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Electronic Supplementary Information

Synthesis of Ester Side Chain Functionalized All-Conjugated Diblock Copolythiophenes via the Rieke Method

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1. Experimental section

Materials and methods

All manipulations were carried out on a dual manifold vacuum/Ar system. Lithium (granular, 99+%) from Acros was stored in a schlenk tube under Ar. Lithium, naphthalene and benzothiophene were weighed in air as needed and transferred to a schlenk tube under a stream of Ar. Naphthalene (Acros, 99+%) and benzothiophene (Sigma-Aldrich, 98%) were stored in a desiccator over phosphorous pentoxide. Zinc chloride (Acros, analysis grade 98.5%) was transferred into small vials inside a glove box and stored in a separate desiccator over phosphorous pentoxide. Zinc chloride was dried by treating it with thionyl chloride and heating with a Bunsen burner, and subsequently removed under a stream of Ar gas. THF was freshly distilled from Na/benzophenone under a N_2 atmosphere at atmospheric pressure prior to use. Brass cannulas were stored in an (air) oven at 110 °C and cleaned immediately after use with acetic acid (in the case of Zn* remnant), acetone (to clean non-polymeric residues), or hot chloroform (for polymer-based contaminations).

NMR chemical shifts (δ, in ppm) were determined relative to the residual $CHCl_3$ absorption (7.26 ppm) or the ^{13}C resonance shift of $CDCl_3$ (77.16 ppm). Polymer molar masses and distributions were determined by size exclusion chromatography (SEC). Analysis was performed on a Tosoh EcoSEC system, comprising of an autosampler, a PSS guard column SDV (50 × 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 µm, 300 × 7.5 mm), and a differential refractive index detector (Tosoh EcoSEC RI) 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 (Polymer Labs) ranging from 474 to 7.5×10^6 g/mol ($K = 14.1 \times 10^{-5}$ dL/g and $\alpha = 0.70$). Polymer concentrations were in the range of 3–5 mg/mL. FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer with a resolution of 4 cm^{-1} (16 scans) using films drop-casted on a NaCl disk. UV-Vis absorption measurements were performed with a scan rate of 600 nm min^{-1} in a continuous run from 200 to 800 nm. 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.[1] RHC measurements were performed at 500 K min^{-1} in aluminum crucibles, using neon (6 mL min^{-1}) as a purge gas.

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[1] (*a*) R. L. Danley, P. A. Caulfield and S. R. A. Aubuchon, *Am. Lab.*, 2008, **40**, 9; (*b*) S. Wouters, F. Demir, L. Beenaerts and G. Van Assche, *Thermochim. Acta*, 2012, **530**, 64.

Standard preparation of Rieke Zinc (Zn)*[2]

Two 120 mL schlenk vessels, A and B, were dried by heating with a Bunsen burner under reduced pressure and cooled down to rt under a stream of Ar. Schlenk vessel A, filled with Ar, was weighed and then reassembled to the schlenk line. Under a stream of Ar, $ZnCl_2$ was charged to the vessel. After three Ar/vacuum cycles, $ZnCl_2$ was wetted with a small amount of $SOCl_2$. The schlenk vessel was heated by a Bunsen burner until the $ZnCl_2$ salt melted and a white fume was released, and the schlenk was then cooled down again under an Ar flow. Schlenk flask A was weighed again to determine the exact amount of $ZnCl_2$ and a stirring bar was added. Dried $ZnCl_2$ (1.1 equiv) was dissolved in freshly distilled THF (25 mL/g). Li pellets (2.2 equiv), naphthalene (2.25 equiv) and benzothiophene (0.04 equiv) were weighed in air and charged into schlenk flask B under an Ar stream. Dry THF (the same amount as added to dissolve $ZnCl_2$) was added (the solution turned from colorless to dark green within less than 2 min) and the mixture was stirred further for 2 h to dissolve the Li pellets. The $ZnCl_2$ solution was then transferred dropwise via cannula to the lithium naphthalenide solution over 10-15 min. The resulting black suspension can be stirred for an additional hour to consume the undissolved Li or stirring can be stopped right after addition. The highly reactive zinc powder obtained was allowed to settle down for a couple of hours. The supernatant was siphoned off via cannula affording the Zn* powder. Thus prepared reactive Rieke zinc was ready to use further on.

Monomer synthesis

2,5-Dibromo-3-hexylthiophene (M1) was prepared according to a literature method.[3]

6-(2,5-Dibromothiophen-3-yl)hexyl acetate (M2a). 6-Acetoxyhexyl bromide (21.95 g, 98.4 mmol) was added neat, via a syringe, to freshly prepared Zn* (120.5 mmol) in THF (150 mL) at rt, and the reaction mixture was stirred for 3 h at rt. Stirring was stopped and the solution was allowed to stand for a couple of hours to allow the excess of zinc to settle from the dark brown organozinc bromide solution. In a second 500 mL flame-dried 3-neck round bottom flask, LiBr (8.54 g, 98.4 mmol), Ni(dppe)Cl_2 (1.7 g, 3.3 mmol), and 3-bromothiophene (6.22 mL, 66.4 mmol) were dissolved in dry THF (100 mL). The organozinc bromide solution was then transferred via cannula over a period of 30 min to that mixture under stirring at rt, and the mixture was allowed to stir further overnight. The reaction was quenched by the addition of a saturated NH_4Cl solution, followed by extraction with Et_2O, and simple distillation afforded 6-(thiophene-3-yl)hexyl acetate (11.27 g, 75%) in pure form. Dibromination with bromine (2.0

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[2] S. Kudret, W. Oosterbaan, J. D'Haen, L. Lutsen, D. Vanderzande and W. Maes, *Adv. Synth. Catal.*, 2013, **355**, 569.
[3] P. Bauerle, F. Pfau, H. Schlupp, F. Wurthner, K.-U. Gaudl, M. B. Caro and P. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1993, **3**, 489.

equiv) in CH_2Cl_2 for 10 min at rt yielded the corresponding dibrominated compound **M2a** (Scheme 2). The resulting mixture was quenched with a $NaHSO_3$ solution and then neutralized by washing with a saturated $NaHCO_3$ solution. The crude product was distilled under high vacuum to afford a light-yellow oil (17.79 g, 93%). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.75 (s, 1H), 4.03 (t, $J_{H\text{-}H}$ = 6.7 Hz, 2H), 2.49 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 2.03 (s, 3H), 1.66–1.49 (m, 4H), 1.42–1.28 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 143.3, 131.5, 111.1, 108.7, 65.1, 30.1, 30.0, 29.3, 29.1, 26.4, 21.7; GC-MS: *m/z* 381/383/385 [M^+] (≥ 98%); FT-IR (NaCl, cm^{-1}): υ_{max} 3091, 2934, 2857, 1738, 1541, 1463, 1418, 1387, 1364, 1241.

Ethyl 6-(2,5-dibromothiophene-3-yl)hexanoate (M2b).[4,5] Ethyl 6-bromohexanoate (28.5 mL, 160 mmol) was added, via a syringe, to a freshly prepared Zn* (195.6 mmol) solution in THF (250 mL) at rt, and the reaction mixture was stirred for 3 h at rt. Stirring was stopped and the solution was allowed to stand for a couple of hours to allow the excess of zinc to settle from the dark brown (6-ethoxy-6-oxohexyl)zinc(II) bromide solution. In a second 500 mL flame-dried 3-neck round bottom flask, LiBr (13.9 g, 160 mmol), Ni(dppe)Cl_2 (4.81 g, 8.9 mmol), and 3-bromothiophene (12.5 mL, 133.3 mmol) were dissolved in dry THF (150 mL). The organozinc bromide solution was then transferred via a cannula over a period of 45 min to that mixture under stirring at rt, and the reaction mixture was allowed to stir further overnight. The reaction was quenched with a saturated NH_4Cl solution, followed by extraction with Et_2O. Kugelrohr distillation of the crude product afforded ethyl 6-(thiophene-3-yl)hexanoate in pure form (22.02 g, 73%). Dibromination with bromine (2.0 equiv) in CH_2Cl_2 for 10 min at rt yielded the corresponding dibrominated compound **M2b** (Scheme 2). Work-up and purification of the crude product was performed according to a literature procedure (34.76 g, 93%).[5] Material purity and identity were confirmed by NMR and MS.

Poly(3-hexylthiophene)-*block*-poly[6-(thiophene-3-yl)hexyl acetate] (P3HT-*b*-P6THA or P1). The feed molar ratio of **M1** and **M2a** was either 50:50 or 85:15. The synthesis procedure for the **P3HT-*b*-P6THA** diblock copolymers (illustrated for the 50:50 feed molar ratio) was as follows: 2,5-Dibromo-3-hexylthiophene (**M1**) (1.010 g, 3.10 mmol) in THF (6 mL) was added via a cannula to freshly prepared Rieke zinc (3.72 mmol) at -78 °C. The mixture was stirred for 1 h at this temperature and then allowed to warm to 0 °C gradually. The unreacted Zn* was allowed to settle down overnight and the formed organozinc supernatant was then transferred by cannula via a 0.45 µm acrodisc filter into a flame-dried schlenk tube and further diluted to 0.015 M by the addition of freshly distilled THF. Organozinc solution I was heated up to 40 °C and 1 mol% of

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[4] B. Campo, D. Bevk, J. Kesters, J. Gilot, H. J. Bolink, J. Zhao, J.-C. Bolsée, W. Oosterbaan, S. Bertho, J. D’Haen, J. Manca, L. Lutsen, G. Van Assche, W. Maes, R. A. J. Janssen and D. Vanderzande, *Org. Electron.*, 2013, **14**, 523.

[5] S.-H. Kim and J.-G. Kim, *Bull. Korean Chem. Soc.*, 2009, **30**, 2283.

Ni(dppe)Cl_2 (0.028 g, 0.053 mmol) was added in one portion. After stirring at this temperature for 15 min, the conversion of the monomer and the molar mass of the polymer formed were evaluated by taking a small aliquot of the reaction mixture (0.927 mmol), which was withdrawn via a syringe, quenched with 2M HCl, and extracted with $CHCl_3$. Organozinc solution II, prepared by reacting 6-(2,5-dibromothiophene-3-yl)hexyl acetate (**M2a**) (0.833 g, 2.17 mmol) with Rieke Zn* (2.60 mmol) in the same manner as for organozinc I, was added via a syringe to the first solution, and the resulting mixture was stirred for an additional 30 min. The reaction was quenched by adding 2M HCl aq. into the solution and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was added to methanol to give a black precipitate, which was filtered off and washed several times with methanol. The crude polymer was purified via sequential Soxhlet extractions with methanol and hexanes, respectively. Polymer **P1 85/15** was synthesized in the same manner.

P1 50/50: UV-Vis (film, λ_{max}, nm): 549, 605sh; SEC (THF): M_n 10.2 x 10^3 g mol^{-1}, D 1.29; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (s), 4.05 (t), 2.77/2.55 (t), 2.02 (s), 1.85–1.14 (m), 0.89 (t); ^{13}C NMR ($CDCl_3$, 100 MHz): 171.2, 139.9, 130.4, 128.6, 64.5, 31.7, 30.5, 30.4, 29.4, 29.3, 29.2, 28.6, 25.8, 22.6, 21.0, 14.1; FT-IR (NaCl, cm^{-1}): υ_{max} 3054, 2953, 2928, 2857, 1740, 1510, 1456, 1365, 1240, 1049, 820.

P1 85/15: UV-Vis (film, λ_{max}, nm): 515, 600; SEC (THF): M_n = 8.8 x 10^3 g mol^{-1}, D 1.49; ^{1}H NMR (300 MHz, $CDCl_3$): 6.96 (s), 4.04 (t), 2.78/2.55 (t), 2.01 (s), 1.86–1.13 (m), 0.89 (t); ^{13}C NMR ($CDCl_3$, 100 MHz): 171.2, 139.9, 133.7, 130.4, 128.6, 64.6, 31.7, 30.5, 30.4, 29.4, 29.3, 28.5, 25.7, 22.7, 21.0, 14.1; FT-IR (NaCl, cm^{-1}): υ_{max} 3055, 2955, 2927, 2856, 1740, 1510, 1457, 1364, 1238, 1048, 822.

Poly(3-hexylthiophene)-*block*-poly[ethyl 6-(thiophene-3-yl)hexanoate] (P3HT-*b*-PE6TH or P2). The feed molar ratio of **M1** and **M2b** was either 50:50 or 85:15. The synthesis procedure for the **P3HT-*b*-PE6TH** diblock copolymers (illustrated for the feed molar ratio of 50:50) was as follows: 2,5-Dibromo-3-hexylthiophene (**M1**) (3.587 g, 11.0 mmol) in THF (22 mL) was added via a cannula to freshly prepared Rieke Zn* (13.2 mmol) at -78 °C. The mixture was stirred for 1 h at this temperature and then allowed to warm to 0 °C gradually. The unreacted Zn* was allowed to settle down overnight and the formed organozinc supernatant was then transferred by cannula via a 0.45 µm acrodisc filter into a flame-dried schlenk tube and further diluted to 0.1 M by addition of fresh THF. Organozinc solution I was heated up to 40 °C and 3 mol% of Ni(dppe)Cl_2 (0.332 g, 0.63 mmol) was added in one portion. After stirring at this temperature for 15 min, the conversion of the monomer and the molar mass of the polymer formed were evaluated by taking a small aliquot of the reaction mixture (1.0 mmol), which was withdrawn via a syringe, quenched with 2M HCl, and extracted with $CHCl_3$. Organozinc solution II, prepared by reacting ethyl 6-(2,5-dibromothiophene-3-yl)hexanoate (**M2b**) (3.841 g, 10.0 mmol) with Rieke zinc (12.0 mmol) in the same manner as for organozinc I, was added via syringe to the first solution, and the resulting mixture was stirred for an additional 30 min. The reaction was quenched by pouring 2M HCl aq. into the solution and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was added to methanol to give a black precipitate, which was filtered off and washed several times with methanol. The crude polymer was purified via sequential Soxhlet extractions with methanol and hexanes, respectively. Polymer **P2 85/15** was synthesized in the same manner.

P2 50/50: UV-Vis (film, λ_{max}, nm): 550, 605sh; SEC (THF): M_n 10.6 x 10^3 g mol^{-1}, D 1.18; ^1H NMR (300 MHz, $CDCl_3$): δ 6.95 (s), 4.10 (q), 2.79/2.55 (t), 2.31 (t), 1.76–1.18 (m), 0.90 (t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.4, 140.5, 140.2, 134.3, 131.3, 131.1, 129.3, 60.9, 35.0, 32.4, 31.2, 31.0, 30.1, 30.0, 29.8, 25.5, 23.3, 15.0, 14.8; FT-IR (NaCl, cm^{-1}): υ_{max} 3055, 2952, 2928, 2857, 1736, 1510, 1456, 1349, 1214, 1033, 820.

P2 85/15: UV-Vis (film, λ_{max}, nm): 556, 605sh; SEC (THF): M_n 8.3 x 10^3 g mol^{-1}, D 1.10; ^1H NMR (300 MHz, $CDCl_3$): δ 6.96 (s), 4.10 (q), 2.78/2.55 (t), 2.31 (t), 1.78–1.20 (m), 0.90 (t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.4, 140.6, 134.3, 131.2, 129.3, 60.9, 35.0, 32.3, 31.1, 30.9, 30.0, 29.9, 29.7, 25.5, 23.3, 14.9, 14.8; FT-IR (NaCl, cm^{-1}): υ_{max} 3055, 2955, 2927, 2857, 1737, 1510, 1455, 1350, 1214, 820.

2. Size exclusion chromatograms of the block copolymers and respective precursor polymers

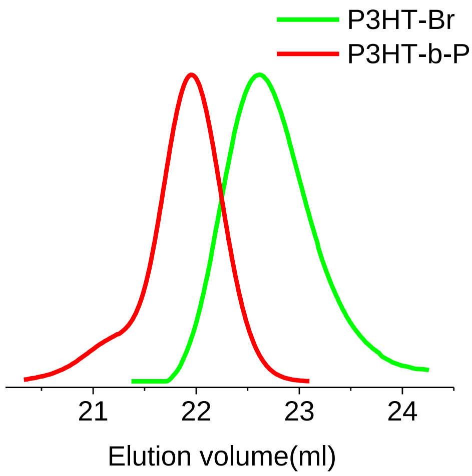

Fig. S1 SEC profiles of **P3HT-*b*-PE6TH-85/15** (**P2-85/15**) and its precursor (not purified by Soxhlet).

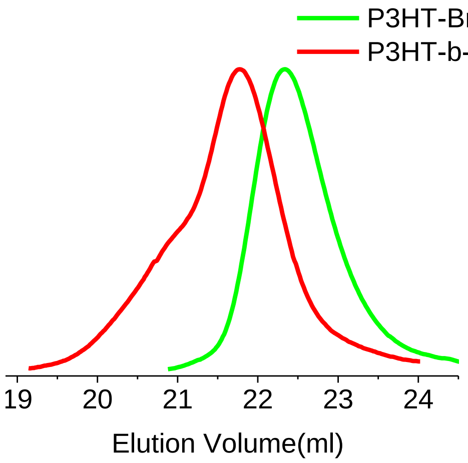

Fig. S2 SEC profiles of **P3HT-*b*-P6THA-85/15** (**P1-85/15**) and its precursor (not purified by Soxhlet).

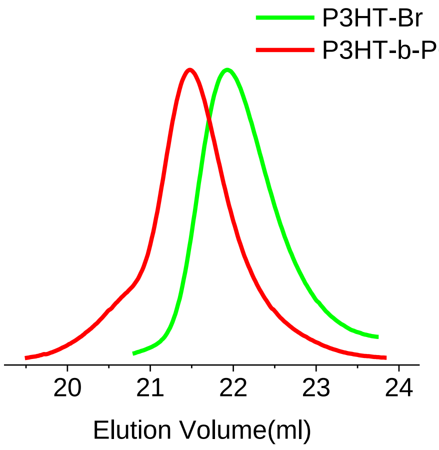

Fig. S3 SEC profiles of **P3HT-*b*-P6THA-50/50** (**P1-50/50**) and its precursor (not purified by Soxhlet).

3. ^{1}H NMR spectra of the block copolythiophenes

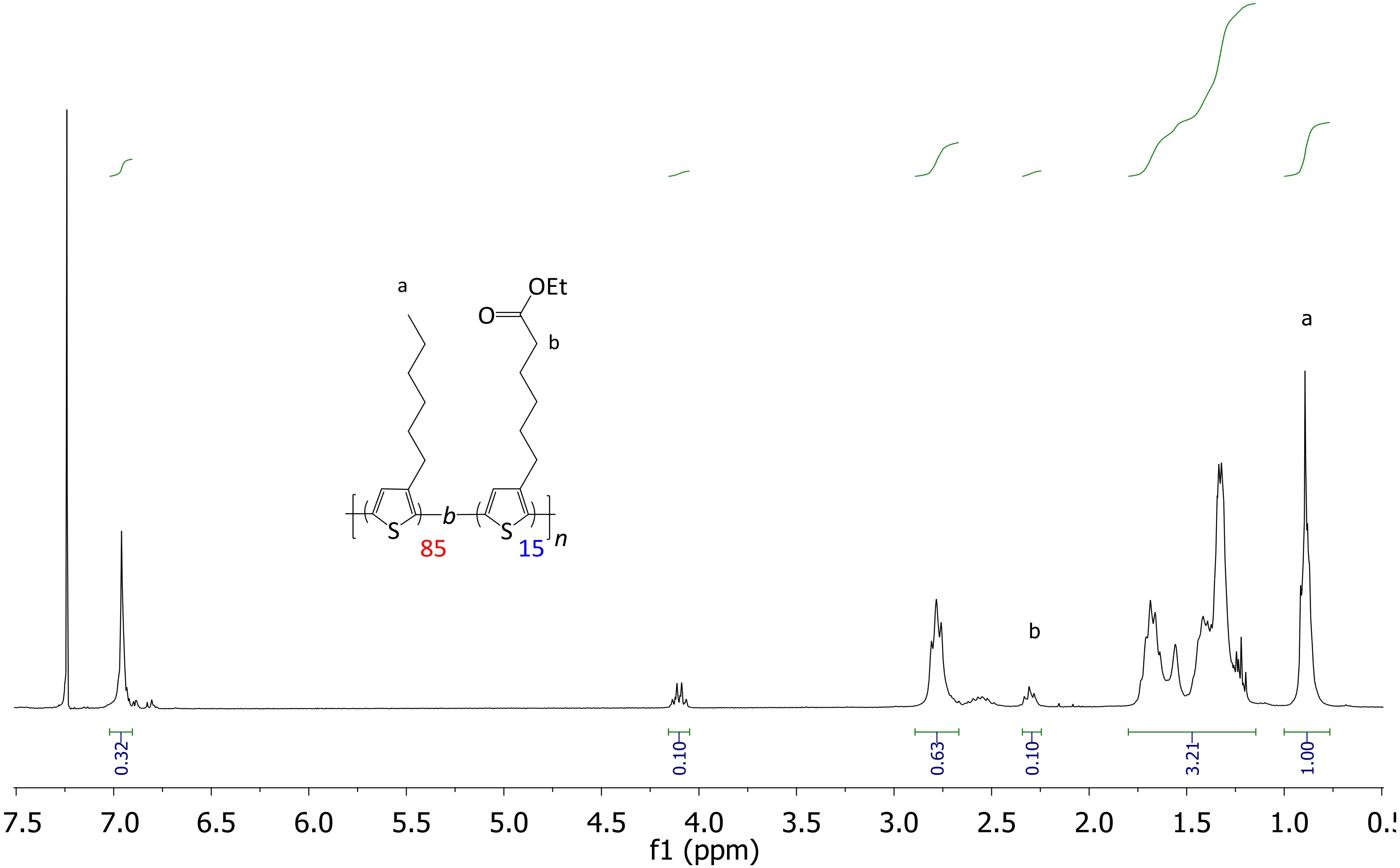

Fig. S4 ^{1}H NMR spectrum of **P3HT-*b*-PE6TH-85/15** (**P2-85/15**).

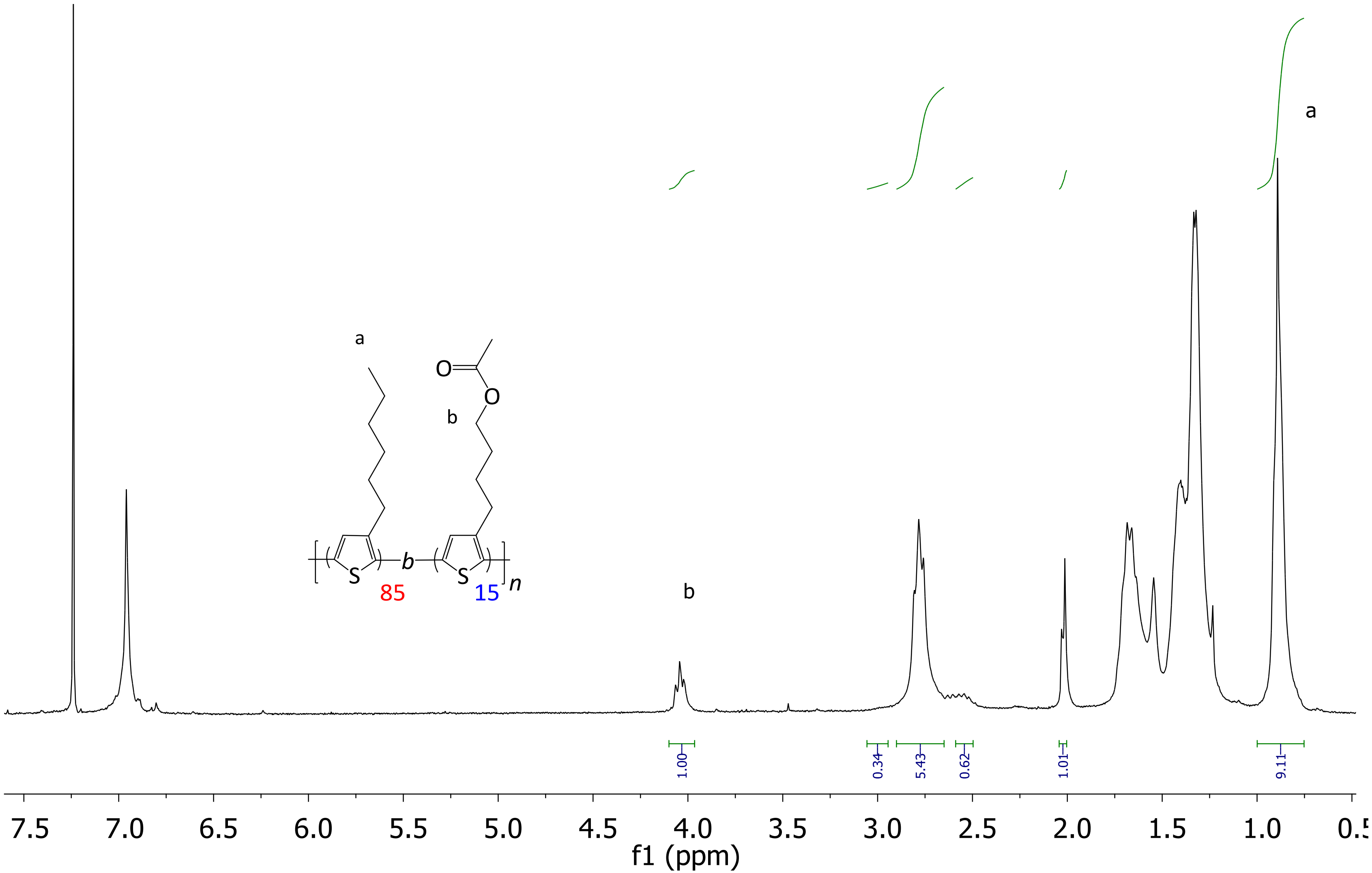

Fig. S5 ^{1}H NMR spectrum of **P3HT-*b*-P6THA-85/15** (**P1-85/15**).

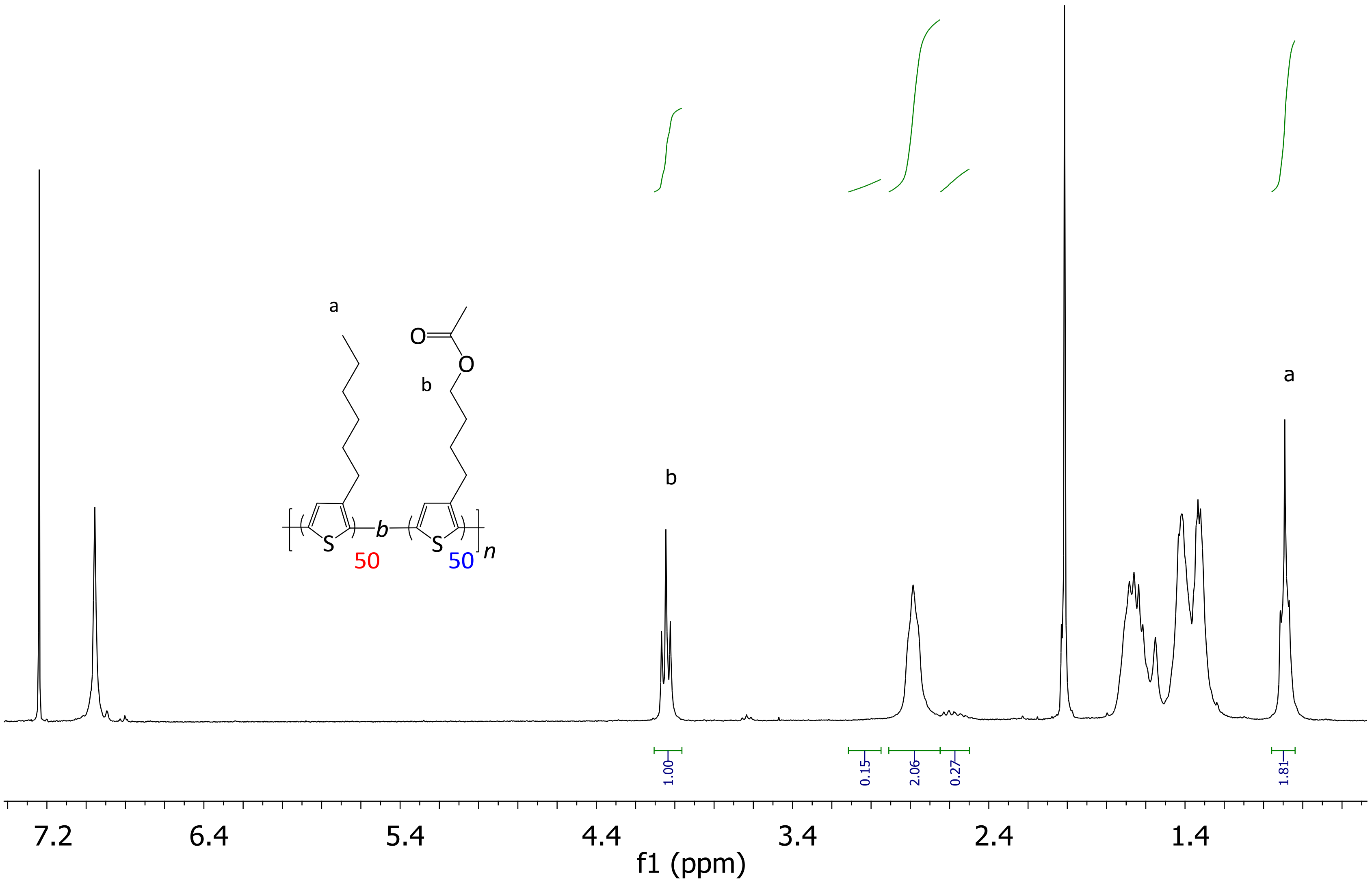

Fig. S6 ^{1}H NMR spectrum of **P3HT-*b*-P6THA-50/50** (**P1-50/50**).