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Supporting Information

Easy and Versatile Synthesis of new Poly(thieno[3,4-*d*]thiazole)s

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Experimental Part

Materials

2-azido-3-bromothiophene[1] **(1)** and 4-methylbenzenesulfonyl azide[2] were synthesized according to the literature. All other starting organic compounds were purchased from Aldrich, Alfa Aesar, Oakwood Products Inc. or TCI and used without any further purification. PySSPy corresponds to 2,2'-dipyridyl disulfide. Tetrabutylammonium tetrafluoroborate (98%, Aldrich) was recrystallized three times in 50/50 mixture of methanol/water and dried at 100 ºC under reduced pressure. The reaction solvents were distilled under inert atmosphere prior to use (THF from sodium/benzophenone, acetonitrile from CaH_2), 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[1,2-b:4,5-b']dithiophene[3], 2,6-bis(trimethyltin)-4,8-di(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophene[4], 4,4-Bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole[5], 5-(9-heptadecanyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione[6], 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione[7] and 6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(N,N'-2-hexyldecyl)isoindigo[8] were synthesized according to the literature.

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Synthesis of monomers and polymers

N-(4-bromothiophenyl)-3-nonanamide **(2a).** In a round bottom flask equipped with an addition funnel, 2-azido-3-bromothiophene **(1)** (4.0g, 19.6 mmol) was dissolved in 160 mL of anhydrous THF. Then, PySSPy (0.864g, 3.92 mmol) and nonanoic acid (3.10g, 19.6 mmol) were added to the solution. The mixture was cooled to 0 °C and trimethylphosphine (60.4 mmol, 60.4 mL of a 1.0 M solution in Toluene) was added dropwise to the solution at 0 °C. After the addition, the reaction was stirred overnight at room temperature. The mixture was then extracted with a saturated solution of sodium bicarbonate and AcOEt. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 90/10 hexane/AcOEt to obtain 4.92 g of the desired product as white powder. (yield : 79 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.90(d, J = 3.6 Hz, 1H); 7.54(s, 1H, NH); 7.22(d, J = 3.6 Hz, 1H); 2.41(t, J = 7.6 Hz, 2H); 1.73(m, 2H); 1.30(m, 10H); 0.88(t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.85; 132.77; 121.50; 110.59; 103.28; 37.45; 32.06; 29.56; 29.45; 29.37; 25.75; 22.89; 14.35.

N-(4-bromothiophen-3-yl)-4-octylbenzamide **(2b)**. In a round bottom flask equipped with an addition funnel, 2-azido-3-bromothiophene **(1)** (2.2g, 10.7 mmol) was dissolved in 90 mL of anhydrous THF. Then, PySSPy (0.475g, 2.15 mmol) and 4-octylbenzoic acid (2.53g, 10.7 mmol) were added to the solution. The mixture was cooled to 0 °C and trimethylphosphine (33.2 mmol, 33.2 mL of a 1.0 M solution in Toluene) was added dropwise to the solution at 0 °C. After the addition, the reaction was stirred

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overnight at room temperature. The mixture was then extracted with a saturated solution of sodium bicarbonate and AcOEt. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 50/50 hexane/DCM to obtain 2.82 g of the desired product as white powder. (yield : 66 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.33(s, 1H, NH); 8.07(d, *J* = 3.6 Hz, 1H); 7.82(d, *J* = 8.1 Hz, 2H); 7.32(d, *J* = 8.1 Hz, 2H); 7.27(d, *J* = 3.6 Hz, 1H); 2.68(t, *J* = 7.6 Hz, 2H); 1.65(m, 2H); 1.30(m, 10H); 0.89(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.78; 148.05; 132.92; 131.46; 129.18; 127.30; 121.59; 110.64; 103.74; 36.14; 32.12; 31.43; 29.69; 29.49; 22.92; 14.38.

N-(4-bromothiophen-3-yl)-4-(octyloxy)benzamide **(2c)**. In a round bottom flask equipped with an addition funnel, 2-azido-3-bromothiophene **(1)** (3.0g, 14.7 mmol) was dissolved in 120 mL of anhydrous THF. Then, PySSPy (0.648g, 2.94 mmol) and 4-(octyloxy)benzoic acid (3.68g, 14.7 mmol) were added to the solution. The mixture was cooled to 0 °C and trimethylphosphine (45.3 mmol, 45.3 mL of a 1.0 M solution in Toluene) was added dropwise to the solution at 0 °C. After the addition, the reaction was stirred overnight at room temperature. The mixture was then extracted with a saturated solution of sodium bicarbonate and AcOEt. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 95/5 hexane/AcOEt to obtain 0.723g of the desired product as white powder. (yield : 12 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.27(s, 1H, NH); 8.05(d, *J* = 3.6 Hz, 1H); 7.87(d, *J* = 8.8 Hz, 2H); 7.28(d, *J* = 3.6 Hz, 1H); 6.99(d, *J* = 8.8 Hz, 2H); 4.03(t, *J* = 6.5 Hz, 2H); 1.81(m, 2H); 1.47(m, 2H); 1.30(m,

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8H) 0.89(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.40; 162.64; 132.95; 129.13; 125.98; 121.61; 114.87; 110.42; 103.69; 68.55; 32.05; 29.58; 29.47; 29.35; 26.24; 22.91; 14.36.

N-(4-bromothiophenyl)-3-nonanamide **(3a)**. In a round bottom flask equipped with a condenser, N-(4-bromothiophenyl)-3-nonanamide **(2a)** (5.25g, 16.5 mmol) was dissolved in 200 mL of anhydrous THF. Lawesson's reagent (10.0g, 24.7 mmol) was then added to the solution. The reaction was refluxed overnight then, it was extracted with AcOEt and a 10 % NaOH solution. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 95/5 hexane/AcOEt to obtain 3.52g of the desired product as a yellow oil. (yield : 64 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.97(d, *J* = 3.6 Hz, 1H); 7.26(d, *J* = 3.6 Hz, 1H); 2.84(t, *J* = 7.6 Hz, 2H); 1.84(m, 2H); 1.26(m, 10H); 0.87(t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.49; 133.57; 121.52; 114.21; 104.96; 49.24; 31.85; 29.59; 29.35; 29.18; 28.86; 22.69; 14.19.

N-(4-bromothiophen-3-yl)-4-octylbenzothioamide **(3b)**. In a round bottom flask equipped with a condenser, N-(4-bromothiophen-3-yl)-4-octylbenzamide **(2b)** (2.5g, 6.3 mmol) was dissolved in 80 mL of anhydrous THF. Lawesson's reagent (3.85g, 9.5 mmol) was then added to the solution. The reaction was refluxed overnight then, it was extracted with AcOEt and a 10 % NaOH solution. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 50/50 hexane/DCM to obtain 2.04g of the

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desired product as a yellow powder. (yield : 78 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.56(s, 1H, NH); 9.17(d, *J* = 3.6 Hz, 1H); 7.83(d, *J* = 8.0 Hz, 2H); 7.35(d, *J* = 3.6 Hz, 1H); 7.27(d, *J* = 7.0 Hz, 2H); 2.67(t, *J* = 7.6, 2H); 1.64(m, 2H); 1.30(m, 10H); 0.89(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.06; 147.43; 140.49; 134.26; 129.13; 126.95; 121.79; 113.88; 105.40; 36.02; 32.11; 31.42; 29.68; 29.50; 29.48; 22.91; 14.35.

N-(4-bromothiophen-3-yl)-4-(octyloxy)benzothioamide **(3c)**. In a round bottom flask equipped with a condenser, N-(4-bromothiophen-3-yl)-4-(octyloxy)benzamide **(2c)** (0.650g, 1.58 mmol) was dissolved in 20 mL of anhydrous THF. Lawesson's reagent (0.960g, 2.37 mmol) was then added to the solution. The reaction was refluxed overnight then, it was extracted with AcOEt and a 10 % NaOH solution. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 90/10 hexane/AcOEt to obtain 0.540g of the desired product as a yellow powder. (yield : 80 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.49(s, 1H, NH); 9.13(d, *J* = 3.6 Hz, 1H); 7.90(d, *J* = 8.7 Hz, 2H); 7.33(d, *J* = 3.6 Hz, 1H); 6.94(d, *J* = 8.7 Hz, 2H); 4.01(t, *J* = 6.5 Hz, 2H); 1.81(m, 2H); 1.47(m, 2H); 1.31(m, 8H); 0.90(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.12; 162.39; 135.10; 134.29; 128.80; 121.75; 114.71; 113.75; 105.46; 68.61; 32.06; 29.58; 29.48; 29.34; 26.24; 22.92; 14.38.

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2-octylthieno[3,4-d]thiazole **(4a).** In a round bottom flask equipped with a condenser, N-(4-bromothiophenyl)-3-nonanamide **(3a)** (3.5g, 10.5 mmol) was dissolved in 150 mL of anhydrous THF. Then, copper (I) iodide (0.100g, 0.52 mmol), neocuproine (0.218g, 1.05 mmol) and potassium carbonate (2.17g, 15.7 mmol) were quickly added to the stirring solution. The reaction was refluxed overnight and then extracted with AcOEt and water. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 90/10 hexane/AcOEt to obtain 2.37g of the desired product as a yellow oil. (yield : 90 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45(d, J = 2.6 Hz, 1H); 7.16(d, J = 2.6 Hz, 1H); 2.98(t, J = 7.6 Hz, 2H); 1.84(m, 2H); 1.36(m, 10H); 0.88(t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 179.16; 160.17; 134.36; 109.97; 109.61; 35.59; 32.05; 29.49; 29.37; 29.15; 22.89; 14.35.

2-(4-octylphenyl)thieno[3,4-d]thiazole **(4b).** In a round bottom flask equipped with a condenser, N-(4-bromothiophen-3-yl)-4-octylbenzothioamide **(3b)** (1.9g, 4.63 mmol) was dissolved in 65 mL of anhydrous THF. Then, copper (I) iodide (0.044g, 0.23 mmol), neocuproine (0.096g, 0.46 mmol) and potassium carbonate (0.959g, 6.94 mmol) were quickly added to the stirring solution. The reaction was refluxed overnight and then extracted with AcOEt and water. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 90/10 hexane/AcOEt to obtain 1.41g of the desired product as a white powder. (yield : 93 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93(d, J = 8.2 Hz, 2H); 7.58(d, J = 2.6 Hz, 1H); 7.29(d, J = 8.2 Hz, 2H); 7.23(d, J = 2.6

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Hz, 1H); 2.67(t, *J* = 7.6 Hz, 2H); 1.65(m, 2H); 1.30(m, 10H); 0.89(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 174.60; 160.73; 147.27; 133.75; 131.54; 129.30; 127.72; 110.54; 110.17; 36.20; 32.12; 31.45; 29.70; 29.54; 29.50; 22.92; 14.37.

2-(4-(octyloxy)phenyl)thieno[3,4-d]thiazole **(4c).** In a round bottom flask equipped with a condenser, N-(4-bromothiophen-3-yl)-4-(octyloxy)benzothioamide **(3c)** (0.512g, 1.20 mmol) was dissolved in 16 mL of anhydrous THF. Then, copper (I) iodide (0.011g, 0.06 mmol), neocuproine (0.025g, 0.12 mmol) and potassium carbonate (0.249g, 1.8 mmol) were quickly added to the stirring solution. The reaction was refluxed overnight and then extracted with AcOEt and water. The organic fractions were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica in a mixture of 90/10 hexane/AcOEt to obtain 0.270g of the desired product as a white powder. (yield : 65 %) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.94(d, *J* = 8.8 Hz, 2H); 7.52(d, *J* = 2.6 Hz, 1H); 7.20(d, *J* = 2.6 Hz, 2H); 6.97(d, *J* = 8.8 Hz, 2H); 4.01(t, *J* = 6.5 Hz, 2H); 1.81(m, 2H); 1.40(m, 10H); 0.90(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 174.15; 162.08; 160.99; 133.84; 129.32; 126.59; 115.05; 110.01; 109.99; 68.50; 32.06; 29.60; 29.49; 29.40; 26.26; 22.92; 14.37.

4,6-dibromo-2-octylthieno[3,4-d]thiazole **(5a).** To a solution of 2-octylthieno[3,4-d]thiazole **(4a)** (0.590g, 23.3 mmol) in 80 mL of tetrahydrofuran (THF), n-bromosuccinimide (NBS) (0.870g, 48.9 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 $MgSO_4$ and concentrated under

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reduce pressure. The crude product was purified by flash chromatography in 90/10 hexanes/AcOEt to obtain 0.743g of an orange oil. (yield: 82 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.97 (t, *J* = 7.6 Hz, 2H); 1.81 (m, 2H); 1.34 (m, 10H); 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.69; 156.92; 135.91; 95.58; 94.49; 35.86; 32.02; 29.44; 29.36; 29.32; 29.30; 22.88; 14.35.

4,6-dibromo-2-(4-octylphenyl)thieno[3,4-d]thiazole **(5b).** To a solution of 2-(4-octylphenyl)thieno[3,4-d]thiazole **(4b)** (1.41g, 42.7 mmol) in 150 mL of tetrahydrofuran (THF), n-bromosuccinimide (NBS) (1.6g, 89.8 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 $MgSO_4$ and concentrated under reduce pressure. The crude product was purified by flash chromatography in 80/20 hexanes/DCM to obtain 1.60g of an orange powder. (yield: 77 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91(d, *J* = 8.2 Hz, 2H); 7.28(d, *J* = 8.2 Hz, 2M); 2.67(t, *J* = 7.6 Hz, 2H); 1.65(m, 2H); 1.30(m, 10H); 0.89(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 175.20; 157.70; 148.08; 135.43; 130.92; 129.34; 127.99; 96.64; 95.48; 36.25; 32.12; 31.40; 29.69; 29.52; 29.49; 22.92; 14.37.

4,6-dibromo-2-(4-(octyloxy)phenyl)thieno[3,4-d]thiazole **(5c).** To a solution of 2-(4-(octyloxy)phenyl)thieno[3,4-d]thiazole **(4c)** (0.270g, 0.79 mmol) in 25 mL of tetrahydrofuran (THF), n-bromosuccinimide (NBS) (0.292g, 1.64 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

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$MgSO_4$ and concentrated under reduce pressure. The crude product was purified by flash chromatography in 90/10 hexanes/AcOEt to obtain 0.332g of an orange powder. (yield: 84 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91(d, *J* = 8.6 Hz, 2H); 6.94(d, *J* = 8.6 Hz, 2M); 4.01(t, *J* = 6.5 Hz, 2H); 1.81(m, 2H); 1.47(m, 2H); 1.30(m, 8H) 0.90(t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 174.75; 162.66; 157.72; 135.42; 129.72; 125.81; 115.06; 95.97; 95.34; 68.57; 32.06; 29.59; 29.48; 29.37; 26.25; 22.92; 14.37.

P2

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

In a 25 mL flask fitted with a condenser, 0.386g (0.500 mmol) of 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene, 0.244g (0.500 mmol) of 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5b)**, 9.0mg (0.010 mmol) of Pd_2dba_3, 12.2mg (0.040 mmol) of triphenylarsine ($AsPh_3$), 5 mL of degassed toluene and 0.5 mL of degassed DMF were added. The reaction mixture was vigorously stirred for 48 h at 110 ºC. After reaction completion, 5.3 µL (0.05 mmol) of bromobenzene was added, then one hour later 9.1 µL (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 µm 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

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through 0.45 μm nylon filter and air-dried to give 0.368 g of the desired polymer. (yield: 95%).

P3

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

In a 25 mL flask fitted with a condenser, 0.350g (0.453 mmol) of 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-b:4,5-b']dithiophene, 0.228g (0.453 mmol) of 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5c)**, 8.3mg (0.0091 mmol) of Pd_2dba_3, 11.1mg (0.036 mmol) of triphenylarsine ($AsPh_3$), 5 mL of degassed toluene and 0.5 mL of degassed DMF were added. The reaction mixture was vigorously stirred for 48 h at 110 ºC. After reaction completion, 5.3 μL (0.05 mmol) of bromobenzene was added, then one hour later 9.1 μL (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 μm 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 μm nylon filter and air-dried to give 0.050 g of the desired polymer. (yield: 14%).

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P5

Poly[2,6-(4,4-Bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole)-alt-4,6-(2-n-octyl)thieno[3,4-d]thiazole]

In a 25 mL flask fitted with a condenser, 0.375g (0.504 mmol) of 4,4-Bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole, 0.197g (0.480 mmol) of 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5a)**, 8.8mg (0.0096 mmol) of Pd_2dba_3, 11.7mg (0.038 mmol) of triphenylarsine ($AsPh_3$), 5 mL of degassed toluene and 0.5 mL of degassed DMF were added. The reaction mixture was vigorously stirred for 48 h at 110 ºC. After reaction completion, 5.3 µL (0.05 mmol) of bromobenzene was added, then one hour later 9.1 µL (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 µm 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 µm nylon filter and air-dried to give 0.256 g of the desired polymer. (yield: 76%).

P6

*Poly[4,6-(*2-octylthieno[3,4-d]thiazole)-alt-1,3-(5-(heptadecan-9-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione)]

5-(heptadecan-9-yl)-5H-thieno[3,4-*c*]pyrrole-4,6-dione (0.150g, 0.38 mmol), 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5a)** (0.157g, 0.38 mmol), *trans*-di(µ-

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acetato)bis[*o*-(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) **(** 7.2mg, 2% mol), pivalic acid (11.7 mg, 30% mol), tris(2-methoxyphenyl)phosphine (10.7mg, 4% mol) and cesium carbonate (250.0 mg 0.76mmol) were put in a Biotage microwave vial (size 2 to 5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen. 1.5 mL of degased THF was added and the reaction was heated with an oil bath at 120^{o}C (reaction under pressure) for 24h. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45 µm 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 µm nylon filter and air-dried to give 0.100 g of the desired polymer. (yield: 41%).

P7

Poly[4,6-(2-octylthieno[3,4-d]thiazole)-alt-3,6-bis(thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione]

3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.112g, 0.109 mmol), 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5a)** (0.028g, 0.109 mmol), *trans*-di(µ-acetato)bis[*o*-(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) **(**1.8mg, 2% mol), pivalic acid (3.1 mg, 30% mol), tris(2-methoxyphenyl)phosphine (2.8 mg, 4% mol) and cesium carbonate (74.9 mg 0.4mmol) were put in a Biotage microwave vial (size 2 to 5 mL) with a magnetic stirring bar. The vial was sealed with a cap and then purged with nitrogen to remove the oxygen.

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1 mL of THF was added and the reaction was heated with an oil bath at 120°C (reaction under pressure) for 24h. Then the reaction was cooled to room temperature and the polymer precipitated in methanol, filtered through 0.45 µm 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 µm nylon filter and air-dried to give 0.072 g of the desired polymer. (yield: 60%).

P8

Poly[4,6-(2-octylthieno[3,4-d]thiazole)-alt-6,6'-(N,N'-2-hexyldecyl)isoindigo]

In a 25 mL flask fitted with a condenser, 0.150g (0.156 mmol) of 6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(N,N'-2-hexyldecyl)-dibromoisoindigo, 0.064g (0.156 mmol) of 2-octyl-4,6-dibromo-thieno[3,4-d]thiazole **(5a)**, 0.7mg (0.18 µmol) of Pd_2dba_3, 0.9mg (3.12 µmol) of tri-*o*-tolylphosphine (P(*o*-tol)$_3$), 5 mL of degassed toluene and 1 mL of degassed DMF were added. The reaction mixture was vigorously stirred for 48 h at 110 ºC. After reaction completion, 5.3 µL (0.05 mmol) of bromobenzene was added, then 1 hour later 9.1 µL (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 µm 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 µm nylon filter and air-dried to give 0.037 g of the desired polymer. (yield: 25%).

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Characterization

^{1}H and ^{13}C NMR were recorded using a Varian AS400 in deuterated chloroform or acetone solution at 298 K. Chemicals shifts were reported as δ 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 ^{o}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 ^{o}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

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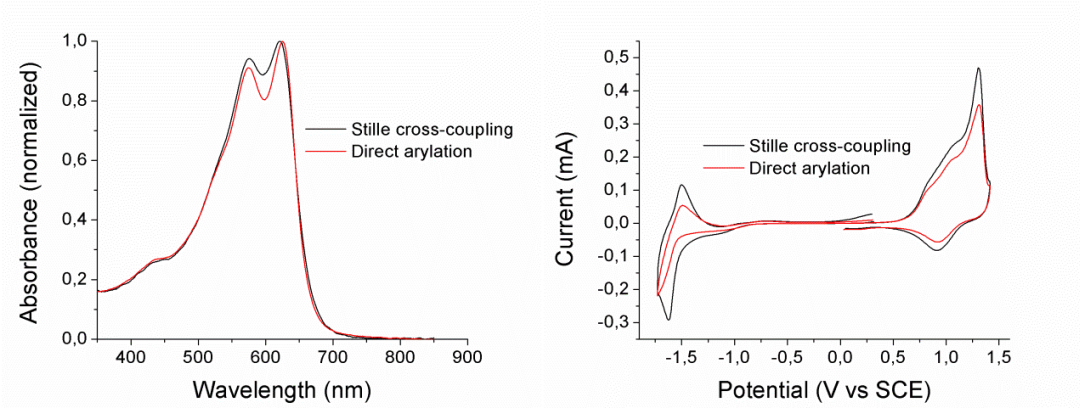
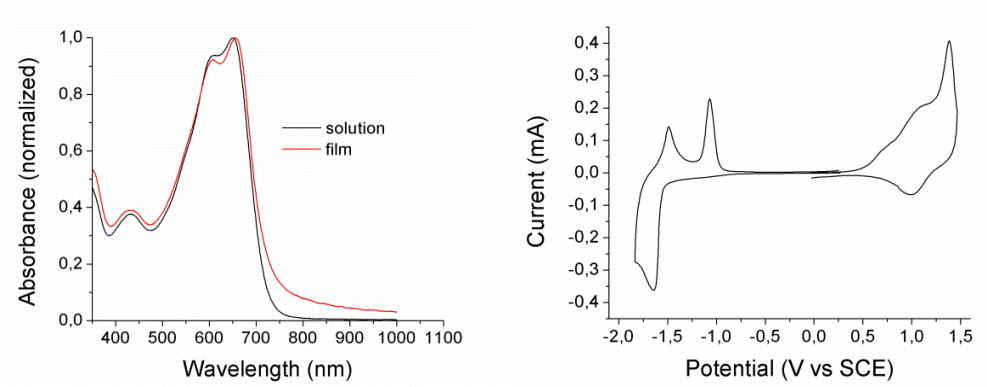
electrodes at a scan rate of 50 mVs^{-1} and a Ag/Ag^{+} (0.1 M of $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and argon saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets, assuming an SCE electrode to be at -4.7 eV from vacuum.



S1: UV-vis absorption spectra and cyclic voltammograms of **P1** synthesized by a Stille cross-coupling or by (hetero)direct arylation polymerization.



S2: UV-vis absorption spectra and cyclic voltammograms of **P2**

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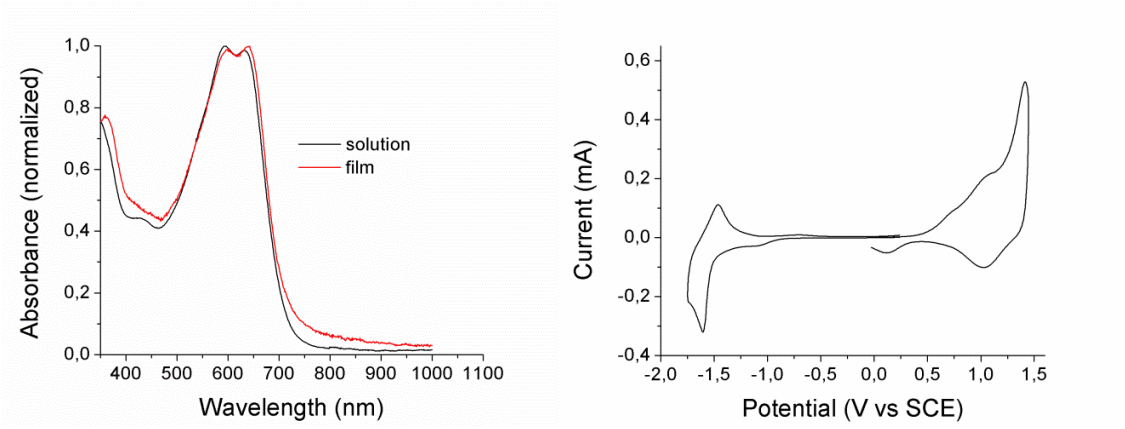
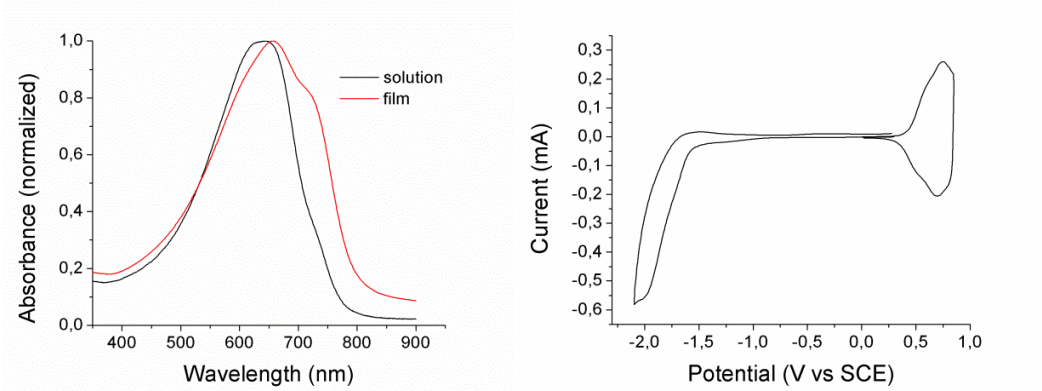
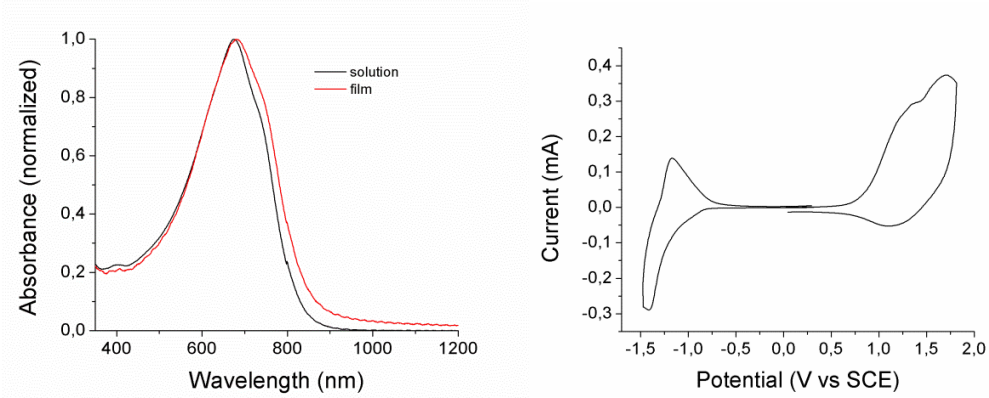


S3: UV-vis absorption spectra and cyclic voltammograms of **P3**



S4: UV-vis absorption spectra and cyclic voltammograms of **P5**



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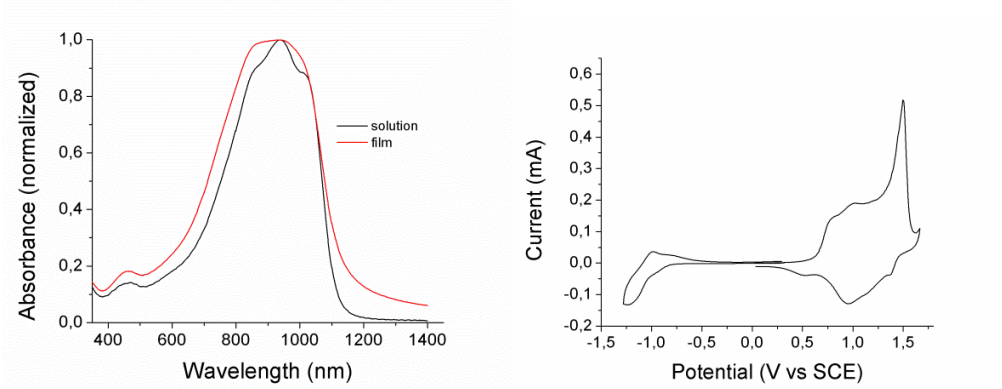
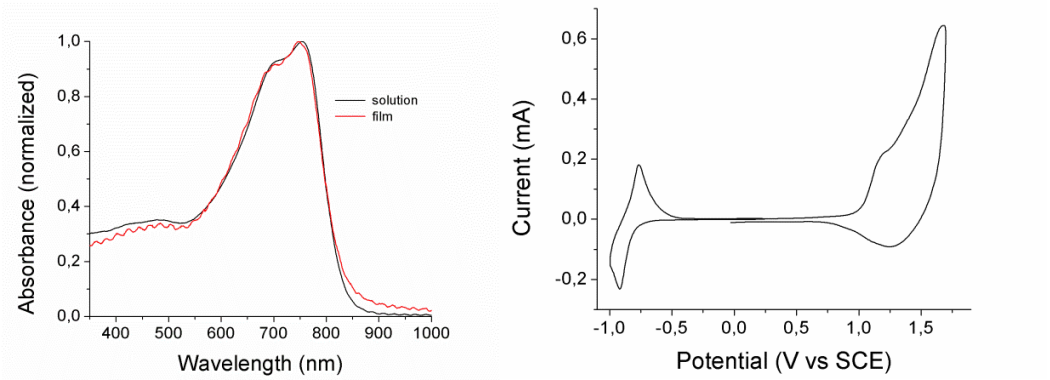
S5: UV-vis absorption spectra and cyclic voltammograms of **P6**



S6: UV-vis absorption spectra and cyclic voltammograms of **P7**



S7: UV-vis absorption spectra and cyclic voltammograms of **P8**

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