

End Group Modification of Regioregular Polythiophene through Postpolymerization Functionalization

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ABSTRACT: HT-poly(3-hexylthiophenes) (HT-PHT) with H/Br end group composition were prepared via a modified McCullough method using anhydrous $ZnCl_2$ for the transmetalation step. These bromine-terminated HT-PHT can be end group modified at the ω end through a cross-coupling reaction with thienylzinc compounds bearing a THP-protected hydroxy or STABASE-protected amino groups. After deprotection, HT-PHTs with $-OH$ or $-NH_2$ functional groups at the ω end were obtained. In addition, HT-PHT with pure H/H end group composition were also modified by treatment with Vilsmeier reagent and functionalized with formaldehyde groups at both the α and ω chain ends. Reduction of the formaldehyde groups produced the HT-PHT diol. MALDI-TOF is a powerful tool to monitor each step of these end group functionalizations.

Introduction

Poly(3-alkylthiophenes) represent an important class of conducting polymers due to their excellent solubility, stability, and processing ability.¹ Control over the regiochemistry and cross-coupling of 3-substituted thiophene monomers has been achieved by using either organo-magnesium² or organo-zinc³ cross-coupling methods on active thiophene intermediates using Kumada catalysts.⁴ Such head-to-tail coupled, regioregular poly(alkylthiophenes) (HT-PATs) have well-defined primary structure and improved electronic and photonic properties over their regiorandom analogues.² As an example, very high conductivities in regioregular PATs have been reported, and regioregular polythiophenes have been found to exhibit very interesting properties in photonics and in electronic devices.^{5,6} Recently, efficient solar cells have been fabricated with regioregular PATs by Alivisatos.⁷

To tune the properties and explore the full potential of these functional materials, chemical modifications of PATs have been actively performed.^{8–12} Most of these efforts are focused on side-chain functionalization of the conjugated polymers. Literature procedures to functionalize end groups of conjugated polymers, however, are very scarce.¹³ End group functionalization of π -conjugated conducting polymers would extend the range of applications of these polymers by allowing preparation of block copolymers, attachment of specific electroactive end groups, the grafting of conjugated polymers onto surfaces, or access of π -conjugated building blocks for some supramolecular self-assembly entities.¹⁴ Recently, our group¹⁵ and others¹⁴ have demonstrated the feasibility of end group modification of HT-PATs. Herein, we present end group functionalization of regioregular poly(3-hexylthiophene) through postpolymerization modification methods. Our postpolymerization modification allows us to obtain well-defined PATs with high molecular weight and pure end functionality such as $-OH$ and $-NH_2$. In addition, we can not only functionalize one end of the PAT chain but also introduce functionality to both ends of the poly(alkylthiophene) chains.

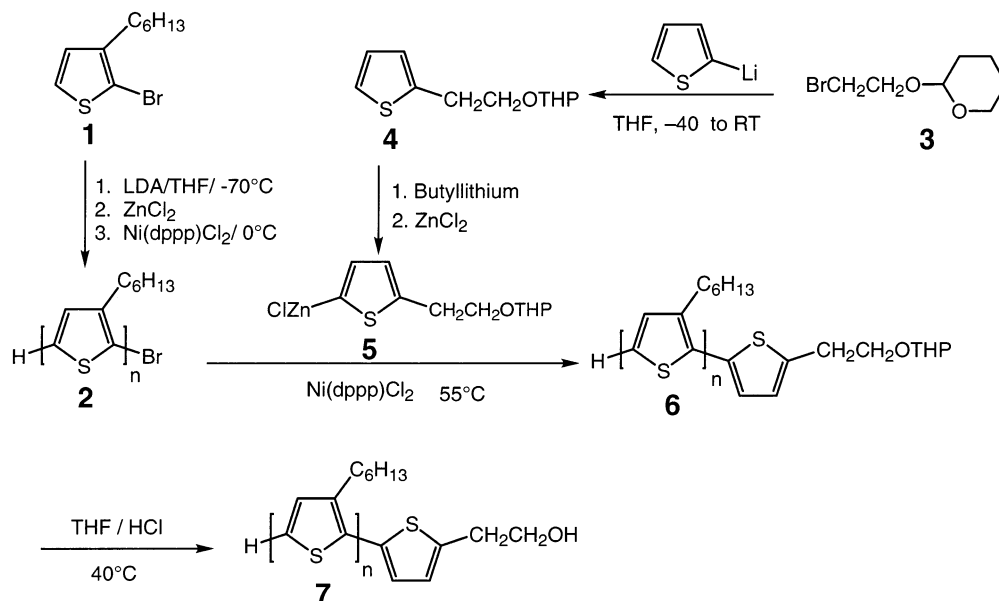
The ability to synthesize regioregular polythiophenes with specific end groups allows for further chemistry to occur at the chain ends and has led to the creation of

new materials such as conducting block copolymers of conducting polymers and commodity polymers. The importance of these new materials is that they will have greatly improved mechanical and processing properties relative to typical regioregular polythiophene. In addition, new block copolymers could self-assemble into a number of nanoscale morphologies such as lamellar, spherical, cylindrical, and vesicular structures, leading to the possibility that new electronic/structural copolymers could be designed, synthesized, and assembled as components in new nanodevices.

We have used the presented methods to prepare a large number of well-defined block copolymers and polyurethane elastomers containing regioregular polythiophenes.¹⁶ Despite having low percentages of regioregular polythiophenes, these new copolymers have very high conductivities (of the order of few to hundreds of $S\text{ cm}^{-1}$) and form very well-defined nanowires reaching the lengths of microns. In addition, we have found that simply changing the solvent or evaporation conditions allows us to control the nanowire formation and the electrical conductivity of the block copolymer.¹⁶

Results and Discussion

Hydroxy Functionalization at the ω End of HT-Poly(3-hexylthiophene). Our approach to synthesizing $-OH$ functionalized HT-PATs is shown in Scheme 1. The first step of our synthesis is to prepare poly(3-hexylthiophene) with well-defined end group structure and high regioregularity. Similar to methods published previously by our group,² the starting material 2-bromo-3-hexylthiophene (**1**) was treated with lithium diisopropylamide (LDA), followed by transmetalation with $ZnCl_2$. The formed 5-bromo-4-hexyl-2-thienyl zinc chloride was polymerized under the catalysis of [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($Ni(dppp)Cl_2$) to give polymer **2** with regioregularity $>98\%$. Transmetalation with anhydrous $ZnCl_2$ is much easier to carry out at low temperature than with $MgBr_2 \cdot Et_2O$, because $ZnCl_2$ is very soluble in THF solvent at $-76\text{ }^\circ\text{C}$ while $MgBr_2 \cdot Et_2O$ is not very soluble even at $-40\text{ }^\circ\text{C}$. Thus, using anhydrous $ZnCl_2$ can minimize the metal-halogen exchange side reactions caused by LDA at elevated temperature.

Scheme 1. Synthesis of HT-Poly(3-hexylthiophene) with Hydroxy Functionality at ω End

Our group¹⁵ and others¹⁴ have recently reported that HT-PATs synthesized through either the McCullough² or Rieke³ route usually have three types of end group composition due to the presence of side reactions in the cross-coupling polymerization. The polymer chains can be terminated with a proton at one end and a bromine at the other end (H/Br), a proton at both ends (H/H), or a bromine at both ends (Br/Br). However, polymer **2** with fairly pure H/Br end group composition (>90%) was synthesized after we optimized the polymerization conditions. It appears that the impurities in the monomer, such as traces of 3-hexylthiophene, can contribute significantly to H/H chains.¹⁵ Therefore, highly pure 2-bromo-3-hexylthiophene (100% determined by GC) was employed to eliminate such problems. One of the other required conditions is that the amount of LDA used should not be more than 1 equiv of the monomer. Because of the metal-halogen exchange reaction, even a very small excess of LDA will contribute a great deal to the production of H/H chains in the product. The titration of LDA was performed to make sure the amount of LDA was not in excess. In addition, we found that longer polymerization times can give rise to higher H/H chain abundance. Therefore, a shorter polymerization time is preferred to obtain H/Br with better purity, although it has a tradeoff of lower yield of polymer product. To obtain well-defined HT-PHT, Soxhlet extraction with hexane was performed to remove the low molecular weight fraction and reduce the polydispersity of **2**.

Figure 1a shows the MALDI-TOF MS of a sample of polymer **2**. The MALDI-MS not only gives information about the absolute molecular weight but also unambiguously reveals the end group composition of the polymer. For example, the peak of 7729.0 Da corresponds well to the H/Br chain with degree of polymerization (DP) of 46 (the calculated mass of this chain is 7730.1). Although H/H and Br/Br peaks can still be seen, they are within the noise of the spectrum, and H/Br chains are highly dominant (>90%). Its average molecular weight determined by MALDI is 7734, while GPC measurement of M_n is 16 800. This is typical since M_n of poly(alkylthiophene) by GPC (polystyrene as standards) is found to be off by a factor of 1.5–2.¹⁵

Using this well-defined HT-PHT with H/Br end group structure (**2**), we performed end group modification as shown in Scheme 1. Since poly(alkylthiophenes) are chemically stable polymers, the ability to modify the end groups off one side of the polymer is similar to polymer or bead supported organic synthesis.¹⁶ Excess of reagents were used to drive the modification reactions to completion to give >95% yield for all of steps after the synthesis of HT-PHT. Purification of all steps was achieved by simple precipitation and filtration; therefore, each step of the end group modification has high yield (>95%) and is facile to accomplish. The HT-PHT (**2**) is made functional by a reaction with an organozinc reagent bearing tetrahydropyran-protected hydroxyl group (**5**) and Ni(dppp)Cl₂ to yield polymer **6** (Scheme 1). Interestingly, temperature is very critical in this coupling reaction. Both NMR and MALDI have revealed that the reaction did not occur at room temperature even after several days. However, when we raised the temperature to 60 °C, the coupling reaction was completed successfully, and polymer **6** was produced with high yield in only a couple of hours. Incorporation of the pyranyl-protected ethoxy moiety is shown by ¹H NMR analysis of polymer **6** (Figure 2). The diastereotopic methylene protons at δ 3.6–4 ppm, the acetal methine proton at δ 4.64 ppm, and the benzylic methylene group at δ 3.1 ppm, are consistent with the incorporation of 2-(2-thienyl)ethoxytetrahydro-2H-pyran (**4**) into polymer **6**. MALDI MS of **6** (Figure 1b) also clearly reveals the end group transformation. The H/Br peaks disappear completely, and the new peaks, according to mass calculation, correspond very well to the chains with THP-protected thienylethoxy moiety. As an example, the 7861.58 Da matches 7861.20, which is the calculated mass of polymer **6** provided that the DP = 46 (Figure 1b).

Deprotection of the thienylethanol end groups of **6** was achieved by treatment of a THF or chloroform solution of the polymer with dilute aqueous HCl and was verified by MALDI-TOF (Figure 1c). For instance, the peak of 7777.67 Da is consistent with the calculated mass of 7777.2 for a polymer of DP = 46 with terminal end groups of H and thienylethanol (Figure 1c). Deprotection of thienylethanol was also confirmed by ¹H NMR

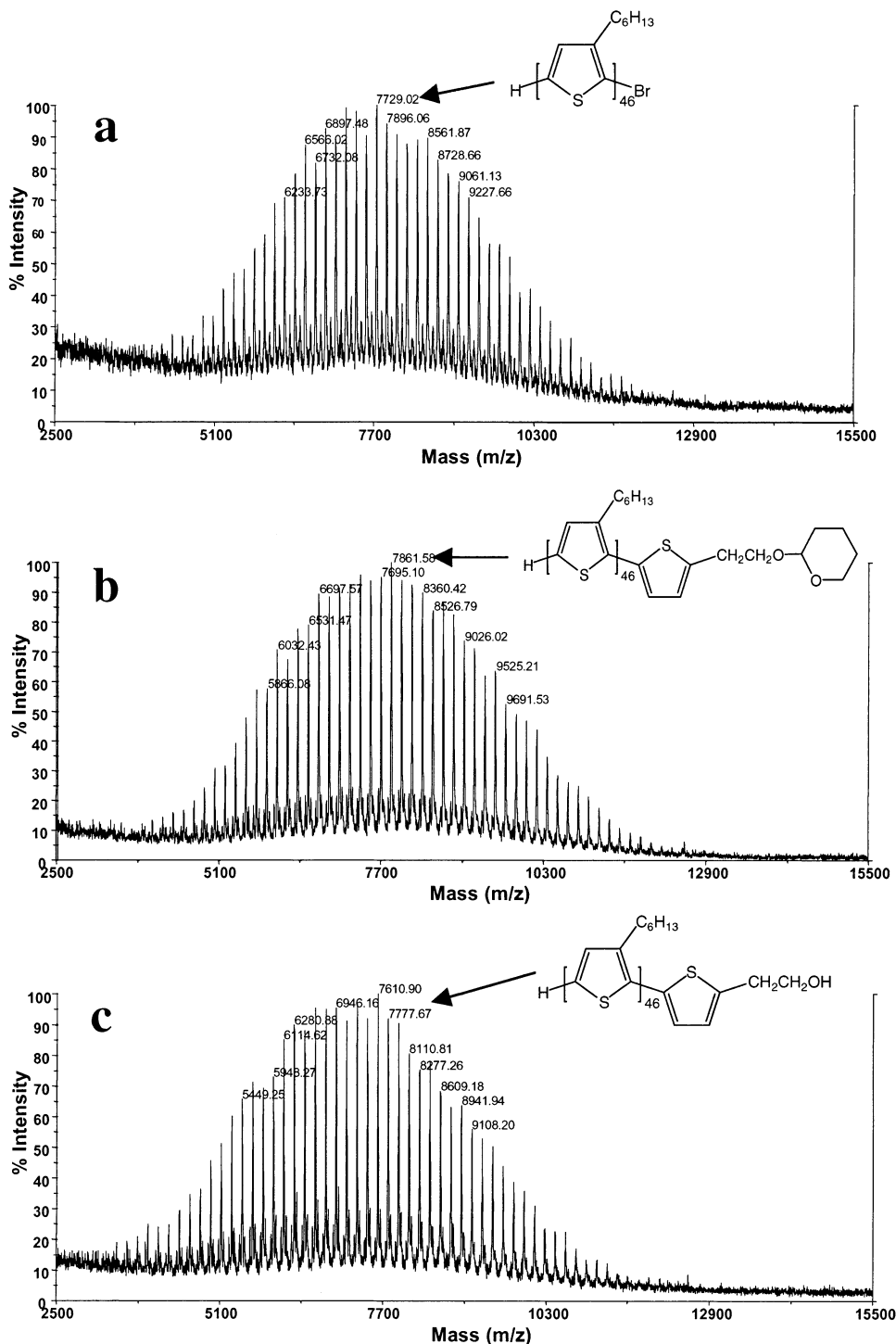


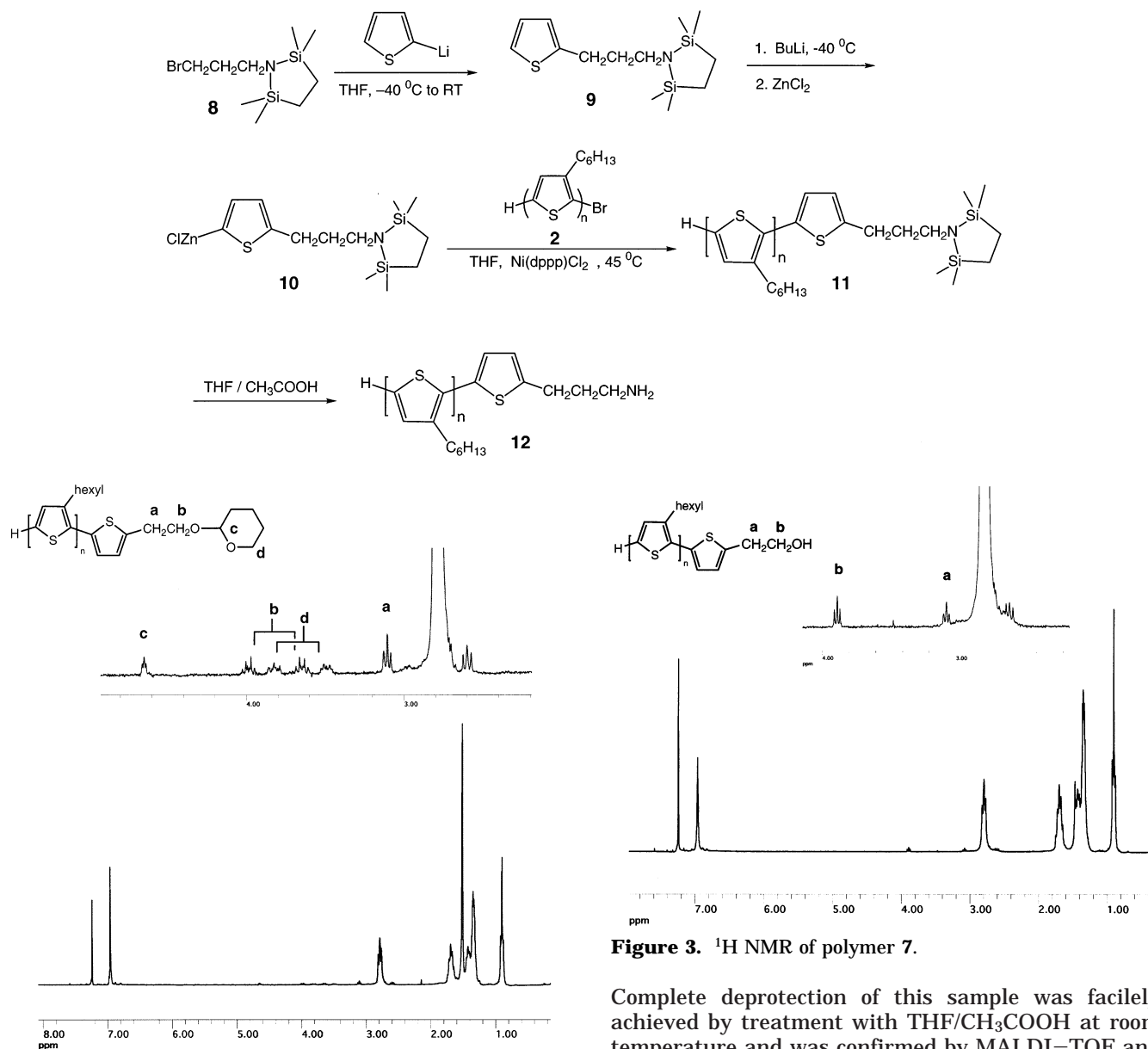
Figure 1. MALDI-TOF MS of polymer **2** (a), polymer **6** (b), and polymer **7** (c).

analysis of polymer **7** (Figure 3). The above procedure leads to a well-defined HT-PHT with $-OH$ functionality at one end in good yield.

Amino Functionalization at the ω End of HT-PHT. Employing a similar strategy as shown in Scheme 1, the incorporation of amino group onto the ω end of HT-PHT was achieved. In Scheme 2 is shown the reactions used to functionalize the end of HT-PHT with a thienylpropylamino group. The thiophene derivative bearing STABASE¹⁷-protected amino group (**9**) was obtained via a substitution reaction of thienyllithium with 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (**8**). Compound **9** was then deprotected by butyllithium followed by transmetalation with

$ZnCl_2$; the resulting organozinc (**10**) then underwent a cross-coupling reaction with the ω end of polymer **2** to yield polymer **11**. Temperature was also very critical in this cross-coupling reaction. At room temperature, the reaction does not go to completion. When the reaction temperature was raised to 60 °C, the reaction yield was 96%, which contained a mixture of the desired polymer **11**, the deprotected polymer **12**, and either the H/H polymer or the polymer **11** that loses an alkylamine in the MS experiment.

We have considered alkylamine loss in the MALDI experiment and believe that only a very small percentage of alkylamine is lost in the MALDI analysis. One experiment of support is the analysis of product of **2** and

Scheme 2. Synthesis of HT-Poly(3-hexylthiophene) with Amino Functionality at ω EndFigure 2. ^1H NMR of polymer 6.

10 by MALDI as a function of power yields little change in the amount of H/H in the sample. We also looked at polymer **2** as a function of power in the MALDI experiment and found little increase in the H/H polymer. As the power increases, the increase of fragmentation of the polymer is generally seen. Therefore, if alkylamine cleavage is occurring to a large extent, these two experiments can to some extent address that concern. In addition, it is important to note that the sample of **2** used to couple with **10** contained around 15–20% of H/H polymer, which is 5–10% more than in typical samples.

Figure 4 shows the MALDI–TOF MS of the polymer product **11** after 5 h of coupling reaction at 60 °C. Apparently, the STABASE protection is too labile, and partial deprotection happened during the reaction. The relatively low coupling yield could be attributed to this partial deprotection during the reaction or is lost in the MALDI experiment. The presence of H/H chains could be attributed to the metal–halogen exchange¹⁸ side reactions during the cross-coupling reaction of **2** and **10**.

Figure 3. ^1H NMR of polymer 7.

Complete deprotection of this sample was facily achieved by treatment with THF/ CH_3COOH at room temperature and was confirmed by MALDI–TOF and NMR.

α,ω Difunctionalization of HT-Polyhexylthiophene. In addition to the end group functionalization at the ω end, regioregular HT-PHT can also be functionalized on both the α and ω ends (Scheme 3). Polymer **13** can be prepared by either our original method^{2a,b} or the method shown in Scheme 2. It unimportant to control the end group chemistry, since the next step in Scheme 3 is simple debromination. As in our preceding discussion, a regioregular PHT (**13**) can have three types of end group structures.^{14,15} However, it can be debrominated by a Grignard metathesis reaction and quenched with methanol to yield a pristine HT-PHT with only H/H end groups (**14**) as confirmed by MALDI analysis and elemental analysis.¹⁵ After the debromination, a Vilsmeier electrophilic reaction¹⁹ was used to introduce formaldehyde groups on each end of the polymer chain to give polymer **15**. The Vilsmeier reaction had good selectivity, and side reactions on the 4-positions of the 3-hexylthiophene repeating units were rarely seen. To drive the reaction to completion, polymer **14** was treated with a large excess of Vilsmeier reagent at 75 °C.

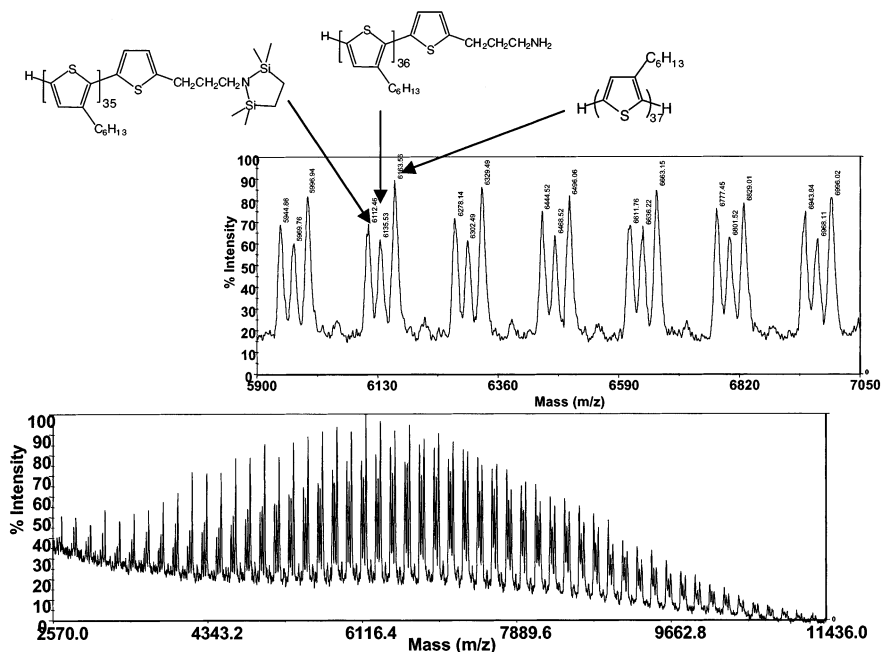
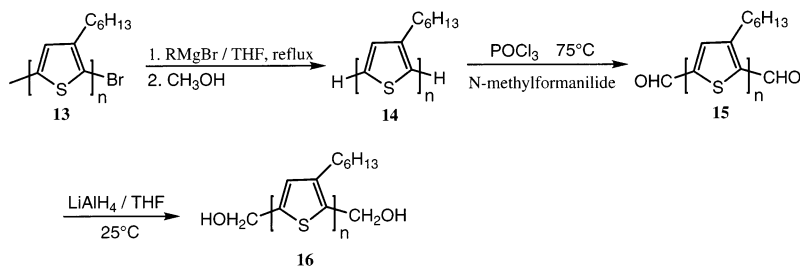


Figure 4. MALDI–TOF MS of polymer **11** indicates the presence of three types of chains in the polymer.

Scheme 3. Synthesis of HT-Poly(3-hexylthiophene) with Hydroxy Difunctionality at Ends



MALDI MS has been used to monitor the kinetic process of the Vilsmeier reaction (Figure 5). While only signals of poly(hexylthiophene) with H/H end group composition can be seen in the MALDI MS of polymer **14** before the reaction (Figure 5a), a small amount of mono-formaldehyded chains was found after 1 h of the Vilsmeier reaction (Figure 5b). After the reaction has proceeded for 8 h, the starting H/H polymer was completely modified and cannot be detected in the MALDI analysis (Figure 5c). However, the presence of mono-formaldehyded species indicated that difunctionalization on the chain ends was not completed yet. After another 16 h of reaction (totally 24 h of reaction), the MALDI MS (Figure 5d) revealed only the presence of diformaldehyde chains in the product (**15**), which confirmed the clean accomplishment of the end group difunctionalization.

One concern may arise here is whether the MALDI can accurately reveal the relative abundance of poly-(hexylthiophene) chains with different end group compositions. To answer this question, we have investigated the MALDI of mixtures of HT-PHTs with different end groups and found that end group composition would not significantly affect the desorption/ionization efficiencies of the HT-PHT chains. For example, when we intentionally mixed 1 equiv of polymer **14** (H/H) with 1 equiv of polymer **15** (CHO/CHO) and subjected this mixture to MALDI–TOF analysis, we found comparable signal intensities of the two types of chains, H/H and CHO/CHO (see Supporting Information). These results demonstrate that MALDI–TOF is a powerful tool to monitor

the end group functionalization of poly(alkylthiophenes). Because of the accurate monitoring of the end group transformation during the Vilsmeier reaction, we can find the optimal reaction time that ensures the completion of the functionalization and minimizes side reactions.

Compared with the MALDI analysis, NMR analysis of polymer **15** is intriguing. Figure S2 (Supporting Information) shows the NMR of polymer **15**. Two δ_{CHO} peaks of different intensity can be seen. According to literature information,²⁰ the peak at $\delta = 10.00$ should be assigned to the proton of $-\text{CHO}$ at the 2-position end, and the other at $\delta = 9.96$ is presumably assigned to the $-\text{CHO}$ at the 5-position end. The peak at chemical shift of 10.00 is highly dominant. Therefore, the NMR data indicate that 2-position chain ends have much higher abundance than 5-position ends in our polymers. At first instance this result is surprising and unexpected. However, it could be attributed to a tail-to-tail coupling that occurs in the first step of the cross-coupling mechanism leading to a polymer that grows head-to-tail, thus giving two symmetric end groups on each polymer chain; i.e., both end groups of a polymer chain are on the 2-position of the 3-hexylthiophene ring and make 2-position end groups dominant. This explanation is supported by our recent studies on Ni(II)-catalyzed cross-coupling polycondensation, which indicate the origin of a tail-to-tail defect in most of the HT-PHT chains.²¹

The formaldehyde end groups of **15** are reduced with LiAlH_4 to yield a HT-PHT terminated by methylene

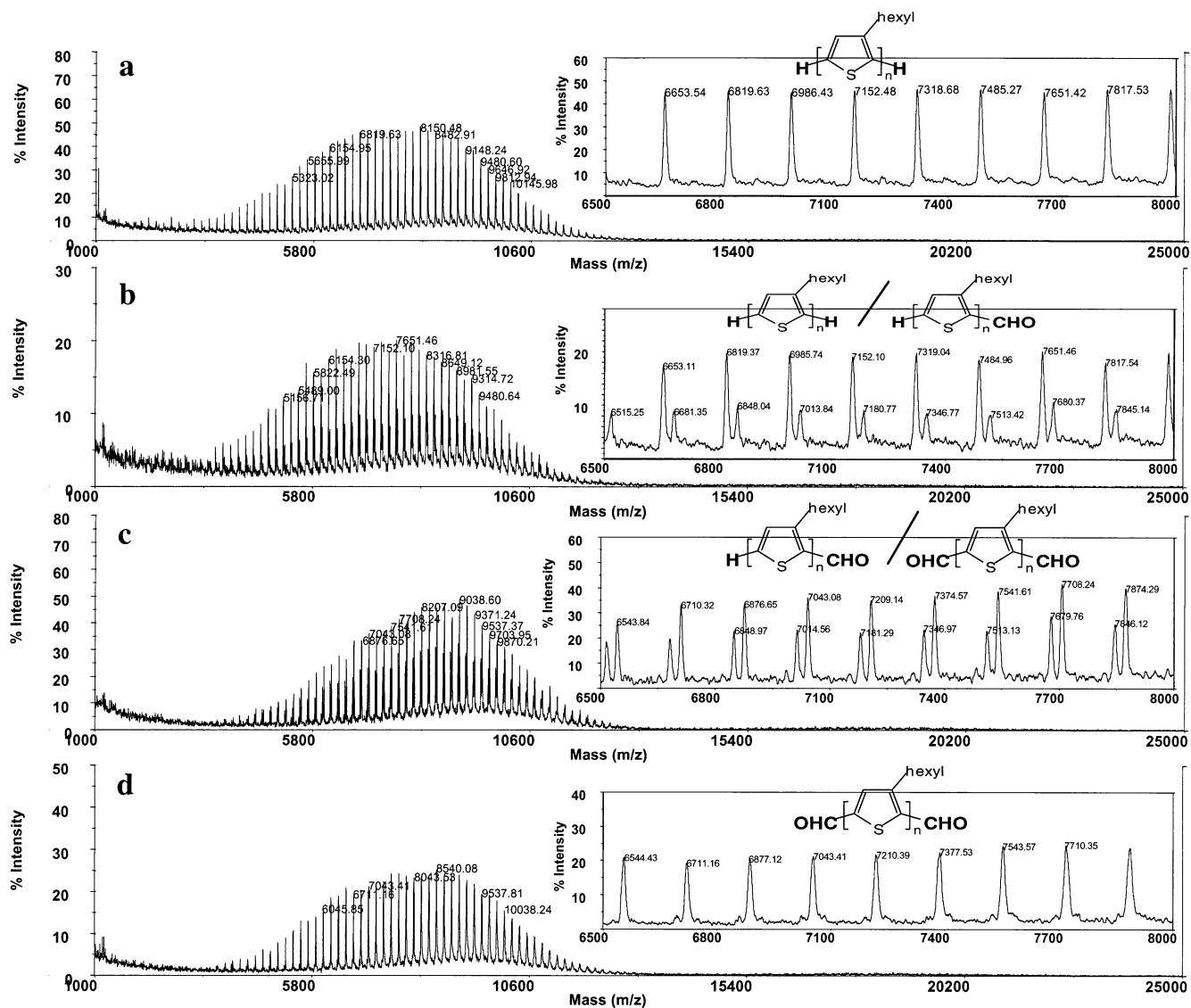


Figure 5. MALDI-TOF MS monitors the process of Vilsmeier reaction: (a) before reaction; (b) after 1 h of reaction; (c) after 8 h of reaction; (d) after 24 h of reaction.

hydroxy groups (**16**). NMR analysis has confirmed the accomplishment of the reduction. The δ_{CHO} peaks disappear, and two new doublet peaks at $\delta = 4.76$ (strong) and 4.73 (weak) can be assigned to the $-\text{CH}_2\text{OH}$.²² In addition, the small triplet at $\delta = 2.94$ in Figure 6, which can be assigned to the benzylic methylene proton on the end unit, also disappears, and a new small triplet at $\delta = 2.59$ shows up. This change is consistent with the achievement of reduction because $-\text{CHO}$ is a deshielding group, while the $-\text{CH}_2\text{OH}$ is a shielding group, for the benzylic methylene proton. Since this step of the transformation does not significantly change the mass of each chain (CHO/CHO to $\text{CH}_2\text{OH}/\text{CH}_2\text{OH}$, mass difference is only 4), therefore reaction monitoring by MALDI-TOF is difficult in this case.

Conclusion

Postpolymerization modification can be used to functionalize HT-poly(3-hexylthiophenes) at one chain end or at both chain ends. The synthesis of HT-PHTs with functional ω end groups began with the preparation of HT-PHT with H/Br end group composition via a modified McCullough method using anhydrous ZnCl_2 for transmetalation. These polymers can be modified at the

ω end through a cross-coupling reaction with thienylzinc compounds bearing THP-protected hydroxy or STA-BASE-protected amino groups. After deprotection, HT-PHTs with $-\text{OH}$ or $-\text{NH}_2$ functional groups at the ω end can be obtained. Employing this methodology, we may also incorporate other functional groups into the chain ends of the conducting polymers and therefore would expand the application of these materials. In addition, HT-PHT can be made functional at both chain ends through treatment of H/H species with Vilsmeier reagent followed by reduction with LiAlH_4 . MALDI-TOF is a powerful tool to monitor end group transformation of HT-PATs.

Experimental Section

Materials. 2-(2-Bromoethoxy)tetrahydro-2H-pyran (**3**), 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (**8**), $\text{Ni}(\text{dppp})\text{Cl}_2$, anhydrous ZnCl_2 beads, phosphorus oxychloride, *N*-methylformanilide, and lithium aluminum hydride (1.0 M in THF) were purchased from Aldrich Chemical Co. and used as received. *n*-Butyllithium (2.5 M in hexane, Aldrich) was titrated per the method of Love.²³ The 2-bromo-3-hexylthiophene was synthesized according to the literature procedure^{2b} and purified through fractionation distillation (purity was >99.8% according to GC analysis). Thiophene

(Aldrich) was freshly distilled from calcium hydride prior to use. Tetrahydrofuran and toluene were dried over Na/benzophenone ketyl and freshly distilled prior to use.

Measurements. ^1H and ^{13}C NMR spectra were recorded on an IBM Bruker FT300 spectrometer operating at 300 and 75 MHz, respectively. All NMR samples were dissolved in CDCl_3 , unless otherwise stated. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. 2,2':5',2''-Terthiophene (Aldrich) was used as the matrix for all samples. MALDI spectra were recorded using the linear mode, in which samples were irradiated under high vacuum using a nitrogen laser (wavelength 337 nm, 2 ns pulse). The accelerating voltage was 20 kV, and the grid voltage and low mass gate were 90.0% and 500.0 Da, respectively. GPC measurements were carried out on a Waters 2690 separation module equipped with three 5 μm Phenogel columns connected in series (guard, 10⁵, 1000, and 100 Å) and a Waters 2487 dual λ absorbance UV detector. Analyses were performed at 30 °C using chloroform as the eluent, and the flow rate was 1.0 $\mu\text{L}/\text{min}$. Calibration was based on polystyrene standards obtained from Polymer Standards Service. GC-MS analysis was performed on a Hewlett-Packard 59970 GC-MS workstation incorporated with a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsilicone as the stationary phase. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

Regioregular Head-to-Tail Poly(3-hexylthiophene) (HT-PHT) (2). In 50 mL of dry THF was placed 1.4 mL of distilled diisopropylamine (10 mmol) and 3.7 mL of 2.58 M *n*-BuLi (9.5 mmol) at -78 °C, and then the mixture was warmed to room temperature for 5 min and then cooled to -78 °C. The monomer 2-bromo-3-hexylthiophene (2.5 g, 10 mmol) was added to the freshly generated LDA and the reaction stirred at -70 °C for 1 h. Then anhydrous ZnCl_2 (1.43 g, 10.5 mmol) was added at -70 °C, and the reaction was stirred for 1 h. The reaction was warmed to 0 °C, and 35 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.065 mmol, 0.6 mol %) was added. The mixture was warmed to room temperature and then stirred an additional half hour. Polymer **2** was precipitated with methanol. The polymer was washed/fractionated by Soxhlet extraction with methanol, hexane, methylene chloride, and THF. The THF fraction was characterized and used. ^1H NMR (CDCl_3): 6.98 (s, 1H), 2.79 (t, $J = 7.68$ Hz, 2H), 1.62 (m, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.90 (t, $J = 6.33$ Hz, 3H). MALDI MS: $M_n = 7634$, PDI = 1.14, end group %: H/Br ~95%, H/H ~4%, Br/Br ~1%; GPC $M_n = 16\ 800$, PDI = 1.28.

2-(2-Thiopheneethoxy)tetrahydro-2H-pyran (3). 8.4 g (0.1 mol) of thiophene was dissolved in 40 mL of anhydrous THF. 40 mL of 2.5 M butyllithium solution was then added to the solution at -40 °C. After stirring at that temperature for 0.5 h, 20.9 g (0.1 mol) of 2-(2-bromoethoxy)tetrahydro-2H-pyran was added. The solution was then warmed to room temperature and stirred overnight. After extraction with water/ether, the organic layer was dried with sodium carbonate. After removing the solvent, the product was distilled at 75 °C (0.05 mmHg). 16.6 g of product was obtained (yield 78%). ^1H NMR (300 MHz, CDCl_3), δ : 7.11 (1 H, dd, $J = 5.13$ Hz, 1.47 Hz), 6.91 (1 H, dd, $J = 5.13$ Hz, 3.66 Hz), 6.84 (1 H, dd, $J = 3.66$ Hz, 1.47 Hz), 4.62 (1 H, t, $J = 3.67$ Hz), 3.83 (2 H, m), 3.64 (2 H, m), 3.11 (2 H, t, $J = 6.59$ Hz), 1.5–1.8 (6 H, m). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$: C, 62.22; H, 7.61; O, 15.07; S, 15.10. Found: C, 62.04; H, 7.33; O, 15.64; S, 14.99.

HT-PHT Ended with 2-(2-Thiopheneethoxy)tetrahydro-2H-pyran (6). To a 100 mL flask were added 20 mL of anhydrous THF and 0.64 g of **4** (0.003 mol). The flask was cooled to -40 °C, and 1 mL of butyllithium solution (2.5 M) was added. The solution was kept at -40 °C for 0.5 h, followed by the addition of 0.5 g of anhydrous ZnCl_2 . The solution was then slowly warmed to room temperature. This organozinc solution was transferred to a THF (30 mL) solution with 0.2 g of polymer **2**. After the addition of 0.04 g of $\text{Ni}(\text{dppp})\text{Cl}_2$, the solution was kept stirring at 58 °C for 5 h. The polymer was then precipitated out in methanol. After filtration, the polymer was dissolved in THF followed by reprecipitation in methanol.

After filtration and drying, 0.19 g of polymer **6** was obtained. The yield of the product is 96%. ^1H NMR: 6.98 (s, 49H), 6.89 (d, $J = 3.30$, 1H), 6.80 (d, $J = 3.30$ Hz, 1H), 4.65 (t, $J = 3.66$ Hz, 1H), 3.82 (m, 2H), 3.65 (m, 2H), 3.11 (t, $J = 6.59$ Hz, 2H), 2.79 (t, $J = 7.63$ Hz, 100H), 1.62 (m, 98H), 1.48–1.36 (m, 300H), 0.9 (t, $J = 6.33$ Hz, 150H); GPC $M_n = 17\ 000$, $M_w/M_n = 1.28$.

HT-PHT Ended with 2-(2-Thiophene)ethanol (7). 0.15 g of polymer **6** was dissolved in 100 mL of THF. This was followed by the addition of 5 mL of 3 M HCl solution and 20 mL of acetic acid. The solution was warmed to 60 °C and stirred at that temperature for 2 h. The polymer was precipitated with methanol and purified by Soxhlet extraction with methanol. The polymer was then dissolved in THF followed by reprecipitation in methanol. After filtration and drying, 0.145 g of final product was obtained (97%). ^1H NMR: 6.98 (s, 49H), 3.89 (t, $J = 6.59$ Hz, 2H), 3.07 (t, $J = 6.59$ Hz, 2H), 2.79 (t, $J = 7.63$ Hz, 99H), 1.62 (m, 99H), 1.48–1.36 (m, 300H), 0.9 (t, $J = 6.33$ Hz, 148H); GPC $M_n = 16\ 740$, PDI = 1.28.

1-(3-(2-Thienyl)propyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (9). Thiophene (3.78 g, 0.045 mol) was dissolved in anhydrous THF (30 mL). To this solution 2.5 M *n*-butyllithium (16 mL, 0.04 mol) was added at -40 °C. After the reaction mixture was stirred at -40 °C for half an hour, 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (**8**, 10.0 g, 0.036 mol) was added. The solution was then warmed to room temperature and kept stirring at that temperature overnight. After extraction with water/ether, the organic layer was dried with sodium carbonate. After removing the solvent, the crude product was purified via Kugelrohr distillation (45 °C, 0.05 mmHg) to eliminate the impurities of low boiling points. Yellow oil product (7.7 g, 77% yield) was finally obtained and used without further purification. Purity > 98% by GC. ^1H NMR: δ 7.08 (1 H, dd, $J = 5.12$ Hz, 1.46 Hz), 6.89 (1 H, dd, $J = 5.12$ Hz, 3.66 Hz), 6.76 (1 H, dd, $J = 3.66$ Hz, 1.46 Hz), 2.85 (2 H, t, $J = 7.33$ Hz), 2.79 (2 H, t, $J = 7.33$ Hz), 1.78 (2 H, m), 0.68 (4 H, s), 0.035 (12 H, s). Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{NSSi}_2$: C, 55.05; H, 8.88; N, 4.94; S, 11.28. Found: C, 54.84; H, 8.62; N, 4.98; S, 11.06.

Polymer 11. To a 100 mL flask were added 20 mL of anhydrous THF and 0.80 g of **9** (0.0028 mol). The flask was cooled to -40 °C, and 1 mL of butyllithium solution (2.5 M) was added. The solution was kept at -40 °C for 0.5 h, followed by the addition of 0.4 g of anhydrous ZnCl_2 . The solution was then slowly warmed to room temperature. This organozinc solution was transferred to a THF (30 mL) solution with 0.2 g of polymer **2**. After the addition of 0.04 g of $\text{Ni}(\text{dppp})\text{Cl}_2$, the solution was kept stirring at 60 °C for 5 h. The polymer was then precipitated out in methanol. After filtration and drying, 0.19 g of polymer was obtained (96%). The polymer was dissolved in THF and subject to MALDI analysis.

Polymer 12. To a 100 mL flask, polymer **11** (0.1 g) and THF (50 mL) were added. After the polymer was completely dissolved, acetic acid (10 mL) was added, and the solution was stirred at room temperature for 2 h. The solution was poured into methanol (200 mL) to precipitate the polymer. After filtration, the polymer was further purified by washing with hot methanol via Soxhlet extraction apparatus. Polymer **12** was obtained as black crystalline solid (0.176 g, 94%). ^1H NMR: δ 6.98 (s, 95 H), 3.02 (t, $J = 6.59$ Hz, 2 H), 2.92 (t, $J = 6.73$ Hz, 2 H), 2.79 (t, $J = 7.63$ Hz, 190 H), 2.04 (m, 2 H), 1.62 (m, 190 H), 1.48–1.36 (m, 570 H), 0.9 (t, $J = 6.33$ Hz, 280 H). GPC $M_n = 17\ 100$, $M_w/M_n = 1.28$.

Regioregular Head-to-Tail Poly(3-hexylthiophene) (13). Anhydrous diisopropylamine (1.4 mL, 10 mmol) and anhydrous THF (50 mL) were placed in a 100 mL flask. This mixture was cooled to -76 °C, and 4 mL of 2.5 M butyllithium was added. The solution was warmed to 0 °C, stirred at that temperature for 5 min, and cooled back to -76 °C. To this reaction mixture containing LDA was added 2-bromo-3-hexylthiophene (2.47 g, 10 mmol), and the solution was stirred at -50 °C for 1 h. This was followed by addition of anhydrous $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ (2.6 g, 10 mmol) at -60 °C, and the reaction was stirred at that temperature for 1 h. The reaction was then slowly allowed to warm to 0 °C, whereupon all $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$

had reacted. To the above mixture 35 mg of Ni(dppp)Cl₂ was added, and the mixture was stirred at room temperature for half hour. The polymer was then precipitated with methanol. After filtration, the polymer was purified by Soxhlet extraction with methanol, hexane, CH₂Cl₂, and finally THF. 0.32 g of polymer was obtained from the THF fraction after removing the THF (yield is 37%). The further reactions were carried out using this THF fraction polymer (**10**), which has M_n of 17.9K and PDI (M_w/M_n) of 1.23 (determined by GPC with polystyrene as standard).

Regioregular Head-to-Tail Poly(3-hexylthiophene) with H/H End Group (14). Polymer **13** (0.3 g, about 0.04 mmol) was dissolved in anhydrous THF (80 mL). 2 M *tert*-butylMgCl in THF (5 mL) was then added. The mixture was warmed to 70 °C and stirred at that temperature for 2 h. After cooling to room temperature, 2 M HCl aqueous solution (5 mL) was added to neutralize the solution. After precipitation in methanol and purification by washing with hot methanol via Soxhlet apparatus, polymer **13** (0.3 g, yield is 100%) was obtained. MALDI MS confirmed the H/H end group composition (Figure 4a); GPC M_n = 17 900, M_w/M_n = 1.23. Elemental Anal. Calcd: C, 72.23; H, 8.50; S, 19.28. Br, 0. Found: C, 71.62; H, 8.48; S, 17.97; Br, undetectable.

Regioregular Head-to-Tail Poly(3-hexylthiophene) with CHO/CHO End Group (15). Polymer **14** (0.3 g) was dissolved in anhydrous toluene (80 mL) under nitrogen. *N*-Methylformamide (2 mL, 0.016 mol) and POC₃ (1.3 mL, 0.014 mol) were then added. The reaction was carried out at 75 °C for 24 h. The solution was cooled to room temperature, followed by the adding of saturated aqueous solution of sodium acetate. The solution was stirred for another 2 h. The polymer was precipitated in methanol and purified by Soxhlet extraction with methanol. After drying in a vacuum, 0.29 g of polymer was obtained. Yield is 97%. ¹H NMR: δ 10.02 and 9.96 (a strong singlet at 10.00 and a weak singlet at 9.96, 2H totally), 6.96 (s, 56H), 2.94 (t, J = 7.63 Hz, 2H), 2.79 (t, J = 7.63 Hz, 120H), 1.62 (m, 112H), 1.48–1.36 (m, 340H), 0.9 (t, J = 6.33 Hz, 170H); GPC M_n = 17 900, PDI = 1.28.

Regioregular Head-to-Tail Poly(3-hexylthiophene) with CH₂OH/CH₂OH End Group (16). Polymer **15** (0.28 g, 0.035 mmol) was dissolved in anhydrous THF (80 mL) under nitrogen. LiAlH₄ solution in THF (1 M, 1.0 mL) was then added. The mixture was kept stirring at room temperature for 40 min. HCl (1 M, 1 mL) was then added to quench the excess of LiAlH₄. The polymer was precipitated in methanol and purified by Soxhlet extraction with methanol. After drying in a vacuum, 0.26 g of polymer **16** was obtained. Yield is 93%. ¹H NMR: δ 6.96 (s, 75H), 4.76 and 4.73 (a strong doublet at 4.76 and a weak doublet at 4.73, 4H totally, J = 5.62 Hz), 2.79 (t, J = 7.63 Hz, 150H), 2.59 (t, J = 7.63 Hz, 4H), 1.62 (m, 150H), 1.48–1.36 (m, 450H), 0.9 (t, J = 6.33 Hz, 225H); GPC M_n = 17 900, PDI = 1.28.

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Supporting Information Available: MALDI–TOF MS of a mixture of polymer **14** and polymer **15** (1:1 in wt %), indicating that **14** and **15** have comparable desorption/ionization efficiency (Figure S1); ¹H NMR of polymer **15**, where the highly dominant δ_{CHO} peak at 10.00 may indicate two symmetric end groups in most of the polymer chains (Figure S2); ¹H NMR of polymer **16** (Figure S3); and MALDI–TOF MS of polymer **16** (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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