sub>. The chloroform fraction was characterized and used. 60 mg of the copolymer **3a1** was obtained (yield: 65%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87, 1.27-1.52, 2.65, 7.72-7.72 (m). UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 271, 319 (sh), 363, and 605 nm. IR: 3050, 3012, 2912, 2849, 1605, 1498, 1461, 1437, 1333, 1226, 1187, 1094, 1059, 1004, 781. TGA (Ar, 2.2% weight loss): 357.8 °C; (Ar, 23.54% weight loss): 484.7 °C. DSC: T<sub>g</sub> = 92 °C. GPC (THF): M<sub>n</sub> = 18.000, PDI = 1.90. Sulphur Elem. Anal. Calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>S: S 4.33. Found: S 3.85.

**Copolymer based on 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 5,8-dibromo-2,3-bis(4'-octylbiphenyl-4-yl)quinoxaline (3a2).** The copolymer **3a2** was prepared by employing the already described procedure (for **3a1**). 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (60.2 mg, 0.12 mmol) was used as the second coupling monomer. After extracting with ethyl acetate the copolymer **3a2** was obtained in 65% yield (70.3 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89, 1.26, 1.53, 7.42-7.72 (m). UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 271, 312 (sh), 387, and 614 nm. IR: 3060, 3021, 2911, 2857, 1494, 1462, 1435, 1339, 1227, 1186, 1050, 1050, 1005, 783. TGA (Ar, 2.3 % weight loss): 308.5 °C; (Ar, 34.0 % weight loss): 484.8 °C. DSC: T<sub>g</sub> = 131.9 °C. GPC (THF): M<sub>n</sub> = 62.700, PDI = 1.83. Sulphur Elem. Anal. Calcd. for C<sub>56</sub>H<sub>58</sub>N<sub>2</sub>S<sub>2</sub>: S 7.79. Found: S 8.81.

**Copolymer based on 2,5-bis(trimethylstannyl)thiophene and 2,3-bis(4'-octylbiphenyl-4-yl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (3a3).** Copolymer **3a3** was prepared by employing the already described procedure (for **3a1**). 0.1 mmol of both monomers have been reacted. After extracting with ethyl acetate the copolymer **3a3** was obtained in 73% yield (70 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.84, 1.26-1.53, 2.86, 6.88-7.82 (m). UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 271, 382 (sh), 363, and 606 nm. IR: 3021, 2911, 2841, 1556, 1523, 1497, 1437, 1335, 1227, 1187, 1005, 965, 799. TGA (Ar, 37.6% weight loss): 485.3 °C. DSC: T<sub>g</sub> = 95.4 °C. GPC (THF): M<sub>n</sub> = 40.500, PDI = 2.54. Sulphur Elem. Anal. Calcd. for C<sub>60</sub>H<sub>60</sub>N<sub>2</sub>S<sub>3</sub>: S 10.63. Found: S 10.74.

**Copolymer based on 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 2,3-bis(4'-octylbiphenyl-4-yl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (3a4).** The polymer **3a4** was prepared by employing the already described procedure (for **3a1**). 0.2 mmol of both monomers have been reacted. After extracting with ethyl acetate the copolymer **3a4** was obtained in 54% yield (107 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.84 (s) 1.27-1.48 (m). UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 271, 380 (sh), and 605 nm. IR: 3058, 3027, 2918, 2841, 1603, 1494, 1377, 1334, 1226, 1187, 1097, 1056, 1004, 961, 782. TGA (Ar, 28.2% weight loss): 335.3 °C. DSC: T<sub>g</sub> = 70.4 °C. GPC (THF): M<sub>n</sub> = 26.000, PDI = 1.65. Sulphur Elem. Anal. Calcd. for C<sub>64</sub>H<sub>62</sub>N<sub>2</sub>S<sub>4</sub>: S 12.99. Found: S 12.03.

### Synthesis: **3b**-series

The synthesis of the **3b**-series follows the protocol described for the **3a**-series. The copolymers were washed/fractionated by Soxhlet extraction with methanol, toluene and CHCl<sub>3</sub>. After precipitation into MeOH the copolymers have been isolated by centrifugation. The estimation of the molecular weights by GPC was impossible due to the very poor solubility.

**Copolymer based on 2,5-bis(trimethylstannyl)thiophene and 5,8-dibromo-2,3-dioctylquinoxaline (3b1).** 5,8-dibromo-2,3-dioctylquinoxaline (**1b**) (93.6 mg, 0.18 mmol) was reacted with 2,5-bis(trimethylstannyl)thiophene (73.75 mg, 0.18 mol). **3b1** was obtained in 97% yield (80.5 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 0.83 (m), 1.25-2.04 (m), 3.12 (m), 7.45-7.73 (m). UV-Vis (thiophene): λ<sub>max</sub> = 283, 348 (sh), 533, and 629 nm. IR: 3058, 2918, 2848, 1558, 1522, 1459, 1434, 1393, 1377, 1286, 1144, 1097, 829, 798, 753, 720, 689, 664. TGA (Ar, 6.03% weight loss): 283.2 °C; (Ar, 50.58% weight loss): 466.5%. DSC: T<sub>g</sub> = 76.98°C.

**Copolymer based on 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 5,8-Dibromo-2,3-dioctylquinoxaline (3b2).** 5,8-dibromo-2,3-dioctylquinoxaline (**1b**) (98.6 mg, 0.19 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (94.65 mg, 0.19 mmol) have been reacted. **3b2** was obtained in 88% yield (90 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.81(s) 1.17-1.40 (m), 3.05 (m), 7.19-8.02. UV-Vis (thiophene): λ<sub>max</sub> = 273; λ<sub>shoulder</sub> = 273, 376 (sh), 571, and 627 nm. IR: 3066, 2918, 2841, 1564, 1513, 1469, 1434, 1387, 1374, 1336, 1286, 1165, 1144, 1052, 922, 821, 782, 722, 689. TGA (Ar, 4.14% weight loss): 298.8 °C; (Ar, 57.52% weight loss): 472%. DSC: T<sub>g</sub> = 87.23°C.

**Copolymer based on 2,5-bis(trimethylstannyl)thiophene and 2,3-dioctyl-5,8-bis(5-bromothiophen-2-yl)quinoxaline (3b3).** 2,3-dioctyl-5,8-bis(5-bromothiophen-2-yl)quinoxaline (**2b**) (204.2 mg, 0.30 mmol) and 2,5-bis(trimethylstannyl)thiophene (123.7 mg, 0.30 mmol) have been reacted. **3b3** was obtained in 91% yield (185 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.84 (s) 1.27-1.48 (m), 3.15 (m), 7.49-7.70 (m). UV-Vis (thiophene): λ<sub>max</sub> = 290, 391 (sh), 578, and 632 nm. IR: 3058, 2911, 2841, 1558, 1461, 1436, 1395, 1375, 1288, 1165, 1140, 1066, 831, 784, 753, 720, 687, 668, 644. TGA (Ar, 2.92% weight loss): 295 °C; (Ar, 49.91% weight loss): 472%. DSC: T<sub>g</sub> = 84.6°C.

**Copolymer based on 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 2,3-dioctyl-5,8-bis(5-bromothiophen-2-yl)quinoxaline (3b4).** 2,3-dioctyl-5,8-bis(5-bromothiophen-2-yl)-quinoxaline (**2b**) (194.6 mg, 0.28 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (141.5 mg, 0.28 mmol) have been reacted. **3b4** was obtained in 95% yield (182 mg).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 0.84 (m), 1.26-1.52 (m), 3.12 (m), 7.51-8.08 (m). UV-Vis (thiophene):  
 $\lambda_{\text{max}}$  = 271, 567 (sh) and 621nm. IR: 3058, 2918, 2848, 1568, 1461, 1436, 1372, 1290, 1163, 1142,  
1070, 831, 786, 753, 722, 691. TGA (Ar, 46.58% weight loss): 472.7 °C. DSC:  $T_g$  = 85.8°C.

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