

Simple Procedure for Mono- and Bis-end-functionalization of Regioregular Poly(3-hexylthiophene)s using Chalcogens

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1. Instrumentation and Materials

^1H NMR spectra were obtained on Bruker AV-300 and AV-400 spectrometers using CDCl_3 as solvent (peak position $\delta^1\text{H} = 7.26$ ppm) and tetramethylsilane was used as an internal standard for ^1H NMR spectra (0.00 ppm) and $^{31}\text{P}\{^1\text{H}\}$ spectra were referenced to external H_3PO_4 (0.00 ppm). Number average molecular weight (M_n) were determined using end group analysis by ^1H NMR,¹ and size exclusion chromatography (Viscotek model 305 triple detector array at 30 °C (RI, viscometer, light scattering), columns: Viscotek I-MBHMW-3078 ($\times 2$), mobile phase: THF, flow rate: 1 mL/min, injection volume: 100 μL , the molecular weights of polymers and the polydispersities (PDI) were determined by GPC relative to polystyrene standards). MALDI-TOF mass spectra were recorded on a Bruker Autoflex II spectrometer using terthiophene as the sample matrix. Samples were prepared by dissolving ca. 0.5 mg in 100 μL of matrix solution in dichloromethane and approximately 1.5 μL of this solution was deposited on the plate. The MALDI experiments were performed in both the linear positive mode and reflectron positive mode.

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. 2-bromo-3-hexylthiophene, (diacetoxyiodo)benzene, iodine, 2.0 M *i*-PrMgCl THF solution, Ni(dppp)Cl₂, sulphur powder, DBU, triisopropylsilanethiol (TIPS-SH), selenium powder, anhydrous carbon disulfide (CS_2), 2,2':5',2''-terthiophene (for a MALDI-TOF mass matrix), all solvents (anhydrous THF, CHCl_3 , hexenes, acetone, methanol), aqueous HCl were purchased from Aldrich, Alfa Aesar or Fisher Scientific and used without further purification. The monomer 2-bromo-5-iodo-3-hexylthiophene and the catalyst 2-tolylNi(PPh₃)₂Br were synthesized according to literature procedures.²

2. General Procedure for Polymer Synthesis

The general procedure (Table 1, entry 1) for the synthesis of selectively end-capped P3HT is as follows. A Schlenk tube was charged with 2-bromo-5-iodo-3-hexylthiophene (1.0 mmol, 0.373 g), well-dried LiCl (2.0 mmol, 0.086 g), and THF (9.5 mL). 2.0 M *i*-PrMgCl THF solution (0.5 mL, 1.0 mmol) was added *via* syringe at 0 °C for 10 min, then the reaction mixture was allowed to stir at room temperature for 1 h. Ni(dppp)Cl₂ (43.4 mg, 8 mol%) was added in one portion at room temperature. After the reaction mixture had been stirred at room temperature for 1 h, it was equally divided into two portions (5 mL × 2).

Proton termination for αBr/ωH P3HT

One of the portions was quenched with 5 M HCl and the residue was added to 50 mL MeOH. The precipitate was washed with MeOH and acetone. The washed polymer was dried *in vacuo* to afford rr-P3HT (75% yield).

¹H NMR (300 MHz, CDCl₃): δ 6.98 (s, 1 H), 2.80 (t, *J* = 7.7 Hz), 2.61 (α CH₂ peak of ω-end 3-hexylthiophene-5-yl), 2.57 (α CH₂ peak of α-end 2-bromo-3-hexylthiophene-5-yl, the total number of proton between δ 2.83-2.57 is 2 H) 1.71 (quint, *J* = 7.6 Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H). ¹H NMR, DP = 10.0 (number average molecular weight: *M*_n = 1.6k),¹ MALDI-TOF MS peak top: DP = 12.6 (2.1k).

Thiol termination for αBr/ωSH P3HT

The other portion was poured into the mixture of sulphur power (S₈, 1.25 mmol, 40 mg) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.16 mmol (ca. 1/8 eq of S₈), 23.4 μL). The reaction mixture was stirred for 30 min, and 5 M HCl (10 mL) was added. Following the above purification procedure for 5 M HCl quenched P3HT, polymer powder was obtained (77% yield).

¹H NMR (300 MHz, CDCl₃): δ 6.98 (s, 1 H), 2.80 (t, *J* = 7.7 Hz), 2.54 (α CH₂ peak of α-end 2-bromo-3-hexylthiophene-5-yl, the total number of proton between δ 2.83-2.51 is 2 H) 1.71 (quint, *J* = 7.6 Hz, 2 H), 1.48-1.23 (m, 6 H), 0.91 (t, *J* = 7.2 Hz, 3 H). ¹H NMR: DP = 10.0 (*M*_n = 1.6k), MALDI-TOF MS peak top: DP = 12.0 (2.1k).

Dithiol termination for αSH/ωSH P3HT

After standard P3HT synthesis, the reaction was quenched with a premixed solution of TIPS-SH/*i*-PrMgCl 1:1 (TIPS-SH, 1.0 mmol, 0.215 mL and 2 M *i*-PrMgCl THF solution, 0.5 mL). The reaction mixture was refluxed for 30 min with stirring. Following the above purification procedure for 5 M HCl quenched P3HT, polymer powder was obtained. The

isolated α S-TIPS / ω S-TIPS P3HT was treated with 0.3 M TBAF CHCl_3 solution (50 mL) and after 10 min, the residue was washed with 0.1 M HCl (70 mL \times 2). After the solvent was removed under reduced pressure, unprotected α SH/ ω SH P3HT was obtained (70%, yield).

^1H NMR (300 MHz, CDCl_3): δ 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz, 2 H), 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.30 (m, 6 H), 0.91 (t, $J = 7.2$ Hz, 3 H). NMR: DP = unknown, due to no clear signals of end group on NMR spectra (Fig. S3), MALDI-TOF MS peak top: DP = 11.0 (1.9k).

CS₂ termination for α Br/ ω CS₂Ni(dppp) P3HT

To the 1.0 mmol scale polymerization reaction mixture, carbon disulfide (CS_2 , 1.0 mmol, 61 μL) was added. After the CS_2 -quenched reaction mixture was stirred for 30 min, 5 M HCl (10 mL) was added to the reaction mixture. Following the above purification procedure for 5 M HCl quenched P3HT, polymer powder was obtained.

^1H NMR (300 MHz, CDCl_3): δ 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz), 2.57 (α CH_2 peak of α -end 2-bromo-3-hexylthiophene-5-yl, the total number of proton between δ 2.80-2.57 is 2 H), 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H), 7.75 (m, dppp), 7.30 (m, dppp), 1.19 (m, dppp), 0.85 (m, dppp). ^{31}P NMR (202 MHz, CDCl_3): δ 9.4 ppm. ^1H NMR, DP = 16.0 ($M_n = 2.6\text{k}$), MALDI-TOF MS peak top: DP = 5.0 (1.6k).

Externally initiated rr-P3HTs was prepared according to published procedures¹ and the above Grignard monomer preparation using 8 mol% of 2-tolylNi(PPh_3)₂Br. The polymerization reaction mixtures were quenched using the above quenching methods unless otherwise noted.

α 2-tol/ ω H P3HT

^1H NMR (300 MHz, CDCl_3): δ 7.43 (m, 2 H), 7.24 (m, 2 H), 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz), 2.61 (α CH_2 peak of ω -end 3-hexylthiophene-5-yl, the total number of proton between δ 2.80-2.61 is 2 H), 2.49 (CH_3 peak of α -end tolyl) 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H). ^1H NMR, DP = 14.0 ($M_n = 2.4\text{k}$),² MALDI-TOF MS peak top: DP = 16.0 (2.7k).

α 2-tol/ ω SH P3HT

^1H NMR (300 MHz, CDCl_3): δ 7.43 (m, 2 H), 7.24 (m, 2 H), 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz, 2 H), 2.49 (CH_3 peak of α -end tolyl) 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H). ^1H NMR, DP = 14.0 ($M_n = 2.4\text{k}$),² MALDI-TOF MS peak top: DP = 16.0 (2.6k).

Selenol termination for α 2-tol/ ω SeH P3HT

The 1.0 mmol scale polymerization reaction mixture was poured into the mixture of well-mixed selenium power (Se, 1.25 mmol, 98.7 mg) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.16 mmol (ca. 1/8 eq of Se), 23.4 μ L). After the selenium quenched reaction mixture was stirred overnight, 5 M HCl (10 mL) was added to the reaction mixture. Following the above purification procedure for 5 M HCl quenched P3HT, polymer powder was obtained.

^1H NMR (300 MHz, CDCl_3): δ 7.43 (m, 2 H), 7.24 (m, 2 H), 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz, 2 H), 2.49 (CH_3 peak of α -end tolyl), 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H). ^1H NMR: DP = 10.0 ($M_n = 1.8\text{k}$), MALDI-TOF MS peak top: DP = 13.0 (2.3k).

α 2-tol/ ω CS₂Ni(dppp)Br P3HT

^1H NMR (300 MHz, CDCl_3): δ 7.43 (m, 2 H), 7.24 (m, 2 H), 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz, 2 H), 2.49 (CH_3 peak of α -end tolyl), 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48-1.38 (m, 2 H), 1.37-1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H), 7.73 (m, dppp), 7.30 (m, dppp), 1.19 (m, dppp), 0.85 (m, dppp). ^{31}P NMR (202 MHz, CDCl_3): δ 9.4 ppm. ^1H NMR: DP = 8.2 ($M_n = 1.4\text{k}$), MALDI-TOF MS peak top: DP = 10.0 (2.3k).

3. ^1H NMR spectra of $\alpha\text{Br}/\omega\text{H}$ P3HT, $\alpha\text{Br}/\omega\text{SH}$ P3HT, and $\alpha\text{SH}/\omega\text{SH}$ P3HT

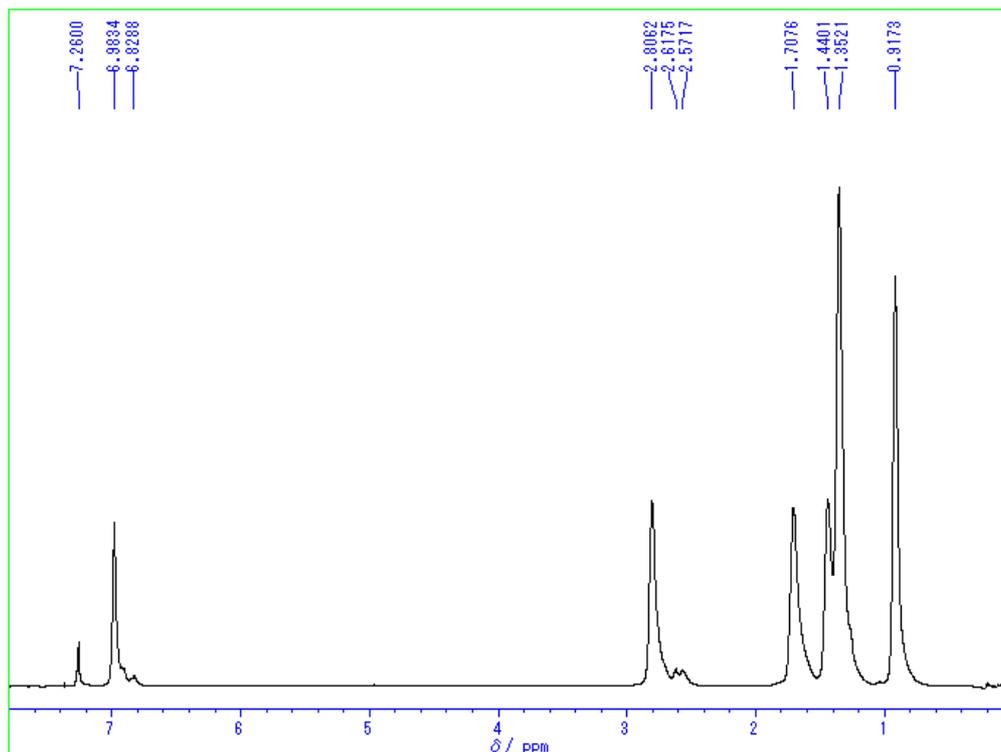


Fig. S1 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of $\alpha\text{Br}/\omega\text{H}$ P3HT.

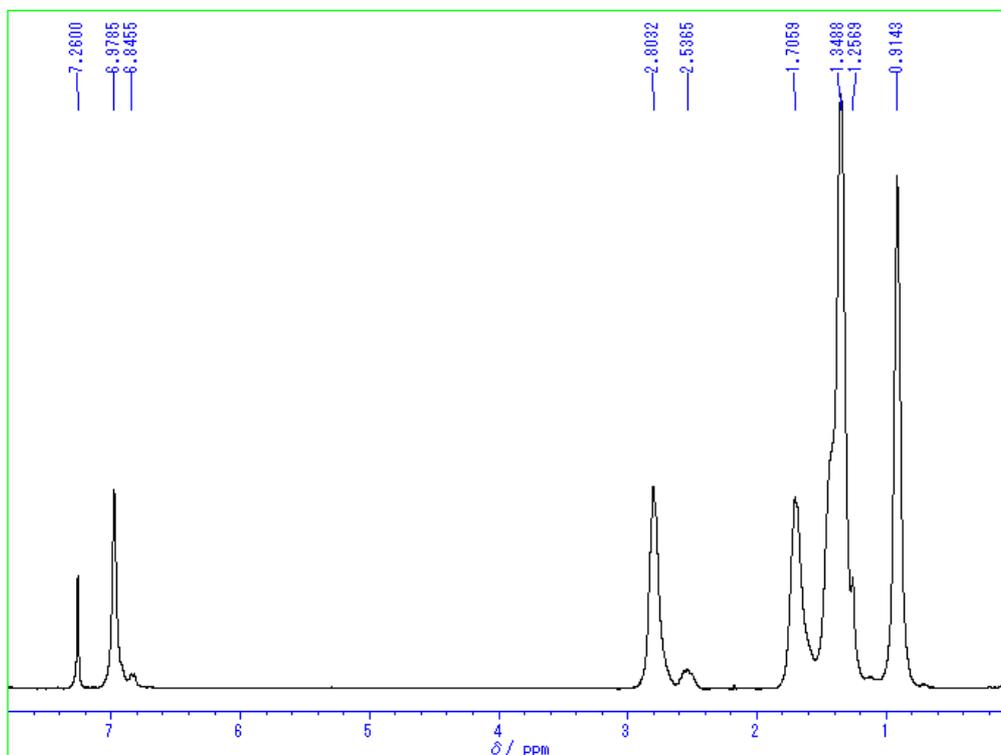


Fig. S2 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of $\alpha\text{Br}/\omega\text{SH}$ P3HT.

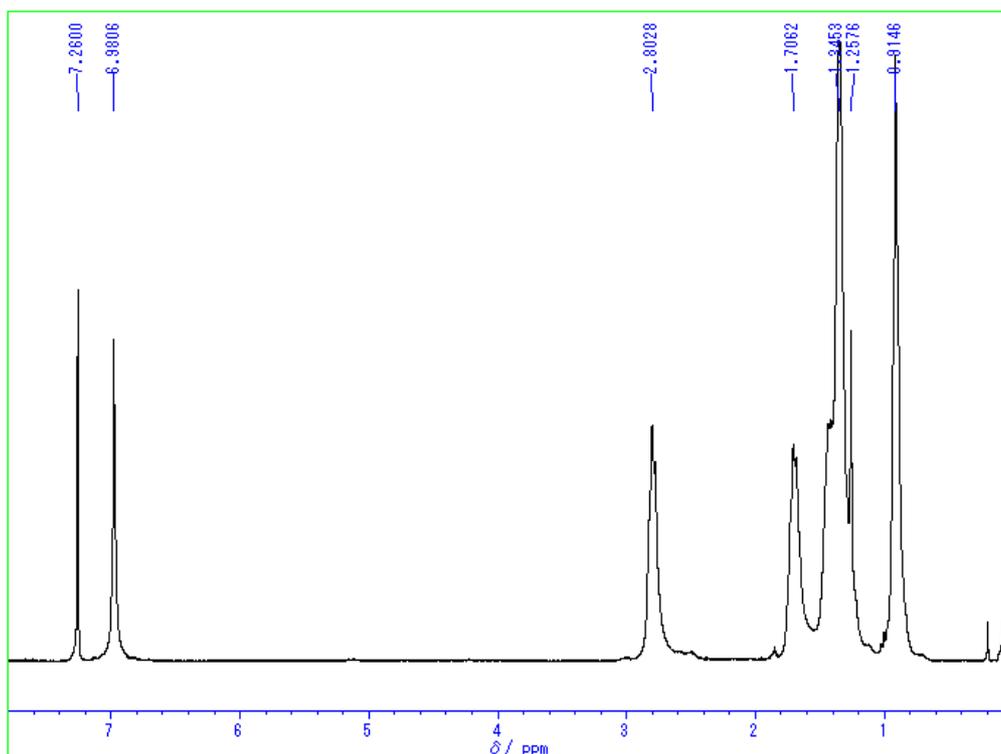


Fig. S3 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of $\alpha\text{SH}/\omega\text{SH}$ P3HT.

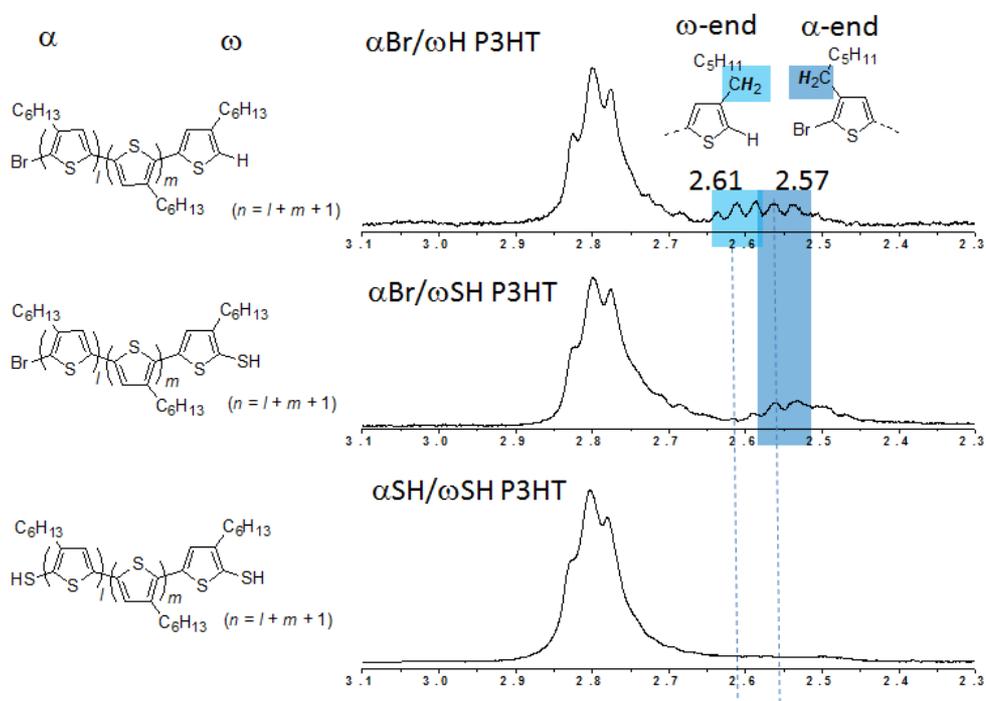


Fig. S4 Expanded $\alpha\text{-CH}_2$ region for Fig. S1-3.

4. MALDI-TOF mass spectra of α TIPSSH/ ω TIPSSH P3HT and α SH/ ω SH P3HT

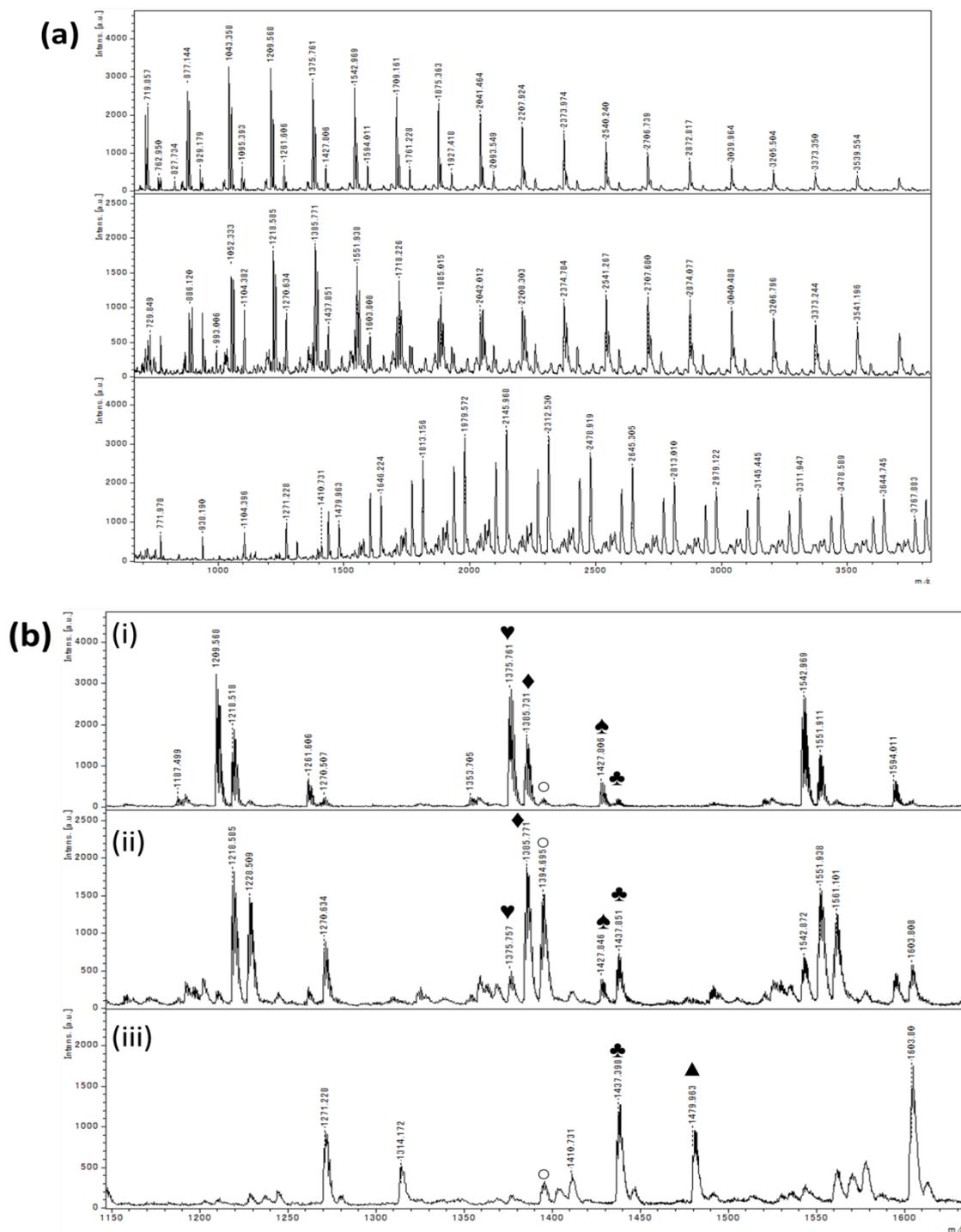


Fig. S5 (a) MALDI-TOF mass spectra of α S-TIPS/ ω S-TIPS P3HT prepared using post-treatment (i) 5 M HCl, (ii) MeOH, and (iii) 0.3 M TBAF in MeOH, (b) zoomed MALDI-TOF mass spectrum of peak top region, notations of 6 sets of peak series, ♥: α S-TIPS / ω S-TIPS P3HT, ♦: α , ω , S-TIPS, SH P3HT, ○: α SH/ ω SH P3HT, ♠: α , ω , S-TIPS, *i*-Pr-S P3HT, ♣ α , ω SH, *i*-Pr-S P3HT ▲ α *i*-Pr-S/ ω *i*-Pr-S P3HT.

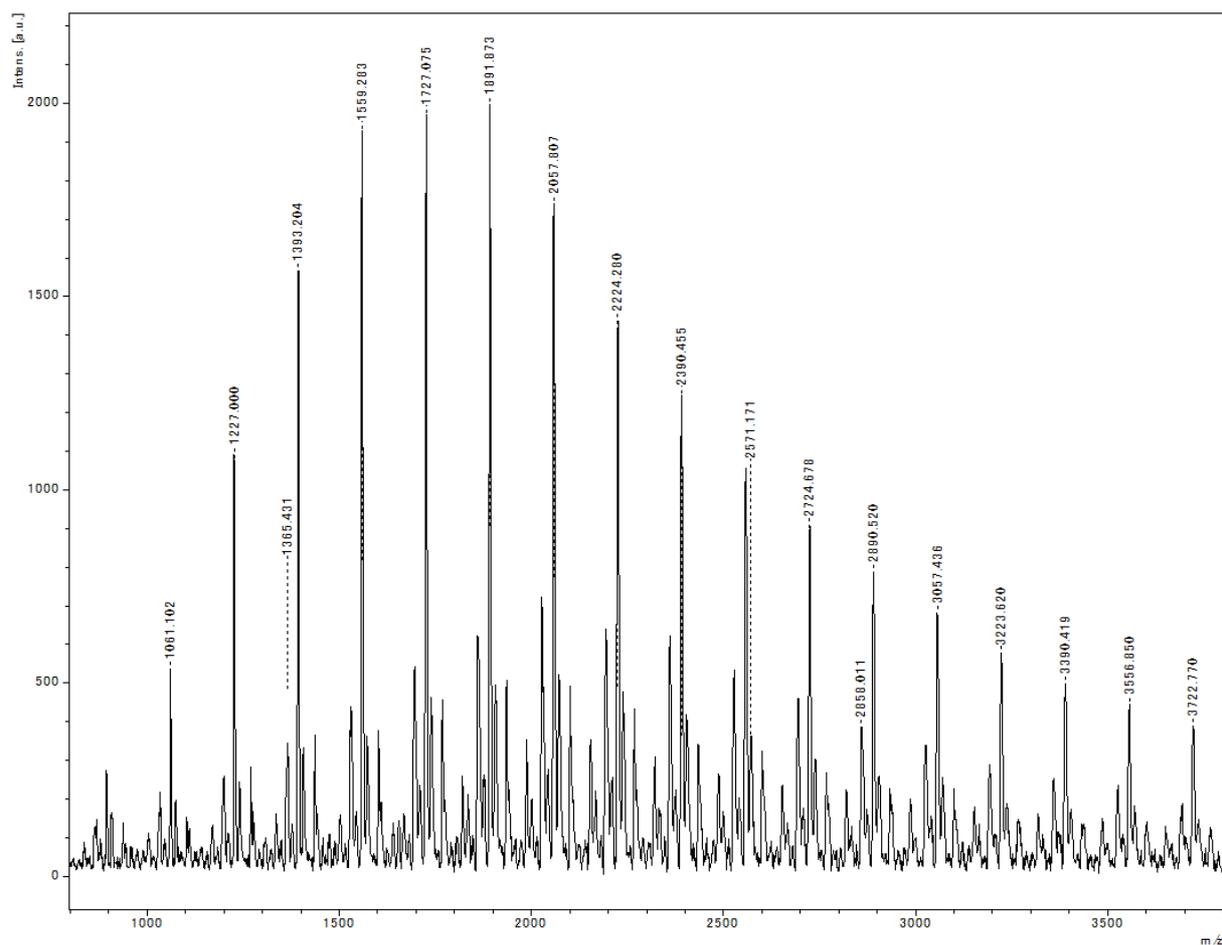


Fig. S6 MALDI-TOF mass spectrum of α SH/ ω SH P3HT.

Calculated mass:

α -end (2-thiol-3-hexylthiophene-5-yl) + poly(3-thiophene-2,5-diyl) + ω -end

(2-thiol-3-hexylthiophene-5-yl) = $199.36 + 166.28 (n - 1) + 199.36 = 66.15$ (thiol-thiol) +
 $166.28 n$ (for example, 1729.0, 1895.2, 2061.5).

5. ^1H NMR spectra of α 2-tol/ ω H P3HT and α 2-tol/ ω SH P3HT

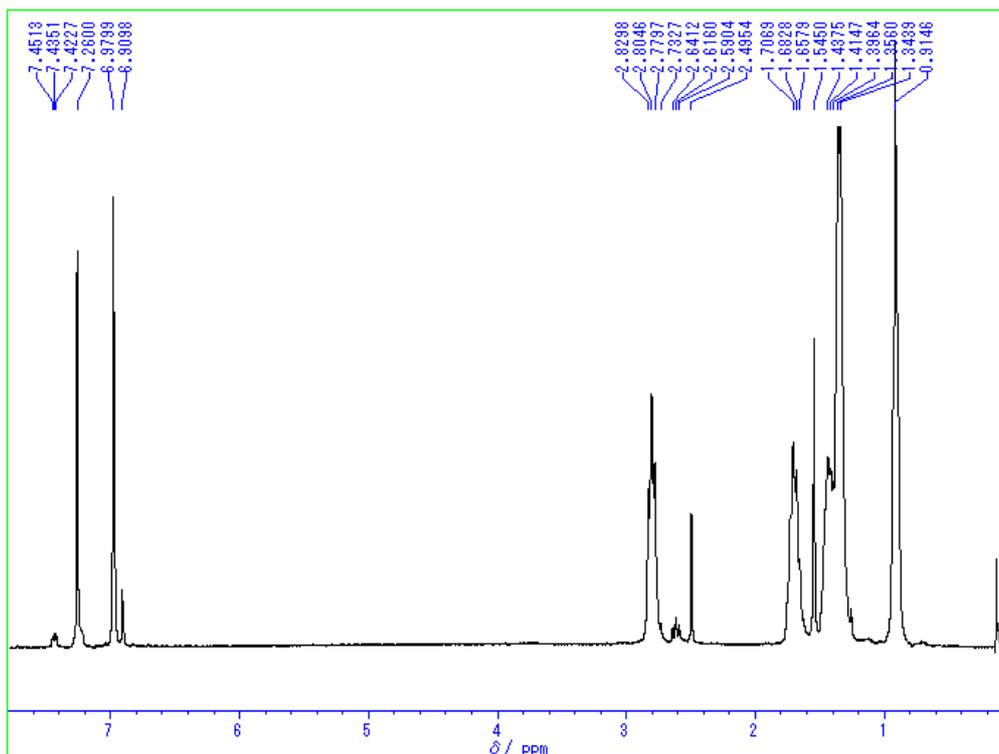


Fig. S7 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of α 2-tol/ ω H P3HT.

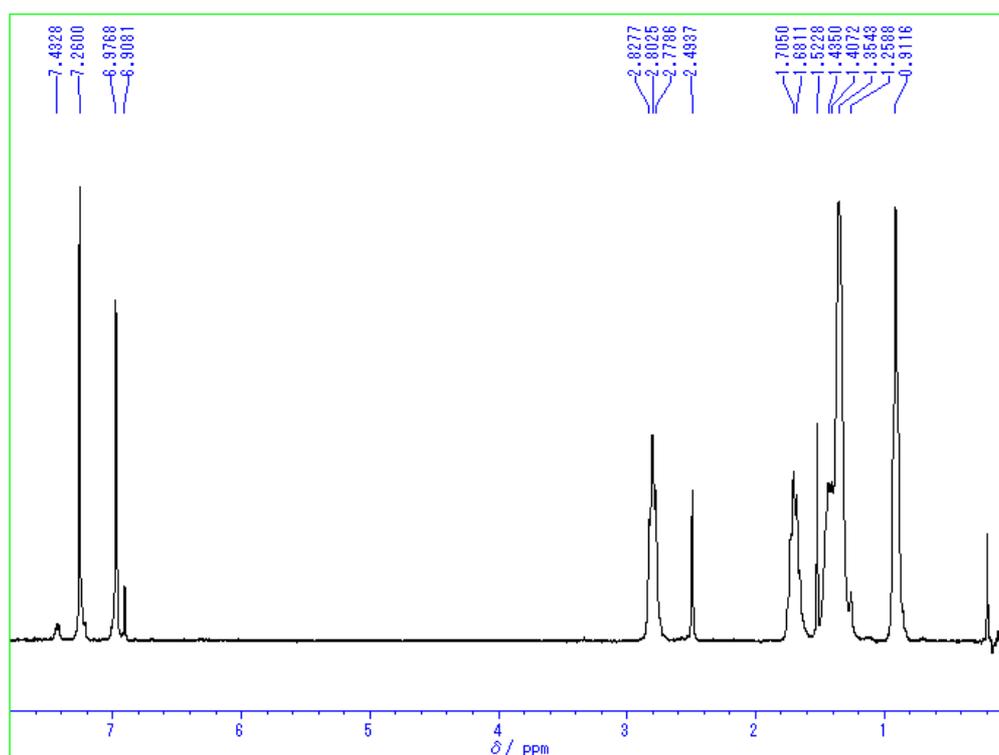


Fig. S8 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of α 2-tol/ ω SH P3HT.

6. MALDI-TOF mass spectra of α 2-tol/ ω H P3HT and α 2-tol/ ω SH P3HT

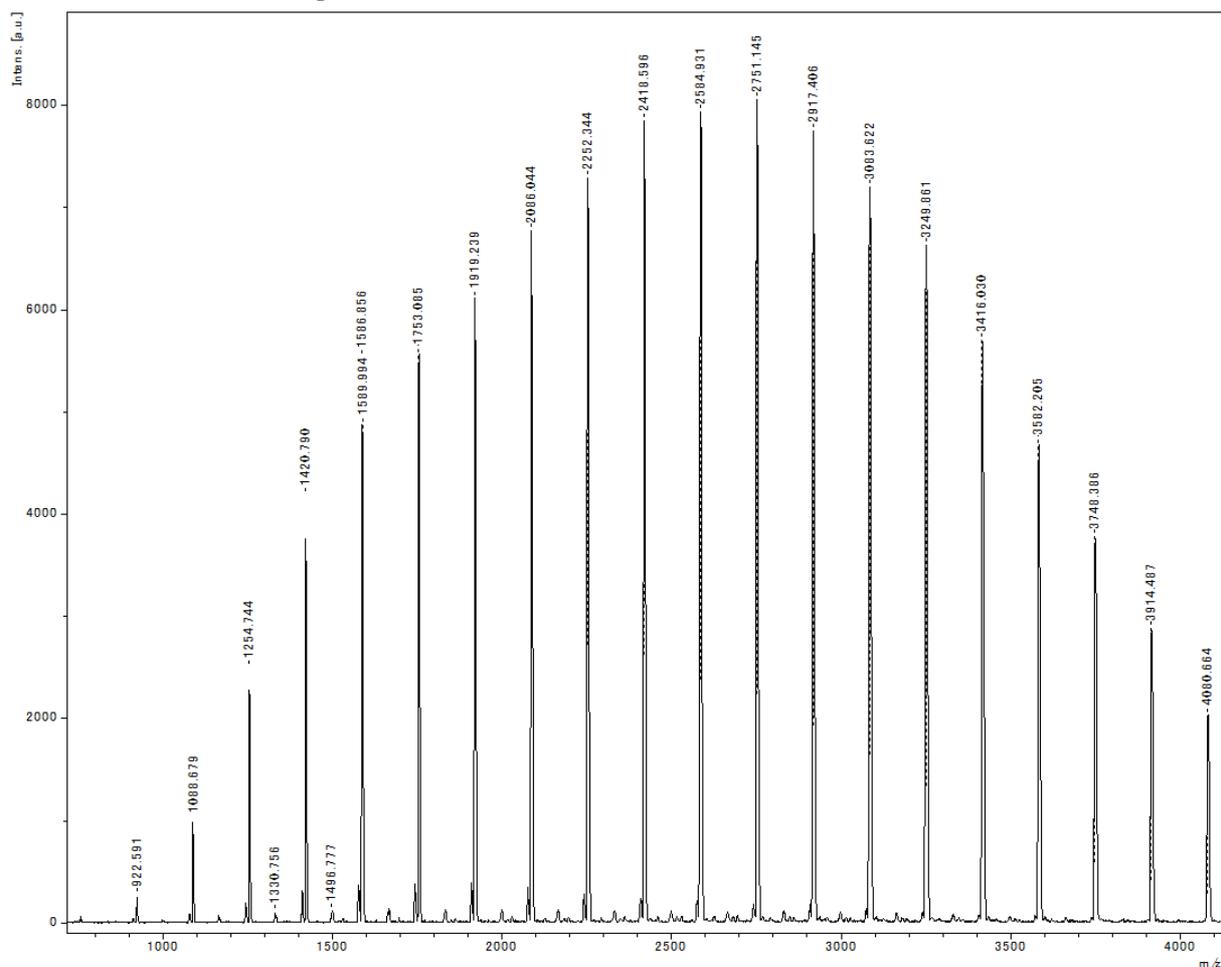


Fig. S9 MALDI-TOF mass spectrum of α 2-tol/ ω H P3HT.

Calculated mass:

α -end (2-tolyl) + poly(3-thiophene-2,5-diyl) + ω -end (3-hexylthiophene-5-yl) = 91.13 +

$166.28 (n - 1) + 167.29 = 92.14$ (tolyl-H) + $166.28 n$

(for example, 2420.1, 2586.3, 2752.6).

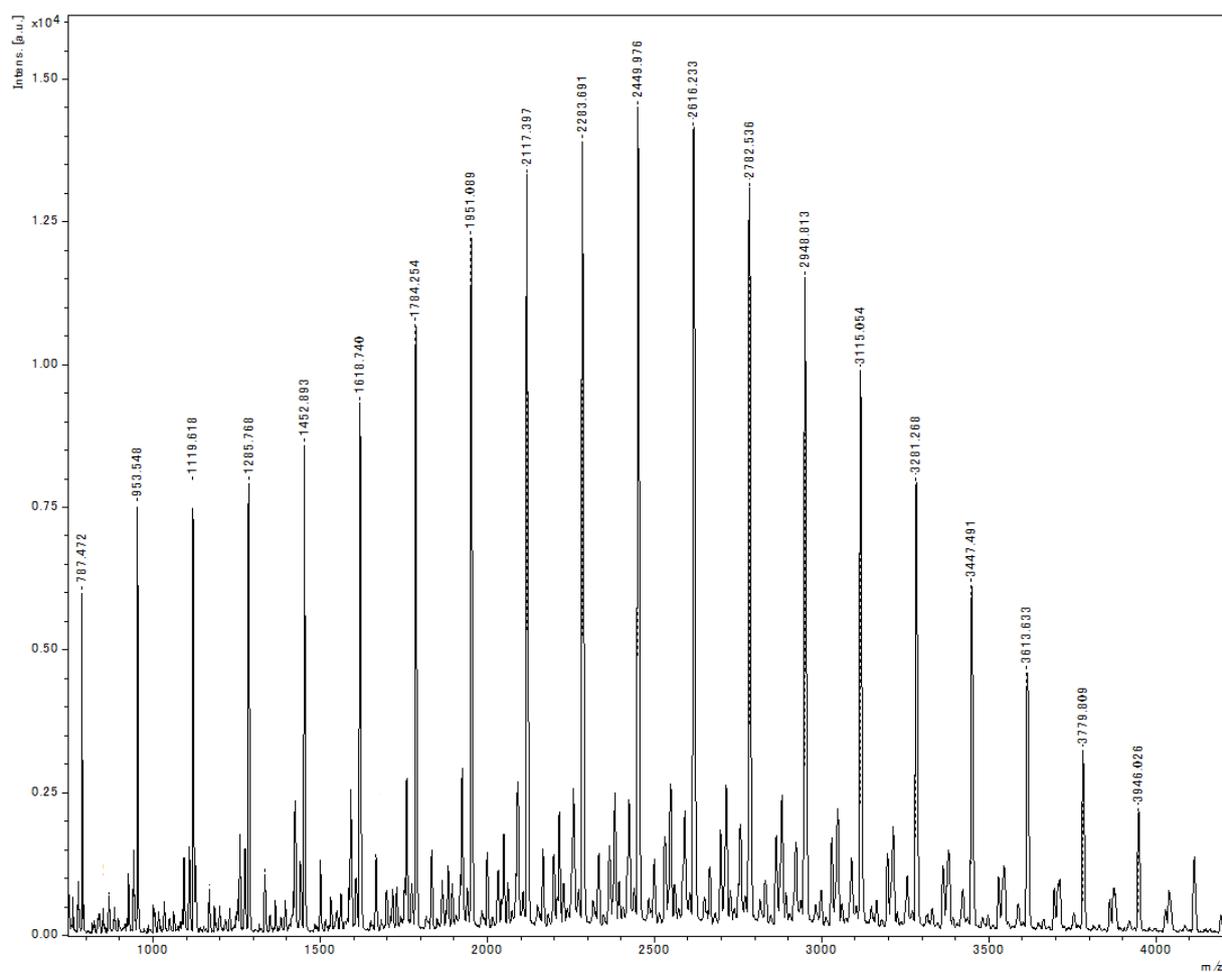


Fig. S10 MALDI-TOF mass spectrum of α 2-tol / ω SH P3HT.

Calculated mass:

α -end (2-tolyl) + poly(3-thiophene-2,5-diyl) + ω -end (2-thiol-3-hexylthiophene-5-yl)

= $91.13 + 166.28 (n - 1) + 199.36 = 124.21$ (tolyl-SH) + $166.28 n$

(for example, calculated Mass: (2119.6, 2285.9, 2452.1).

7. ^1H NMR spectrum of α 2-tol/ ω SeH P3HT

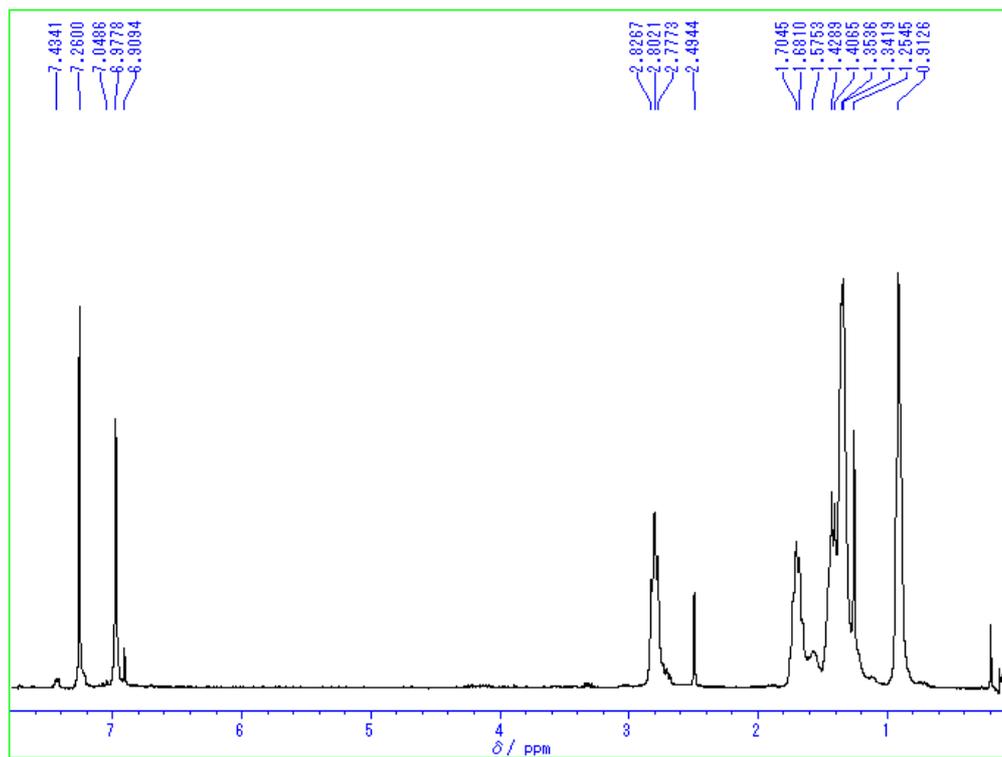


Fig. S11 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of α 2-tol/ ω SeH P3HT.

8. MALDI-TOF mass spectrum of α 2-tol/ ω SeH P3HT

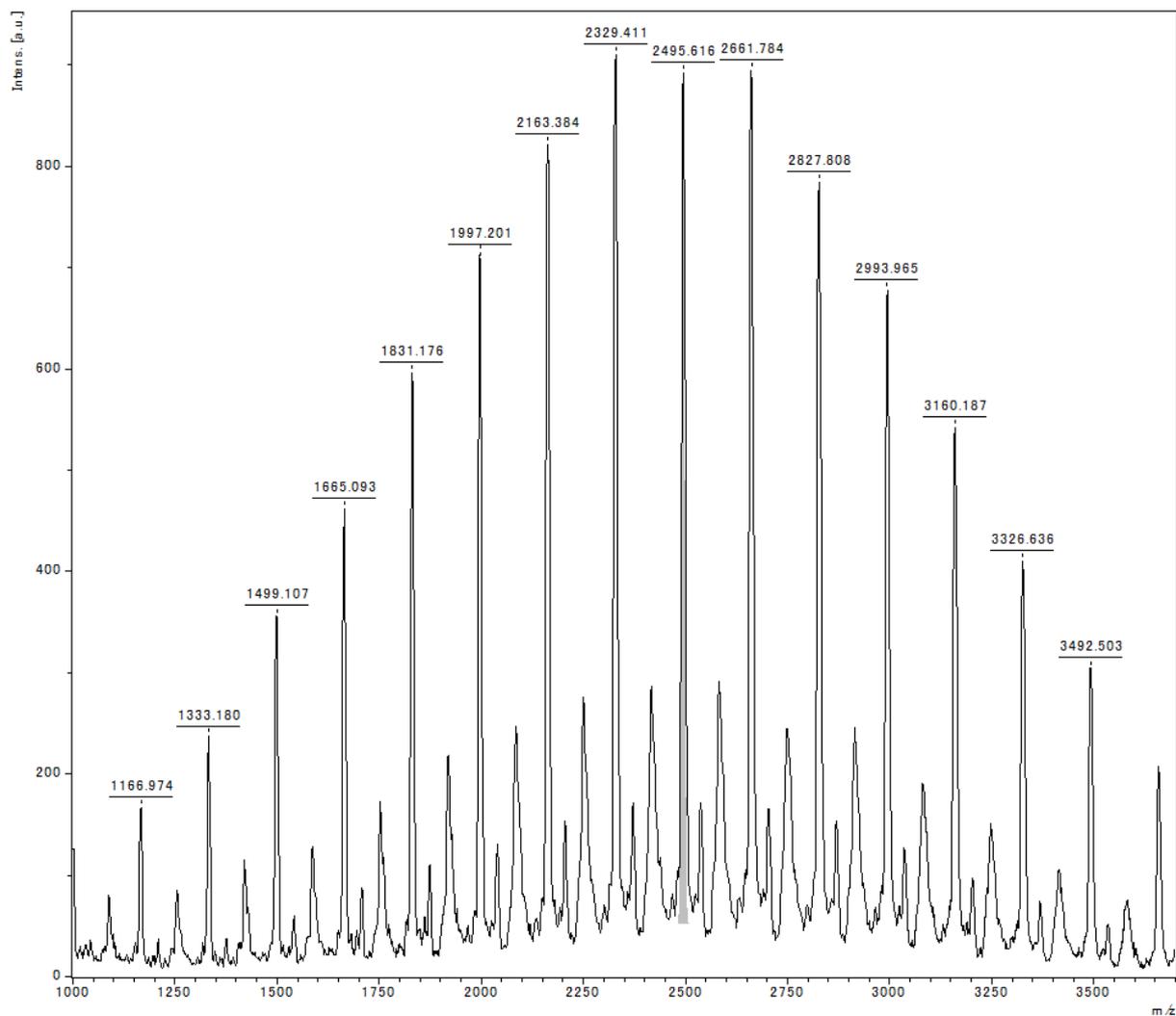


Fig. S12 MALDI-TOF mass spectrum of α 2-tol / ω SeH P3HT.

Calculated mass:

α -end (2-tolyl) + poly(3-thiophene-2,5-diyl) + ω -end (2-selenol-3-hexylthiophene-5-yl)

= $91.13 + 166.28 (n - 1) + 247.01 = 171.10$ (tolyl-selenol) + $166.28 n$

(for example, calculated mass: (2166.5, 2332.7, 2499.0).

9. ^1H NMR spectra of $\alpha\text{Br}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT and $\alpha\text{2-tol}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT

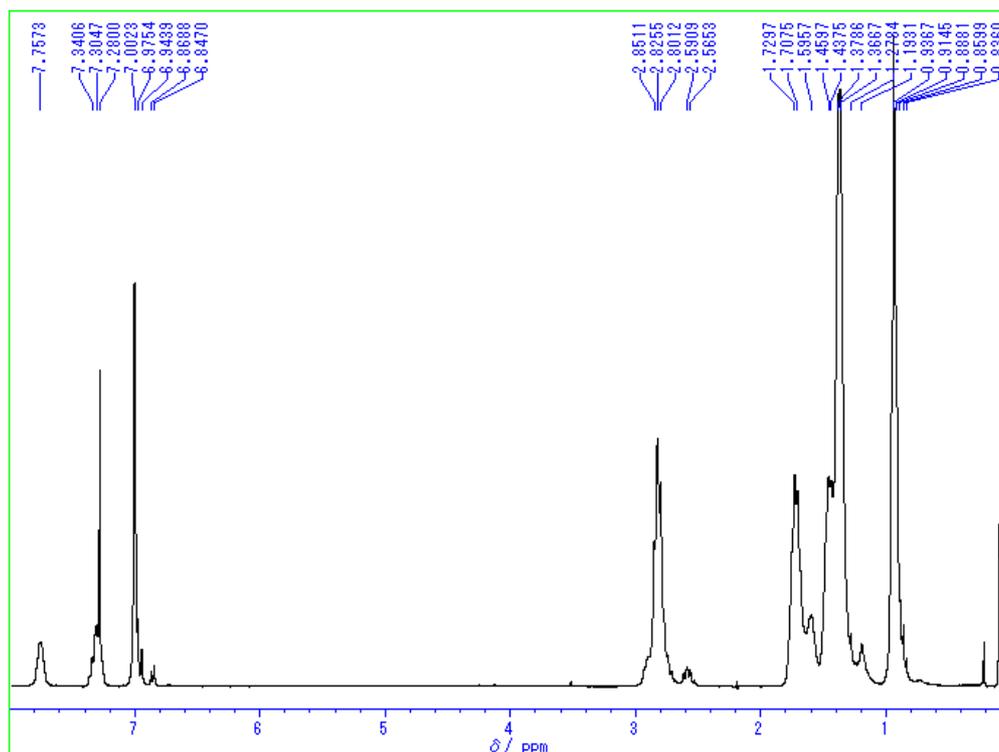


Fig. S13 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of $\alpha\text{Br}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT.

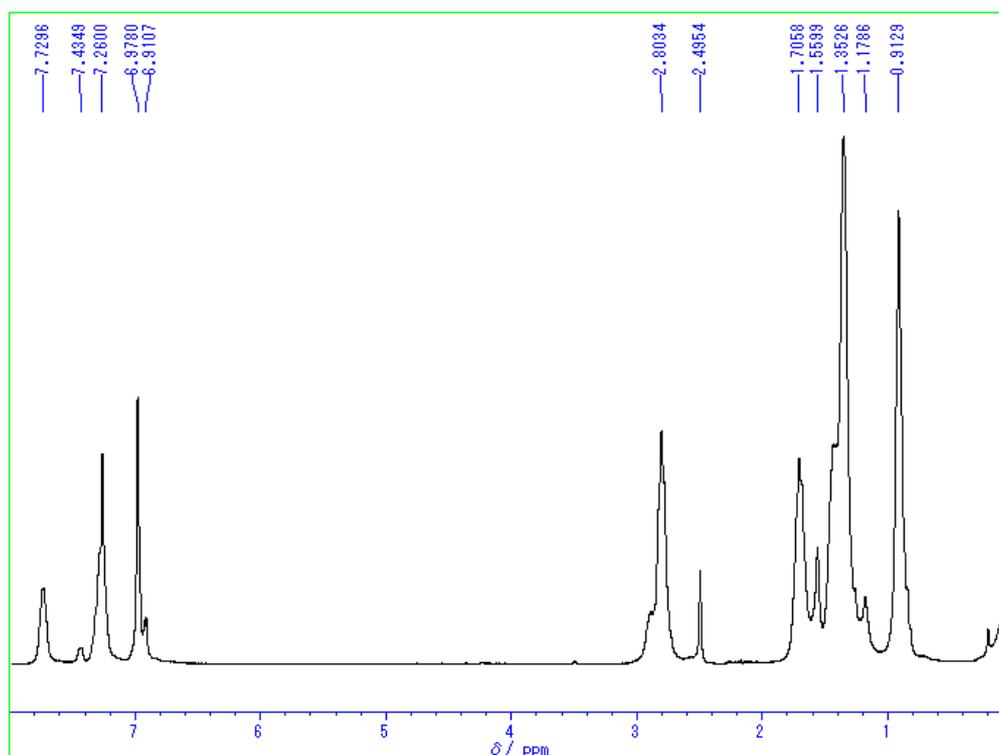


Fig. S14 ^1H NMR spectrum (300 MHz, CDCl_3 , room temperature) of $\alpha\text{2-tol}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT.

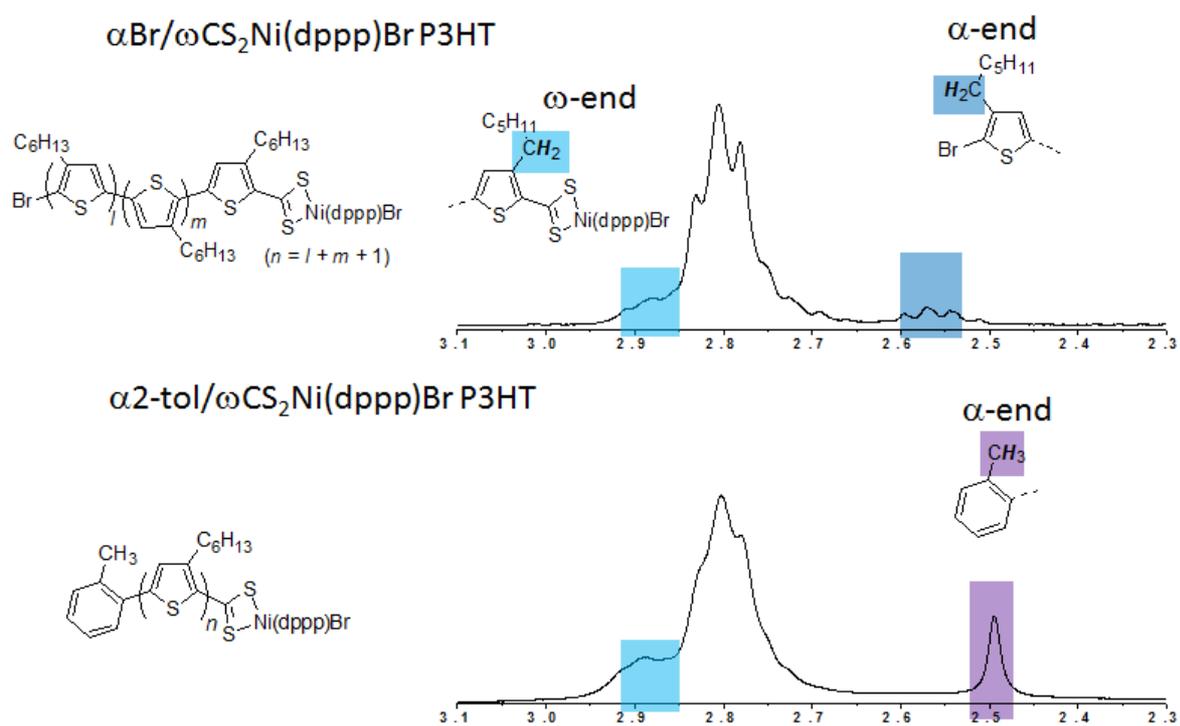


Fig. S15 Expanded $\alpha\text{-CH}_2$ region for Fig. S13 and 14.

10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\alpha\text{Br}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT and $\alpha 2\text{-tol}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT

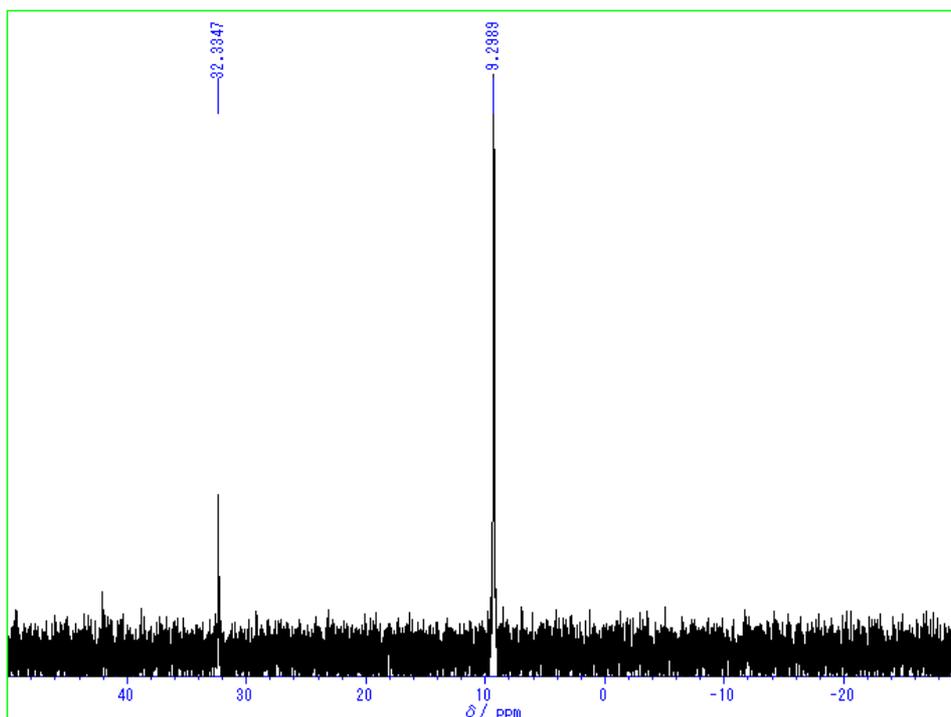


Fig. S16 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CDCl_3 , room temperature) of $\alpha\text{Br}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT (δ 32.3 is unknown peak).

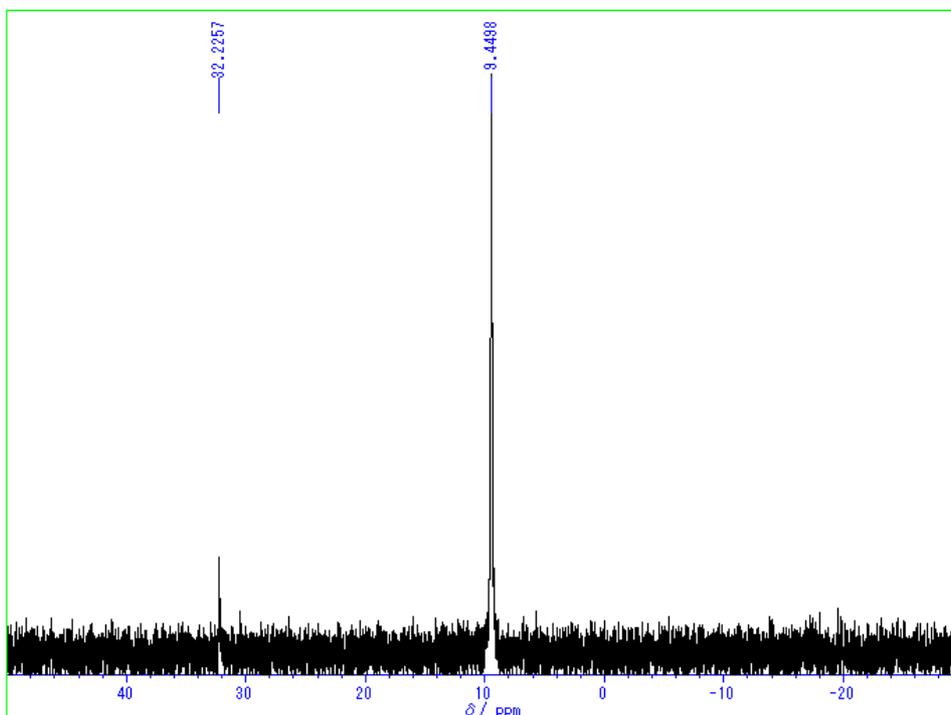


Fig. S17 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CDCl_3 , room temperature) of $\alpha 2\text{-tol}/\omega\text{CS}_2\text{Ni}(\text{dppp})\text{Br}$ P3HT (δ 32.2 is unknown peak).

11. MALDI-TOF mass spectra of α Br/ ω CS₂Ni(dppp) P3HT and α 2-tol/ ω CS₂Ni(dppp) P3HT

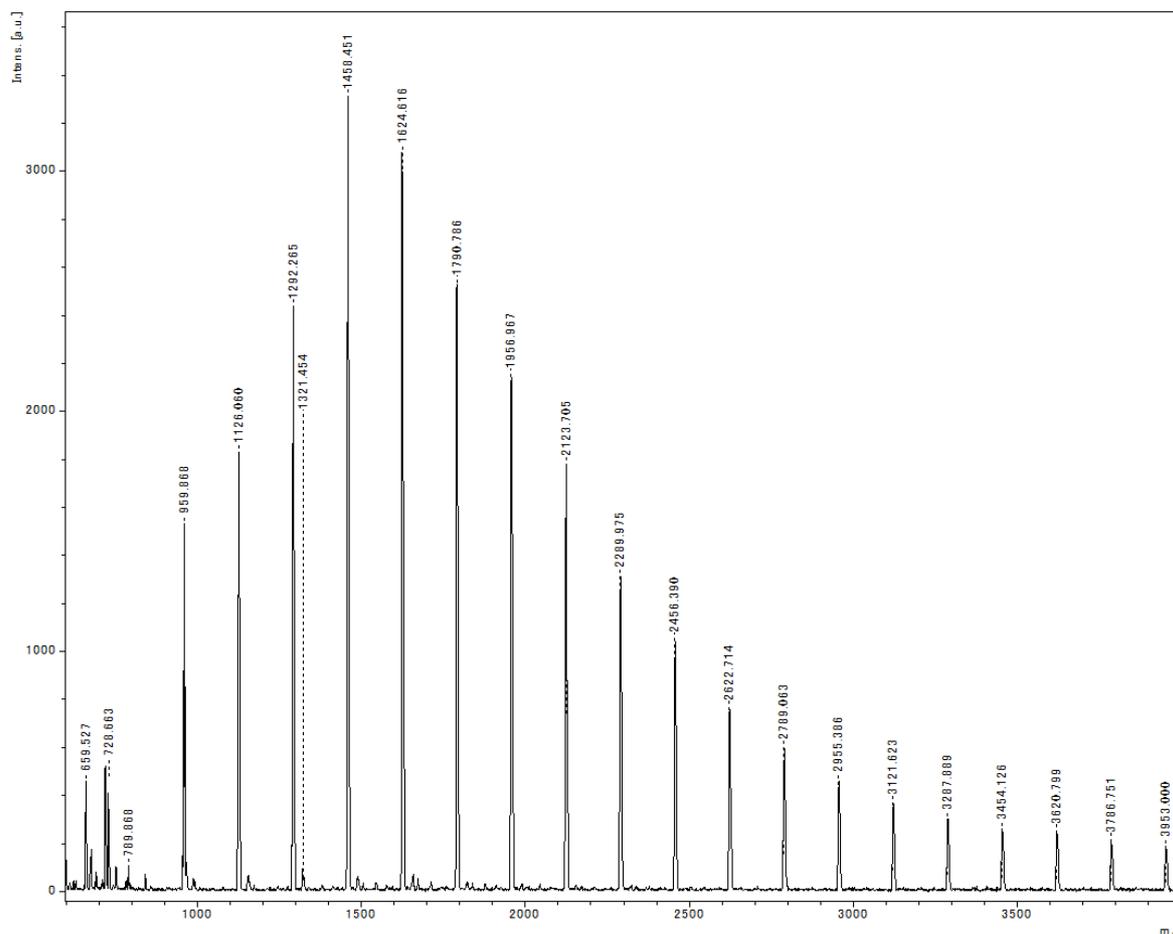


Fig. S18 MALDI-TOF mass spectrum of α Br/ ω CS₂Ni(dppp)Br P3HT.

Calculated mass:

α -end (2-bromo-3-hexylthiophene-5-yl) + poly(3-thiophene-2,5-diyl) + ω -end [1,3-Bis(diphenylphosphino)propane]

bromo(3-hexylthiophene-5-yl-2-carbothionato-*S,S'*)nickel(II) = 246.19 + 166.28 ($l + m - 1$) + 713.56 = 627.18 (Br-Ni(dppp)CS₂) + 166.28 n (for example, calculated. Mass: 1458.6, 1624.9, 1791.1).

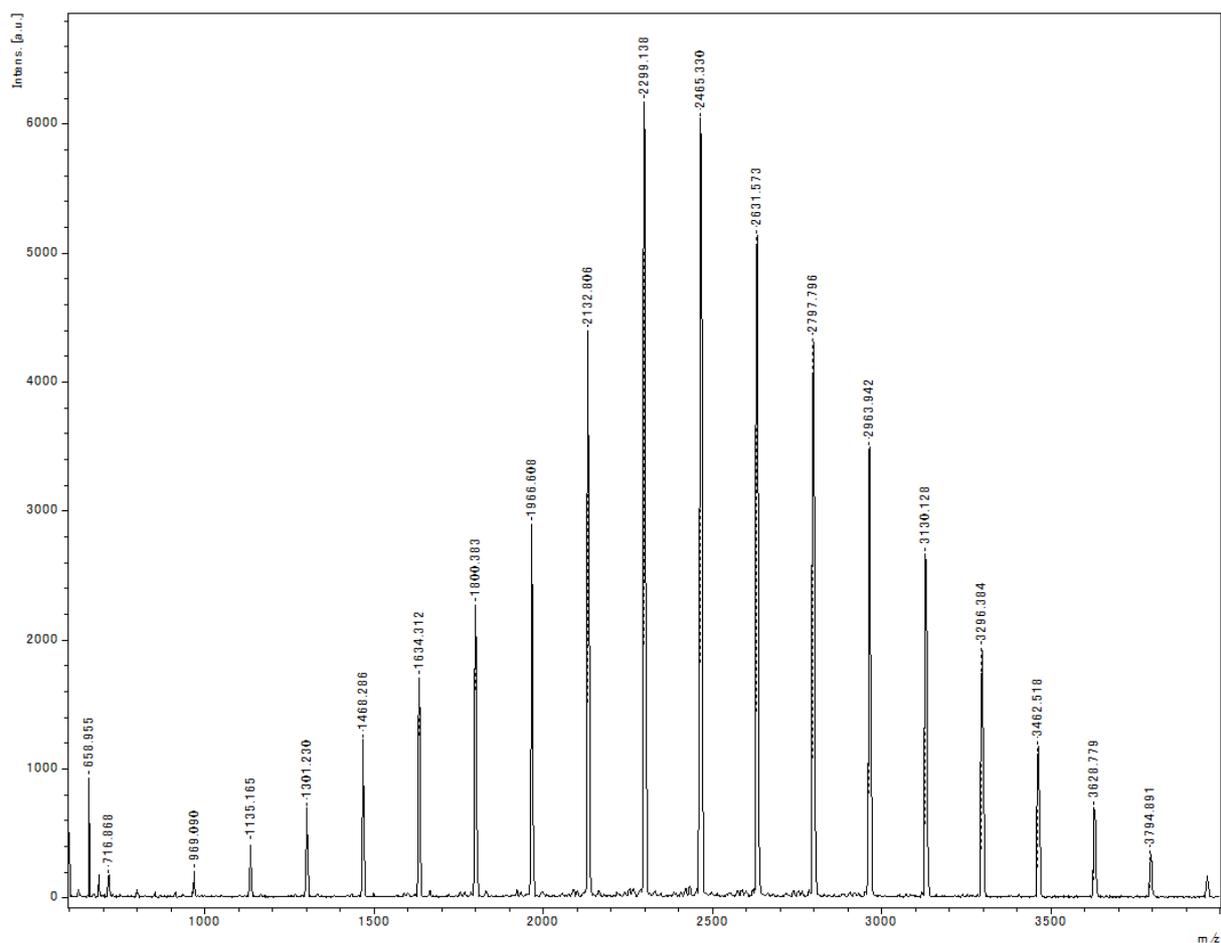
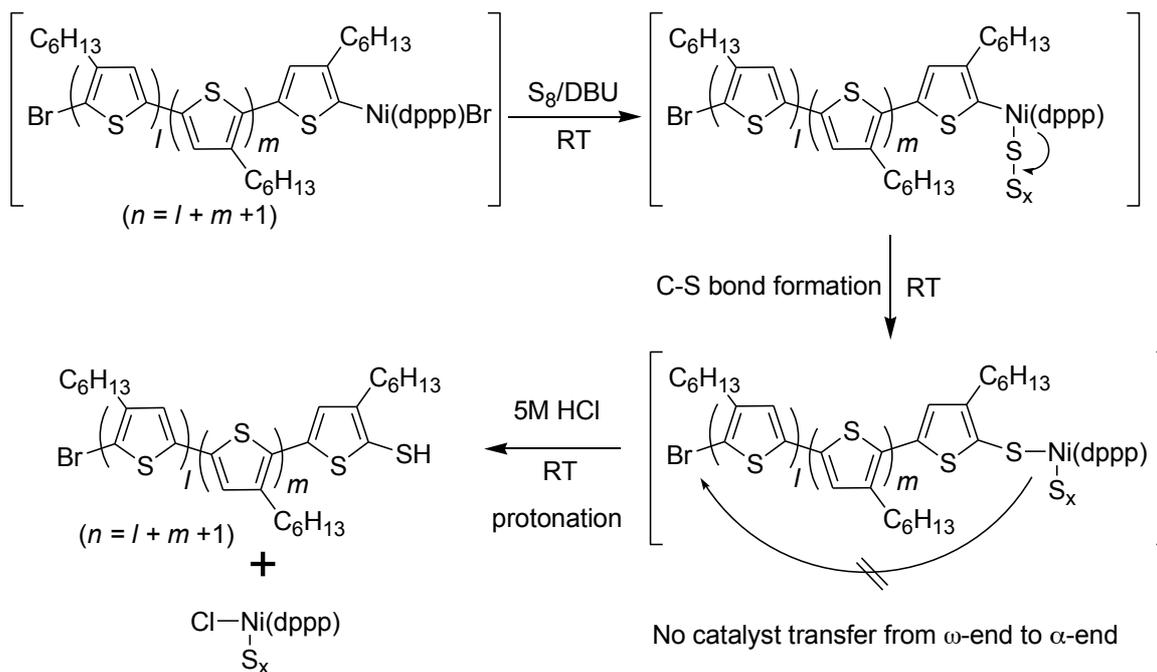


Fig. S19 MALDI-TOF mass spectrum of α -2-tol/ ω -CS₂Ni(dppp)Br P3HT.

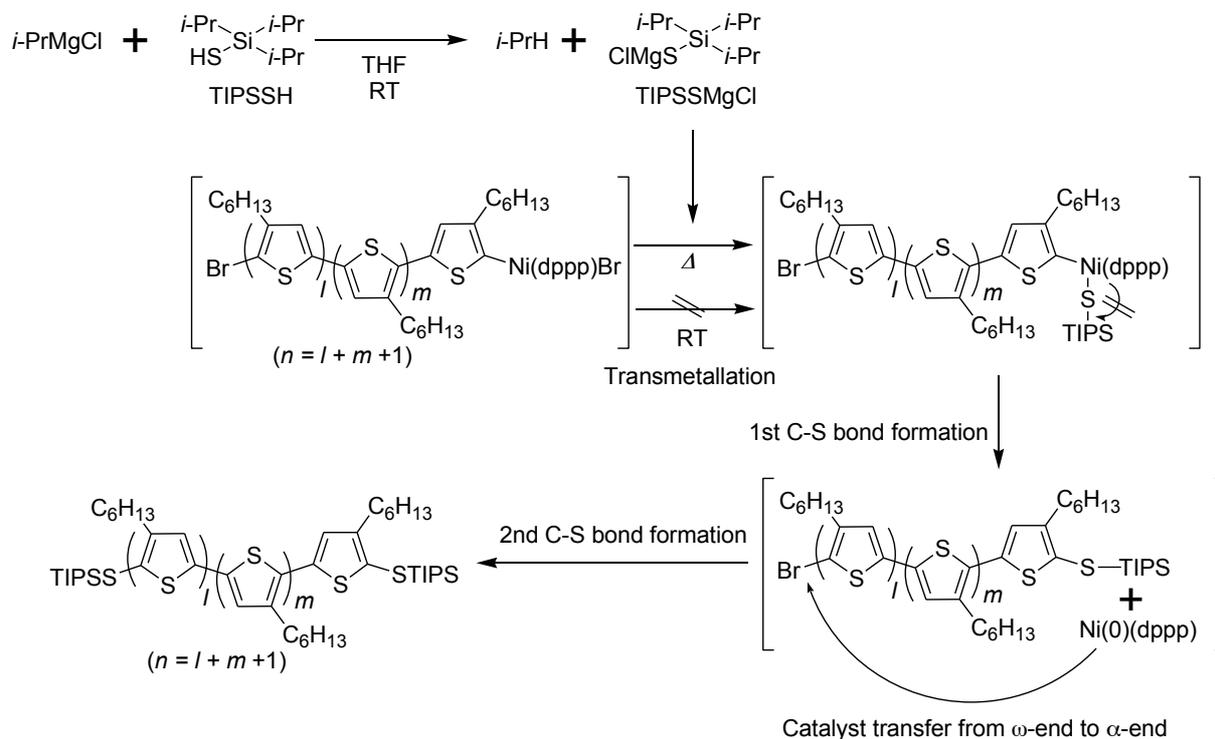
Calculated mass:

α -end(2-tolyl) + poly(3-thiophene-2,5-diyl) + [1,3-Bis(diphenylphosphino)propane]
bromo(3-hexylthiophene-5-yl-2-carbothionato-*S,S'*)nickel(II) = 91.13 + 166.28 (*n-1*) +
713.56 = 638.41 (toluene-CS₂Ni(dppp)) + 166.28 *n* (for example, calculated. Mass: (2134.9,
2301.2, 2467.5)

12. Proposed SH end-capping mechanisms (Scheme S1 and S2)



Scheme S1. Proposed mechanism of ω -end capping by S_8/DBU



Scheme S2. Proposed mechanism of α -end and ω -end capping by $\text{TIPS}/i\text{-PrMgCl}$

Reference

1. End group analysis by NMR;
<http://www.sigmaaldrich.com/technical-documents/articles/material-matters/polymer-analysis-by.html>
2. H. A. Bronstein and C. K. Luscombe, *J. Am. Chem. Soc.*, 2009, **131**, 12894.