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Acceptor (Block) Copolymers via GRIM Polymerization

Supplementary material

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Supporting Information

Synthesis of highly fluorescent all-conjugated alternating donor-acceptor (block) copolymers via GRIM polymerization

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Reagents and instrumentation

All reagents and chemicals were obtained from commercial sources and used without further purification. Diethyl ether and THF were dried using a solvent purification system (MBraun MB-SPS 800). NMR chemical shifts (δ , in ppm) were determined relative to the residual ^1H signal of CHCl_3 (7.26 ppm) or the ^{13}C resonance shift of CDCl_3 (77.16 ppm). High resolution ESI-MS was performed using a LTQ Orbitrap Velos Pro mass spectrometer equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z range 220–2000 using a standard solution containing caffeine, MRFA and Ultramark 1621. Analysis of the molar masses and distributions of the polymer samples was performed on a Tosoh EcoSEC System, comprising of an autosampler, a PSS guard column SDV (50 x 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 μm , 300 x 7.5 mm) and a UV-detector using THF as the eluent at 40 °C with a flow rate of 1.0 mL/min. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5×10^6 g/mol ($K = 14.1 \times 10^{-5}$ dL/g and $\alpha = 0.70$). Preparative size exclusion chromatography (prep-SEC) was performed on a JAI LC-9110 NEXT system equipped with JAIGEL 2H and 3H columns (eluent CHCl_3 , flow rate 3.5 mL/min). MALDI-TOF mass spectra were recorded on a Bruker Daltonics Ultraflex II ToF/ToF. 1 μL of the matrix solution (4 mg/mL DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile) in CHCl_3) was spotted onto an MTP Anchorchip 600/384 MALDI plate. The spot was allowed to dry and 1 μL of the analyte solution (0.5 mg/mL in CHCl_3) was spotted on top of the matrix. Background corrected UV-Vis absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer from Agilent using a band width of 2 nm, full slit height and a scan speed of 600 nm/min. Fully corrected steady-state emission spectra were recorded on a Fluorolog 3-2-2 Tau from Horiba Jobin Yvon, using a band pass of 2 nm and an increment of 1. Samples were dissolved in chloroform. The absorbance at the excitation wavelength was adjusted between 0.01 and 0.1 AU. Absorption and emission spectra were collected at room temperature without deoxygenation. 9,10-Diphenylanthracene dissolved in cyclohexane was used as the reference (quantum yield = 0.90).¹ Calculated quantum yield values were corrected for refractive index variation between solvents. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat using a three-electrode microcell setup with a platinum wire working electrode, a platinum wire counter electrode, a Ag/AgNO₃ reference electrode (silver wire in 0.01 M AgNO₃ / 0.1 M NBu₄PF₆ in anhydrous acetonitrile) and (argon degassed) anhydrous acetonitrile containing 0.1 M NBu₄PF₆ as the electrolyte. The system was calibrated against ferrocene/ferrocenium. Experiments were carried out under a constant flow of argon over the electrolyte surface. The polymer samples were dissolved in CS₂. The working electrode was dipped into this solution and dried at room temperature in air before the measurement. Cyclic voltammograms were recorded at a scan rate of 100 mV/s. The HOMO-LUMO energy levels of the polymers were estimated using the obtained CV data. For the conversion of V to eV, the onset potentials of the first oxidation/reduction peaks were used and referenced to ferrocene/ferrocenium, which has an ionization potential of -4.98 eV vs. vacuum. This correction factor is based on a value of 0.31 eV for Cp₂Fe/Cp₂Fe⁺ vs. a saturated calomel electrode (SCE)² and a value of 4.68 eV for SCE vs. vacuum.³

$$E_{\text{HOMO}} (\text{eV}) = -4.98 - E_{\text{onset, ox}}^{\text{Ag/AgNO}_3} (\text{V}) + E_{\text{onset, Fc/Fc}^+}^{\text{Ag/AgNO}_3} (\text{V})$$

$$E_{\text{LUMO}} (\text{eV}) = -4.98 - E_{\text{onset, red}}^{\text{Ag/AgNO}_3} (\text{V}) + E_{\text{onset, Fc/Fc}^+}^{\text{Ag/AgNO}_3} (\text{V})$$

The accuracy of measuring redox potentials by CV is about 0.01–0.02 V. Reproducibility can be less because the potentials depend on concentration and temperature. Rapid heat-cool calorimetry (RHC) experiments were performed on a prototype RHC of TA Instruments, equipped with liquid nitrogen cooling and specifically designed for operation at high scanning rates. RHC measurements were performed at 500 K/min (after cooling at 20 K/min) using aluminum crucibles filled with samples of 200–250 μg , using helium (10 mL/min) as a purge gas. TGA experiments were performed at 20 K/min in platinum crucibles on a TA Instruments Q5000 TGA using nitrogen (50 mL/min) as purge gas.

Monomer synthesis

2,5-Dibromo-3-hexylthiophene was synthesized according to a literature procedure.^{4,5}

Synthesis of 2-bromo-3-hexylthiophene (1)⁶

A solution of 3-hexylthiophene (7.57 g, 45.0 mmol) in tetrahydrofuran (75 mL) was cooled to 0 °C and protected from light. *N*-bromosuccinimide (8.01 g, 45.0 mmol) was added in portions and the mixture was stirred for 2 h at room temperature and under N₂ atmosphere. The reaction was quenched with H₂O, extracted with diethyl ether (3x) and washed subsequently with a saturated Na₂S₂O₃ solution and H₂O. The organic layer was then dried with MgSO₄, filtered and evaporated under reduced pressure. The product was purified by column chromatography (silica gel, petroleum ether), resulting in a colorless oil (7.98 g, 72%). ¹H NMR (300 MHz, CDCl₃): δ = 7.18 (d, *J* = 5.6 Hz, 1H), 6.79 (d, *J* = 5.6 Hz, 1H), 2.60–2.52 (m, 2H), 1.63–1.52 (m, 2H), 1.37–1.25 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H).

Synthesis of 2-bromo-5-iodopyridine (2)^{7,8}

n-Butyllithium (9.29 mL, 23.2 mmol; 2.5 M in hexanes) was added dropwise to a solution of 2,5-dibromopyridine (5.00 g, 21.1 mmol) in dry diethyl ether (250 mL) at –78 °C and under Ar atmosphere. After stirring for 30 min at –78 °C, an ice-cooled solution of iodine (5.89 g, 23.2 mmol) in dry diethyl ether (50 mL) was added via cannula. The mixture was then stirred for 2 h, whereby it slowly heated up to –40 °C. The reaction was quenched with a saturated Na₂S₂O₃ solution and extracted with diethyl ether (3x). The resulting organic layer was washed with brine and dried with MgSO₄. After filtration and evaporation to dryness, the crude product was purified via column chromatography (silica gel, petroleum ether/ethyl acetate 80/20). The product was finally obtained as a white solid (5.49 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ = 8.59 (d, *J* = 2.4 Hz, 1H), 7.82 (dd, *J* = 8.3 Hz and 2.4 Hz, 1H), 7.29 (dd, *J* = 8.3 Hz and 0.5 Hz, 1H).

Synthesis of 2-bromo-5-(3'-hexylthiophen-2'-yl)pyridine (3)

n-Butyllithium (6.34 mL, 15.8 mmol; 2.5 M in hexanes) was added dropwise to a solution of 2-bromo-3-hexylthiophene (1) (3.56 g, 14.4 mmol) in dry tetrahydrofuran (6 mL) at –78 °C and under Ar atmosphere. The mixture was stirred for 1 h at –78 °C, during which zinc chloride

(2.36 g, 17.3 mmol) was weighed in a flame-dried three-neck flask, dried under vacuum, brought under Ar atmosphere and dissolved in dry tetrahydrofuran (17 mL). This solution was then added via cannula to the lithiated thiophene at $-78\text{ }^{\circ}\text{C}$ and the mixture was allowed to gradually heat up to room temperature over 2 h. Meanwhile, 2-bromo-5-iodopyridine (**2**) (3.68 g, 13.0 mmol) was dissolved in dry tetrahydrofuran (13 mL) and purged with N_2 , after which $\text{Pd}(\text{PPh}_3)_4$ (0.266 g, 0.230 mmol, 1.6 mol%) was added in one portion and the mixture was again purged with N_2 . The formed zinc intermediate was then added to this solution via cannula, the mixture was again purged with N_2 and then it was refluxed overnight. The mixture was cooled down to room temperature, quenched with a saturated NaHCO_3 solution and extracted with chloroform (3x). The resulting organic layer was dried with MgSO_4 , filtered and evaporated to dryness. The crude product was finally purified with column chromatography (silica gel, petroleum ether/dichloromethane 50/50), yielding a yellow oil (2.12 g, 50%). ^1H NMR (400 MHz, CDCl_3): δ = 8.43 (dd, J = 2.5 and 0.7 Hz, 1H), 7.58 (dd, J = 8.2 and 2.5 Hz, 1H), 7.52 (dd, J = 8.2 and 0.7 Hz, 1H), 7.31 (d, J = 5.2 Hz, 1H), 7.01 (d, J = 5.2 Hz, 1H), 2.65–2.56 (m, 2H), 1.63–1.54 (m, 2H), 1.32–1.22 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 150.0 (CH), 140.74 (C), 140.67 (C), 139.1 (CH), 132.2 (C), 130.4 (C), 130.0 (CH), 128.0 (CH), 125.4 (CH), 31.7 (CH_2), 31.1 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ESI-HRMS: found 324.0389, calcd 324.0422 (MH^+).

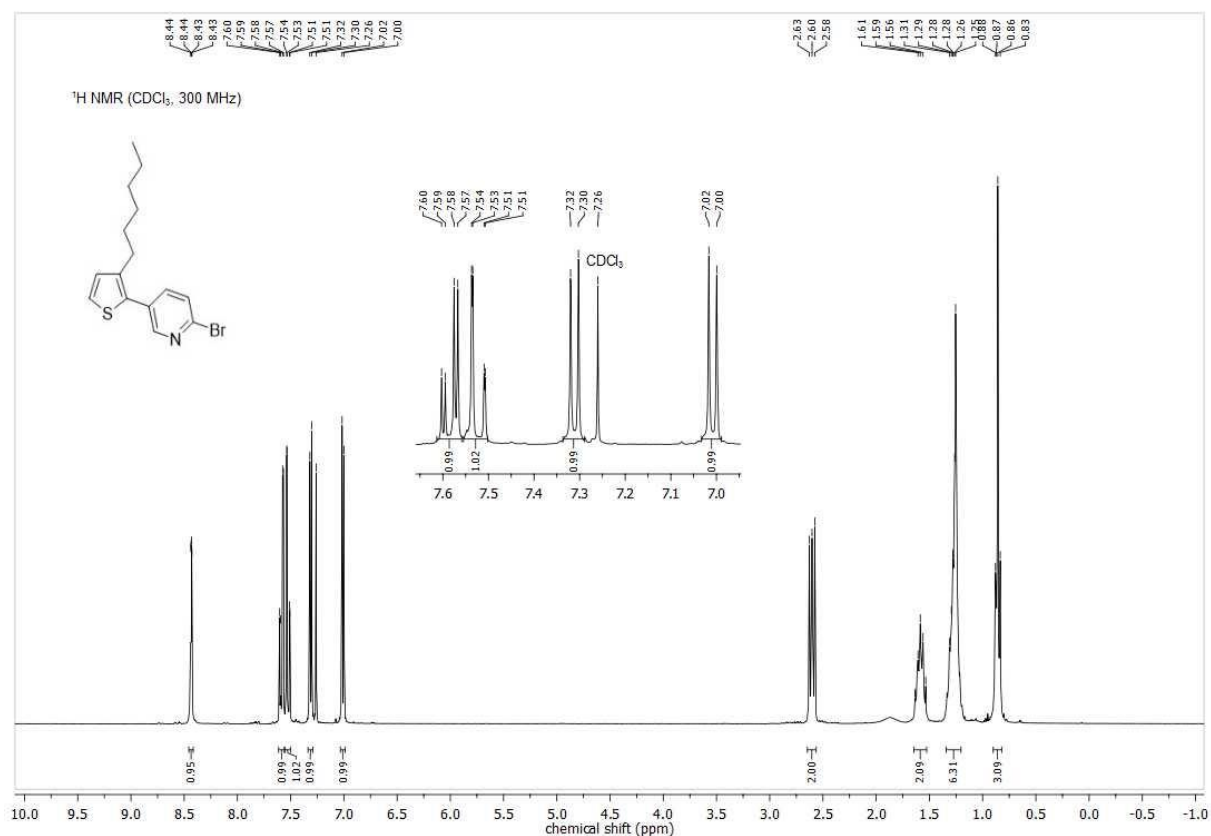


Figure S1. ^1H NMR spectrum of 2-bromo-5-(3'-hexylthiophen-2'-yl)pyridine (**3**).

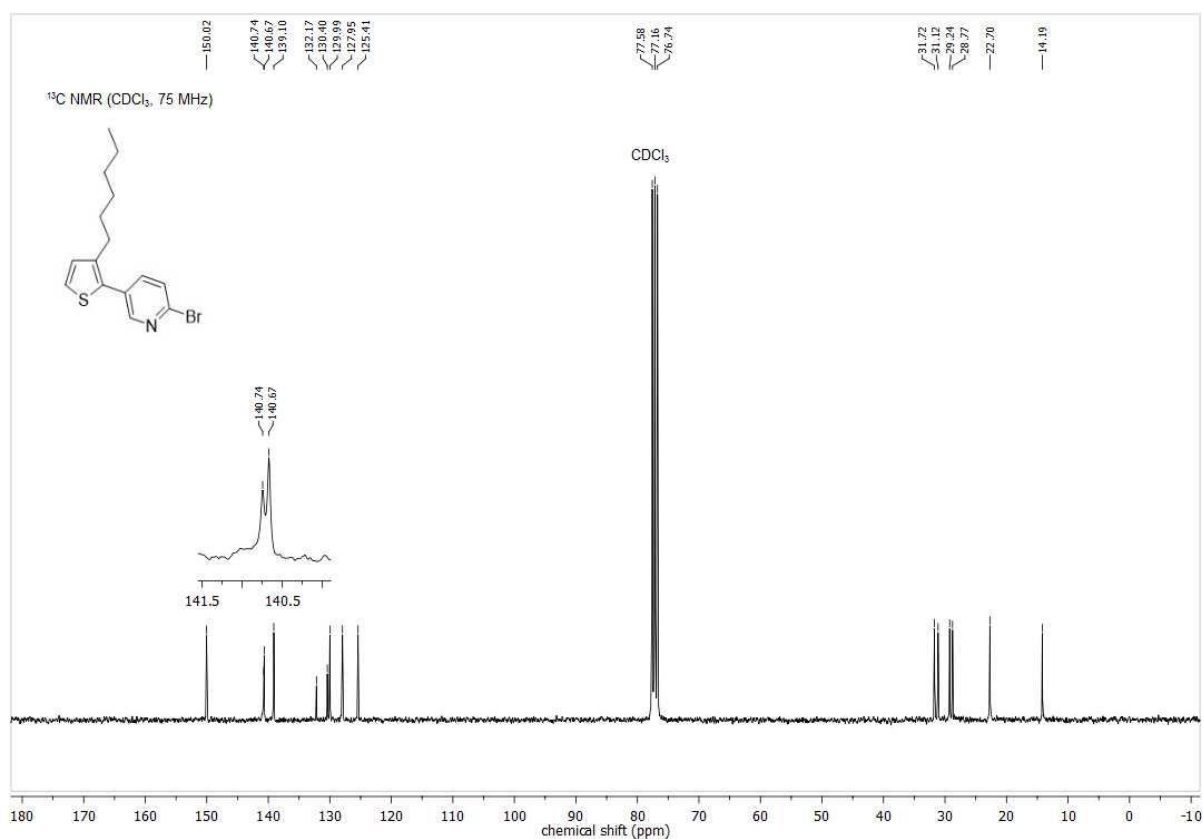


Figure S2. ¹³C NMR spectrum of 2-bromo-5-(3'-hexylthiophen-2'-yl)pyridine (**3**).

Synthesis of 2-bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**)

2-Bromo-5-(3'-hexylthiophen-2'-yl)pyridine (**3**) (2.12 g, 6.54 mmol) was dissolved in chloroform (70 mL) and acetic acid (35 mL), and the solution was protected from light. Then, *N*-iodosuccinimide (2.48 g, 11.0 mmol) was added portion wise and the mixture was stirred overnight at room temperature and under N₂ atmosphere. The reaction was quenched with a saturated NaHCO₃ solution, extracted with hexanes (3x), washed with a saturated Na₂S₂O₃ solution and dried with MgSO₄. After filtration, the solvent was evaporated under reduced pressure and the crude material was purified by column chromatography (silica gel, petroleum ether/dichloromethane 50/50). The product was obtained as a yellow oil (2.56 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ = 8.37 (dd, *J* = 2.1 and 1.1 Hz, 1H), 7.53–7.51 (m, 2H), 7.15 (s, 1H), 2.59–2.50 (m, 2H), 1.59–1.50 (m, 2H), 1.30–1.21 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 149.8 (CH), 142.6 (C), 141.3 (C), 139.6 (CH), 138.8 (CH), 138.2 (C), 129.2 (C), 128.0 (CH), 73.4 (C), 31.6 (CH₂), 31.0 (CH₂), 29.1 (CH₂), 28.4 (CH₂), 22.7 (CH₂), 14.2 (CH₃); ESI-MS: found 449.9350, calcd 449.9388 (MH⁺).

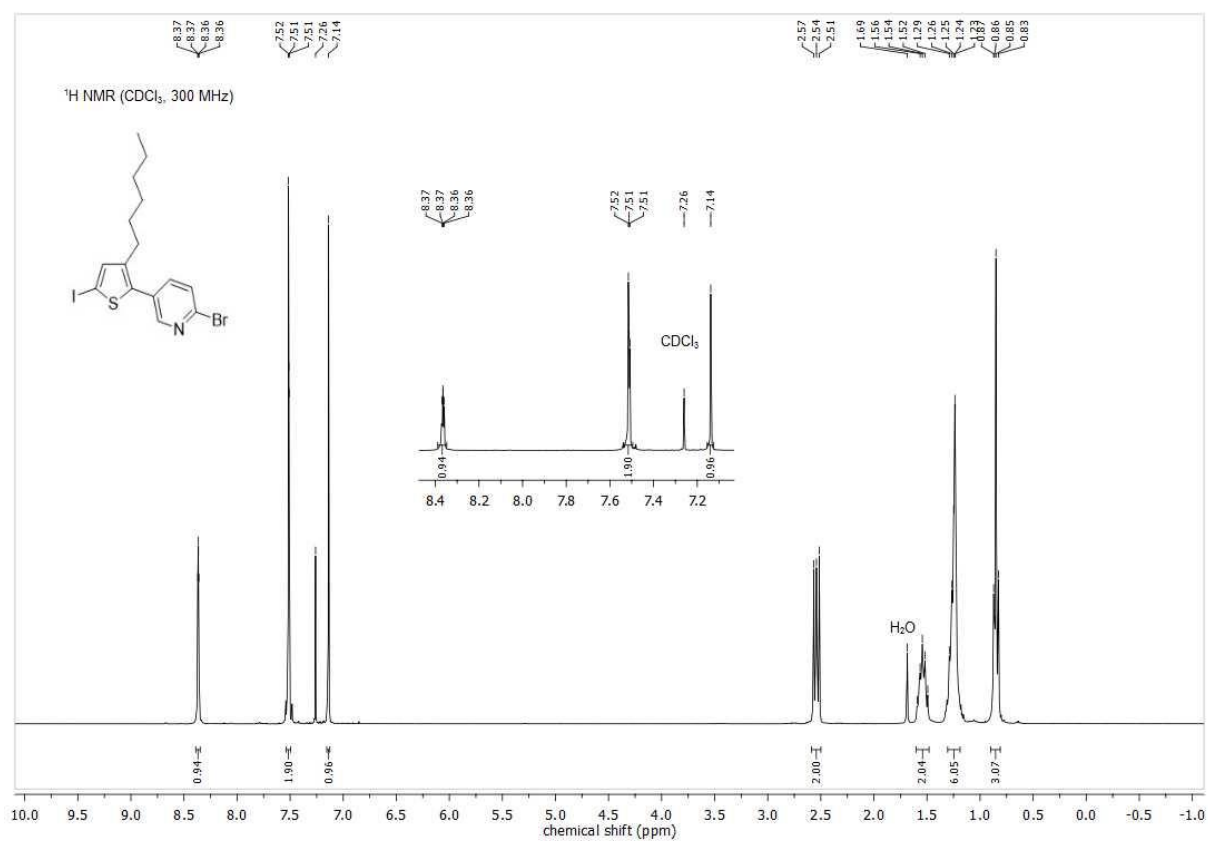


Figure S3. ¹H NMR spectrum of 2-bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**).

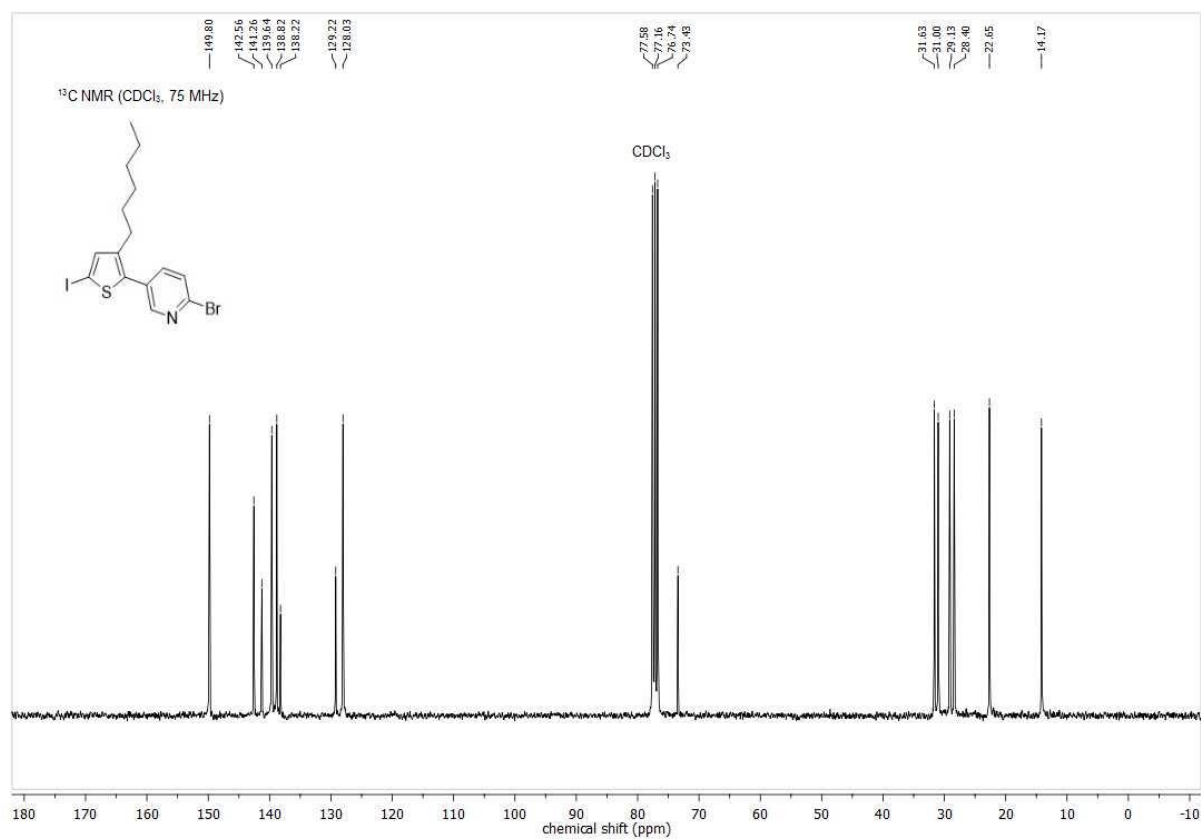


Figure S4. ¹³C NMR spectrum of 2-bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**).

Alternating copolymer synthesis

Polymerization test 1

2-Bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**) (0.225 g, 0.500 mmol), dried overnight under vacuum using P₂O₅ prior to use, was loaded in a three-neck flask and brought under Ar atmosphere, after which dry THF (5 mL) was added via cannula. *i*-PrMgCl·LiCl (0.385 mL, 0.500 mmol; 1.30 M in THF) was added dropwise to this solution at 0 °C to start the Grignard metathesis reaction. After stirring for 1 h at 0 °C, this mixture was cannulated to another three-neck flask containing Ni(dppp)Cl₂ (2.71 mg, 5.00 μmol) and dry THF (2 mL), at RT and under Ar atmosphere. After the start of the polymerization, aliquots were taken at different time intervals and analyzed by gel permeation chromatography (GPC). The polymerization was stopped after 30 min by adding water (0.5 mL). Then, the polymerization mixture was precipitated in methanol, whereafter the precipitate was filtered over a Soxhlet thimble and subsequently purified by means of Soxhlet extractions with methanol, acetone, hexanes and chloroform (dissolving the polymer), respectively. The solvent was evaporated under reduced pressure, after which the polymer was redissolved in pyridine (2 mL) and again precipitated in methanol. The precipitate was filtered off over a PTFE membrane (47 mm/0.45 μm) and dried overnight under vacuum, affording an orange solid (34.1 mg, 28%). ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (d, *J* = 1.8 Hz, 1H), 7.79 (dd, *J* = 8.2 and 1.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.53 (s, 1H), 2.79–2.71 (m, 2H), 1.78–1.69 (m, 2H), 1.45–1.32 (m, 6H), 0.94 (t, *J* = 6.7 Hz, 3H); UV–Vis (CHCl₃): λ_{max} = 413 nm, UV–Vis (film): λ_{max} = 437 nm; GPC (THF, PS standards): *M*_n = 2.6 × 10⁴ g/mol, *M*_w = 3.4 × 10⁴ g/mol, PDI = 1.28.

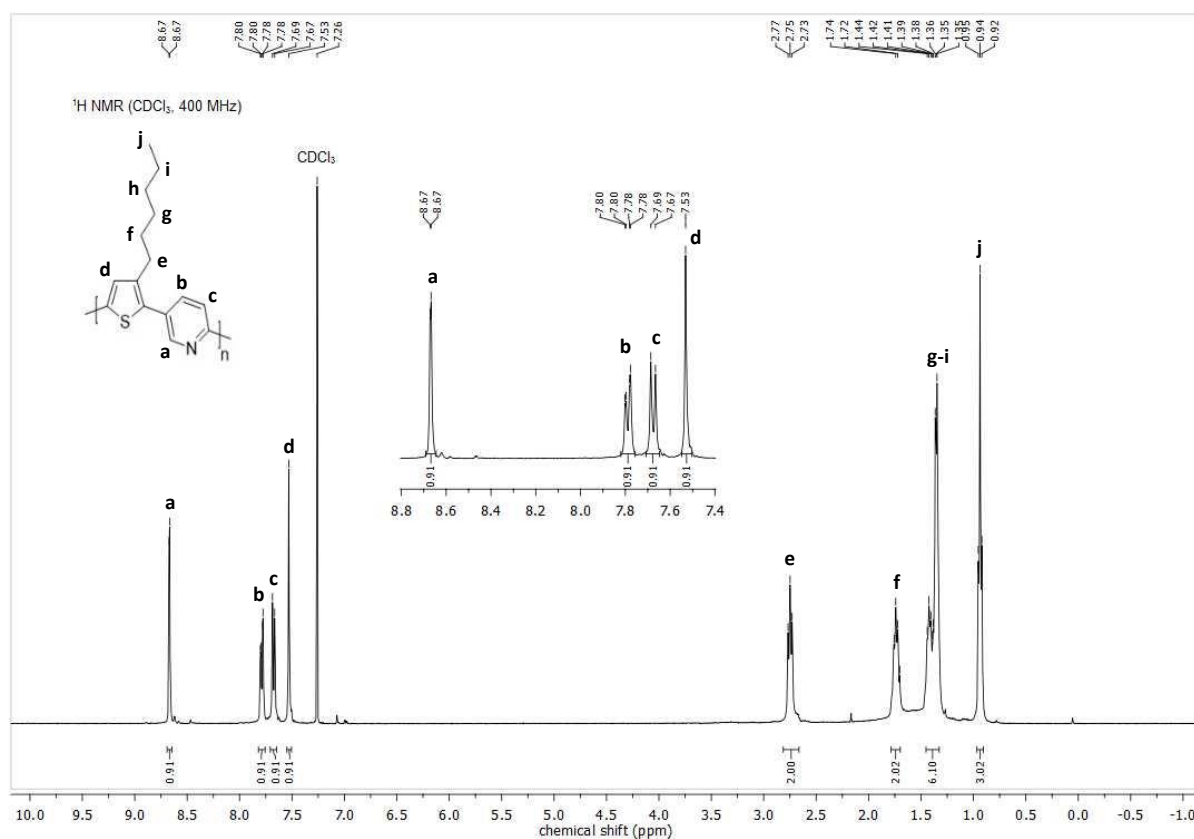


Figure S5. ¹H NMR spectrum of poly[(3-hexylthiophene-5,2-diyl)-*alt*-(pyridine-5,2-diyl)] (**P(3HT-*alt*-P)**).

Polymerization test 9

Similar to polymerization test 1, but Ni(dppe)Cl₂ (2.64 mg, 5.00 μmol) was used instead of Ni(dppp)Cl₂. The polymer was obtained as an orange solid (35.0 mg, 29%). GPC (THF, PS standards): $M_n = 2.3 \times 10^4$ g/mol, $M_w = 3.0 \times 10^4$ g/mol, PDI = 1.29.

Variable catalyst amounts

2-Bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**) (90.0 mg, 0.200 mmol), dried overnight under vacuum using P₂O₅ prior to use, was loaded in a three-neck flask and brought under Ar atmosphere, after which dry THF (2 mL) was added via cannula. *i*-PrMgCl·LiCl (0.154 mL, 0.200 mmol, 1.30 M in THF) was added dropwise to this solution at 0 °C to start the Grignard metathesis reaction. After stirring for 1 h at 0 °C, this mixture was cannulated to another three-neck flask containing each time a different amount of Ni(dppp)Cl₂ (1 mol%: 1.08 mg, 2.00 μmol; 2.5 mol%: 2.71 mg, 5.00 μmol; 5 mol%: 5.42 mg, 10.0 μmol; 10 mol%: 10.8 mg, 20.0 μmol) and dry THF (2 mL), at RT and under Ar atmosphere. The polymerization mixture was stirred for 30 min at RT, whereafter it was quenched with 0.5 mL of water and precipitated in methanol. The precipitate was filtered over a Soxhlet thimble and subsequently purified by means of Soxhlet extractions with methanol, acetone, hexanes and chloroform (dissolving the polymer), respectively. The solvent was evaporated under reduced pressure, after which the polymer was characterized by GPC.

Block copolymer synthesis

2,5-Dibromo-3-hexylthiophene (0.326 g, 1.00 mmol) was loaded in a three-neck flask and brought under Ar atmosphere. Then, dry THF (10 mL) was added via cannula, after which the solution was cooled down to 0 °C. *i*-PrMgCl.LiCl (0.769 mL, 1.00 mmol; 1.30 M in THF) was added dropwise to this solution to start the first Grignard metathesis reaction (GRIM 1). Meanwhile, 2-bromo-5-(3'-hexyl-5'-iodothiophen-2'-yl)pyridine (**4**) (0.135 g, 0.300 mmol), dried overnight under vacuum using P₂O₅ prior to use, was also loaded in a three-neck flask, brought under Ar atmosphere and dissolved in dry THF (3 mL). 15 Min after the start of GRIM 1, *i*-PrMgCl.LiCl (0.231 mL, 0.300 mmol; 1.30 M in THF) was added dropwise to this solution at 0 °C to start the second Grignard metathesis reaction (GRIM 2). Both GRIM reactions were stirred for 1 h at 0 °C. After GRIM 1, the thiophene mixture was cannulated to another three-neck flask containing Ni(dppp)Cl₂ (3.52 mg, 6.50 μmol) and dry THF (3 mL), at RT and under Ar atmosphere. This polymerization mixture was then stirred for 15 min at RT, whereafter half of it (6.5 mL) was quenched with a MeOH/HCl mixture (1 mL, 1 M), while to the other half of the mixture the thiophene-pyridine mixture of GRIM 2 was added at RT. The block copolymerization was stopped after 30 min by quenching with 1 mL of water. Both the **P3HT** homopolymer and the **P3HT-*b*-P(3HT-*alt*-P)** copolymer were precipitated in methanol and filtered over a Soxhlet thimble. Both materials were subsequently purified by means of Soxhlet extractions with methanol, acetone, hexanes and chloroform (dissolving the polymer), respectively. The solvent was evaporated under reduced pressure, after which the polymers were redissolved in chloroform (2 mL) and again precipitated in methanol. The precipitates were filtered off over a PTFE membrane (47 mm/0.45 μm) and dried overnight under vacuum, affording 24.5 mg of **P3HT** and 63.3 mg of the **P3HT-*b*-P(3HT-*alt*-P)** copolymer (41%). ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (br, 0.6H), 7.79 (d, *J* = 8.2 Hz, 0.6H), 7.68 (d, *J* = 8.2 Hz, 0.6H), 7.53 (s, 0.6H), 6.92 (s, 1.4H), 2.91–2.63 (m, 4H), 1.79–1.63 (m, 4H), 1.50–1.33 (m, 12H), 0.99–0.90 (m, 6H); UV–Vis (CHCl₃): λ_{max} = 424 nm, UV–Vis (film): λ_{max} = 447 nm; GPC (THF, PS standards): M_n = 4.1 × 10⁴ g/mol, M_w = 5.6 × 10⁴ g/mol, PDI = 1.37.

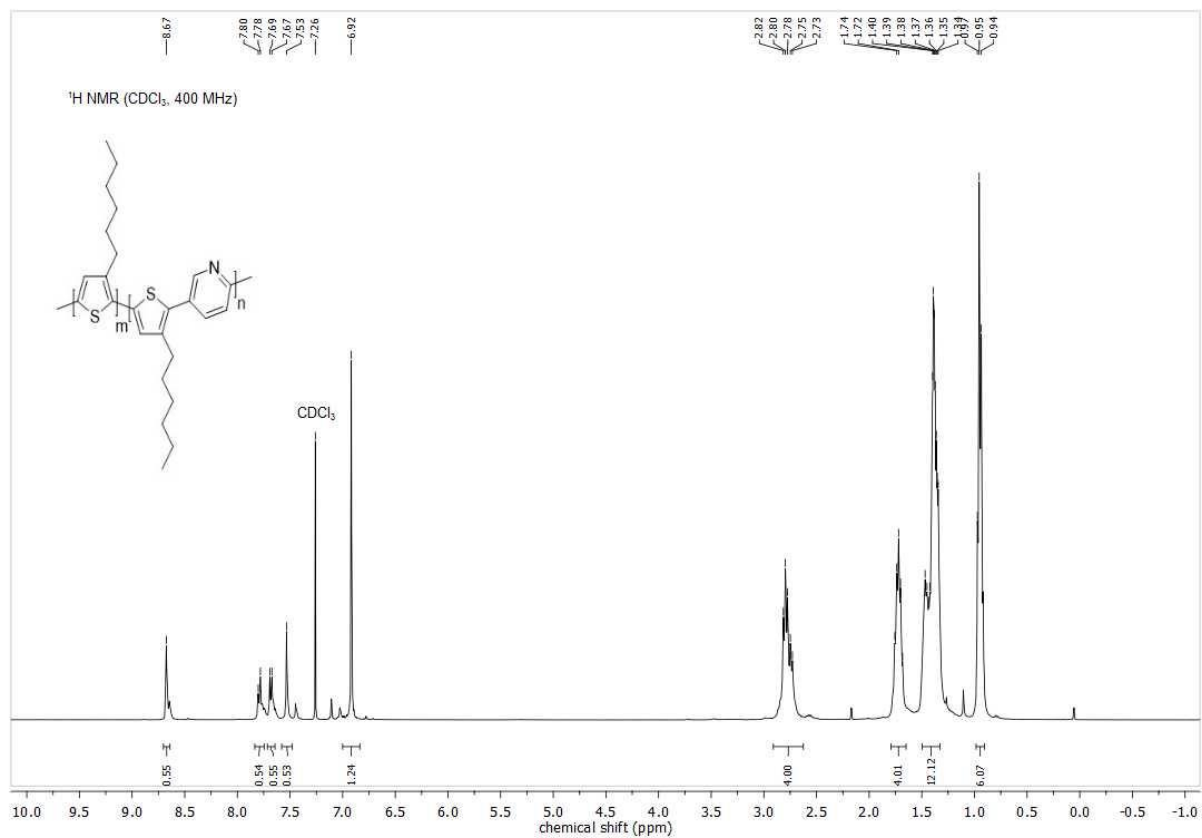


Figure S6. ¹H NMR spectrum of poly{[3-hexylthiophene-5,2-diyl]-*block*-[(3-hexylthiophene-5,2-diyl)-*alt*-(pyridine-5,2-diyl)]} (P3HT-*b*-P(3HT-*alt*-P)).

Polymerization plots

Polymerization test 1

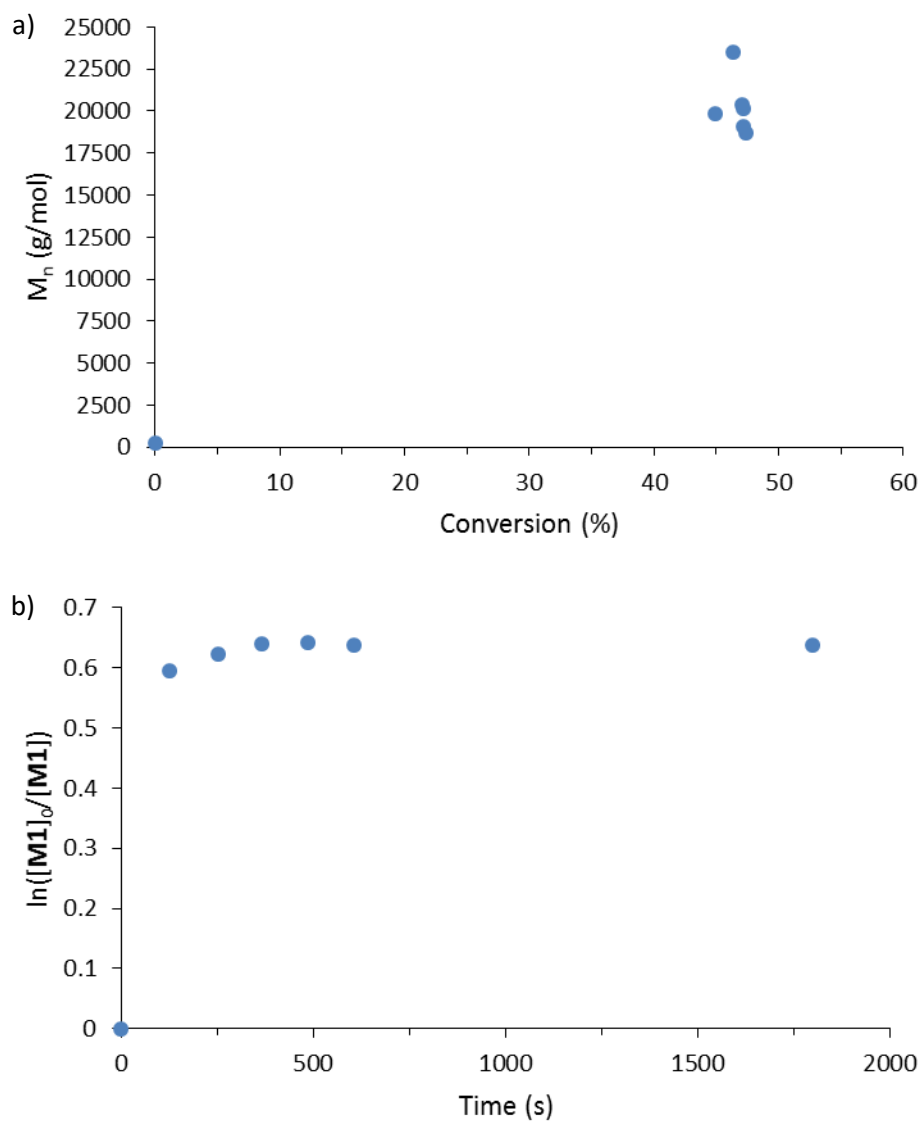


Figure S7. a) Relation between M_n and conversion; b) Relation between $\ln([M1]_0/[M1])$ and time. The polymerization test was run with 1 mol% of Ni(dppp)Cl₂ at RT and $[M1] = 0.075$ M.

Polymerization test 9

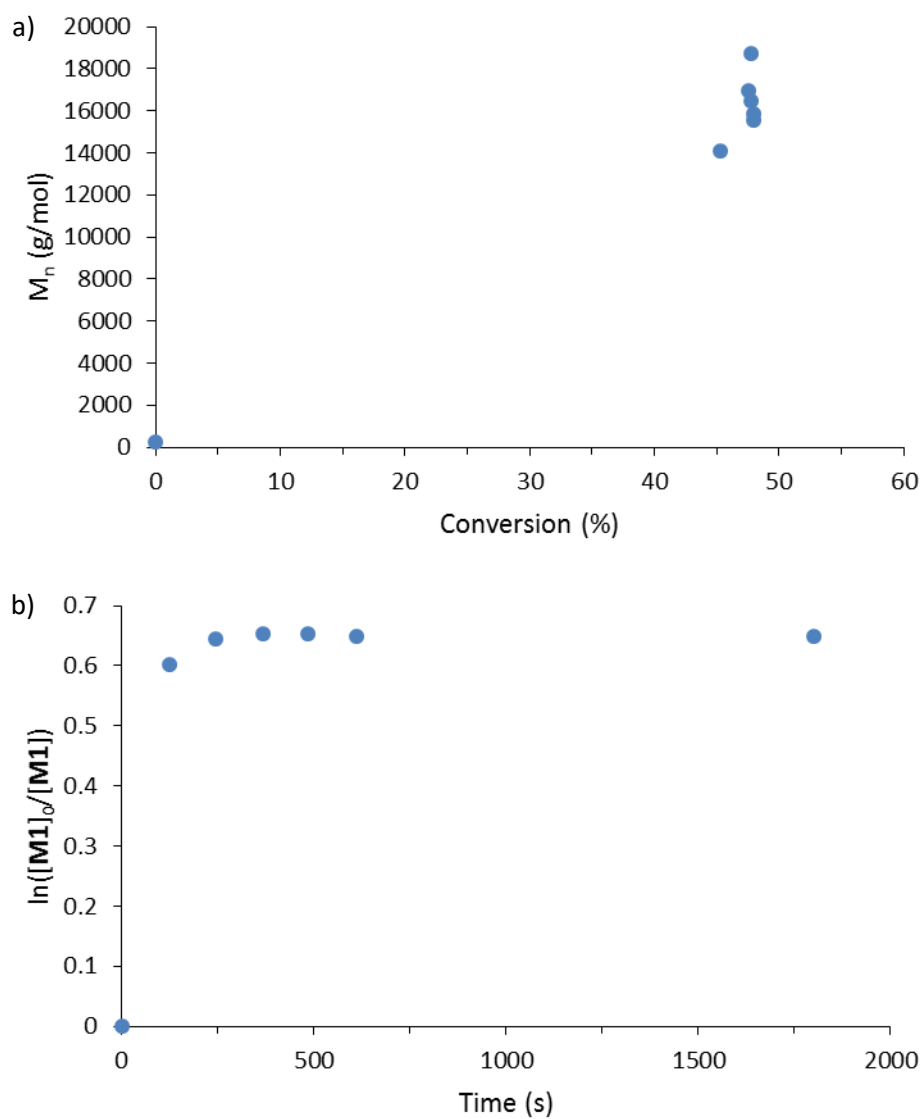


Figure S8. a) Relation between M_n and conversion; b) Relation between $\ln([M1]_0/[M1])$ and time. The polymerization test was run with 1 mol% of Ni(dppe)Cl₂ at RT and $[M1] = 0.075$ M.

MALDI-TOF measurements

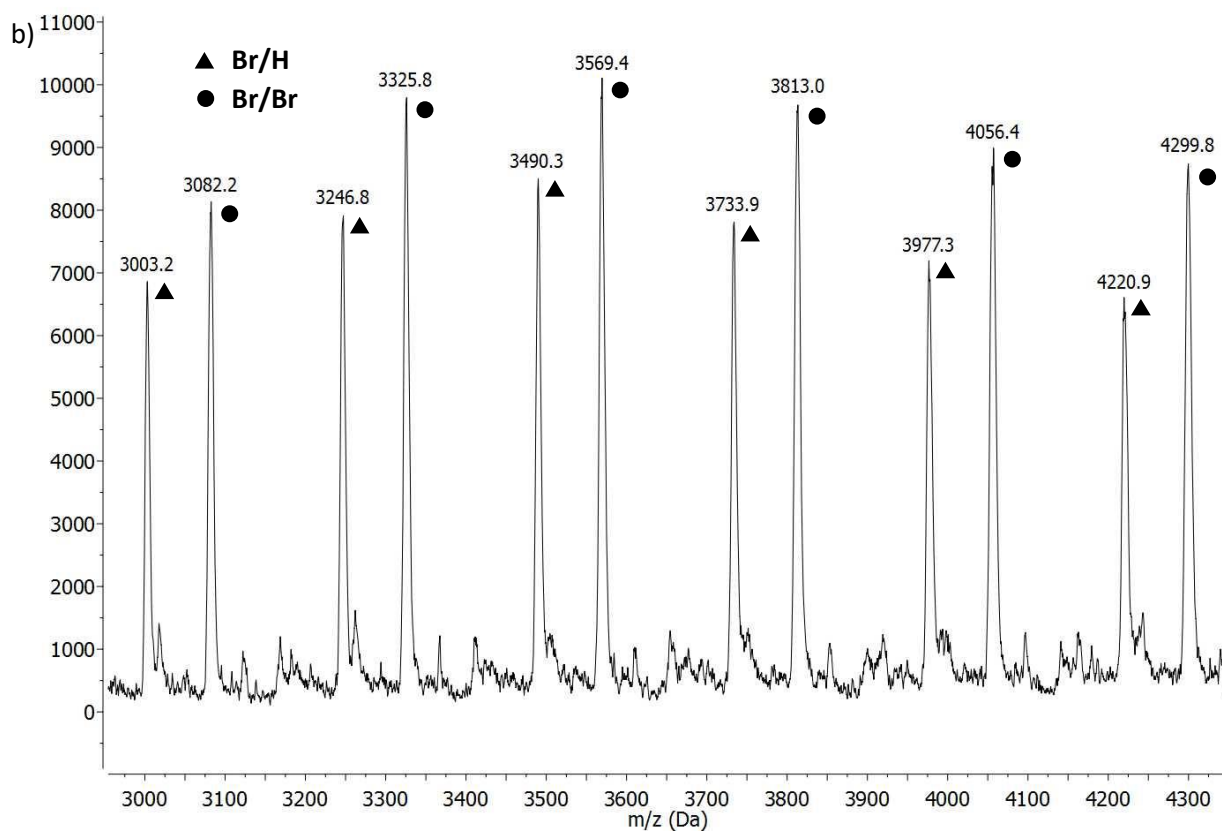
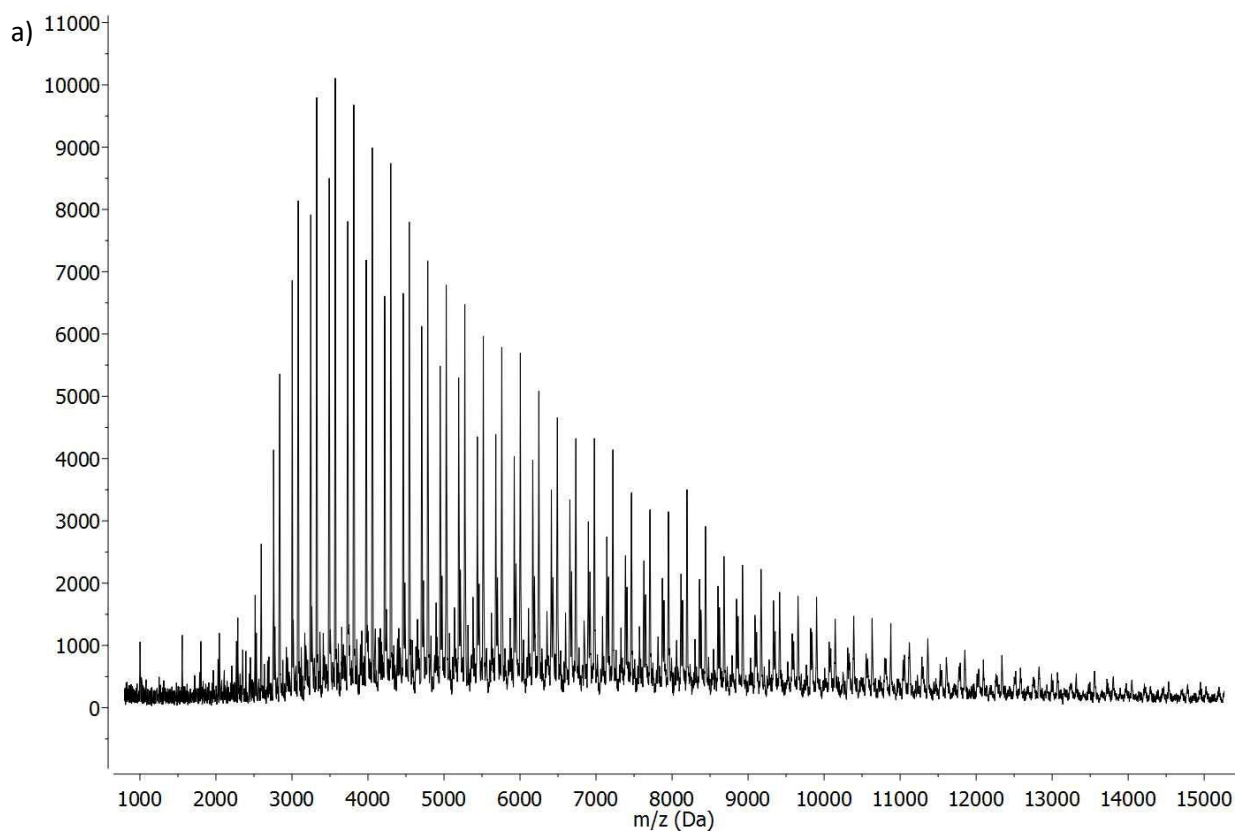


Figure S9. a) MALDI-TOF MS spectrum of **P(3HT-*alt*-P)**; b) Enlarged region (m/z 3000–4300) of the MALDI-TOF MS spectrum of **P(3HT-*alt*-P)**.

Study of the block copolymer purity

GPC

Preparative GPC was performed to cut off the low-molar mass tail of the block copolymer (to evaluate the possible presence of non-chain-extended **P3HT**). The prep-GPC profile is shown in Figure S10. Two fractions (**F1** and **F2**) were collected and evaporated to dryness. The weight percentage of **F2** equals to 19%.

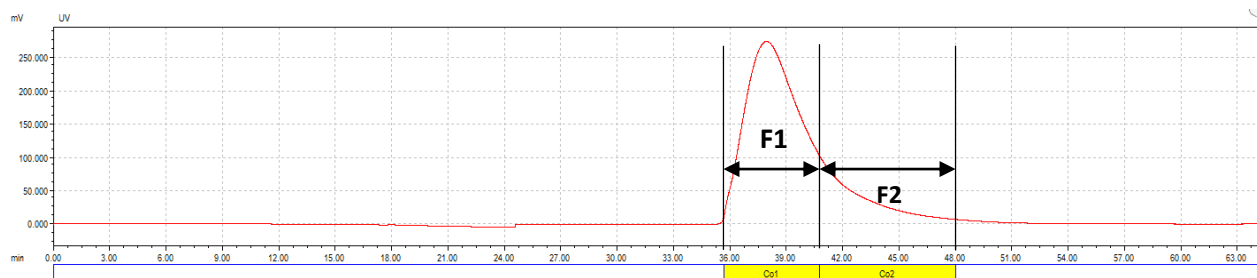


Figure S10. Prep-GPC profile of the **P3HT-*b*-P(3HT-*alt*-P)** copolymer. The tail was cut off at 40.75 min.

Both fractions were then analyzed by analytical GPC and ^1H NMR spectroscopy. From the GPC profiles (Figure S11), it is clear that fraction **F1** (green curve) no longer contains any of the low molar mass polymer species. This fraction can thus be considered as the pure block copolymer.

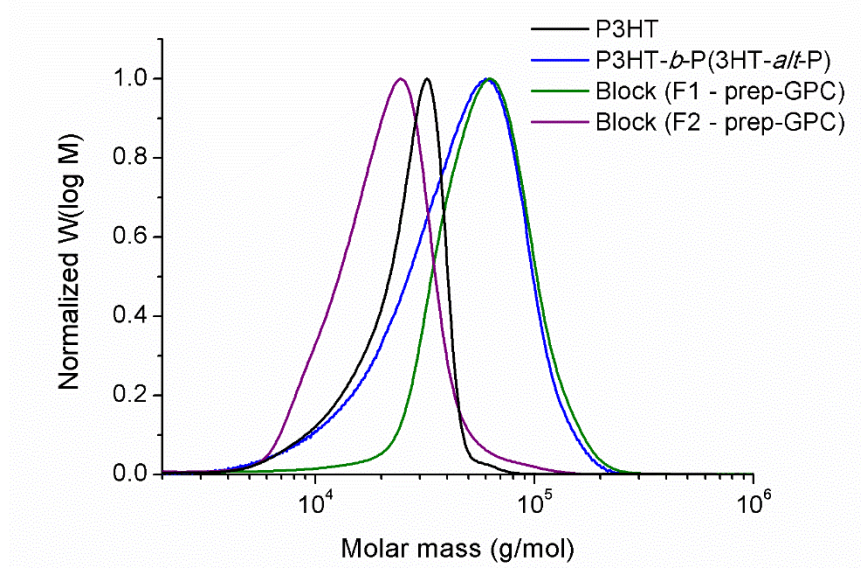


Figure S11. GPC profiles of the **P3HT** homopolymer, the **P3HT-*b*-P(3HT-*alt*-P)** copolymer and the two fractions (**F1** and **F2**) after preparative GPC purification of the block copolymer.

^1H NMR

By comparing the aromatic regions of the ^1H NMR spectra of both fractions (Figure S12), the amount of **P3HT** in the low-molar mass fraction **F2** was determined to be less than 20%. This finding, together with the weight percentage of 19% for **F2**, results in the conclusion that only 3-4% of **P3HT** is present in the block copolymer after the synthesis and standard purification procedure.

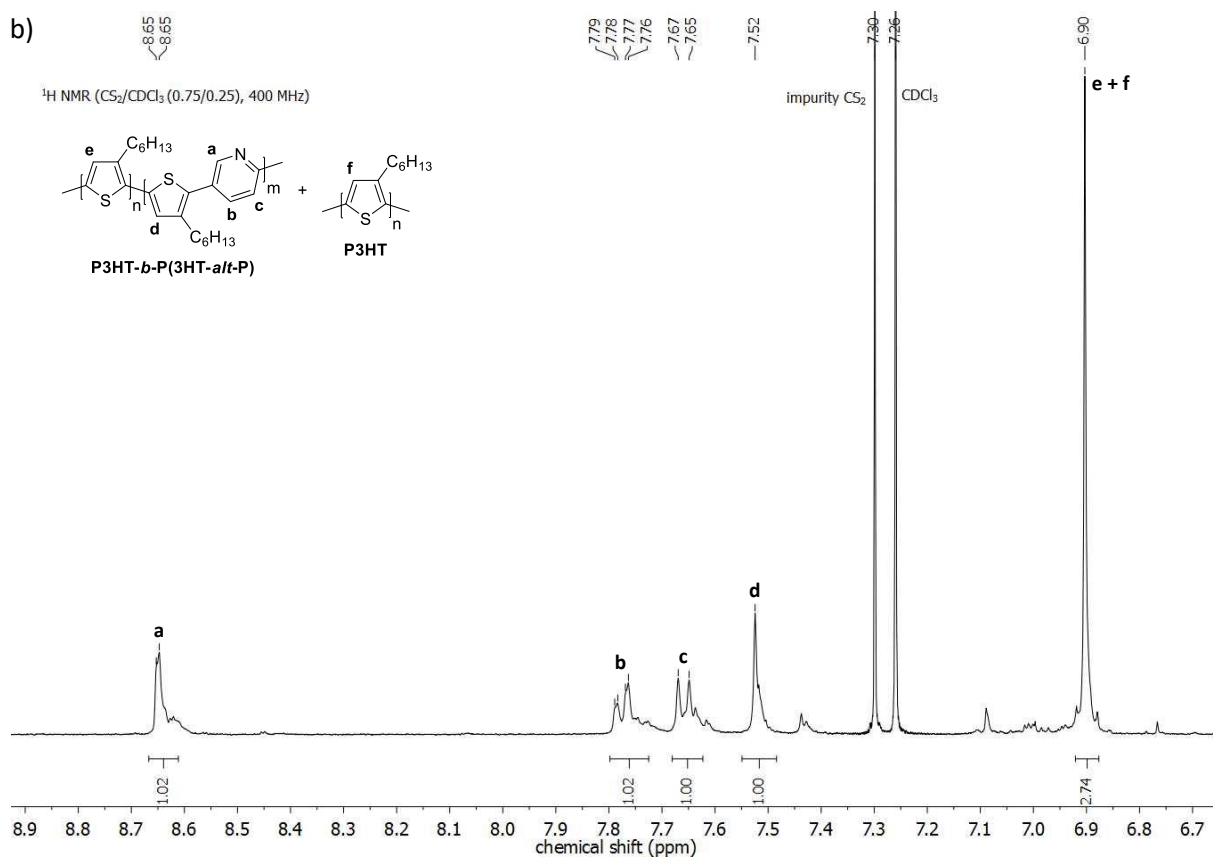
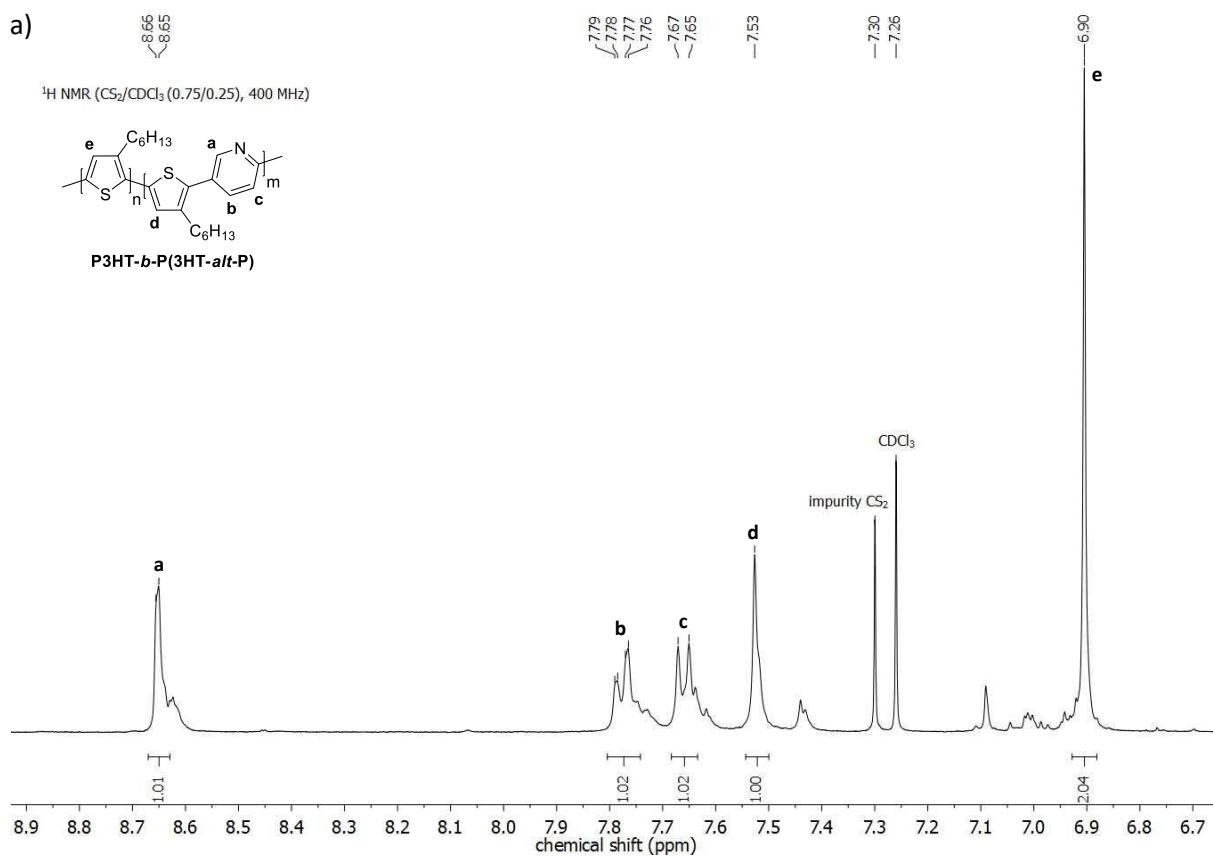


Figure S12. Aromatic regions of the $^1\text{H NMR}$ spectra of a) **F1** and b) **F2**.

Thermal analysis

RHC

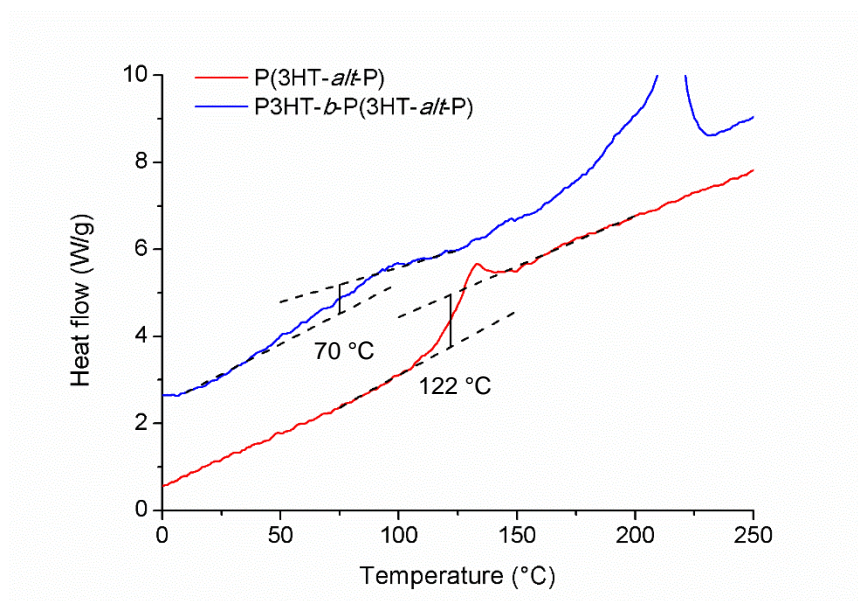


Figure S13. Determination of the glass transition temperatures from the RHC (2nd) heating profiles of **P(3HT-*alt*-P)** and **P3HT-*b*-P(3HT-*alt*-P)** (curves shifted vertically for clarity).

TGA

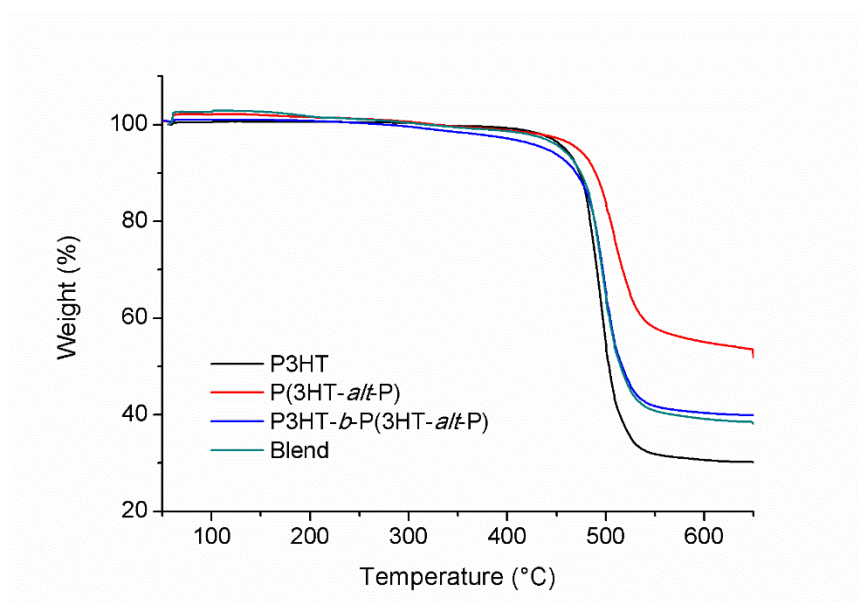


Figure S14. TGA profiles of **P3HT**, **P(3HT-*alt*-P)**, **P3HT-*b*-P(3HT-*alt*-P)** and the physical blend of **P3HT** and **P(3HT-*alt*-P)** (60/40).

Polymer fluorescence



Figure S15. Fluorescence of **P(3HT-*alt*-P)** (left), **P3HT-*b*-P(3HT-*alt*-P)** (middle) and **P3HT** (right) in chloroform solution under a UV lamp at 365 nm.

Paper chromatography

Solutions of **P3HT**, **P(3HT-*alt*-P)**, **P3HT-*b*-P(3HT-*alt*-P)** and the blend of **P3HT** and **P(3HT-*alt*-P)** (60/40) were spotted on chromatography paper (Figure S13a). If all materials are spotted onto the same line and chloroform is used as the eluent, the chromatogram as shown in Figure S13b is obtained. In both cases, a clear distinction can be made between the block copolymer and the blend, whereby the blend is just a superposition of the two polymer constituents.

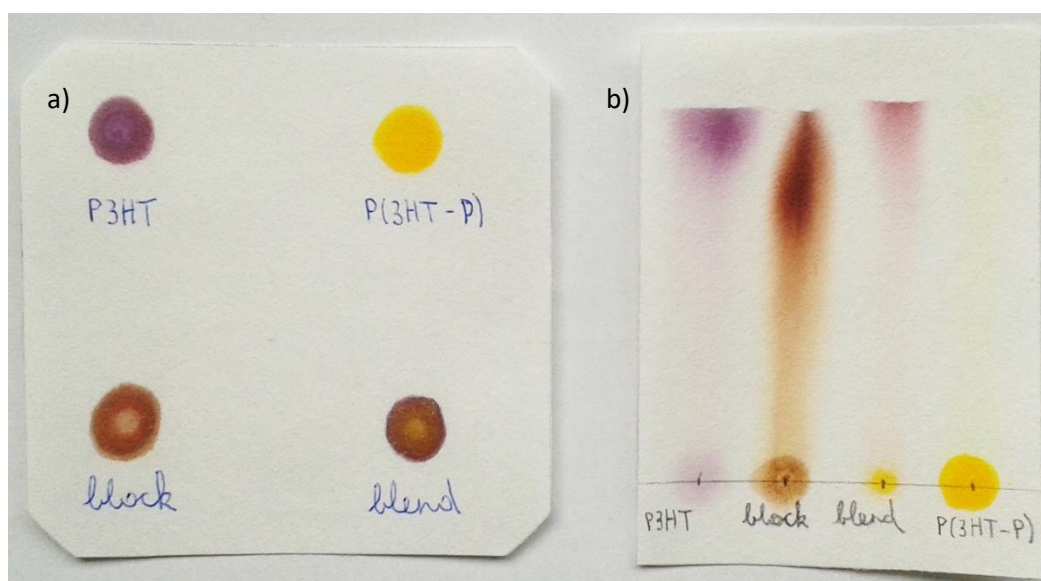


Figure S16. a) Spots of the different polymer materials on chromatography paper; b) Paper chromatogram of the different polymer materials (eluent = CHCl_3).

References

- (1) Hamai, S.; Hirayama, F. Actinometric Determination of Absolute Fluorescence Quantum Yields. *J. Phys. Chem.* **1983**, *87*, 83–89.
- (2) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications, 2nd Edition*; Wiley, 2001.
- (3) Trasatti, S. The Absolute Electrode Potential: An Explanatory Note. *Pure Appl. Chem.* **1986**, *58*, 955–966.
- (4) Pal, B.; Yen, W.-C.; Yang, J.-S.; Su, W.-F. Substituent Effect on the Optoelectronic Properties of Alternating Fluorene-Thiophene Copolymers. *Macromolecules* **2007**, *40*, 8189–8194.
- (5) Yang, Y.-L.; Lee, Y.-H.; Lee, Y.-P.; Chiang, C.-J.; Shen, C.; Wu, C.-C.; Ohta, Y.; Yokozawa, T.; Dai, C.-A. Synthesis and Characterization of Poly(3-hexylthiophene)–poly(3-hexyloxythiophene) Random Copolymers with Tunable Band Gap via Grignard Metathesis Polymerization. *Polym. Int.* **2014**, *63*, 2068–2075.
- (6) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. Chain-Growth Polymerization for Poly(3-hexylthiophene) with a Defined Molecular Weight and a Low Polydispersity. *Macromolecules* **2004**, *37*, 1169–1171.
- (7) Wang, X.; Rabbat, P.; O’Shea, P.; Tillyer, R.; Grabowski, E. J. J.; Reider, P. J. Selective Monolithiation of 2,5-Dibromopyridine with Butyllithium. *Tetrahedron Lett.* **2000**, *41*, 4335–4338.
- (8) Engtrakul, C.; Sita, L. R. Ferrocene-Based Nanoelectronics: 2,5-Diethynylpyridine as a Reversible Switching Element. *Nano Lett.* **2001**, *1*, 541–549.