Electronic Supplementary Information (ESI)

Synthesis of regioblock copolythiophene by Negishi catalyst-transfer polycondensation using $^{t}Bu_2Zn\cdot 2LiCl$

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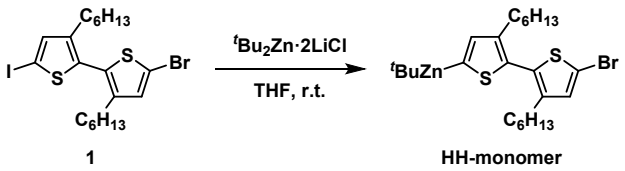
Preparation of a THF solution of HH-monomer



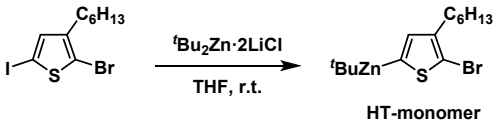
Scheme S1. Synthesis of HH-monomer by zinc-iodine exchange reaction

Table S1. Synthesis of HH-monomer by zinc-iodine exchange reaction using $^{t}Bu_2Zn{\cdot}2LiCl$ under varied conditions.

Run	[$^{t}Bu_2Zn{\cdot}2LiCl$]/[1][a]	[LiCl]/[1][b]	Conc. (M)[c]	Conv. (%)[d]
S1	1.0	0	0.0242	61
S2	2.0	0	0.0213	0
S3	1.0	3.0	0.0239	37
3	1.0	0	0.107	95

[a] Initial molar ratio of $^{t}Bu_2Zn{\cdot}2LiCl$ for **1**. [b] Initial molar ratio of LiCl for **1**. [c] Concentration (mol/L) of reaction mixture for synthesizing HH-monomer. [d] Conversion of zinc-iodine exchange reaction was evaluated by ^{1}H NMR spectroscopy.

Preparation of a THF solution of HT-monomer as the second monomer

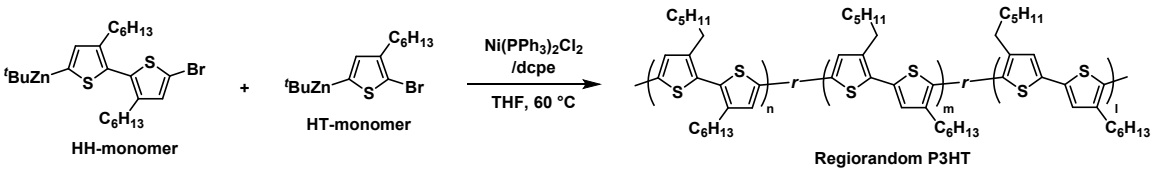


Scheme S2. Synthesis of HT-monomer by zinc-iodine exchange reaction

2-Bromo-3-hexyl-5-iodothiophene (185 mg, 0.496 mmol) was placed in a 5 mL two-necked flask purged with N_2. After dissolving 2-bromo-3-hexyl-5-iodothiophene in dehydrated THF (5 mL), a 0.184 M THF solution of $^{t}Bu_2Zn{\cdot}2LiCl$ (2.7 mL, 0.50

mmol) was added and stirred at room temperature for 30 min to afford the HT-monomer.

Synthesis of regiorandom P3HT



Scheme S3. Synthesis of regiorandom P3HT

1 (112 mg, 0.207 mmol) and 2-bromo-3-hexyl-5-iodothiophene (154 mg, 0.413 mmol) were placed in a 20 mL two-necked flask purged with N_2. After dissolving them in dehydrated THF (2 mL), a 0.184 M THF solution of ^{t}Bu$_2$Zn·2LiCl (3.4 mL, 0.62 mmol) was added at 0 °C and stirred at room temperature for 1 h. Then, the reaction mixture was diluted with 10 mL of dehydrated THF. The Ni catalyst (0.0092 mmol) solution (5 mL), which was prepared in another batch by mixing $Ni(PPh_3)_2Cl_2$ (6.0 mg, 0.0092 mmol) and dcpe (9.7 mg, 0.023 mmol) in THF (5 mL), was added to start the polymerization. The polymerization was carried out at 60 °C for 30 min, followed by quenching with 5 M HCl aq. (2 mL). The quenched solution was extracted with chloroform, washed with water, and analyzed by SEC directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtrating and drying under

vacuum, the crude HHTT-P3HT was obtained as a dark red solid (91 mg, 66%). SEC: M_n = 11,200, M_w/M_n = 1.46. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.10-6.91 (m, 1H), 2.88-2.68 (m, 1H), 2.66-2.42 (m, 1H), 1.78-1.50 (m, 2H), 1.49-1.15 (m, 6H), 0.99-0.80 (m, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 143.52, 143.00, 140.44, 140.02, 139.92, 137.11, 136.91, 135.82, 134.96, 133.89, 130.76, 130.62, 130.52, 129.75, 128.73, 128.44, 127.52, 127.28, 126.69, 125.94, 125.26, 31.99, 30.83, 30.66, 29.61, 29.41, 29.29, 22.93, 22.75, 14.27.

^{1}H and ^{13}C NMR spectra

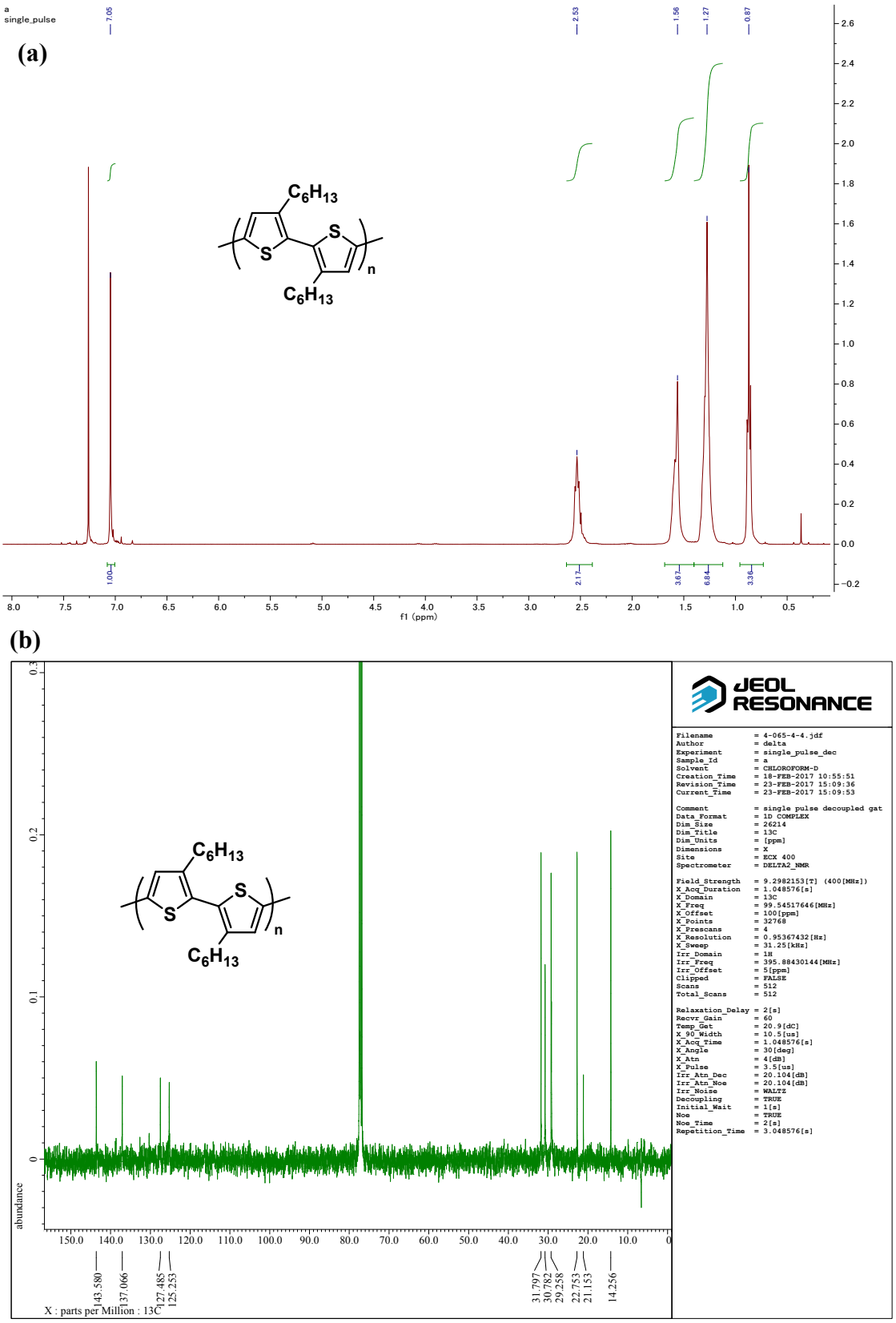


Figure S1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HHTT-P3HT (Run 4).

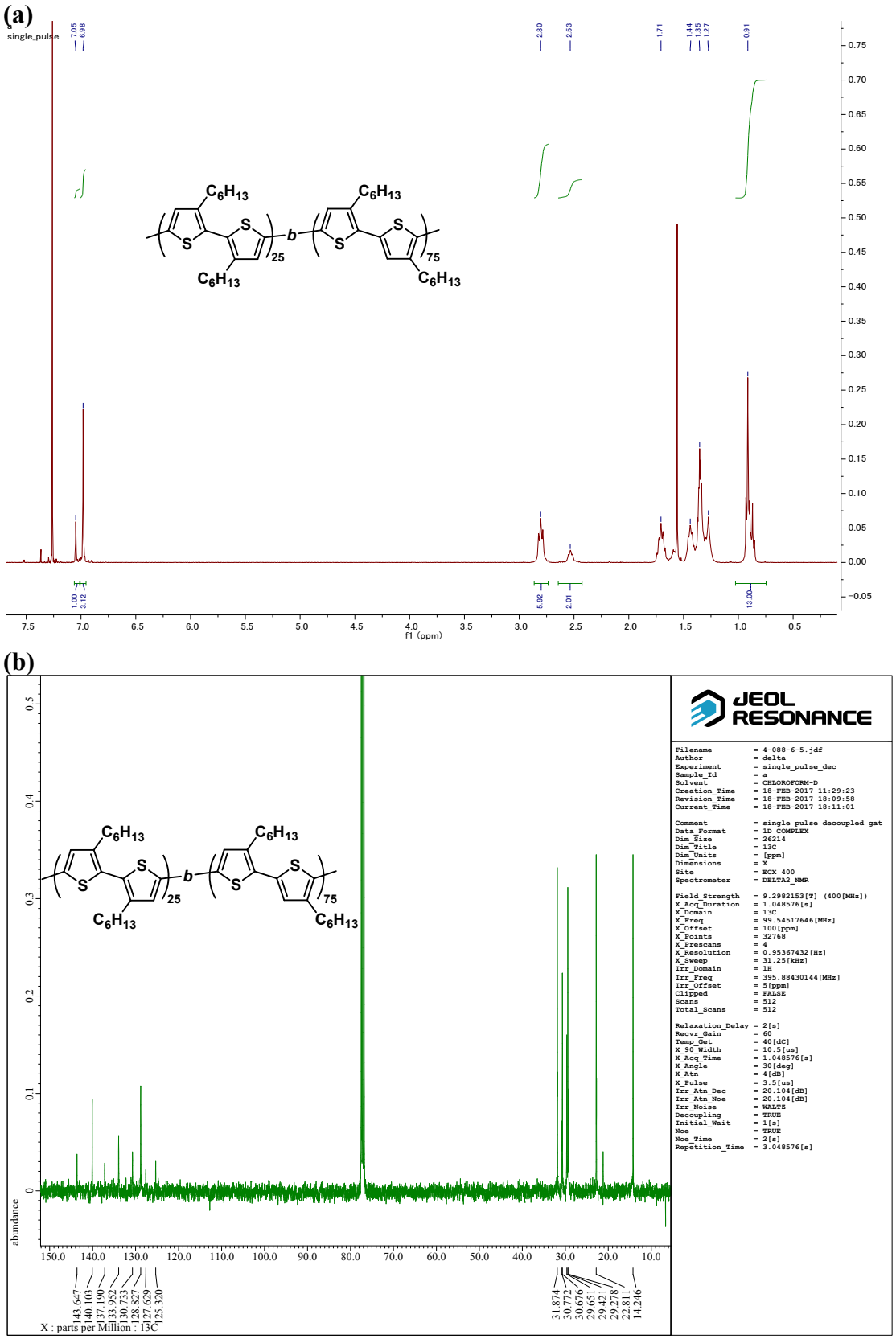


Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of regioblock P3HT ($HHTT_{25}HT_{75}$, Run 6).

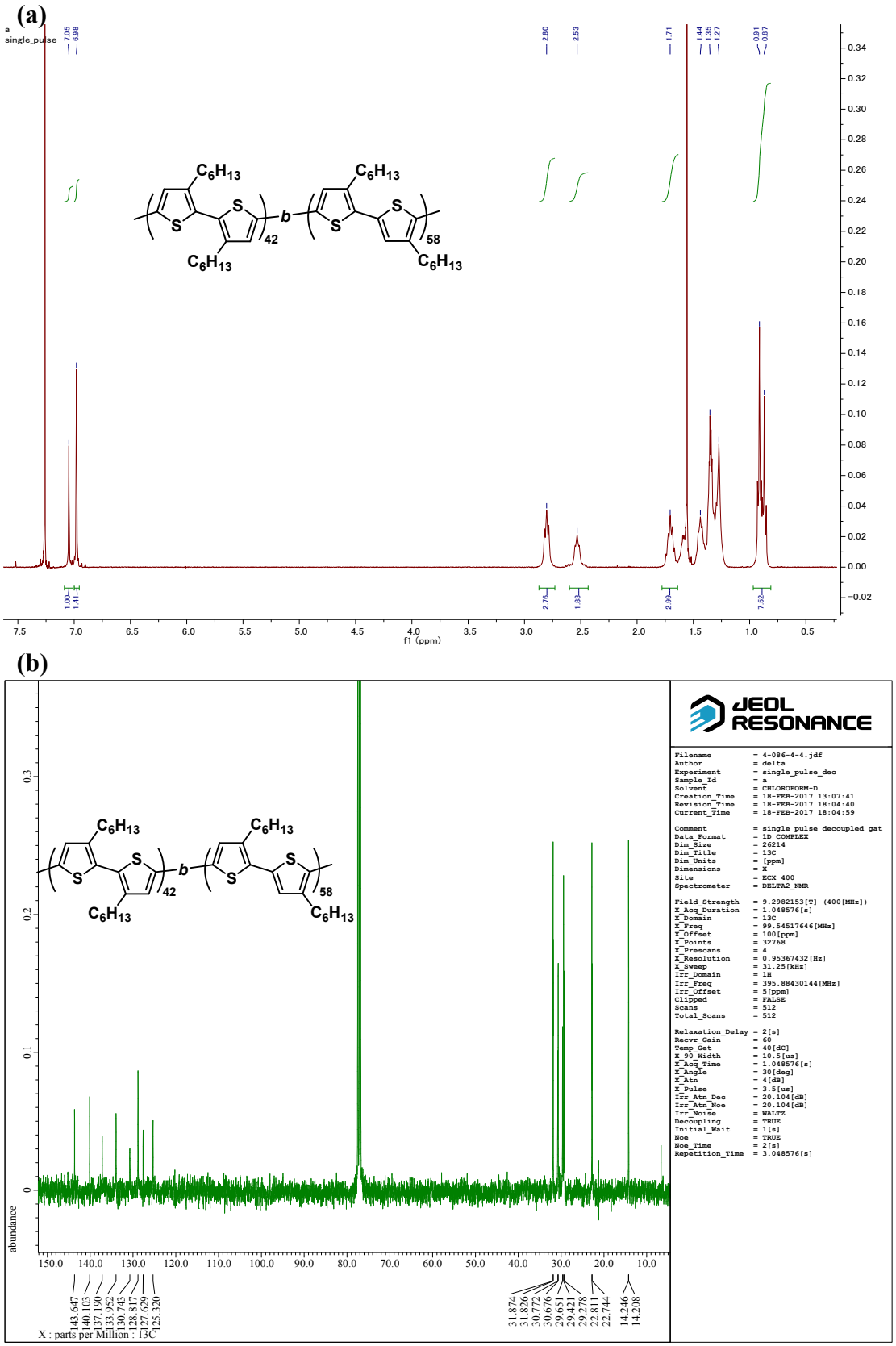


Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of regioblock P3HT ($HHTT_{42}HT_{58}$, Run 7).

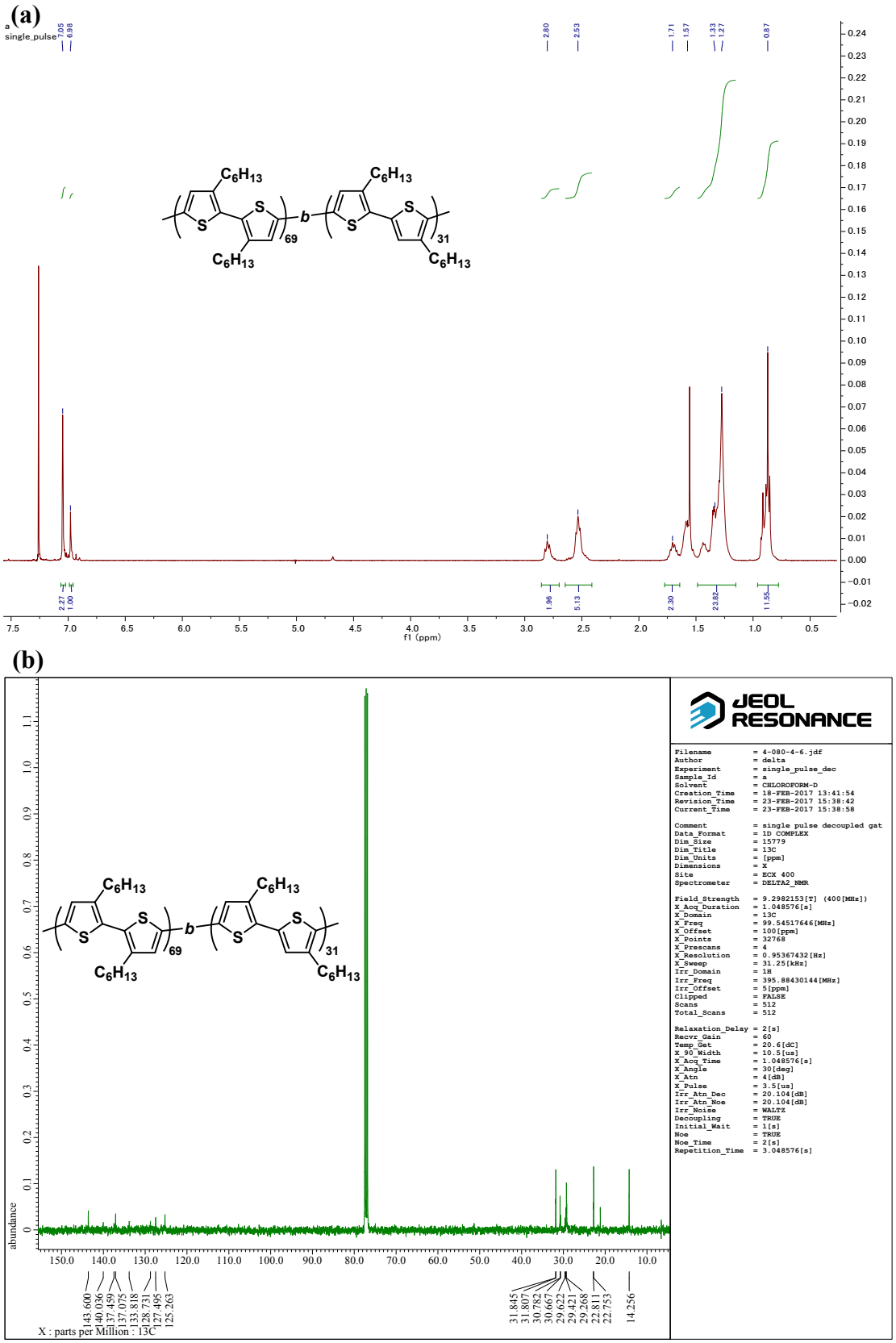


Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of regioblock P3HT ($HHTT_{69}HT_{31}$, Run 8).

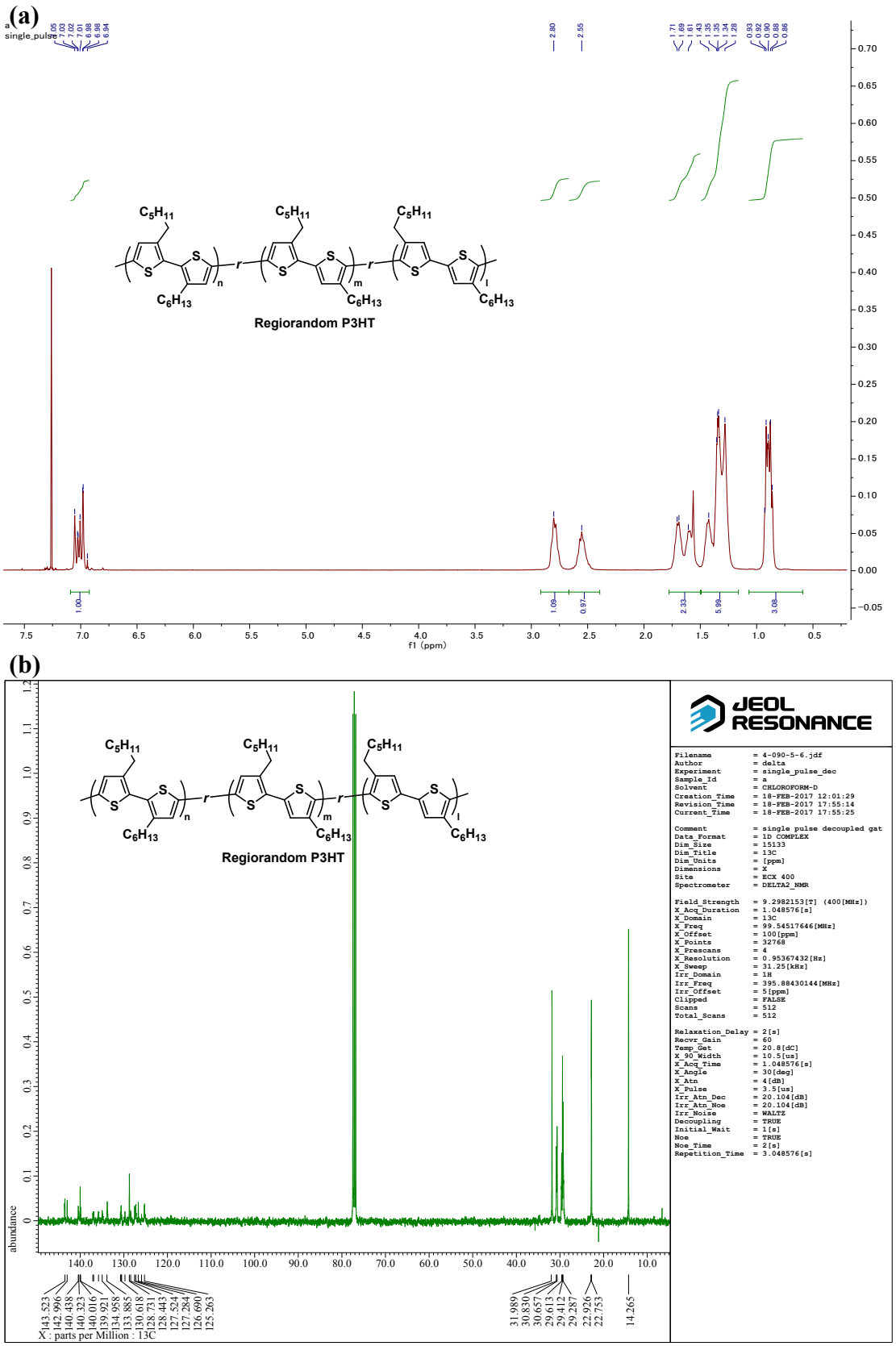


Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of regiorandom P3HT.

SEC UV traces of HHTT-P3HT and regioblock P3HT

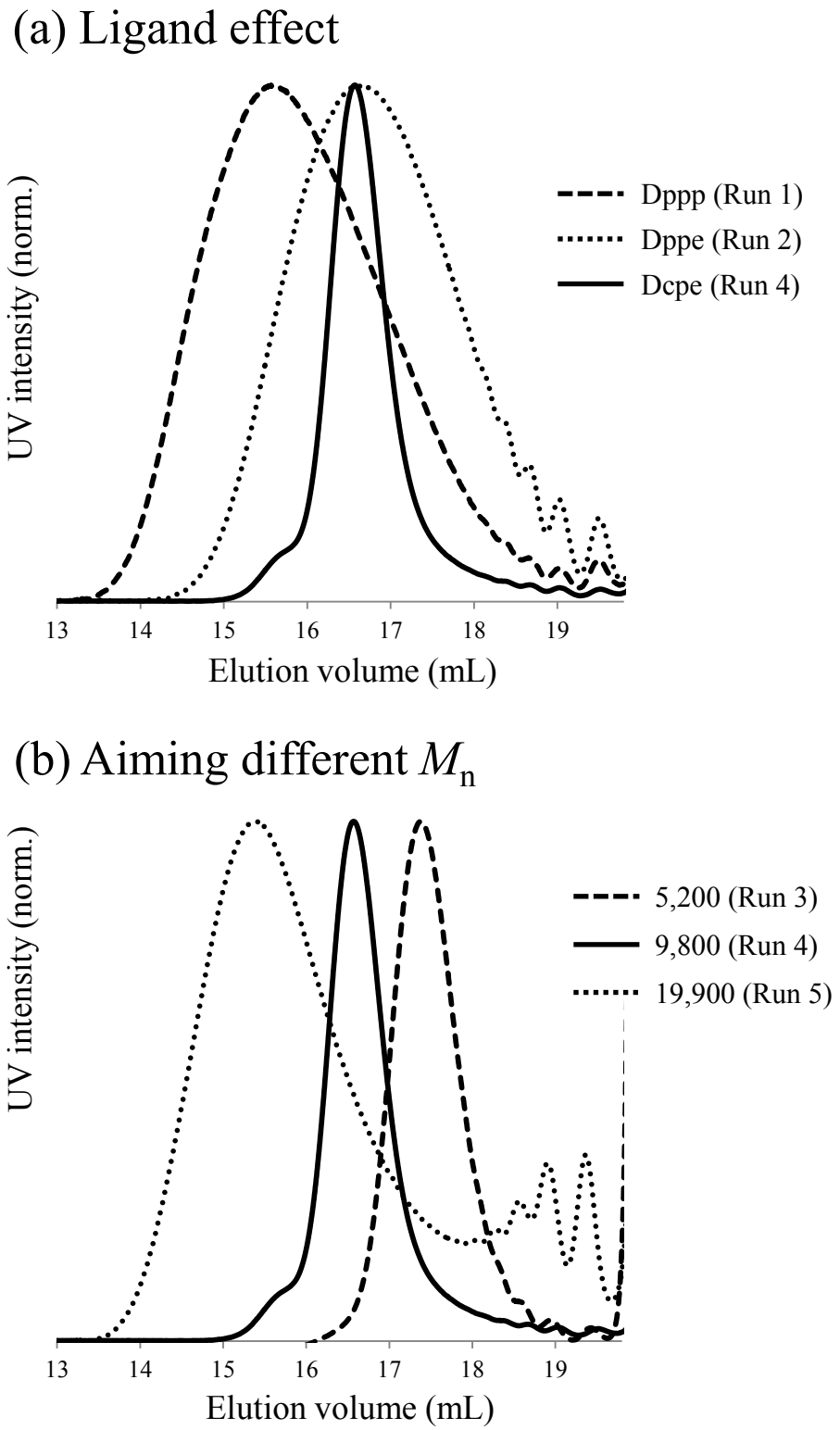


Figure S6. SEC UV traces of HHTT-P3HTs with (a) different ligands (Runs 1, 2 and 4) and (b) different [**1**]/$Ni(PPh_3)_2Cl_2$ (Runs 3-5).

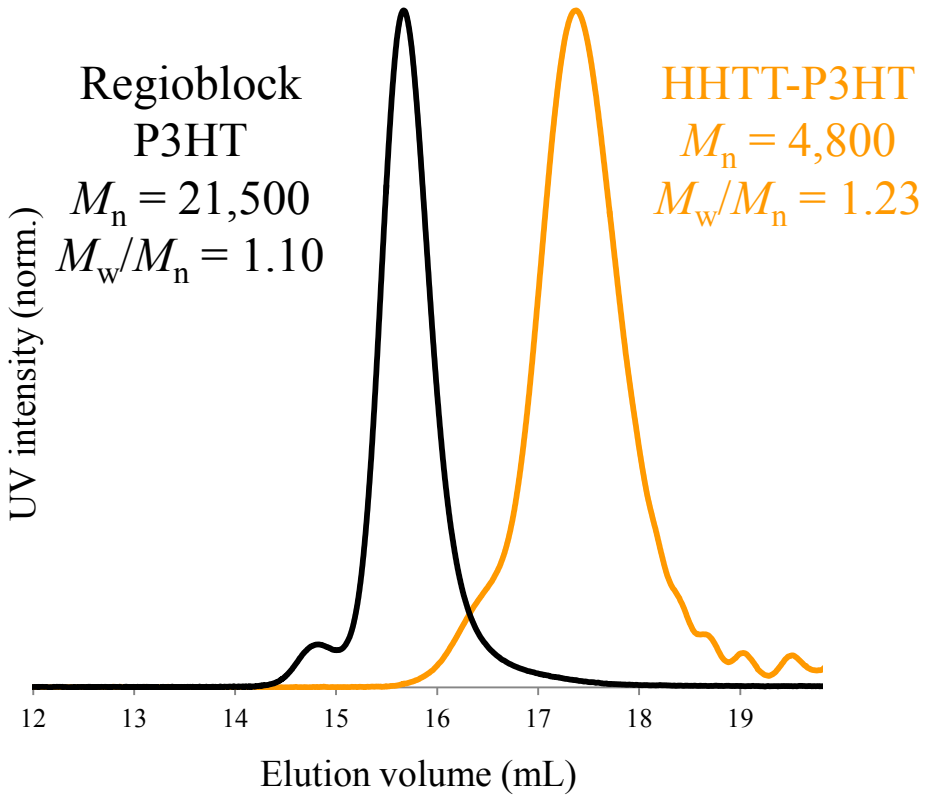


Figure S7. SEC UV traces of HHTT-P3HT (1st block, orange) and regioblock P3HT ($HHTT_{25}HT_{75}$, Run 6, black) after the successive addition of the HT-monomer (2nd block).

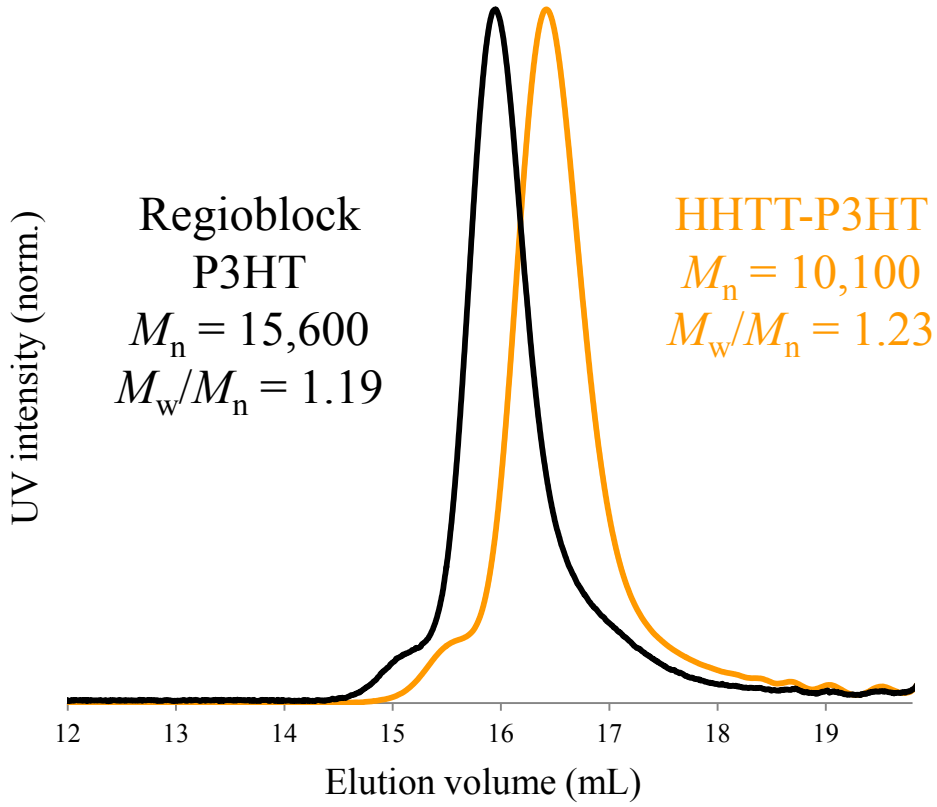


Figure S8. SEC UV traces of HHTT-P3HT (1st block, orange) and regioblock P3HT ($HHTT_{69}HT_{31}$, Run 8, black) after the successive addition of the HT-monomer (2nd block).

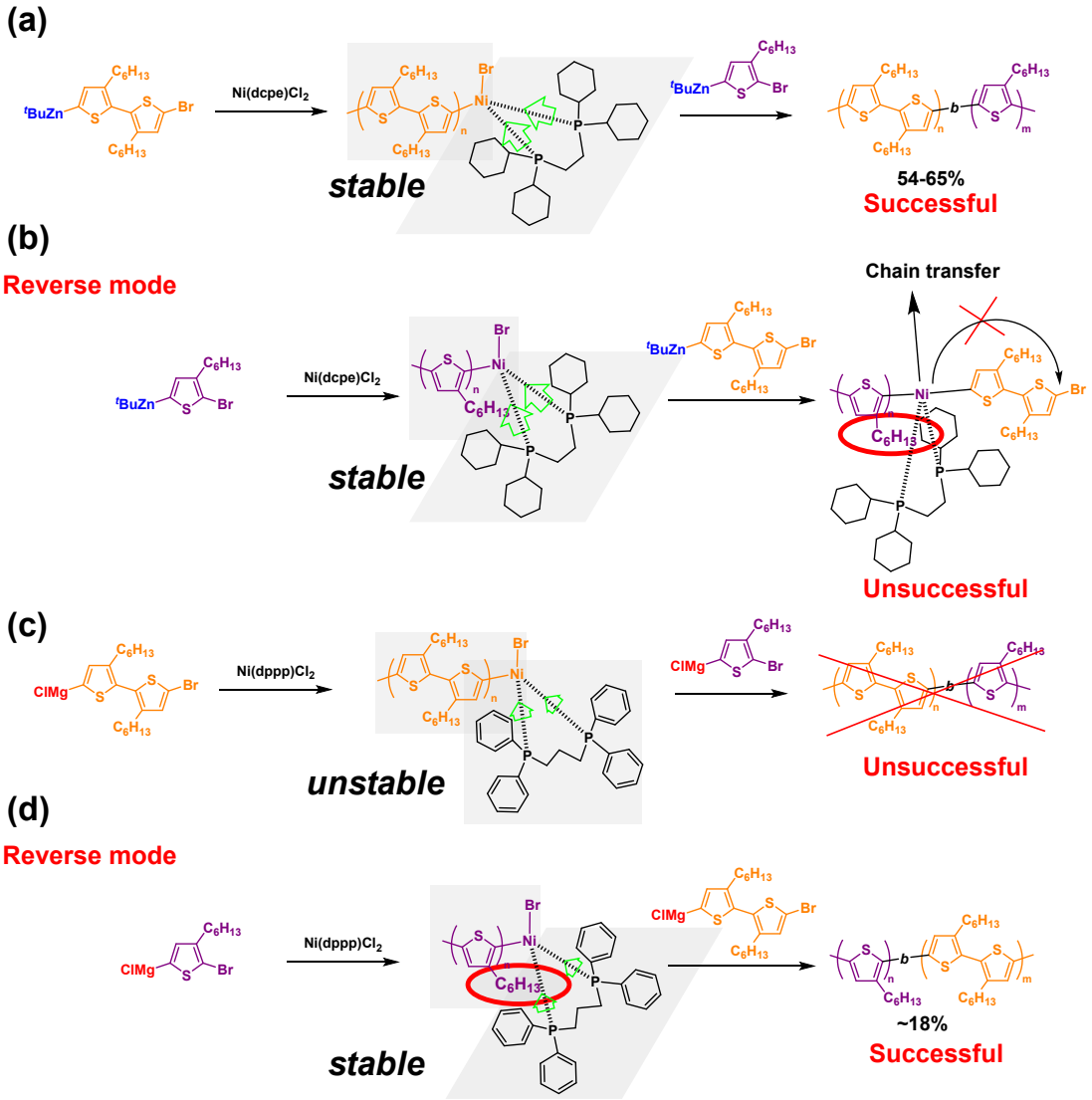


Figure S9. Schematic illustrations of plausible structures/mechanisms for (a) successful and (b) unsuccessful monomer addition sequences in NCTP and (c) unsuccessful and (d) successful monomer addition sequences in the conventional KCTP[1] for the synthesis of regioblock copolythiophenes.

In-plane 1D GIWAXS profiles

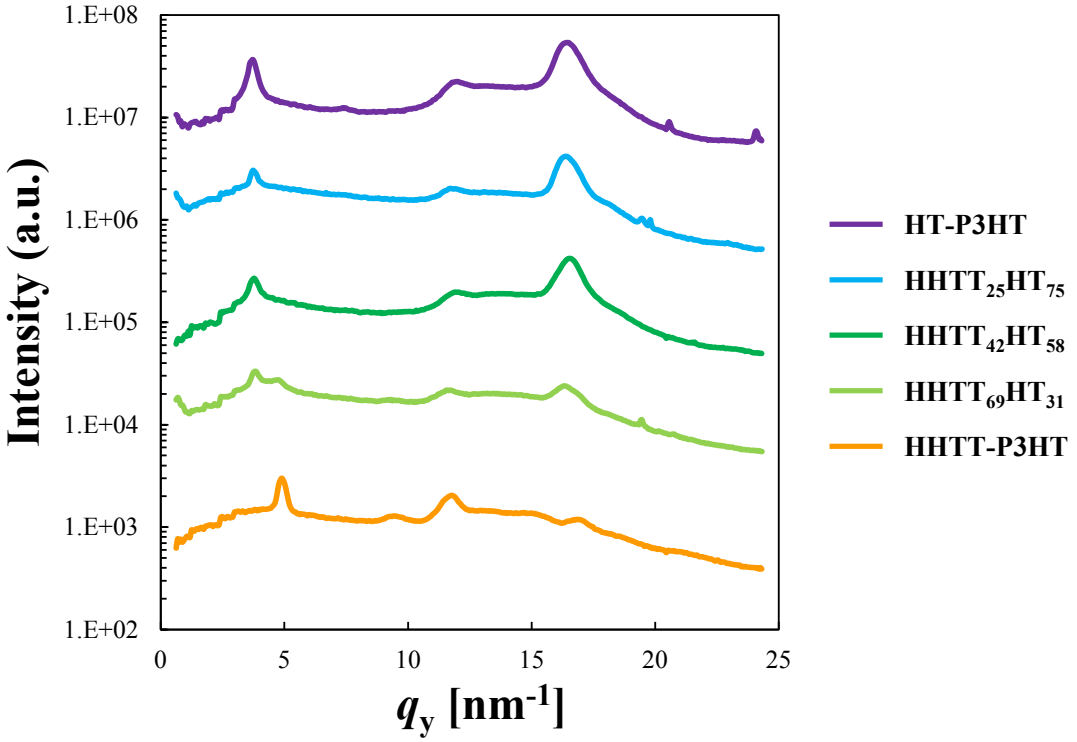


Figure S10. In-plane 1D GIWAXS profiles of HT-P3HT, HHTT$_{25}$HT$_{75}$, HHTT$_{42}$HT$_{58}$, HHTT$_{69}$HT$_{31}$ and HHTT-P3HT. All of the films were spin-casted on a Si wafer and annealed at 150 °C for 1 h under vacuum.

2D GISAXS patterns

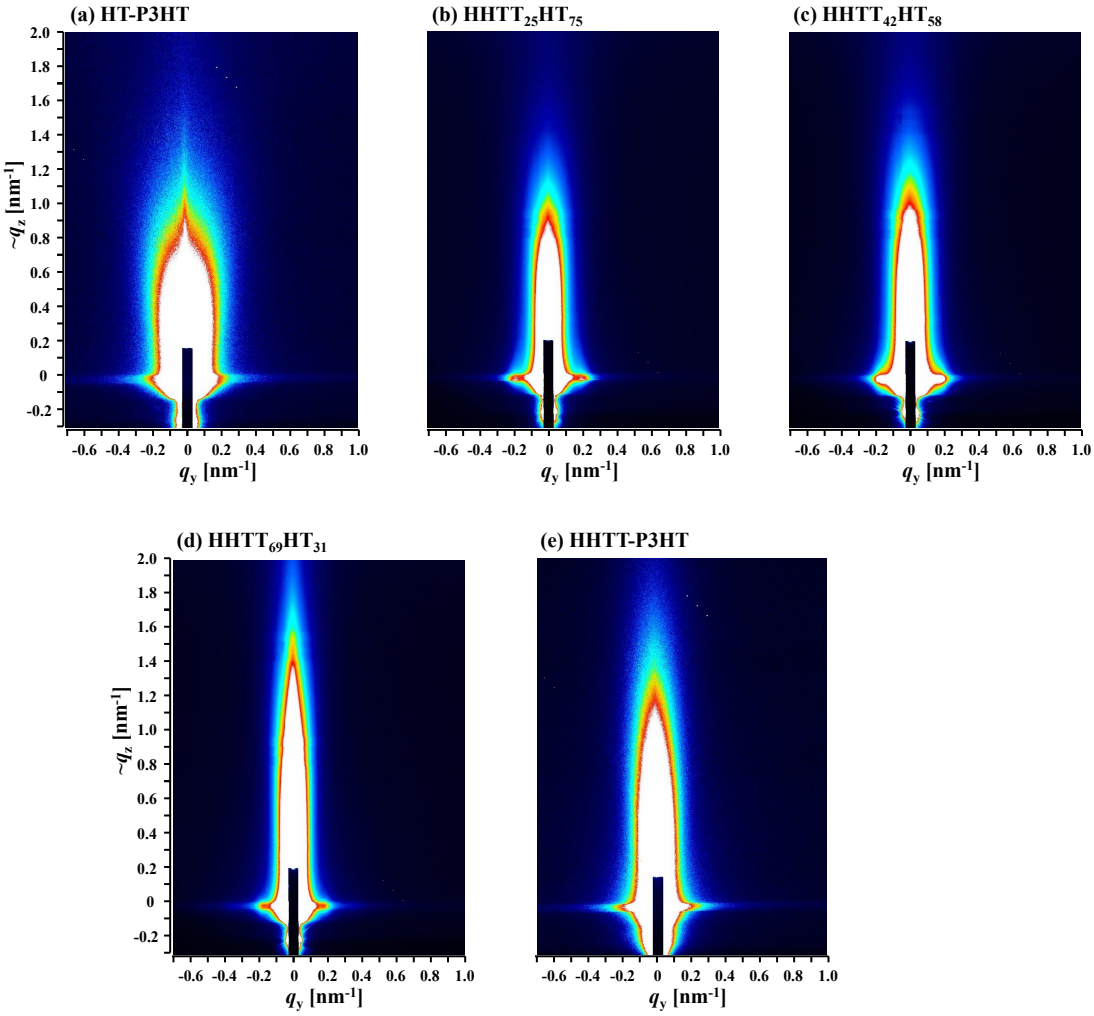


Figure S11. 2D GISAXS patterns of (a) HT-P3HT, (b) $HHTT_{25}HT_{75}$, (c) $HHTT_{42}HT_{58}$, (d) $HHTT_{69}HT_{31}$ and (e) HHTT-P3HT. All of the films were spin-casted on a Si wafer and annealed at 150 °C for 1 h under vacuum.

Temperature dependency of in-plane 1D GISAXS profiles

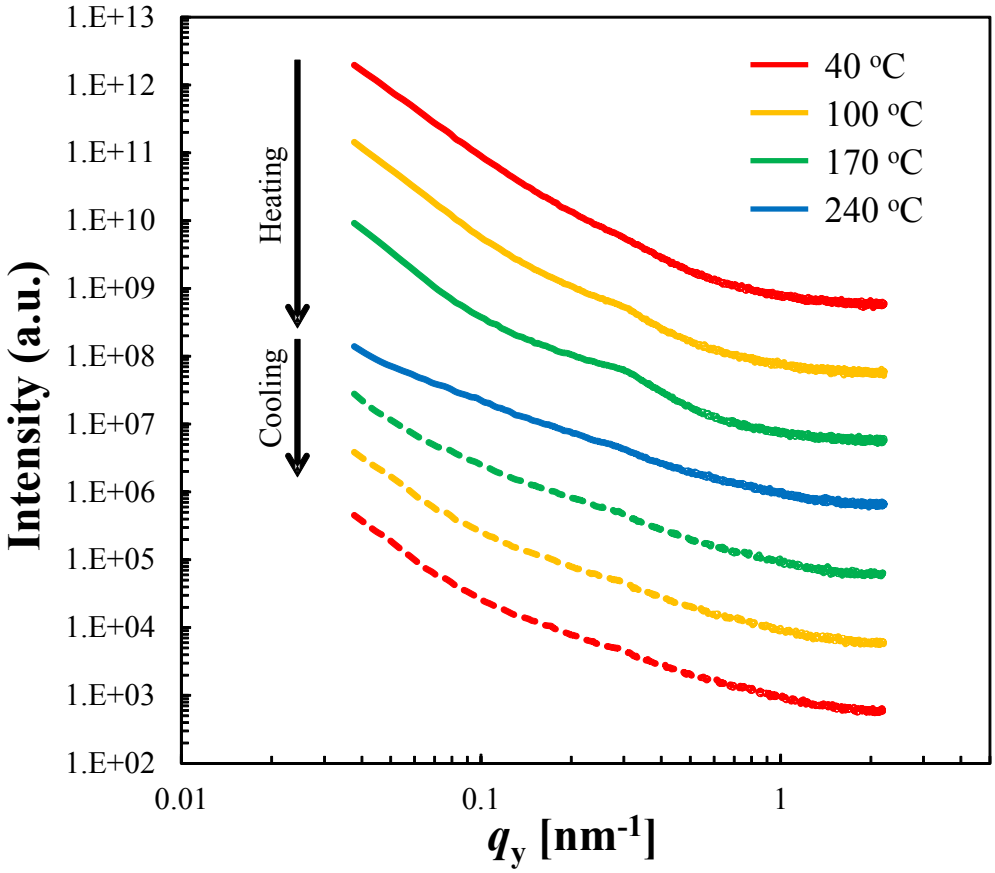


Figure S12. Temperature dependency of in-plane 1D GISAXS profiles of regioblock P3HT ($HHTT_{42}HT_{58}$, Run 7). The film was spin-casted on a Si wafer and heated up and cooled down gradually.

TGA thermograms

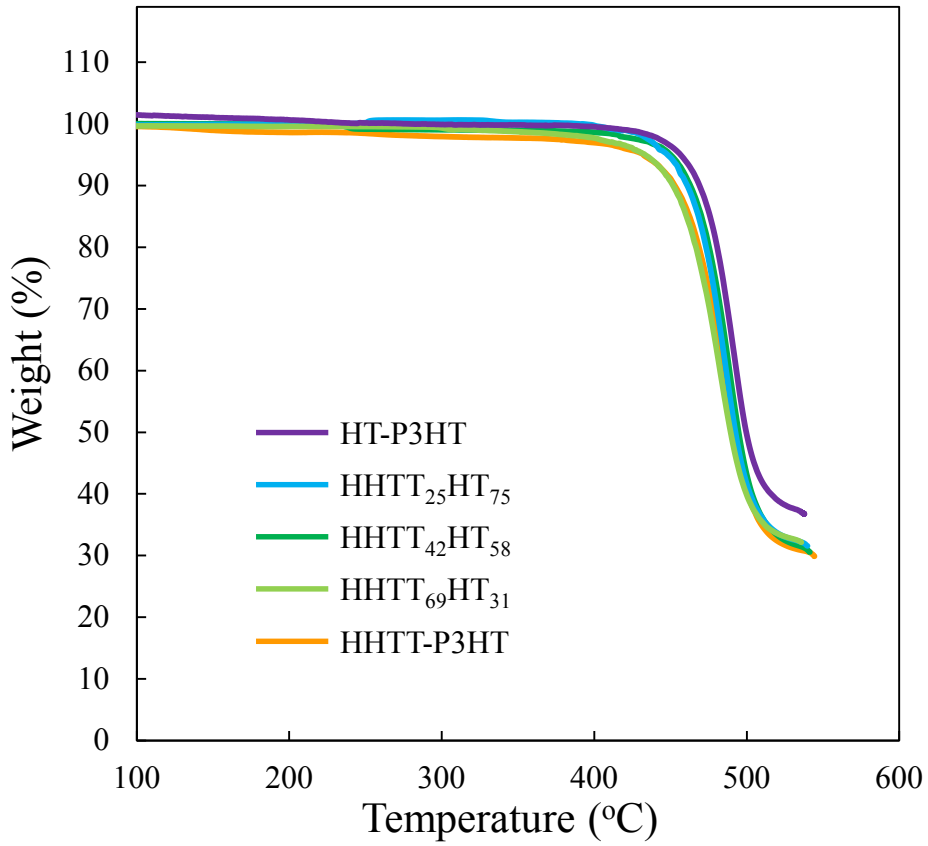


Figure S13. TGA curves of HT-P3HT, $HHTT_{25}HT_{75}$, $HHTT_{42}HT_{58}$, $HHTT_{69}HT_{31}$ and HHTT-P3HT at the heating scan rate of 10 °C/min in N_2.

DSC thermograms

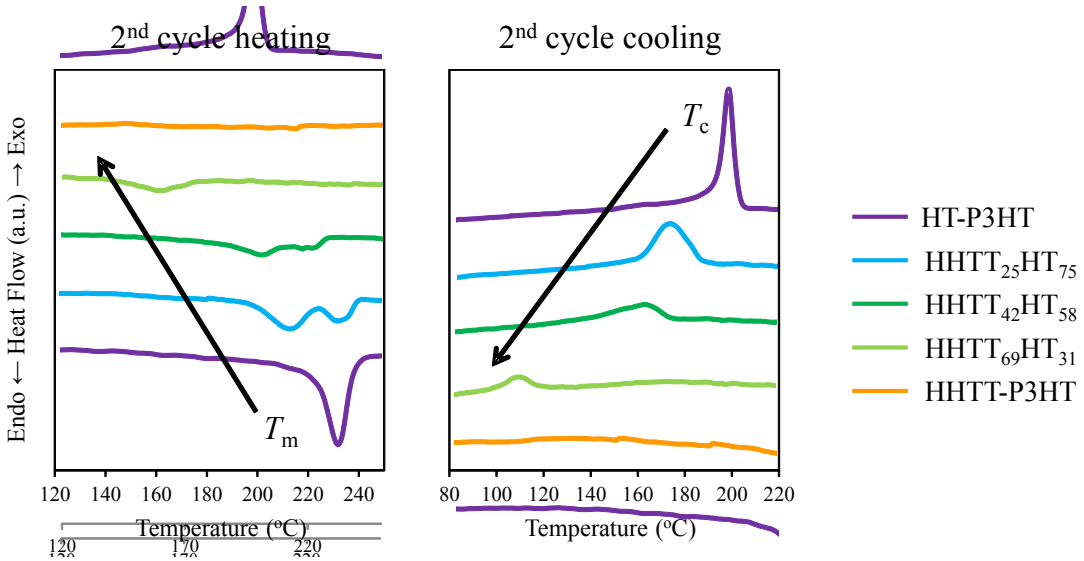


Figure S14. DSC curves at the 2nd cycle heating and 2nd cycle cooling scans of HT-P3HT, $HHTT_{25}HT_{75}$, $HHTT_{42}HT_{58}$, $HHTT_{69}HT_{31}$ and HHTT-P3HT at the heating and cooling rate of 10 °C/min in N_2.

Table S2. Thermal properties of HT-P3HT, HHTT-P3HT and regioblock P3HTs measured by TGA and DSC.

	$T_{d5\%}$ (°C)[a]	T_m (°C)[b]	ΔH_m (J/g)[c]	T_c (°C)[b]	ΔH_c (J/g)[c]	X_c[d]
HT-P3HT	456	233.4	19.7	199.2	17.3	59.7
$HHTT_{25}HT_{75}$	448	213.8	12.5	172.8	10.5	37.9
$HHTT_{42}HT_{58}$	450	201.6	8.57	163.9	4.98	26.0
$HHTT_{69}HT_{31}$	434	160.4	2.74	107.9	2.40	8.30
HHTT-P3HT	432	-	-	-	-	-

[a] The 5% weight-loss temperatures were evaluated by TGA at 10 °C/min in N_2. [b] The melting and crystallizing temperature were evaluated by DSC at 10 °C/min in N_2. [c] The melting and crystallizing enthalpies were evaluated from the integrated peaks of DSC. [d] Crystallinities were calculated from the comparison between evaluated ΔH_m and an ideal melting enthalpy (33 J/g)[2].

UV-vis absorption

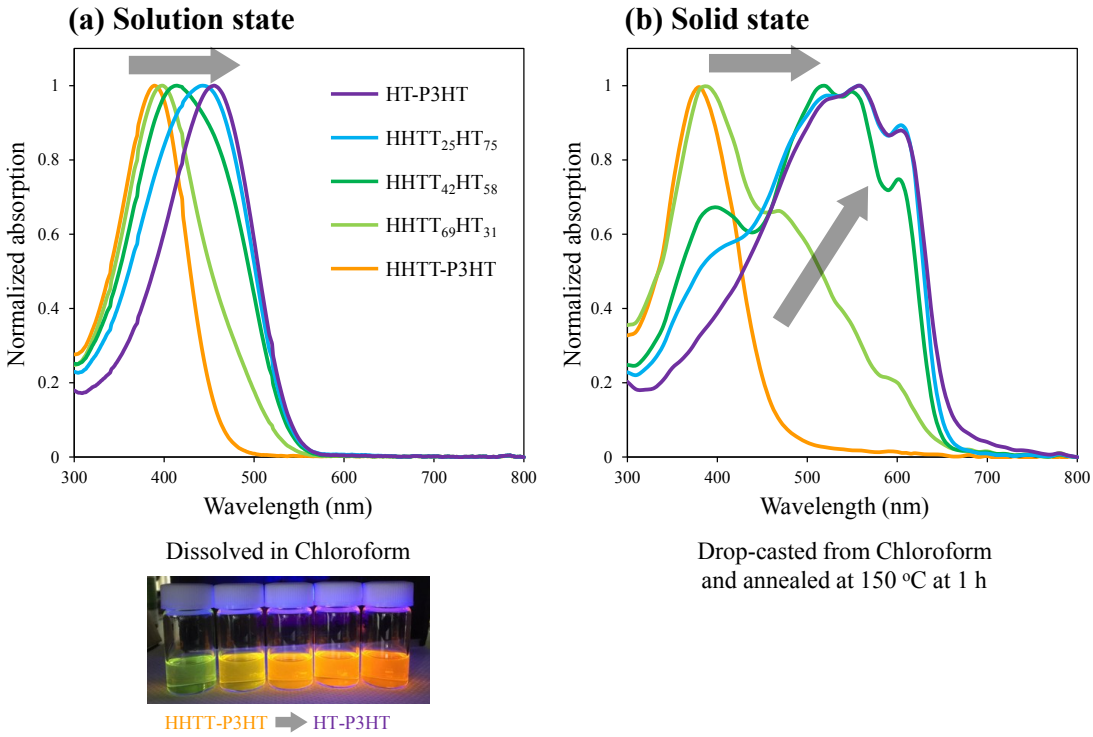


Figure S15. UV-vis absorption spectra of HT-P3HT, $HHTT_{25}HT_{75}$, $HHTT_{42}HT_{58}$, $HHTT_{69}HT_{31}$ and HHTT-P3HT (a) dissolved in chloroform and (b) drop-casted from chloroform and annealed at 150 °C at 1 h under vacuum.

Reference

1 X. Li, P. J. Wolanin, L. R. Macfarlane, R. L. Harniman, J. Qian, O. E. C. Gould, T. G. Dane, J. Rudin, M. J. Cryan, T. Schmaltz, H. Frauenrath, M. A. Winnik, C. F. J. Faul and I. Manners, *Nat. Commun.*, 2017, **8**, 15909.

2 J. Balko, R. H. Lohwasser, M. Sommer, M. Thelakkat and T. Thurn-Albrecht, *Macromolecules*, 2013, **46**, 9642–9651.