Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for the Paper

π-Conjugated Polymers with Thermocleavable Substituents for Use as Active Layers in Organic Photovoltaics

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General Procedures and Starting Materials. The reagents 6-bromo-1-hexanol, 6-chloro-1-hexanol, 8-chloro-1-octanol, dihydropyran (DHP), *p*-toluenesulfonic acid monohydrate (pTSA), magnesium, [1,3-bis(diphenylphosphino)propane] dichloronickel(II) (Ni(dppp)Cl_2), 3-bromothiophene, *N*-bromosuccinimide (NBS), 3,4-ethylenedioxythiophene (EDOT), *n*-butyllithium (2.5 M in hexanes), magnesium bromide ethyl etherate ($MgBr_2{\cdot}Et_2O$), dimethylformamide (DMF), diisopropylamine and methylmagnesium bromide (1.0 M in butyl ether) were obtained commercially (all from Aldrich) and used as received. All solvents were of at least reagent grade. All reactions were carried out under inert conditions unless otherwise stated.

6-Bromo-1-tetrahydropyranyloxyhexane (**1a: X = Br**). *p*-Toluenesulfonic acid monohydrate (90 mg, 0.473 mmol) was added to a solution of 6-bromo-1-hexanol (3.0 mL, 21.9 mmol) and DHP (3.0 mL, 33.0 mmol) in DCM (3.0 mL) at 0 °C under Ar(g). After 20 min the reaction mixture was brought to RT and stirred for 16 hr then poured onto water and extracted with DCM. The organic phase was separated, washed with $NaHCO_3$ (aq), dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford crude **1a** (X = Br) (6.23 g, 107%). The product was filtered through a silica plug with a solvent mixture of hexanes and DCM (3:2) affording pure **1a** (X = Br) (4.15 g, 71.6%) as a clear colorless liquid. ^{1}H NMR (δ, $CDCl_3$): 4.58 (1H, dd, J = 4.25 Hz), 3.88 (1H, m), 3.75 (1H, tt, J = 6.75), 3.51 (1H, m), 3.44 – 3.38 (3H, m), 1.91 – 1.39 (14 H, m).

6-Chloro-1-tetrahydropyranyloxyhexane (**1a: X = Cl**). *p*-Toluenesulfonic acid monohydrate (285 mg, 1.50 mmol) was added to a solution of 6-chloro-1-hexanol

(10.0 mL, 74.9 mmol) and DHP (10.2 mL, 112.5 mmol) in DCM (20 mL) at 0 °C under Ar(g). After 20 min the reaction mixture was brought to RT and stirred for 16 hr then poured onto water and extracted with DCM. The organic phase was separated, washed with $NaHCO_3$ (aq) and dried over $MgSO_4$. The solvent was subsequently removed under reduced pressure and further purification by filtration through a silica plug using hexanes/DCM (3/2) afforded **1a** (X = Cl) (15.3 g, 92.3 %) as a clear colorless liquid. ^{1}H NMR (δ, $CDCl_3$): 4.54 (1H, dd, J = 4.5 Hz), 3.83 (1H, m), 3.71 (1H, dt, J = 6.75 Hz), 3.52 – 3.45 (3H, m), 3.35 (1H, dt, J = 6.5 Hz), 1.81 – 1.35 (14H, m).

8-Chloro-1-tetrahydropyranyloxyoctane (**1b: X = Cl**). *p*-Toluenesulfonic acid monohydrate (340 mg, 1.79 mmol) was added to a solution of 8-chloro-1-octanol (15.0 mL, 88.9 mmol) and DHP (12.0 mL, 132.4 mmol) in DCM (20 mL) at 0 °C under Ar(g). After 20 min the reaction mixture was brought to RT and stirred for 16 hr then poured onto water and extracted with DCM. The organic phase was separated, washed with $NaHCO_3$ (aq) and dried over $MgSO_4$. The solvent was subsequently removed under reduced pressure and further purification by filtration through a silica plug using hexanes/DCM (3/2) afforded **1b** (X = Cl) (19.9 g, 90 %) as a clear colorless liquid. ^{1}H NMR (δ, $CDCl_3$): 4.55 (1H, dd, J = 4.25 Hz), 3.84 (1H, m), 3.70 (1H, dt, J = 7.00 Hz), 3.52 – 3.45 (3H, m), 3.35 (1H, dt, J = 6.5 Hz), 1.83 – 1.29 (18H, m).

3-(6-(2-Tetrahydropyranyloxy)hexyl)thiophene (**2a**). A solution of **1a** (X = Cl) (13.9 g, 63.0 mmol) in THF (20 mL) was added to magnesium ribbons (1.54 mg, 63.5 mmol) and a few crystals of iodine. The reaction mixture was heated to reflux and stirred for 6h. Upon cooling to room temperature, the prepared Grignard reagent was transferred to a dropping funnel and slowly added to a solution of 3-bromothiophene (4.7 mL, 50.1 mmol) in THF (10 mL) in the presence of Ni(dppp)Cl_2 (275 mg, 0.51 mmol). The reaction mixture was heated to reflux and stirred for 16 h. After cooling to room temperature, the reaction mixture was poured onto water and extracted with DCM. The organic layer was separated, washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Distillation to remove the by-product followed by filtration through a silica plug with DCM afforded **2a** as a clear colourless liquid (6.13g, 45.6%) ^{1}H NMR (δ, $CDCl_3$): 7.21 (1H, dd, J = 5.0 Hz), 6.92 – 6.89 (2H, m), 4.56 – 4.54 (1H, m), 3.87 – 3.82 (1H, m), 3.71 (1H, dt, J = 7.0Hz), 3.50 – 3.46 (1H, m), 3.36 (1H, dt, J = 6.5 Hz), 2.61 (2H, t, J = 7.75 Hz), 1.84 – 1.35 (14H, m).

3-(8-(2-Tetrahydropyranyloxy)octyl)thiophene (**2b**). A solution of **1b** (X = Cl) (10.0 g, 40.2 mmol) in THF (20 mL) was added to magnesium ribbons (1.085 g, 44.6 mmol) and a few crystals of iodine. The reaction mixture was heated to reflux and stirred for 4h. Upon cooling to room temperature, the prepared Grignard reagent was transferred to a dropping funnel and slowly added to a solution of 3-bromothiophene (3.0 mL, 32.1 mmol) in THF (15 mL) in the presence of Ni(dppp)Cl_2 (180 mg, 0.332 mmol). The reaction mixture was heated to reflux and stirred for 16 h. After cooling to room temperature, the reaction mixture was poured onto water and extracted with DCM. The organic layer was separated, washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Distillation to remove the by-product followed by filtration through a silica plug with DCM afforded **2b** as a clear colourless liquid (4.3 g, 45.2 %) ^{1}H NMR (δ, $CDCl_3$): 7.21 (1H, dd, J = 4.86 Hz), 6.92 – 6.89 (1H, m), 4.56 - 4.55 (1H, m), 3.85 – 3.83 (1H, m), 3.71 (1H, dt, J = 6.93 Hz), 3.49 – 3.47 (1H, m), 3.36 (1H, dt, J = 6.71 Hz), 2.61 – 2.58 (2H, m), 1.82 – 1.23 (18H, m).

2-Bromo-3-(6-(2-tetrahydropyranyloxy)hexyl)thiophene (**3a**). NBS (2.49 g, 14.0 mmol) was added in small aliquots to a solution of **2a** (3.71 g, 13.8 mmol) in $CHCl_3$:acetic acid (1:1, 15 mL) at 0 °C. The reaction was slowly brought to RT and after stirring for 16 h poured onto water and extracted with DCM. The organic layer was washed with $NaHCO_3$ (aq), dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by column chromatography with hexanes/DCM (3/2) afforded the desired product **3a** as a clear yellow liquid (3.28 g, 68.3 %). ^{1}H NMR (δ, $CDCl_3$): 7.16 (1H, d, J = 5.5 Hz), 6.77 (1H, d, J = 5.5 Hz), 4.55 (1H, dd, J = 4.5 Hz), 3.87 – 3.82 (1H, m), 3.71 (1H, dt, J = 7.0 Hz), 3.50 – 3.45 (1H, m), 3.36 (1H, dt, J = 6.75 Hz), 2.54 (2H, t, J = 7.5 Hz), 1.84 – 1.33 (14H, m).

2-Bromo-3-(8-(2-tetrahydropyranyloxy)octyl)thiophene (**3b**). NBS (2.51 g, 14.1 mmol) was added in small aliquots to a solution of **2b** (4.3 g, 14.5 mmol) in $CHCl_3$:acetic acid (1:1, 20 mL) at 0 °C. The reaction was slowly brought to RT and after stirring for 16 h poured onto water and extracted with DCM. The organic layer was washed with $NaHCO_3$ (aq), dried over $MgSO_4$ and the solvent removed under reduced pressure to afford the crude product as a yellow liquid (5.28 g, 99.8 %). Purification by column chromatography with hexanes/DCM (3/2) provided the desired product **3b** as a clear colorless liquid (2.79 g, 52.7 %). ^{1}H NMR (δ, $CDCl_3$): 7.16 (1H, d, J = 5.58 Hz), 6.77 (1H, d, J = 5.58 Hz), 4.56 - 4.55 (1H, m), 3.86 – 3.83 (1H, m), 3.71 (1H, dt, J = 6.93 Hz), 3.49 – 3.47 (1H, m), 3.36 (1H, dt, J = 6.68 Hz), 2.55 – 2.52 (2H, m), 1.84 – 1.33 (18H, m).

McCullough Polymerization of 2-Bromo-3-(6-(2-tetrahydropyranyloxy)hexyl) thiophene. *n*-BuLi (2.3 mL, 2.5 M in hexanes) was added dropwise to a solution of diisopropylamine (0.81 mL, 5.74 mmol) in THF (20mL) at RT. The stirring solution was then cooled to -40 °C and 40 min then cooled further to -78 °C at which time a solution of **3a** (2.0 g, 5.76 mmol) in THF (5 mL) was added dropwise slowly. The reaction mixture was allowed to warm to -40 °C and stirred for 40 min. The reaction mixture was cooled back down to -78 °C and magnesium bromide diethyletherate (1.5 g, 5.81 mmol) was added. After stirring for 20 min at -78 °C, the mixture was allowed to slowly warm to -5 °C and Ni(dppp)Cl_2 (34 mg, 0.0627 mmol) was added and the mixture warmed to RT. After stirring for 18 hr, the reaction was quenched with MeOH (400 mL) and filtered to afford a dark red solid. Purification by Soxhlet extraction with MeOH and hexanes, followed by extraction with chloroform and evaporation of the solvent afforded the desired polymer **4a** as a dark red solid (480 mg). The polymer had average molecular weight M_w = 13603 and M_n = 8978 with a polydispersity index (PDI) of 1.515 determined by GPC. ^{1}H NMR (δ, $CDCl_3$): 6.94 (1H, s), 4.55 (1H, s), 3.89 – 3.79 (1H, m), 3.75 – 3.70 (1H, m), 3.50 – 3.43 (1H, m), 3.41 – 3.30 (1H, m), 2.83 – 2.70 (2H, m), 1.85 – 1.33 (14H, m).

McCullough Polymerization of 2-Bromo-3-(8-(2-tetrahydropyranyloxy)octyl) thiophene. *n*-BuLi (1.47 mL, 2.5 M in hexanes) was added dropwise to a solution of diisopropylamine (0.52 mL, 3.68 mmol) in THF (15mL) at RT. The stirring solution was then cooled to -40 °C and 40 min then cooled further to -78 °C at which time a solution of **3b** (1.38 g, 3.68 mmol) in THF (5 mL) was added dropwise slowly. The reaction mixture was allowed to warm to -40 °C and stirred for 40 min. The reaction mixture was cooled back down to -78 °C and magnesium bromide diethyletherate (950 mg, 3.68 mmol) was added. After stirring for 20 min at -78 °C, the mixture was allowed to slowly warm to -5 °C and Ni(dppp)Cl_2 (20 mg, 0.0369 mmol) was added and the mixture warmed to RT. After stirring for 18 hr, the reaction was quenched with MeOH (400 mL) and filtered to afford a dark red solid. Purification by Soxhlet extraction with MeOH and hexanes, followed by extraction with chloroform and evaporation of the solvent afforded the desired polymer **4b** (300 mg). Dissolution into chloroform followed by precipitation in MeOH afforded the purified polymer as a sticky dark red/purple solid. The polymer had average molecular weight M_w = 7312 and M_n = 6089 with a polydispersity index (PDI) of 1.2 determined by GPC. ^{1}H NMR (δ, $CDCl_3$): 7.10 (1H, s), 4.55 - 4.50 (1H, m), 3.84 – 3.78 (1H, m), 3.71 – 3.64 (1H, m), 3.47 – 3.41 (1H, m), 3.37 – 3.30 (1H, m), 2.85 – 2.75 (2H, m), 1.85 – 1.30 (18H, m).

3,4-Ethylenedioxy-3’-(6-(2-tetrahydropyranyloxy)hexyl)-2,2’-bithiophene (7). *n*-Butyllithium (2.3 mL, 2.5 M in hexanes) was added to a solution of EDOT (0.61 mL, 5.72 mmol) in THF (10 mL) at -78 °C. After 1h, the reaction mixture was warmed to 0 °C and $MgBr_2 \cdot Et_2O$ (1.49 g, 5.77 mmol) was added in one portion. After 45 min, the reaction mixture was allowed to warm to RT. The freshly prepared Grignard reagent was added to a THF (10 mL) solution of **3a** (2.09 g, 6.02 mmol) in the presence of $Ni(dppp)Cl_2$ (70 mg, 0.129 mmol). After refluxing for 16h, the reaction mixture was poured onto water and extracted with DCM. The combined organic phases were washed with NaCl (aq) and water then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the crude product as a dark brown oil (2.42 g, 98.4 %). Purification by column chromatography with DCM provided the desired product **7** as a clear colorless liquid (1.47 g, 63 %). ^{1}H NMR (δ, $CDCl_3$): 7.21 (1H, d, J = 5.22 Hz), 6.90 (1H, d, J = 5.22 Hz), 6.34 (1H, s), 4.55 - 4.54 (1H, m), 4.25 – 4.20 (4H, m), 3.85 – 3.82 (1H, m), 3.69 (1H, dt, J = 6.90 Hz), 3.48 – 3.46 (1H, m), 3.35 (1H, dt, J = 6.65 Hz), 2.67 – 2.64 (2H, m), 1.79 – 1.34 (14H, m).

3,4-Ethylenedioxy-5,5’-dibromo-3’-(6-(2-tetrahydropyranyloxy)hexyl)-2,2’-bithiophene (8). Under subdued light, a solution of NBS (1.32 g, 7.42 mmol) in DMF (10 mL) was added dropwise to a solution of **7** (1.45 g, 3.55 mmol) in DMF (10 mL) at 0 °C. The reaction was slowly brought to RT and after stirring for 16 h poured onto water and extracted with DCM. The organic layer was washed with copious amounts of saturated NaCl (aq), dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by column chromatography with DCM afforded the desired product **8** as a dark brown oil (1.496 g, 74.4 %). ^{1}H NMR (δ, $CDCl_3$): 6.85 (1H, s), 4.55 - 4.54 (1H, m), 4.28 – 4.23 (4H, m), 3.85 – 3.82 (1H, m), 3.70 (1H, dt, J = 6.84 Hz), 3.49 – 3.47 (1H, m), 3.35 (1H, dt, J = 6.57 Hz), 2.59 – 2.56 (2H, m), 1.83 – 1.32 (14H, m).

Grim Polymerization of 3,4-Ethylenedioxy-5,5'-dibromo-3'-(6-(2-tetrahydropyranyloxy)hexyl)-2,2'-bithiophene. Methylmagnesium bromide (4.75 mL, 1.0 M in butyl ether) was added to a solution of **8** (2.243 g, 3.96 mmol) in THF (20mL) and the reaction was brought to reflux for 5 h. Ni(dppp)Cl_2 (20.0 mg, 0.0369 mmol) was added and stirred at reflux overnight. The reaction was cooled to RT then quenched with MeOH (400 mL) and filtered to afford a dark red solid. Purification by Soxhlet extraction with MeOH and hexanes, followed by extraction with chloroform and evaporation of the solvent afforded the desired polymer **9** as a dark purple solid (115 mg). The polymer had average molecular weight $M_w = 6809$ and $M_n = 5445$ with a polydispersity index (PDI) of 1.25 determined by GPC. ^{1}H NMR (δ, $CDCl_3$): 7.07 (1H, s), 4.56 (1H, s), 4.37 (4H, m), 3.90 – 3.81 (1H, m), 3.79 – 3.68 (1H, m), 3.52 – 3.43 (1H, m), 3.42 – 3.32 (1H, m), 2.85 – 2.64 (2H, m), 1.90 – 1.10 (14H, m).