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

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1. Instrumentation and Materials

$^1$H NMR spectra were obtained on Bruker AV-300 and AV-400 spectrometers using CDCl$_3$ as solvent (peak position $\delta^1H = 7.26$ ppm) and tetramethylsilane was used as an internal standard for $^1$H NMR spectra (0.00 ppm) and $^{31}$P{$^1$H} spectra were referenced to external H$_3$PO$_4$ (0.00 ppm). Number average molecular weight ($M_n$) were determined using end group analysis by $^1$H 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)Cl$_2$, 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(PPh$_3$)$_2$Br 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/oH 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: Mn = 1.6k), 1 MALDI-TOF MS peak top: DP = 12.6 (2.1k).

Thiol termination for αBr/oSH 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 (Mn = 1.6k), MALDI-TOF MS peak top: DP = 12.0 (2.1k).

Dithiol termination for αSH/oSH 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 αS–TIPS /ωS–TIPS P3HT was treated with 0.3 M TBAF CHCl₃ solution (50 mL) and after 10 min, the residue was washed with 0.1 M HCl (70 mL × 2). After the solvent was removed under reduced pressure, unprotected αSH/ωSH P3HT was obtained (70%, yield).

¹H NMR (300 MHz, CDCl₃): 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 αBr/ωCS₂Ni(dppp) P3HT
To the 1.0 mmol scale polymerization reaction mixture, carbon disulfide (CS₂, 1.0 mmol, 61 µL) was added. After the CS₂-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, CDCl₃): δ 6.98 (s, 1 H), 2.80 (t, J = 7.7 Hz), 2.57 (α CH₂ 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). ³¹P NMR (202 MHz, CDCl₃): δ 9.4 ppm. ¹H NMR, DP = 16.0 (Mn = 2.6k), 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(PPh₃)₂Br. The polymerization reaction mixtures were quenched using the above quenching methods unless otherwise noted.

α2-tol/ωH P3HT
¹H NMR (300 MHz, CDCl₃): 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 CH₂ peak of ω-end 3-hexylthiophene-5-yl, the total number of proton between δ 2.80-2.61 is 2 H), 2.49 (CH₃ 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 (Mn = 2.4k),² MALDI-TOF MS peak top: DP = 16.0 (2.7k).

α2-tol/ωSH P3HT
¹H NMR (300 MHz, CDCl₃): 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 (CH₃ 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 (Mn = 2.4k),² MALDI-TOF MS peak top: DP = 16.0 (2.6k).
**Selenol termination for α2-tol/ωSeH 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 µL). 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.

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.43 \text{ (m, 2 H), 7.24 \text{ (m, 2 H), 6.98 \text{ (s, 1 H), 2.80 } (t, J = 7.7 Hz, 2 H), 2.49 \text{ (CH}_3\text{ peak of } \alpha-\text{end tolyl), 1.71 \text{ (quint, } J = 7.6 \text{ Hz, 2 H), 1.48-1.38 \text{ (m, 2 H), 1.37-1.30 \text{ (m, 4 H), 0.91 } (t, J = 7.2 Hz, 3 H)}.} \]

\[ ^1\text{H NMR: } \text{DP = 10.0(} M_n = 1.8k), \text{ MALDI-TOF MS peak top: } \text{DP = 13.0 (2.3k).} \]

**α2-tol/ωCS}_2\text{Ni(dppp)}\text{Br P3HT**}

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.43 \text{ (m, 2 H), 7.24 \text{ (m, 2 H), 6.98 \text{ (s, 1 H), 2.80 } (t, J = 7.7 Hz, 2 H), 2.49 \text{ (CH}_3\text{ peak of } \alpha-\text{end tolyl), 1.71 \text{ (quint, } J = 7.6 \text{ Hz, 2 H), 1.48-1.38 \text{ (m, 2 H), 1.37-1.30 \text{ (m, 4 H), 0.91 } (t, J = 7.2 Hz, 3 H), 7.73 \text{ (m, dppp), 7.30 \text{ (m, dppp), 1.19 \text{ (m, dppp), 0.85 \text{ (m, dppp).} 31}\text{P NMR (202 MHz, CDCl}_3\text{): } \delta 9.4 \text{ ppm.}} \]

\[ ^1\text{H NMR: } \text{DP = 8.2 (} M_n = 1.4k), \text{ MALDI-TOF MS peak top: } \text{DP = 10.0 (2.3k).} \]
3. $^1$H NMR spectra of $\alpha$Br/$\omega$H P3HT, $\alpha$Br/$\omega$SH P3HT, and $\alpha$SH/$\omega$SH P3HT

**Fig. S1** $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha$Br/$\omega$H P3HT.

**Fig. S2** $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha$Br/$\omega$SH P3HT.
Fig. S3 $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha$SH/$\omega$SH P3HT.

Fig. S4 Expanded $\alpha$-CH$_2$ region for Fig. S1-3.
4. MALDI-TOF mass spectra of αTIPSSH/ωTIPSSH P3HT and αSH/ωSH P3HT

Fig. S5 (a) MALDI-TOF mass spectra of αS–TIPS/ωS–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, ♥: αS–TIPS /ωS–TIPS P3HT, ♦: α, ω, S–TIPS, SH P3HT, o: αSH/ωSH 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 αSH/ωSH P3HT.

Calculated mass:

\[
\text{α-end (2-thiol-3-hexylthiophene-5-yl)} + \text{poly(3-thiophene-2,5-diyl)} + \text{ω-end (2-thiol-3-hexylthiophene-5-yl)} = 199.36 + 166.28 \ (n - 1) + 199.36 = 66.15 \ \text{(thiol-thiol)} + 166.28 \ n \ \text{(for example, 1729.0, 1895.2, 2061.5).}
\]
5. $^1$H NMR spectra of α2-tol/ωH P3HT and α2-tol/ωSH P3HT

**Fig. S7** $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of α2-tol/ωH P3HT.

**Fig. S8** $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of α2-tol/ωSH P3HT.
6. MALDI-TOF mass spectra of α2-tol/ωH P3HT and α2-tol /ωSH P3HT

**Fig. S9** MALDI-TOF mass spectrum of α2-tol/ωH P3HT.

Calculated mass:

\[
\alpha\text{-end (2-tolyl)} + \text{poly(3-thiophene-2,5-diyl)} + \omega\text{-end (3-hexylthiophene-5-yl)} = 91.13 + 166.28 (n - 1) + 167.29 = 92.14 \text{ (tolyl-H)} + 166.28 n
\]

(for example, 2420.1, 2586.3, 2752.6).
**Fig. S10** MALDI-TOF mass spectrum of α2-tol/ωSH P3HT.

Calculated mass:

\[
\alpha\text{-end (2-tol)} + \text{poly(3-thiophene-2,5-diyl)} + \omega\text{-end (2-thiol-3-hexylthiophene-5-yl)} \\
= 91.13 + 166.28 \cdot (n - 1) + 199.36 = 124.21 \text{ (tolyl-SH)} + 166.28 \cdot n
\]

(for example, calculated Mass: (2119.6, 2285.9, 2452.1)).
7. $^1$H NMR spectrum of $\alpha_2$-tol/ωSeH P3HT

Fig. S11 $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha_2$-tol/ωSeH P3HT.
8. MALDI-TOF mass spectrum of α2-tol/ωSeH P3HT

Fig. S12 MALDI-TOF mass spectrum of α2-tol/ωSeH P3HT.

Calculated mass:

\[
\alpha\text{-end (2-tolyl) + poly(3-thiophene-2,5-diyl) + \omega\text{-end (2-selenol-3-hexylthiophene-5-yl)}} \\
= 91.13 + 166.28 (n - 1) + 247.01 = 171.10 \text{ (tolyl-selenol)} + 166.28 n
\]

(for example, calculated mass: (2166.5, 2332.7, 2499.0).)
9. $^1$H NMR spectra of $\alpha$Br/$\omega$CS$_2$Ni(dppp)Br P3HT and $\alpha$2-tol/$\omega$CS$_2$Ni(dppp)Br P3HT

Fig. S13 $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha$Br/$\omega$CS$_2$Ni(dppp)Br P3HT.

Fig. S14 $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of $\alpha$2-tol/$\omega$CS$_2$Ni(dppp)Br P3HT.
Fig. S15 Expanded α-\(\text{CH}_2\) region for Fig. S13 and 14.
10. $^{31}P\{^1H\}$ NMR spectra of $\alpha$Br/$\omega$CS$_2$Ni(dppp)Br P3HT and $\alpha$2-tol/$\omega$CS$_2$Ni(dppp)Br P3HT

Fig. S16 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CDCl$_3$, room temperature) of $\alpha$Br/$\omega$CS$_2$Ni(dppp)Br P3HT ($\delta$ 32.3 is unknown peak).

Fig. S17 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CDCl$_3$, room temperature) of $\alpha$2-tol/$\omega$CS$_2$Ni(dppp)Br P3HT ($\delta$ 32.2 is unknown peak).
11. MALDI-TOF mass spectra of αBr/ωCS₂Ni(dppp) P3HT and α2-tol/ωCS₂Ni(dppp) P3HT

Fig. S18 MALDI-TOF mass spectrum of αBr/ωCS₂Ni(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 α2-tol/ωCS₂Ni(dppp)Br P3HT.

Calculated mass:

\[ \alpha\text{-end}(2\text{-tolyl}) + \text{poly}(3\text{-thiophene-2,5-diyl}) + [1,3\text{-Bis(diphenylphosphino)propane}] \]

\[ \text{bromo}(3\text{-hexylthiophene-5-yl-2-carbothionato-S,S'}\text{nickel(II)}) = 91.13 + 166.28 (n-1) + 713.56 = 638.41 \text{ (toluene-CS}_2\text{Ni(dppp))} + 166.28 n \] (for example, calculated. Mass: (2134.9, 2301.2, 2467.5)
12. Proposed SH end-capping mechanisms (Scheme S1 and S2)

\[
\begin{align*}
\text{Proposed mechanism of } \omega\text{-end capping by } S_8/\text{DBU} \\
\begin{array}{c}
\text{i-PrMgCl} + \text{i-Pr} \text{Si} \text{Si-Pr} \text{ClMg} & \xrightarrow{\text{THF RT}} & \text{i-PrH} + \text{i-Pr} \text{Si} \text{Si-Pr} \text{ClMg} \\
\end{array}
\end{align*}
\]

Scheme S1. Proposed mechanism of \(\omega\)-end capping by \(S_8/\text{DBU}\)

\[
\begin{align*}
\text{Transmetallation} & \quad \text{1st C-S bond formation} & \quad \text{2nd C-S bond formation} \\
\end{align*}
\]

Scheme S2. Proposed mechanism of \(\alpha\)-end and \(\omega\)-end capping by TIPS/i-PrMgCl

S20
Reference

1. End group analysis by NMR;
   http://www.sigmaaldrich.com/technical-documents/articles/material-matters/polymer-analysis-by.html