# Supporting Information for

Poly(3-(2,5-dioctylphenyl)thiophene) synthesized by direct arylation polycondensation: End groups, defects and crystallinity

Daniel Schiefer<sup>1</sup>, Hartmut Komber<sup>2</sup>, Fanuel Mugwanga Keheze<sup>3</sup>, Susanna Kunz<sup>1</sup>, Ralf
Hanselmann<sup>1</sup>, Günter Reiter<sup>3,4,5</sup> and Michael Sommer<sup>1,4,5</sup>

<sup>1</sup>Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Straße 31, 79104 Freiburg, Germany

<sup>2</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

<sup>3</sup>Institut für Physik, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

<sup>4</sup>Freiburger Materialforschungszentrum FMF, Stefan-Meier-Straße 21, 79104 Freiburg, Germany

<sup>5</sup>Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien FIT, Georges-Köhler-Allee 105, 79110 Freiburg, Germany

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#### 1. Measurements and Chemicals

*NMR spectroscopy.*  $^{1}$ H (500.13 MHz,) and  $^{13}$ C (125.75 MHz) NMR spectra were recorded on a Bruker Avance III spectrometer using a 5 mm  $^{1}$ H/ $^{13}$ C/ $^{19}$ F/ $^{31}$ P gradient probe. Spectra were recorded at 30°C using CDCl<sub>3</sub> as solvent, lock and internal standard ( $\delta$ ( $^{1}$ H) 7.26 ppm,  $\delta$ ( $^{13}$ C) 77.0 ppm).  $^{1}$ H - $^{1}$ H and  $^{1}$ H- $^{13}$ C correlated 2D NMR spectra were recorded to verify the signal assignments using standard pulse sequences included in the Bruker TOPSPIN 3.2 software package.

Size exclusion chromatography (SEC). SEC measurements were carried out on a PSS SeCcurity HP1200 G1310A from PSS with three columns of pore sizes of 10<sup>2</sup>, 10<sup>3</sup>, and 10<sup>4</sup> Å and a guard column (PSS). Calibration was done using polystyrene standards. THF was used as eluent at room temperature at a flow rate of 1.0 mL/min.

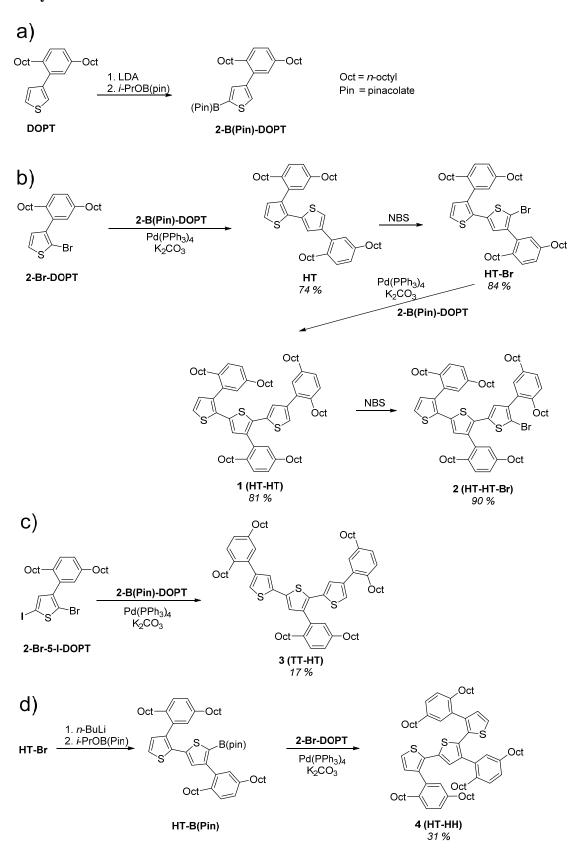
UV/vis spectroscopy. UV/vis measurements were carried out on a Perkin Elmer  $\lambda 1050$  spectrophotometer using a tungsten lamp as the excitation source.

*DSC measurements*. DSC measurements were acquired on a NETZSCH DSC 204 F1 Phoenix under a nitrogen atmosphere. The heating and cooling rate was 10 K/min unless otherwise stated.

MALDI-ToF mass spectrometry. MALDI-ToF-MS measurements were performed with a Bruker Autoflex III TOF/TOF mass spectrometer (Bruker Daltonik GmbH, Germany) operating in positive reflector mode. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) was used as matrix. Matrix and analyte were dissolved in THF and mixed as follows:  $10~\mu L$  dithranol (20~mg/mL),  $1~\mu L$  analyte (1~mg/mL).  $1~\mu L$  of the mixture was spotted on the sample probe and allowed to dry. Poly(ethylene oxide) was used for external calibration.

Chemicals. All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. Herrmann-Beller catalyst was obtained from Sigma Aldrich in 98% purity and used as received. THF was dried over sodium and stored under nitrogen atmosphere. **DOPT**, **2-Br-DOPT** and **2-Br-5-I-DOPT** (**Scheme S-1**) were synthesized according to literature.<sup>[1]</sup>

### 2. Synthesis



**Scheme SI-1.** Synthetic routes to **2-B(Pin)-DOPT** (a) and model compounds 1 - 4 (b – d).

**Synthesis of 2-(4-(2,5-dioctylphenyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [2-B(Pin)-DOPT].** A flask containing 3-(2,5-dioctylphenyl)thiophene (1.00 g, 2.66 mmol, 1.0 eq.) in dry THF (30 mL) was degassed and cooled to -78 °C. Lithium diisopropylamide (1 M in hexane, 3.10 mL, 3.10 mmol, 1.2 eq.) was slowly added and the reaction mixture was stirred at -78 °C for 4 h. The reaction was quenched with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.65 mL, 594 mg, 3.19 mmol, 1.2 eq.) and allowed to warm to room temperature. The reaction mixture was diluted with *iso*-hexanes, extracted with water, dried and concentrated under reduced pressure and high vacuum. The colorless oil was used without further purification.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62 (d, 1H, H<sub>3</sub>), 7.45 (d, 1H, H<sub>5</sub>), 7.19 - 7.05 (m, 3H, H<sub>Ar</sub>), 2.63 - 2.52 (4H, α-CH<sub>2</sub>), 1.68 - 1.09 (36 H, CH<sub>2</sub>), 0.92-0.83 ppm (6H, CH<sub>3</sub>).

**Synthesis of 3,4'-bis(2,5-dioctylphenyl)-2,2'-bithiophene [HT].** 2-(4-(2,5-dioctylphenyl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2-B(Pin)-DOPT**, 330 mg, , 0.65 mmol, 1.5 eq.), 2-bromo-3-(2,5-dioctylphenyl)thiophene (200 mg, 0.43 mmol, 1.0 eq.), K<sub>2</sub>CO<sub>3</sub> (480 mg, 3.46 mmol, 8.0 eq.), toluene (3.0 mL) and H<sub>2</sub>O (1.7 mL) were added to a 10 mL microwave vial and degassed. Tetrakis(triphenylphosphine)palladium(0) (15.0 mg, 3 mol-%) was added and the reaction mixture was heated to 80 °C in the microwave for 3 h. The reaction mixture was diluted with *iso*-hexanes, washed with water, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product was purified by flash chromatography (iso-hexanes) and obtained as colorless oil (245 mg, 74 %).

APCI-MS: m/z = 767.56110 (100), 768.56415 (57.52), 769.56921 (13.11) [M+H]<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.22 (d, 1H; 4'), 7.20 (d, 1H; 7'), 7.15 (dd, 1H; 8'),7.13 (d, 1H; 7), 7.07 (d, 1H; 10'), 7.06 (dd, 1H; 8), 6.99 (d, 1H; 10), 6.95 (d, 1H; 3), 6.94 (d, 1H; 3'), 6.89 (d, 1H; 1), 2.59 (t, 2H; 11,  $R_{2^{\circ}}$ ), 2.56 (t, 2H; 11,  $R_{2}$ ), 2.51 (t, 2H; 11,  $R_{1}$ ), 2.40 (t, 2H; 11,  $R_{1^{\circ}}$ ), 1.7 – 1.1 (48H; 12 – 17), 0.9 – 0.8 ppm (12H; 18).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.1 (2), 140.4 (9°), 140.1 (9), 139.1 (6°), 138.2 (2°), 137.8 (6), 136.0 (5), 135.9 (4), 135.6 (5°), 132.8 (1°), 131.1 (3°), 130.7 (10°), 129.9 (10), 129.2 (7°), 129.1 (7), 128.2 (8°), 127.4 (8), 127.0 (3), 122.6 (4°), 122.1 (1), 35.5 (11, R<sub>2</sub>), 35.4 (11, R<sub>2</sub>°), 32.9 (11, R<sub>1</sub>°), 32.8 (11, R<sub>1</sub>), 31.9 (16), 31.6 – 30.8 (12), 30 – 29 (13 - 15), 22.7 (17), 14.1.ppm (18).

Synthesis of 5'-bromo-3,4'-bis(2,5-dioctylphenyl)-2,2'-bithiophene [HT-Br]. A flask containing 3,4'-bis(2,5-dioctylphenyl)-2,2'-bithiophene (290 mg, 0.38 mmol, 1.0 eq.) in CHCl<sub>3</sub>/AcOH (1:1, 19 mL) was degassed and cooled to 0 °C. NBS (66.1 mg, 0.37 mmol. 0.98 eq.) was added in one potion. The reaction was carried out under the exclusion of light at 0 °C for 3 h and then allowed to warm to room temperature. The reaction mixture was diluted with CHCl<sub>3</sub>, washed with H<sub>2</sub>O and sat. NaHCO<sub>3</sub> solution, extracted with *iso*-hexanes, dried and concentrated under reduced pressure. The product was purified by flash chromatography (*iso*-hexanes) and obtained as colorless oil (278 mg, 87 %).

APCI-MS:  $m/z = 845.47162 (93.48), 847.46930 (100) [M+H]^{+}$ .

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.23 (d, 1H; 4'), 7.21 (d, 1H; 7'),7.17 (dd, 1H; 8'), 7.16 (d, 1H; 7), 7.11 (dd, 1H; 8), 7.05 (d, 1H; 10'), 6.94 (d, 1H; 10), 6.92 (d, 1H; 3'), 6.78 (s, 1H; 3), 2.60 (t, 2H; 11, R<sub>2</sub>·), 2.58 (t, 2H; 11, R<sub>2</sub>), 2.40 (t, 4H; 11, R<sub>1</sub> and R<sub>1</sub>·), 1.7 – 1.1 (48H; 12 – 17), 0.9 – 0.8 ppm (12H; 18).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.8 (2), 140.5 (9°), 140.0 (9), 139.0 (6°), 138.6 (2° and 6), 136.2 (4), 135.0 (5°), 134.4 (5), 132.2 (1°), 131.1 (3°), 130.6 (10°), 130.2 (10), 129.4 (7°), 129.0 (7), 128.6 (8°), 128.2 (8), 126.8 (3), 123.0 (4°), 110.3 (1), 34.4 (11, R<sub>2</sub> and R<sub>2</sub>·), 33.0 (11, R<sub>1</sub>·), 32.8 (11, R<sub>1</sub>), 31.9 (16), 31.6 – 30.8 (12), 30 – 29 (13 - 15), 22.7 (17), 14.1.ppm (18).

Synthesis of 3,4',4''-tris(2,5-dioctylphenyl)-2,2':5',2''-terthiophene [1, HT-HT]. A microwave vial containing 5'-bromo-3,4'-bis(2,5-dioctylphenyl)-2,2'-bithiophene (87.4 mg , 0.103 mmol, 1.0 eq.), 2-(4-(2,5-dioctylphenyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (78.8 mg, 0.155 mmol, 1.5 eq.),  $K_2CO_3$  (114 mg, 0.824 mmol, 8.0 eq.), toluene (1.0 mL) and  $H_2O$  (0.4 mL) was degassed. Tetrakis(triphenylphosphin)palladium(0) (2.40 mg, 2 mol-%) was added and the reaction was carried out in the microwave at 80°C for 3 h. The

reaction mixture was diluted, washed with water, extracted with *iso*-hexanes and concentrated under reduced pressure. The product was purified by flash chromatography (*iso*-hexanes) and obtained as colorless oil (96.0 mg, 81 %).

ESI-MS: m/z = 1148.82214 (92.80), 1149.82642 (100), 1150.82910 (52.71) [M]<sup>+</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data are given in **Table S-1**.

**Synthesis of 5"-bromo-3,4',4"-tris(2,5-dioctylphenyl)-2,2':5',2"-terthiophene [2, HT-HT-Br].** A flask containing 3,4',4"-tris(2,5-dioctylphenyl)-2,2':5',2"-terthiophene (**1**, 51.1 mg, 0.042 mmol, 1.0 eq.) in CHCl<sub>3</sub>/AcOH (1:1, 5 mL) was degassed and cooled to 0 °C. NBS (7.25 mg, 0.041 mmol. 0.98 eq.) was added in one potion. The reaction was carried out under the exclusion of light at 0 °C for 3 h and then allowed to warm to room temperature. The reaction mixture was diluted with CHCl<sub>3</sub>, washed with H<sub>2</sub>O and sat. NaHCO<sub>3</sub> solution, extracted with *iso*-hexanes, dried and concentrated under reduced pressure. The product was purified by flash chromatography (*iso*-hexanes) and obtained as pale yellow oil (49.3 mg, 90 %).

ESI-MS: m/z = 1226.73352 (84.45), 1227.73706 (76.00), 1228.73181 (100), 1229.73438 (83.30)  $[M]^+$ .

<sup>1</sup>H and <sup>13</sup>C NMR data are given in **Table S-1**.

**Synthesis of 4,3',4''-tris(2,5-dioctylphenyl)-2,2':5',2''-terthiophene [3, TT-HT].** A flask containing 2-bromo-3-(2,5-dioctylphenyl)-5-iodothiophene (150 mg, 0.25 mmol, 1.0 eq.), 2-(4-(2,5-dioctylphenyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (299 mg, 0.59 mmol, 2.3 eq.), K<sub>2</sub>CO<sub>3</sub> (650 mg, 4,72 mmol, 8.0 eq.), toluene (2.5 mL) and H<sub>2</sub>O (2.4 mL) was degassed. Tris(dibenzylideneacetone)dipalladium(0) (2.7 mg, 0.5 mol-%) and triphenylphosphine (3.1 mg, 2 mol-%) were added and the reaction mixture was heated to 80 °C for 72 h. The reaction mixture was diluted with *iso*-hexanes, washed with water, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product was purified by flash chromatography (*iso*-hexanes) and obtained as pale yellow oil (50.4 mg, 17 %).

ESI-MS: m/z = 1148.82288 (90.45), 1149.82715 (100), 1150, 83215 (41.37), 1151.83789 (10.47)  $[M]^+$ .

<sup>1</sup>H and <sup>13</sup>C NMR data are given in **Table S-1**.

**Synthesis of 2-(3',4-bis(2,5-dioctylphenyl)-2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [HT-B(Pin)].** A flask containing 5'-bromo-3,4'-bis(2,5-dioctylphenyl)-2,2'-bithiophene (100 mg, 0.118 mmol, 1.0 eq) in dry THF (5 mL) was cooled to -78 °C. nBuLi (2.5 M in hexane, 0.047 mL, 1.0 eq.) was slowly added and the solution was stirred for 2 h. The reaction was quenched with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29 mg, 0.153 mmol, 1.3 eq.) and allowed to warm to room temperature. The reaction was diluted with *iso*-hexanes, extracted with water, dried and concentrated under reduced pressure and high vacuum. The colorless oil was used without further purification.

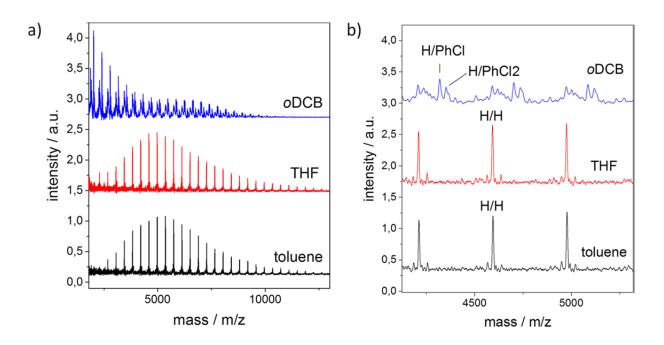
Synthesis of 3,4',3"-tris(2,5-dioctylphenyl)-2,2':5',2"-terthiophene [4, HT-HH]. A microwave vial containing 2-(3',4-bis(2,5-dioctylphenyl)-2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (76 mg, 0.085 mmol, 1.0 eq), 2-bromo-3-(2,5-dioctylphenyl)thiophene (39.4 mg, 0.085 mmol, 1.0 eq) and K<sub>2</sub>CO<sub>3</sub> (93.9 mg, 0.68 mmol, 8.0 eq) in H<sub>2</sub>O (0.35 mL) and toluene (0.85 mL) was degassed with N<sub>2</sub>. Tetrakis(triphenylphosphin)palladium(0) (1.90 mg, 2 mol-%) was added and the reaction was carried out in the microwave at 80°C for 3 h. The reaction mixture was diluted with *iso*-hexane, washed with water, dried and concentrated under reduced pressure. The product was purified by flash chromatography (*iso*-hexanes) and obtained as colorless oil (31.3 mg, 27 %).

General procedure for the DAP of PDOPT in solution. A HT-GPC vial was loaded with 2-bromo-3-(2,5-dioctylphenyl)thiophene (50 mg, 0.11 mmol, 1.0 eq.), Cs<sub>2</sub>CO<sub>3</sub> (53 mg, 0.17 mmol, 1.5 eq.), pivalic acid (3.3 mg, 33 µmol, 0.3 eq.) and the solvent to be examined (2.2 mL). After degassing with nitrogen, *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (Herrmann-Beller catalyst, 2.1 mg, 2 mol-%) and tris(*o*-methoxyphenyl)phosphine (1.6 mg, 4 mol-%) were added and the reaction vessel was sealed. The reaction occurred at 120 °C for 72 h. The reaction was diluted, washed with water, extracted with *iso*-hexanes and concentrated under reduced pressure. The end groups of the formed oligomeres were analyzed by MALDI-TOF spectrometry.

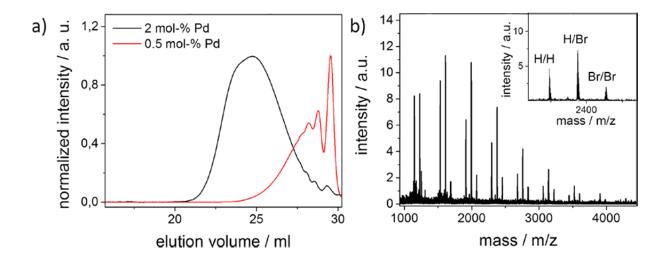
<sup>&</sup>lt;sup>1</sup>H and <sup>13</sup>C NMR data are given in **Table S-1**.

General procedure for the DAP of PDOPT in bulk. A 1 mL vial was loaded with 2-bromo-3-(2,5-dioctylphenyl)thiophene (200 mg, 0.43 mmol, 1.0 eq.) and Cs<sub>2</sub>CO<sub>3</sub> (154 mg, 0.47 mmol, 1.1 eq.) and stirred under vacuum for 10 min. *Trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (Herrmann-Beller catalyst, 8.0 mg, 2 mol-%) and tris(*o*-methoxyphenyl)phosphine (6.0 mg, 4 mol-%) were added and the reaction vessel was sealed and heated to the desired reaction temperature for 72 h. The reaction was diluted with *iso*-hexanes, washed with water, extracted with *iso*-hexane and concentrated under reduced pressure. The polymer was purified by Soxhlet extraction with acetone and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was filtered over a plug silica-plug and concentrated under reduced pressure to obtain the desired polymer.

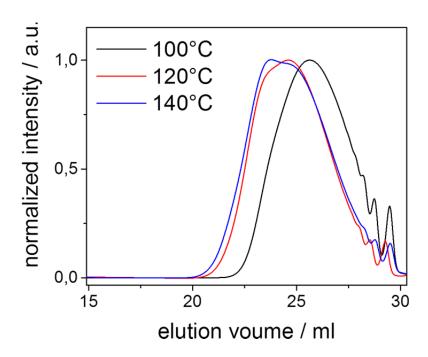
### 3. Additional MALDI-ToF mass spectra, SEC curves and optical properties



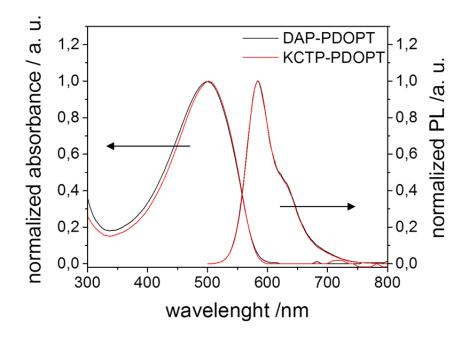
**Figure SI-1.** MALDI-ToF mass spectra of DAP polymers synthesized in different solvents. a) complete spectra and b) enlarged region.



**Figure SI-2.** a) SEC curves of DAP PDOPT **4** and **9** synthesized with 2 mol-% and 0.5 mol-% Pd loading, respectively. b) MALDI-ToF mass spectrum of the PDOPT oligomers obtained with 0.5 mol-% Pd loading.



**Figure SI-3.** SEC curves of PDOPT synthesized by DAP at different temperatures under bulk conditions (entries **11-13**).



**Figure SI-4.** Comparison of UV/vis and PL spectra of DAP-PDOPT **12** and KCTP-PDOPT **16** with  $M_n \sim 9$  kg/mol.

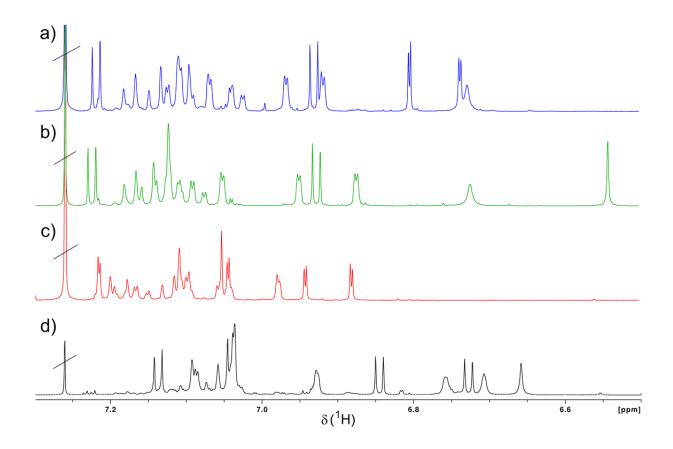
## 4. $^{1}$ H and $^{13}$ C NMR spectroscopy of PDOPT and model compounds 1 - 4

**Table SI-1.**  $^{1}$ H and  $^{13}$ C chemical shifts (in ppm) of **PDOPT** and model compounds 1-4 (CDCl<sub>3</sub>,  $30^{\circ}$ C)

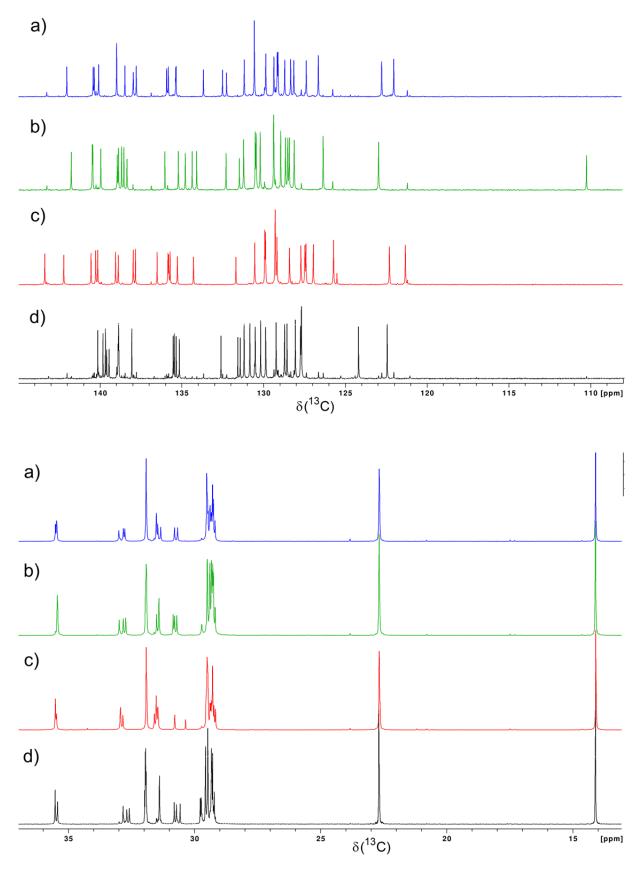
Compound	PDOPT	1	2	3	4
Position	<sup>13</sup> C NMR				
1	131.7	122.0	110.2	121.3	131.6
2	138.3	142.0	141.8	143.3	139.6
3	128.4	126.6	126.4	125.7	129.9
4	133.8	135.8	136.0	136.5	124.2
1'	-	132.3	131.5	131.7	131.4
2'	-	138.0	138.4	138.9	139.4
3'	-	128.7	128.7	127.4	127.7
4'	-	133.7	134.1	134.3	135.2
1''	-	132.5	132.3	122.3	132.6
2''	-	138.5	138.7	142.2	138.1
3''	-	131.2	131.2	126.9	131.2
4''	-	122.8	123.0	135.7	122.4
5	135.1	135.9	134.4	135.8	135.5
6	138.7	137.8	138.5	138.0	138.9
7	129.2	129.1	128.9	129,3	128.7
8	128.4	127.4	128.1	127.7	127.7
9	140.4	140.1	139.9	140.3	139.7
10	130.4	129.9	130.2	129.9	130.5
5'	-	135.4	134.8	135.3	135.5
6'	-	139.0	138.9	139.3	138.9

7'	l <u>-</u>	129.2	129.4	129.3	128.6
8'	_	128.2	128.5	128.4	127.7
9'	_	140.4	140.5	140.6	139.7
10'	_	130.6	130.5	130.5	130.8
5"	_	135.3	135.2	135.8	135.3
6"	_	139.0	139.0	137.8	138.9
7''	_	129.4	129.4	129.2	129.2
8''	_	128.3	128.5	127.5	128.1
9''		140.4	140.4	140.1	140.2
10"	_	130.6	130.5	129.9	130.2
11 in		150.0	150.5	127.7	150.2
$R_1$	32.7	32.8	32.7	32.8	32.8
$R_2$	35.4	35.5	35.5	35.5	35.5
$R_{1}$	_	32.8	32.8	32.9	32.7
$R_{2}$	_	35.4	35.5	35.5	35.5
R <sub>1</sub> "	_	33.0	33.0	32.9	32.6
R <sub>2</sub>		35.4	35.5	35.5	35.5
162		33.4	33.3	33.3	33.3
Position			<sup>1</sup> H NMR		
1	-	6.81	-	7.05	-
3	6.51	6.74	6.54	7.22	6.73
4	_	_	_	-	7.04
3'	-	6.73	6.73	7.06	6.66
1"	-	-	-	6.88	-
3"	_	6.93	6.93	6.94	6.84
4''	-	7.22	7.22	-	7.14
7	7.13	7.10	7.13	7.19	7.09
8	7.08	7.03	7.08	7.10	7.04
10	6.94	6.92	6.88	7.11	6.71
7'	-	7.14	7.15	7.21	7.06
8'	-	7.11	7.12	7.16	7.04
10'	_	6.97	6.95	7.11	6.76
7''	-	7.17	7.17	7.13	7.09
8''	-	7.11	7.12	7.05	7.09
10"	-	7.07	7.05	6.98	6.93
11 in					
$R_1$	2.28	2.45	2.34	2.64	2.16
$R_2$	2.51	2.55	2.55	2.59	2.49
R <sub>1</sub> ·	-	2.32	2.32	2.46	2.22
$R_{2}$	_	2.55	2.55	2.59	2.49
R <sub>1"</sub>	-	2.41	2.40	2.50	2.28
R <sub>2"</sub>	1	İ	2.57	2.55	2.55

Further signals of the alkyl chains:  $^{13}$ C (ppm): 31.9 (16), 31.7 - 30.7 (12), 30 - 29 (13 - 15), 22.7 (17), 14.1 (18).  $^{1}$ H (ppm): 1.65 - 1.4 (12), 1.4 - 1 (13 - 17), 0.95 - 0.8 (18).



**Figure SI-5.**  $^{1}$ H NMR spectra (aromatic protons) of model compounds  $\mathbf{1} - \mathbf{4}$  (a – d). Solvent: CDCl<sub>3</sub>, 30°C.



**Figure SI-6.**  $^{13}$ C NMR spectra of model compounds 1 - 4 (a – d). Solvent: CDCl<sub>3</sub>, 30°C.

#### 5. <sup>13</sup>C chemical shift increments

**Table SI-2.** <sup>13</sup>C chemical shift increments (solvent: CDCl<sub>3</sub>)

Position	replace H by Br in	replace H by PDOPT	replace H by PDOPT	
	position 1 <sup>a)</sup>	in position 1 <sup>b)</sup>	in position 4 <sup>c)</sup>	
1	-11.8	+9.7	-0.8	
2	-0.2	-3.7	-0.2	
3	-0.2	+1.8	-2.8	
4	+0.2	-2.0	+11.0	

a) calculated from 1 and 2.

# 6. Assignment of <sup>1</sup>H and <sup>13</sup>C chemical shifts to PDOPT end groups and regioirregularities I – VII

III: 
$$X = H (H-HT-)$$

1 (positions 1-4) I:

2 (positions 1-4) II:

1 and 2 (positions 1'' - 4'') III:

3 (positions 1-4) **IV**:

b) calculated from **PDOPT** and **1** (positions 1 – 4). c) calculated from **PDOPT** and **1** (positions 1'' – 4'').

V: calculated  $^{13}$ C chemical shifts based on **3** (positions 1 – 4) and Br increments (**Table S-3**)

**VI**: calculated  $^{13}$ C chemical shifts based on **3** (positions 1 – 4) and PDOPT increments increments (**Table S-3**);  $^{1}$ H chemical shift should be similar to 3' of **3** 

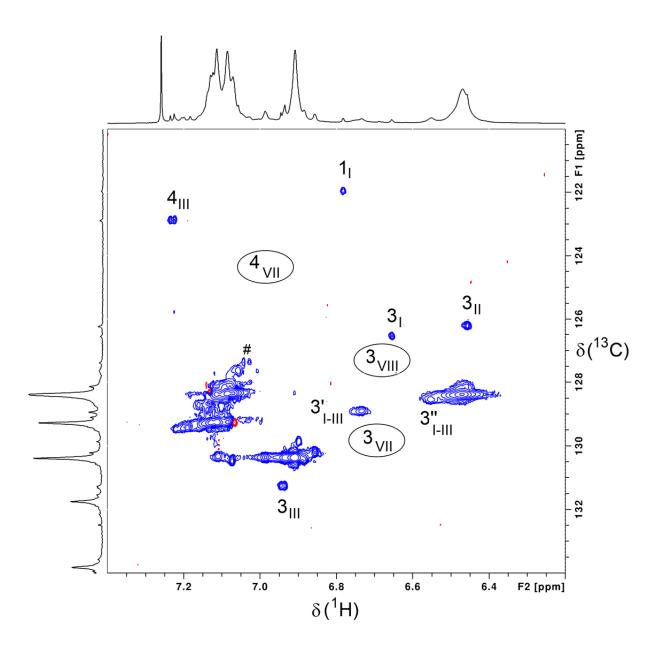
**VII**: 4 (positions 1-4)

**VIII**: calculated <sup>13</sup>C chemical shifts based on **4** (positions 1 – 4) and PDOPT increments increments (**Table S-3**); <sup>1</sup>H chemical shift should be similar to 3' of **4** 

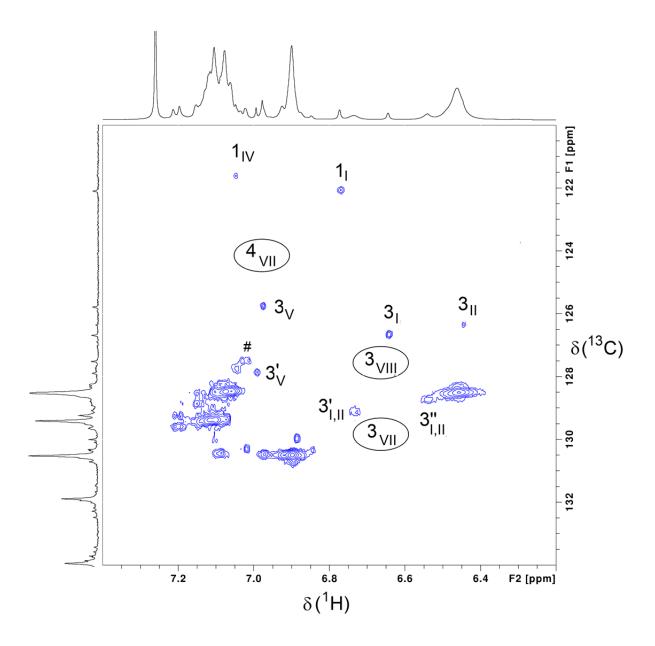
**Table SI-3.** Estimation of <sup>13</sup>C chemical shifts based on model compounds' data and chemical shift increments (in brackets) to identify Br-TT end group and TT and HH units in the PDOPT backbone

Position	3	1-Br- <b>3</b>	1-PDOPT- <b>3</b>	4	4-PDOPT- <b>4</b>
1	121.3	109.5 (-11.8)	131.0 (+ 9.7)	131.6	130.8 (-0.8)
2	143.3	143.1 (-0.2)	139.6 (-3.7)	139.6	139.4 (-0.2)
3	125.7	125.5 (-0.2)	127.5 (+1.8)	129.9	127.1 (-2.8)
4	136.5	136.7 (+ 0.2)	134.5 (-2.0)	124.2	135.2 (-11.0)
1'	131.7	131.7	131.7	131.4	131.4
2'	138.9	138.9	138.9	139.4	139.4
3'	127.4	127.4	127.4	127.7	127.7
4'	134.3	134.3	134.3	135.2	135.2

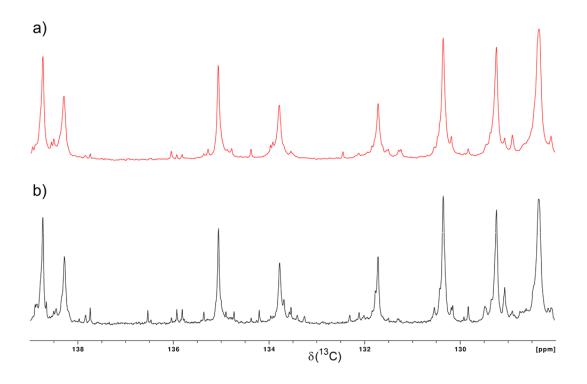
# 7. Additional $^{13}$ C NMR and HSQC spectra of PDOPT synthesized from DAP and KCTP



**Figure SI-7.** HSQC spectrum (aromatic carbons' region) of PDOPT synthesized by DAP (entry **11**). The carbons atoms  $3_{VII}$ ,  $3_{VII}$  and  $4_{VII}$  could not be observed by correlation peaks in the marked regions. # Signal of DOP moiety. Solvent: CDCl<sub>3</sub>.



**Figure SI-8.** HSQC spectrum (aromatic carbons' region) of PDOPT synthesized by KCTP (entry **15**). The carbons atoms  $3_{VII}$ ,  $3_{VII}$  and  $4_{VII}$  could not be observed by correlation peaks in the marked regions. # Signal of DOP moiety. Solvent: CDCl<sub>3</sub>.



**Figure SI-9.** Aromatic carbons' region of PDOPT synthesized by DAP (entry **11**; a) and KCTP (entry **15**; b) not shown in Figure 5. Solvent: CDCl<sub>3</sub>.

## 8. References

[1] D. Schiefer, T. Wen, Y. Wang, P. Goursot, H. Komber, R. Hanselmann, P. Braunstein, G. Reiter, M. Sommer, *ACS Macro Lett.* **2014**, *3*, 617–621.