# Synthesis, characterization and device optimisation of new poly(benzo[1,2-*b*:4,5-*b*']dithiophene-*alt*-thieno[3,4-*d*]thiazole) derivatives for solar cell applications.

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### **Experimental Part**

#### Materials

4,6-Dibromo-2-octylthieno[3,4-d]thiazole (1) and 2-(pentadecan-7-yl)thieno[3,4d]thiazole (2) were synthesized according to the literature<sup>1,2</sup>. All other starting organic compounds were purchased from Aldrich, Alfa Aesar, Oakwood Products Inc. or TCI and used without any further purification. Tetrabutylammonium tetrafluoroborate (98%, Aldrich) was recrystallized three times in 50/50 mixture of methanol/water and dried at 100 °C under reduced pressure. The reaction solvents were distilled under inert atmosphere prior to use (THF from sodium/benzophenone, acetonitrile from CaH<sub>2</sub>), the other solvents were usually ACS grade. Column chromatography was carried out on silica gel (size: 300-400 mesh). 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2b:4,5-b']dithiophene<sup>3</sup>, 2,6-bis(trimethyltin)-4,8-bis(2'-ethylhexylthiophene)benzo[1,2b:4,5-b']dithiophene<sup>4</sup> were synthesized according to the literature.

### Synthesis of monomers and polymers

2-octyl-4,6-bis(3-octyl(thienophen-2-yl)thieno[3,4-d]thiazole (3). In a 100 mL flask fitted with a condenser, 1.10g (2.67 mmol) of 4,6-dibromo-2-octylthieno[3,4-d]thiazole (1), 2.41g (6.69 mmol) of trimethyltin-2-octylthiophene, 48.9mg (0.0530 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 65.5mg (0.210 mmol) of triphenylarsine (AsPh<sub>3</sub>) and 35mL of degased toluene were added. The reaction mixture was vigorously stirred at 110 °C overnight. Then, the reaction was quenched with water, extracted with diethyl ether, dried with anhydrous MgSO<sub>4</sub> and concentrated under reduce pressure. The crude product was purified by flash chromatography in hexanes to obtain 1.18g of yellow oil which is used without further purification. (yield: 68 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.30(m, 2H); 6.98(m, 2H); 3.03(m, 2H); 2.84(m, 4H); 1.86(m, 2H); 1.68(m, 4H); 1.33(m, 30H); 0.87(m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  178.41; 155.36; 141.23; 140.36; 132.53; 130.49; 129.93; 129.89; 127.97; 125.92; 124.47; 120.67; 119.93; 35.71; 32.16; 32.13; 32.08; 30.87; 30.83; 29.96; 29.94; 29.91; 29.88; 29.74; 29.70; 29.64; 29.57; 29.54; 29.47; 29.43; 29.41; 29.37; 29.31; 22.95; 22.92; 22.90; 14.36. HRMS for C<sub>37</sub>H<sub>55</sub>NS<sub>4</sub>: Calcd : 641.3217 Found: 641.3228.

### 4,6-bis(5-bromo-3-octylthienophen-2-yl)-2-octylthieno[3,4-d]thiazole (4).

To a solution of 2-octyl-4,6-bis(3-octyl(thienophen-2-yl)thieno[3,4-d]thiazole (3) (1.18g, 1.83 mmol) in 120 mL of tetrahydrofuran (THF), n-bromosuccinimide (NBS) (68.4mg, 3.84 mmol) was added to the reaction. The reaction was allowed to stir at room temperature overnight. Then, the reaction was quenched with water, extracted with diethyl ether, dried with anhydrous MgSO<sub>4</sub> and concentrated under reduce pressure. The crude product was purified by flash chromatography in hexanes to obtain 656mg of yellow oil. (yield: 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  6.93(s, 2H); 3.02(t, *J* = 7.6 Hz, 2H); 2.75(quin, *J* = 7.6 Hz, 4H); 1.85(quin, *J* = 7.6 Hz, 2H); 1.63(m, 4H); 1.34(m, 30H); 0.87(m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  178.61; 155.36; 141.19; 140.88; 132.86; 132.78; 132.29; 130.84; 129.36; 119.69; 118.41; 112.86; 111.42; 35.48; 31.91; 31.88; 31.83; 30.44; 30.38; 29.81; 29.63; 29.59; 29.52; 29.44; 29.40; 29.29; 29.27; 29.25; 29.16; 29.15; 29.03; 22.68; 22.67; 22.66; 14.12. HRMS for C<sub>37</sub>H<sub>53</sub>NS<sub>4</sub>Br<sub>2</sub>: Calcd : 797.1428 Found: 797.1459.

### 2-(pentadecan-7-yl)-4,6-di(thiphen-2-yl)thieno[3,4-d]thiazole (5).

In a 50 mL flask fitted with a condenser, 0.897g (1.76 mmol) of 4,6-dibromo-2-(pentadecan-7-yl)thieno[3,4-d]thiazole of (2), 1.58g (4.22)mmol) 2-(tributylstannyl)thiophene, 32.2mg (0.0350 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 43.2mg (0.140 mmol) of triphenylarsine (AsPh<sub>3</sub>) and 20mL of degased toluene were added. The reaction mixture was vigorously stirred at 110 °C overnight. Then, the reaction was quenched with water, extracted with diethyl ether, dried with anhydrous MgSO<sub>4</sub> and concentrated under reduce pressure. The crude product was purified by flash chromatography in a mixture of 95/5 hexanes/CHCl<sub>3</sub> to obtain 0.331g of yellow oil which is used without further purification. (yield: 36 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.57(m, 1H); 7.29(m, 2H); 7.22(m, 1H); 7.08(m, 2H); 3.09(m, 1H); 1.79(m, 4H); 1.33(m, 20H); 0.88(m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 183.40; 154.45; 136.54; 134.90; 130.48; 128.15; 127.65; 125.34; 124.71; 124.54; 123.25; 120.44; 118.82; 46.27; 35.66; 35.64; 31.90; 31.72; 29.66; 29.46; 29.34; 29.33; 27.35; 27.33; 22.71; 22.68; 14.16; 14.13. HRMS for C<sub>28</sub>H<sub>37</sub>NS<sub>4</sub>: Calcd : 515.1809 Found: 515.1822.

### 4,6-bis(5-bromothienophen-2-yl)-2-(1-hexylnonyl)thieno[3,4-d]thiazole (6).

To a solution of 2-(pentadecan-7-yl)-4,6-di(thiphen-2-yl)thieno[3,4-d]thiazole (5) (0.331g, 0.642 mmol) in 25 mL of tetrahydrofuran (THF), n-bromosuccinimide (NBS) (0.234g, 1.32 mmol) was added to the reaction. The reaction was allowed to stir at room temperature overnight. Then, the reaction was quenched with water, extracted with diethyl ether, dried with anhydrous MgSO<sub>4</sub> and concentrated under reduce pressure. The

crude product was purified by flash chromatography in hexanes to obtain 0.242g of yellow oil. (yield: 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.13(d, *J* = 3.8 Hz, 1H); 6.98(d, *J* = 3.8 Hz, 2H); 6.88(d, *J* = 3.8 Hz, 1H); 3.05(m, 1H); 1.77(m, 4H); 1.30(m, 20H); 0.88(m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  183.87; 154.59; 137.78; 136.26; 130.92; 130.64; 130.21; 124.19; 123.24; 119.73; 117.96; 112.96; 111.52; 46.25; 35.60; 35.59; 31.91; 31.74; 29.65; 29.48; 29.34; 27.33; 27.31; 22.72; 22.70; 14.17; 14.15. HRMS for C<sub>28</sub>H<sub>35</sub>NS<sub>4</sub>Br<sub>2</sub>: Calcd : 671.0019 Found: 671.0005.

### P1

# Poly[2,6-(4,8-bis-(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene)-alt-4,6-(2-n-octyl)thieno[3,4-d]thiazole]

In a 25 mL flask fitted with a condenser, 0.392g (0.508 mmol) of 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene (7), 0.209g (0.508 mmol) of 2octyl-4,6-dibromo-thieno[3,4-d]thiazole (1), 9.3mg (0.0102 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 12.5mg (0.0406 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 48 h at 110 °C. After reaction completion, 5,3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.341 g of the desired polymer (97 % yield). In a 25 mL flask fitted with a condenser, 0.193g (0.250 mmol) of 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene (7), 0.200g (0.250 mmol) of 4,6bis(5-bromo-3-octylthienophen-2-yl)-2-octylthieno[3,4-d]thiazole (4), 4.5mg (0.005 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 6.1mg (0.02 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 48 h at 110 °C. After reaction completion, 5,3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.200 g of the desired polymer (74 % yield).

### **P3**

In a 25 mL flask fitted with a condenser, 0.275g (0.356 mmol) of 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene (7), 0.239g (0.356 mmol) of 4,6bis(5-bromothienophen-2-yl)-2-(1-hexylnonyl)thieno[3,4-d]thiazole (6), 6.5mg (0.007 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 8.7 mg (0.028 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 48 h at 110 °C. After reaction completion, 5.3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.308 g of the desired polymer (90 % yield).

#### P4

# Poly[2,6-(4,8-bis(2'-ethylhexylthiophene)benzo[1,2-b:4,5-b']dithiophene-alt-4,6-(2-n-octyl)thieno[3,4-d]thiazole]

In a 25 mL flask fitted with a condenser, 0.251g (0.277 mmol) of 2,6-bis(trimethyltin)-4,8-bis(2'-ethylhexylthiophene)benzo[1,2-b:4,5-b']dithiophene (8), 0.114g (0.277 mmol) of 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole (1), 4.9mg (0.0054 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 6.7mg (0.022 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 72 h at 110 °C. After reaction completion, 5.3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.218 g of the desired polymer (95 % yield). In a 25 mL flask fitted with a condenser, 0.178g (0.196 mmol) of 2,6-bis(trimethyltin)-4,8-bis(2'-ethylhexylthiophene)benzo[1,2-b:4,5-b']dithiophene **(8)**, 0.157g (0.196 mmol) of 4,6-bis(5-bromo-3-octylthienophen-2-yl)-2-octylthieno[3,4-d]thiazole **(4)**, 3.6mg (0.0039 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 4.8mg (0.015 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 48 h at 110 °C. After reaction completion, 5.3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.125 g of the desired polymer (52 % yield).

### **P6**

In a 25 mL flask fitted with a condenser, 0.178g (0.197 mmol) of 2,6-bis(trimethyltin)-4,8-bis(2'-ethylhexylthiophene)benzo[1,2-b:4,5-b']dithiophene (8), 0.133g (0.197 mmol) of 4,6-bis(5-bromothienophen-2-yl)-2-(1-hexylnonyl)thieno[3,4-d]thiazole (6), 3.6mg (0.0039 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 4.8mg (0.015 mmol) of triphenylarsine (AsPh<sub>3</sub>), 5 mL of degassed toluene was added. The reaction mixture was vigorously stirred for 48 h at 110 °C. After reaction completion, 5.3  $\mu$ L (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1  $\mu$ L (0.05 mmol) of trimethyl(phenyl)tin was added and the reaction was heated for one more hour. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and washed on Soxhlet apparatus with acetone, hexanes and then chloroform. The chloroform fraction was reduced to 20-30 mL and then precipitated in methanol, filtered through 0.45  $\mu$ m nylon filter and air-dried to give 0.160 g of the desired polymer (74 % yield).

### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR were recorded using a Varian AS400 in deuterated chloroform or acetone solution at 298 K. Chemicals shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. Number-average (Mn) and weight-average (Mw) molecular weights were determined by size exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PLgel Mixed C (300 x 7.5 mm) columns and a PLgel Mixed C guard column. The flow rate was fixed at 1.0 mL/min using 1.2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as eluent. The temperature of the system was set to 110 °C. The samples were prepared at concentration of nominally 1.0 mg/mL in hot TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vial was held at 110 °C with shaking for 1 h for complete dissolution. The solution was filtered through a 2 µm porous stainless steel filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards dissolved in TCB. Thermogravimetric (TGA) measurements were carried out with a Mettler Toledo TGA SDTA 851e apparatus at a heating rate of 20 K/min under a nitrogen atmosphere. The temperature of degradation ( $T_d$ ) corresponds to a 5 % weight loss. UV-vis-NIR absorption spectra were taken using a Varian Cary 500 UV-vis-NIR spectrophotometer using 1 cm path length quartz cells. For solid state measurements, polymer thin films were casted on a glass plate from chloroform solutions. Optical bandgap was calculated from the onset of the absorption band. Cyclic voltammograms (CV) were recorded with a Solartron 1287 potentiostat using platinum electrodes at a scan rate of 50 mVs<sup>-1</sup> and a Ag/Ag<sup>+</sup> (0.1 M of AgNO<sub>3</sub> in acetonitrile) reference electrode in an anhydrous and argon saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) in acetonitrile. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets, assuming an SCE electrode to be at -4.7 eV from vacuum.



S2: <sup>13</sup>C NMR spectrum of 4.



**S4**: <sup>13</sup>C NMR spectrum of **6**.



S5: UV-vis absorption spectra and cyclic voltammograms of P1.



S6: UV-vis absorption spectra and cyclic voltammograms of P2.



S7: UV-vis absorption spectra and cyclic voltammograms of P3.



S8: UV-vis absorption spectra and cyclic voltammograms of P4.



S9: UV-vis absorption spectra and cyclic voltammograms of P5.



S10: UV-vis absorption spectra and cyclic voltammograms of P6.

### Solar cell fabrication and evaluation

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14  $\Omega$  per square) (Naranjo Substrates). The photoactive layer were deposited by spin coating a chloroform solution containing the polymers and the acceptor with different ratio and the appropriate amount of 1,8diiodooctane (DIO). LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at  $\sim 2 \times 10$  –7 mbar as the back electrode. The active area of the cells was 0.09 or 0.16  $cm^2$  and no size dependence was found between these two dimensions. J - Vcharacteristics were measured under  $\sim 100 \text{ mW/cm}^2$  white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50 resistance, using a lockin amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.



S11 : *J*-*V* characteristics and EQE spectra of P1 for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .



**S12** : *J*-*V* characteristics and EQE spectra of **P2** for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .



**S13** : *J*-*V* characteristics and EQE spectra of **P3** for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .



**S14** : *J*-*V* characteristics and EQE spectra of **P4** for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .



**S15** : *J*-*V* characteristics and EQE spectra of **P5** for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .



**S16** : *J-V* characteristics and EQE spectra of **P6** for optimized devices using  $PC_{71}BM$  and  $IC_{61}BA$ .

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