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Regiocontrolled Synthesis of Poly((3-hexylthiophene-ylene)ethynylenes): Their Characterization and Photoluminescent Properties

Juan Li and Yi Pang*

Department of Chemistry & Center for High Performance Polymers and Ceramics, Clark Atlanta University, Atlanta, Georgia 30314

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ABSTRACT: A systematically regiocontrolled synthesis of poly((3-hexylthiophene-ylene)ethynylenes) (P3HTEs) is reported. The polymer structures are characterized by ^{1}H and ^{13}C NMR spectroscopy. The UV−vis absorption λ_{max} for P3HTE of a head-to-tail chain sequence (**5**) is slightly higher (about 4 nm) than that of P3HTE **10** with a head-to-head chain sequence. The fluorescence intensity for **5** in the film state, however, is about 10 times stronger than **10** under identical experimental conditions. Both **5** and **10** in solutions exhibit similar structured emissions of high- and low-energy bands. As the conjugation length of the molecule increases, however, the structured emission characteristic appears to be less prominent. The quantum efficiency of P3HTE increases sharply with the conjugation length when the chain length is shorter than the tetramer. Further extending the conjugation length beyond the tetramer appears to shift the fluorescence emission band to a longer wavelength, but to have little effect on the quantum efficiency of the molecule.

Introduction

Since the first report[1] of poly((thiophene-ylene)ethynylene) (PTE) of low molecular weight, a few studies[2,3] have been carried out to improve the molecular weight. PTE of high molecular weight is insoluble with a I_2-doped conductivity of 10^{-6} s/cm. Recent effort has been focused on poly((3-alkylthiophene-ylene)ethynylenes) (P3ATEs), where an alkyl has been introduced at the β-position of the thiophene ring to improve the solubility. Oligomers of P3ATE with defined chain length show potential applications[4,5] as “molecular wires”. The optical absorbance[5] of poly((3-ethylthiophene-ylene)-ethynylene) increases with chain length, reaching an optical saturation at about 440 nm.[6,7] Other interesting properties observed from P3ATE include strong photoluminescence[8,9] and third-order optical nonlinearity,[9,10] which offers additional reasons for further investigation of this class of material.

Among the many conjugated polymers, little work has been done for the systematically controlled synthesis. An elegant example is the regiocontrolled synthesis[11] of poly(3-alkylthiophenes) (P3ATs) with a high content of head-to-tail chain sequences. The regioregular P3ATs exhibit a conjugation length remarkably longer, as large as 87−173 nm in UV−vis λ_{max} of solid films, than the corresponding regiorandom P3ATs. Regioregularity of P3ATs also has a large impact on many physical properties of the materials, such as conductivities[12] and photoluminescences.[13] The photoluminescence quantum yield of poly(3-hexylthiophene)[13] (P3HT) in solution increases with the content of head-to-tail chain sequences. It appears that structural ordering in conjugated polymers can have a large effect on the nonradiative decay of the photoexcited polymer chains, which accounts for the low photoluminescence quantum yields of the materials.

For poly((3-alkylthiophene-ylene)ethynylene), the 3-alkyl substituent on a thiophene ring can be incorporated into a polymer chain with two different regioregularities: head-to-head (HH) and head-to-tail (HT) (Figure 1). Our previous report[14] indicates that coupling 3-alkyl-2,5-diethynylthiophene with 3-alkyl-2,5-diiodothiophene leads to P3ATE with randomly distributed HH (∼60%) and HT (∼40%) linkages. In the present study we report the synthesis of regioregular P3ATEs and the influence of structural order/disorder on their photophysical properties.

Results and Discussion

Synthesis of Poly((3-hexylthiophene-ylene)ethynylene) (P3HTE) with HT Chain Sequence. The desired HT linkage was achieved through polymerizing 2-ethynyl-5-iodo-3-hexylthiopnene (**4**) at room temperature. In this monomer a terminal acetylene was connected to the 4-position of the thiophene ring, thus leaving the HT linkage as the only possibility during the polymerization. Synthesis of **4** was accomplished in five steps from 3-hexylthiophene[15] (**1**) by selective monoiodination[16] at the 2-position and then coupling[17] with (trimethylsilyl)acetylene, followed by iodination[5] at the 5-position of the thiophene ring (Figure 2).

Synthesis of P3HTE with the HH and TT Chain Sequence. Direct coupling[18] of **2** with acetylene gas conveniently afforded bis(3-hexyl-2-thienyl)ethyne (**6**) with the HH linkage in 91% isolation yield (Figure 3). During the coupling, an acetylene atmosphere from a rubber balloon was found to be effective in achieving the symmetrical coupling. Iodination of **6** using *n*-butyllithium followed by treatment with iodine at −78 °C proceeded in a combined yield of 85%. Subsequent coupling of **7** with (trimethylsilyl)acetylene led to a crystalline product, **8**, which after desilylation provided bis(5-ethynyl-3-hexyl-2-thienyl)ethyne (**9**). Polymer **10** was eventually obtained in high yield via coupling monomers **7** and **9** at room temperature with formation of the TT linkage.

Characterization of P3HTEs. Both P3HTEs **5** and **10** were dark brown resins, which were soluble in organic solvents such as THF, toluene, and chloroform.

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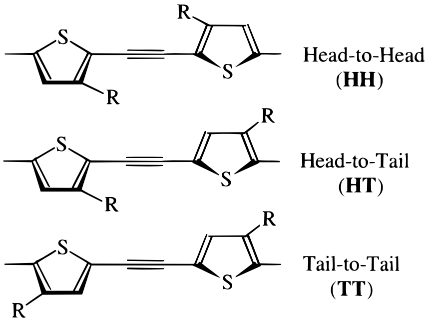


Figure 1. Illustration of coplanar conformations of head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) linkages.

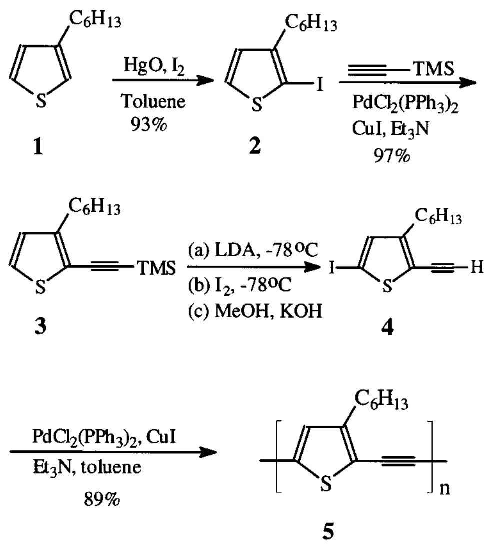


Figure 2. Regiocontrolled synthesis of poly((3-hexylthiophene-ylene)ethynylene) with the head-to-tail (HT) sequence.

Polymer films could be cast from their corresponding solutions. Polymer structures were characterized by solution ^{1}H and ^{13}C NMR. No resonance signals near 3.48 ppm (acetylene protons) were detected in the ^{1}H NMR spectra of P3HTEs **5** and **10**. Complete polymerization in both **5** and **10** was further supported by disappearance of the absorption band near 3309 cm^{-1} (C−H stretching) in IR spectra, which is strong and characteristic in acetylene-containing monomers **4** and **9**. ^{1}H NMR spectra of both regioregular P3HTEs revealed very similar resonance signals. In comparison with regiorandom P3HTE,[9,14] the resonance signals for methylene protons between 1 and 3 ppm (Figure 4) are sharp and well resolved, attributing to the regioregularity in the polymer chain structures.

Quantitative ^{13}C NMR provides a sensitive probe for the alkyl substitution patterns along the polymer backbone. Our previous report[14] has shown that four acetylene carbons of about equal intensity are observed in the regiorandom P3HTE. With the aid of the model compounds, two signals are assigned to the HT linkage, and the other two to HH and TT linkages. In the top spectrum of Figure 5, two acetylene carbons at 86.54 and 89.27 ppm correspond to the HT linkage in P3HTE **5**. The bottom spectrum shows another set of acetylene carbons at 87.19 and 88.81 ppm, attributing to HH and TT linkages in P3HTE **10**. Lack of overlapping in the two sets of acetylene carbons confirms the regioregular structures in both **5** and **10**.

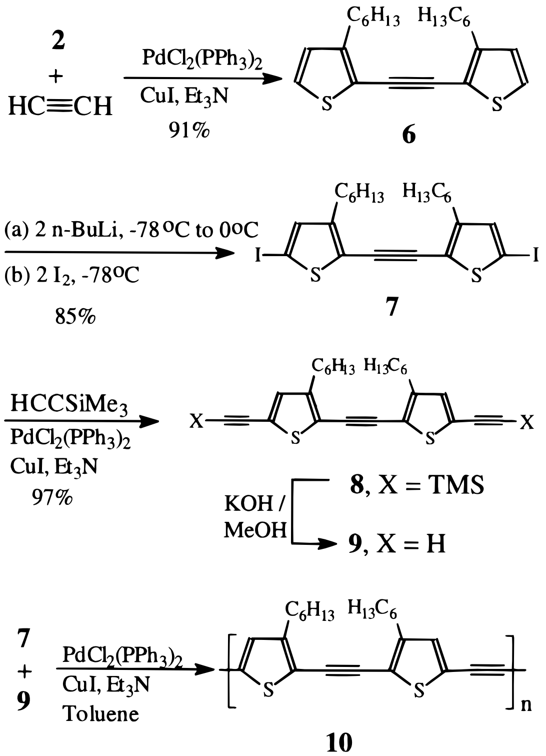


Figure 3. Regiocontrolled synthesis of poly((3-hexylthiophene-ylene)ethynylene) with the head-to-head (HH) and tail-to-tail sequences.

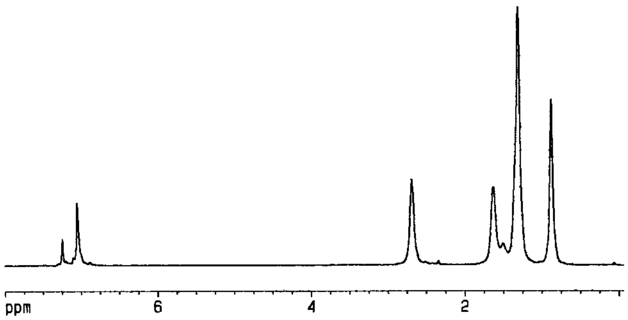


Figure 4. ^{1}H NMR ($CDCl_3$) spectrum of P3HTE **5**. The signal at 7.25 ppm is attributed to $CHCl_3$.

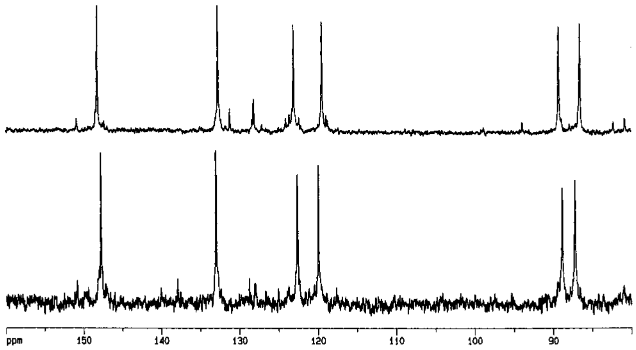


Figure 5. Quantitative ^{13}C NMR spectra of P3HTEs **5** (top) and **10** (bottom), where the alkyl region is omitted for clarity.

Molecular Weights and Chain Stiffness. The molecular weights of P3HTEs were measured in THF eluent by using size exclusion chromatography with on-line refractive index, viscosity, and light-scattering detectors (referred to as SEC^3). By using the SEC^3 setting, the true molecular weights of the polymers were obtained versus the elution volume. A typical SEC^3 chromatogram is shown in Figure 6, indicating that P3HTE **5** has a monomodel distribution. The peak molecular weights from refractive index (RI), viscosity (DP), and light-scattering (LS) detectors were quite comparable, suggesting a linear polymer structure. The

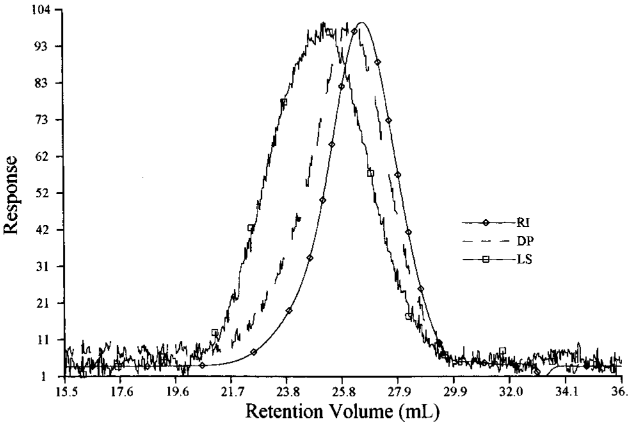
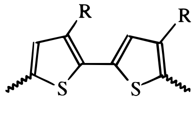


Figure 6. SEC^3 chromatogram of P3HTE **5**.

weight-average molecular weights determined were 20 100 ($M_w/M_n = 1.9$) for **5** and 116 400 ($M_w/M_n = 7.8$) for **10**. The broader molecular weight distribution of **10** could be due to the side reaction[19] of the terminal thienylacetylenes occurring during the polymerization.

For π-conjugating polymers, a fundamental issue is how rigid these molecules are as a result of the extended π-conjugation. Evaluation of their unperturbed molecular dimensions in dilute solutions will help to gain an insight into the extended chain stiffness of these polymers. The Mark–Houwink coefficients in $[\eta] = KM^{\alpha}$, measured by the on-line viscometer, were $\alpha = 0.68$ and $K = 3.52 \times 10^{-4}$ cm^3/g for **5**. It is intriguing to make a comparison with poly(3-hexylthiophene) (P3HT),[20] whose α value is as high as 0.96. The striking low α value for **5** indicates that P3ATE polymers may not have a rigid linear conformation in the dilute solution, which is the minimum-energy conformational form[5] for an oligomer of 16 repeating units. In other words, the conformation for P3ATE could be more coil-like in comparison with P3HT. The observed conformational difference between P3HT and P3HTE may originate from the reduced steric and Coulombic interactions between the adjacent thiophenes in the latter. In light of the energy difference between the molecular fragments **11** and **12**, the probability for **12** to occur in P3HTE is expected to be higher than the one for **11** in P3HT. The random occurrence of **12** along the polymer backbone could be one of the major reasons responsible for P3HTE to deviate from the rigid linear conformation,[5] in which the thiophene rings have to be placed with the sulfur atoms pointing alternately up and down along the entire polymer chain.



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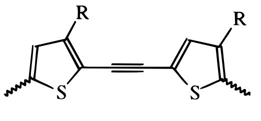

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Photoabsorbance and Photoluminescence. UV–vis spectra of P3HTEs **5** and **10** were measured from THF solutions (Figure 7) and thin films on glass substrates. Under the same conditions, both polymers **5** and **10** showed very similar UV–vis absorbances. Comparing with P3HTE **10**, the absorption λ_{max} of P3HTE **5** was slightly shifted to a longer wavelength (about 4 nm). The regioregularity effect in P3HTEs appeared to be much smaller than that in poly(3-hexylthiophenes) (P3HTs),[11] where a difference of 28 nm in λ_{max} has been reported between regioregular (head-to-tail) and regiorandom P3HTs in CHCl$_3$ solutions. The negligible difference in UV–vis absorption λ_{max} between **5** and **10** suggested that the arrangement of substituents had little effect on the π–π* absorption band and the conjugation length of P3HTE. The diminished regioregularity effect in P3HTE could be explained in terms of the reduced steric interactions between substituents on adjacent thiophene rings and of the reduced interaction between the alkyl side chain and the sp^2 lone pair on the sulfur atoms of the neighbor thiophenes.

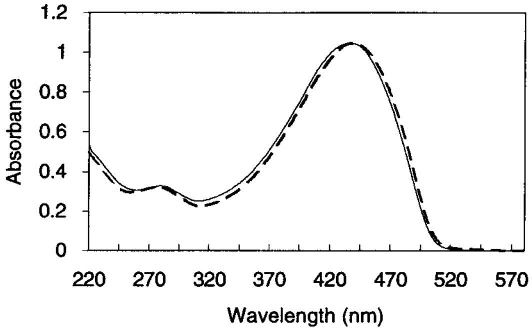
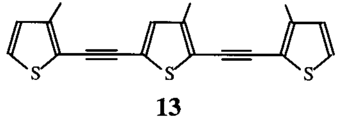


Figure 7. UV–vis spectra of P3HTEs **5** (solid line) and **10** (broken line) measured in the same concentration of THF solutions (0.1 g/L concentration).

Regioregular P3HTE **5** in CHCl$_3$ solvent showed a maximum absorption wavelength at 441 nm (Table 1), which is essentially the same as for poly((3-ethylthiophene-ylene)ethynylene).[5] It appears that the length of the alkyl substituents has a negligible influence on the conjugation length of P3ATE materials. Regiorandom P3HTE,[14] prepared at room temperature as reported previously, exhibited a remarkably longer conjugation length (ca. 35 nm in solution and 41 nm in solid) than the same polymer[9] prepared at an elevated temperature. Thus the polymerization temperature could play an important role in synthesizing P3HTE materials with low electronic gaps. This temperature effect might originate from the instability[19,21] of terminal thienylacetylenes to generate the unwanted structural defects.

Different from P3HT[13] where only one emission band is observed, two emission bands were observed in the fluorescence spectra of P3HTE solutions (Figure 8) with λ_{max} at about 506 and 536 nm. The emission ratios of the two bands for both **5** and **10** were essentially not changed over a wide concentration range ($10^{-6} - 10^{-3}$ M of the repeating unit). Three thiophene-capped model compounds, trimer **13**, tetramer **14**, and hexamer **15**, were synthesized to explore the possible conjugation



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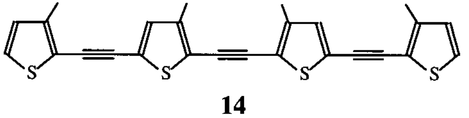

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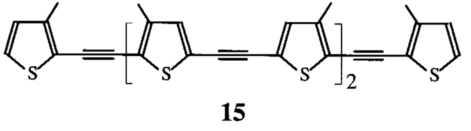

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Table 1. UV–Vis, Fluorescence, and ^{13}C NMR (δ(C≡C)) Data for P3HTEs

	λ_{max} (nm)				
compounds	absorption[a]	fluorescence[a]	excitation[b]	ϕ_n[c]	^{13}C NMR
5	440 (THF), 441 (CHCl$_3$), 486 (film)	506, 536 (THF) 575 (film)	430	0.20	86.54, 89.27
10	436 (THF), 437 (CHCl$_3$), 488 (film)	505, 535 (THF) 575 (film)	420	0.18	87.19, 88.81
random P3HTE	438 (THF), 437 (CHCl$_3$), 487 (film)	505, 535 (THF)	420		86.79, 87.46, 89.02, 89.61
dimer **6**	320 (THF)			≈0	87.67
dimer **8**	367, 393 (THF)	408, 430 (THF)	370	0.07	88.07, 97.01, 99.73
trimer **13**	371 (THF)	414, 436 (THF)	370	0.06	87.28, 87.92, 88.81
tetramer **14**	391 (THF)	450, 476 (THF)	391	0.21	86.98, 87.98, 88.57
hexamer **15**	421 (THF)	484, 514 (THF)	421	0.18	86.79, 87.18, 87.21, 88.69, 89.21

[a] Solvent or the statement of measurement is shown in parentheses. [b] Excitation spectrum is obtained by monitoring at λ_{max} of fluorescence. [c] Quantum efficienty is measured in THF solution.

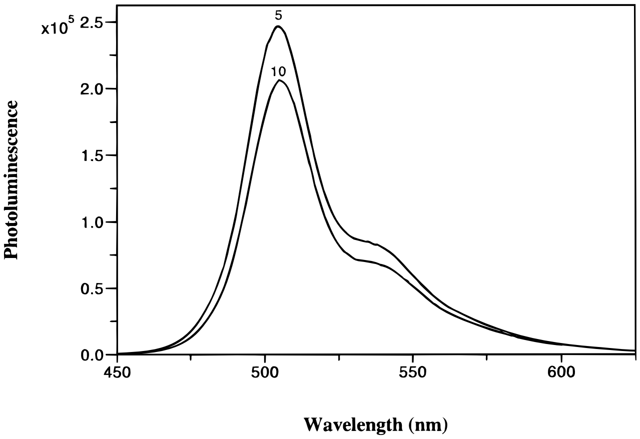

Figure 8. Fluorescence spectra of P3HTEs **5** and **10** showing structured emission bands at about 506 and 536 nm.

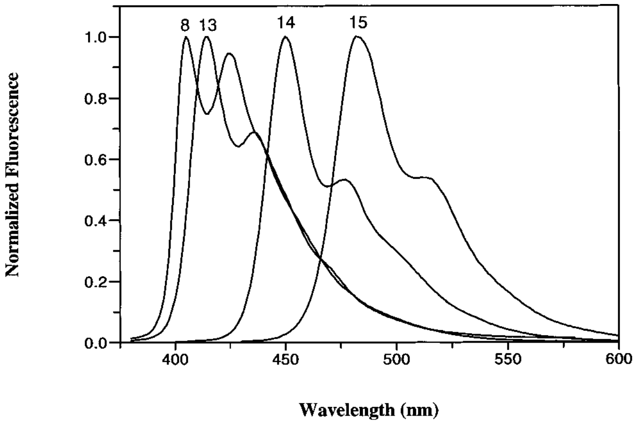

Figure 9. Normalized fluorescence spectra of oligomers **8**, **13**, **14**, and **15**. The relative low-energy band decreases as the conjugation increases.

length effect on the fluorescence characteristics. Fluorescence spectra of **13**–**15** exhibited structured emissions with two resolved bands (Figure 9). The relative fluorescence intensity of the low-energy band appeared to decrease as the conjugation length of the molecule increases.

Quantum Yields of Fluorescence. Fluorescence quantum yields of P3HTEs are listed in Table 1. Since both **5** and **10** have very similar conjugation lengths and the same absorbance, the difference between fluorescent intensities are due primarily to the arrangement of alkyl substituents along the polymer backbone, which affects the nonradiative decay process of the excited states. This regioregularity effect on fluorescence intensity is even larger in the solid state, as polymer **5** of HT linkages fluoresces about 10 times stronger than **10** of HH and TT linkages. The low fluorescence in **10** might be due to relative ease in forming a nonemissive excimer from symmetrically substituted HH and TT linkages, as the TT linkage allows a closer face-to-face proximity interaction with a planar excited-state molecule.[22] Formation of the nonemissive excimer, which has been suggested in P3HT,[13] is consistent with our observation that the fluorescence of P3HTEs decreases by more than 1 order of magnitude from solution to film states. In summary, P3HTE of HT linkages exhibits a stronger fluorescence than the one of HH and TT linkages in both the solution and film states.

It is well documented that the conjugation length[23] of a molecule plays an important role in affecting the quantum yield. Bis(3-hexyl-2-thienyl)ethyne (**6**) gave essentially no fluorescence when excited in its entire photoabsorbance range (300–450 nm), due primarily to the small size[23] of the π-system. Addition of two triple bonds to the thiophene rings made the molecule fluorescent, as shown in bis[3-hexyl-5-[(trimethylsilyl)-ethynyl]-2-thienyl]ethyne (**8**). The quantum yield of trimer **13** was still low (about 6%). Interestingly, the quantum yield of tetramer **14** sharply increased to 21% in repeated measurements, a value comparable with those of P3HTE polymers. Further extending the conjugation length beyond **14** appeared to have little effect on the fluorescence quantum efficiency of the molecule, but to shift the fluorescence emission to longer wavelength.

Experimental Section

Materials and Instrumentation. 3-Hexyl-2-iodothiophene,[16] 2,5-diiodo-3-hexylthiophene,[16,19] and 2,5-diethynyl-3-hexylthiophene[19] were synthesized according to literature procedures. All reagents and solvents were purchased from Acros Organics. Solvents were dried, distilled, and stored under argon. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. UV–vis spectra were recorded in THF solvent on a Beckman DU640 spectrophotometer at 23 °C. NMR spectra were acquired on a Bruker ARX400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Fluorescence spectra were recorded on a PTI steady state fluorometer at 23 ± 1 °C in THF solution. UV–vis and fluorescence spectra of polymer films were recorded on glass substrates in air. Size exclusion chromatography (SEC) was carried out on a Viscotek SEC assembly consisting of a Model P1000 pump, Model T60 dual detectors, and a Model LR40 laser refractometer. Polymer concentrations for SEC experiments were prepared in a concentration of 2–3 mg/mL.

Preparation of 3-Hexyl-5-iodo-2-[(trimethylsilyl)ethynyl]thiophene. 3-Hexyl-5-iodo-2-[(trimethylsilyl)ethynyl]thiophene was prepared from 3-hexyl-2-iodothiophene.[5] The product was purified by column chromatography with silica gel (hexanes) as a colorless liquid in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (s, 1H), 2.63 (t, 2H, J = 7.4 Hz), 1.55 (m, 2H), 1.29 (br, 6H), 0.88 (t, 3H, J = 5.9 Hz), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 149.9, 137.6, 124.1, 102.3, 95.8, 73.6, 31.2, 29.6, 28.8, 28.4, 22.2, 13.8, −0.42.

Preparation of 2-Ethynyl-5-iodo-3-hexylthiophene (4). 3-Hexyl-5-iodo-2-[(trimethylsilyl)ethynyl]thiophene (1.09 g, 6 mmol) was placed in a 50 mL round-bottomed flask, which contained methanol (15 mL), THF (5 mL), and a catalytic amount of potassium hydroxide. The reaction was monitored by IR and complete after stirring the solution at room temperature for 3−4 h. The solvent was removed on a rotatory evaporator at room temperature. The product, 2-ethynyl-3-hexyl-5-iodothiophene (**4**), was obtained as a colorless liquid in 81% yield after purification on a silica gel column with hexanes. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 (s, 1H), 3.48 (s, 1H), 2.65 (t, J = 6.7 Hz, 2H), 1.57 (m, 2H), 1.29 (broad singlet, 6H), 0.87 (t, J = 6.6 Hz, 3H). Anal. Calcd for $C_{12}H_{15}IS$: C, 45.29; H, 4.75; S, 10.08. Found: C, 45.18; H, 4.72; S, 9.99.

Preparation of Bis(3-hexyl-2-thienyl)ethyne (6). 3-Hexyl-2-iodothiophene (15 g, 51 mmol) was added to a 250 mL flask under an argon atmosphere, which was equipped with a magnetic stirrer and contained toluene (120 mL), triethylamine (27 mL, 0.2 mol), copper(I) iodide (9.5 mg, 0.05 mmol), and bis(triphenylenephosphine)palladium dichloride (79 mg, 0.1 mmol). The flask was pumped to about 100 Torr, and the acetylene gas was introduced and maintained via a balloon. After stirring for 8 h at room temperature, the product, bis(3-hexyl-2-thienyl)ethyne, was filtered out and purified through a silica gel column by using hexanes in 91% yield as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (d, 2H, J = 5.1 Hz), 6.87 (d, 2H, J = 5.1 Hz), 2.74 (t, 4H, 7.6 Hz), 1.63 (m, 4H), 1.32 (m, 12 H), 0.87 (t, 6 H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.1, 127.8, 125.7, 117.9, 87.5, 31.2, 29.9, 29.2, 28.6, 22.2, 13.7. Anal. Calcd for $C_{22}H_{30}S_2$: C, 73.68; H, 8.43. Found: C, 73.74; H, 8.44.

Preparation of Bis(3-hexyl-5-iodo-2-thienyl)ethyne (7). Bis(3-hexyl-2-thienyl)ethyne (1.08 g, 3 mmol) and anhydrous ether (20 mL) were placed in a 50 mL flask, which was fitted with a magnetic stirrer and capped with a rubber septum under an argon atmosphere. The flask was cooled to −78 °C and *n*-butyllithium (6.6 mmol in hexanes) was added via a syringe. A yellow brown suspension was obtained after stirring the solution at −78 °C for 20 min and then 0 °C for 30 min. The mixture was then cooled back to −78 °C, and the anions were titrated with iodine solution (1.68 g, 6.6 mmol in 10 mL dry ether). After addition, the mixture was stirred at −78 °C for 1 h and then gradually warmed to room temperature. The product, bis(3-hexyl-5-iodo-2-thienyl)ethyne, was purified on a silica gel column with hexanes as a yellowish oil in 87% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.013 (s, 2H), 2.667 (t, 4 H, J = 7.65 Hz), 1.591 (m, 4 H), 1.266 (br, 12 H), 0.861 (t, 6 H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.5, 138.1, 123.9, 88.3, 74.4, 31.5, 30.1, 29.3, 28.9, 22.5, 14.0. Anal. Calcd for $C_{22}H_{28}I_2S_2$: C, 43.29; H, 4.62; S, 10.50. Found: C, 43.35; H, 4.64; S, 10.41.

Preparation of Bis[3-hexyl-5-[(trimethylsilyl)ethynyl]-2-thienyl]ethyne (8). Bis(3-hexyl-5-iodo-2-thienyl)ethyne was coupled with (trimethylsilyl)acetylene at room temperature by using the same condition as described in the polymerization of P3HTEs. Purification on a silica gel column with hexanes afforded **8** as yellow crystals, mp 70−71 °C, in 93% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.99 (s, 2H), 2.65 (t, 4H, J = 7.4 Hz), 1.59 (m, 4H), 1.29 (br, 12H), 0.87 (t, 6 H, J = 5.9 Hz), 0.24 (s, 18 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.3, 133.3, 119.2, 99.7, 97.0, 88.1, 31.1, 29.8, 29.3, 28.6, 22.3, 13.7, −0.49. UV−vis λ_{max} (nm, in THF solvent), 367 (ϵ = 3.91 × 10^4), 393 (ϵ = 4.84 × 10^4). Anal. Calcd for $C_{32}H_{46}S_2Si_2$: C, 69.75; H, 8.41; S, 11.64. Found: C, 69.95; H, 8.39; S, 11.76.

Preparation of Bis(5-ethynyl-3-hexyl-2-thienyl)ethyne (9). Trimethylsilyl groups of **8** were removed by using the same procedure for preparing **4**. The product was a yellow oil and had the following spectral properties. ^{1}H NMR ($CDCl_3$): δ 7.03 (s, 2H), 3.35 (s, 2H), 2.66 (t, 4H, 7.6 Hz), 1.60 (m, 4H), 1.29 (br, 12H), 0.87 (t, 6H, 6.5 Hz). Anal. Calcd for $C_{26}H_{30}S_2$: C, 76.79; H, 7.43. Found: C, 76.61; H, 7.48.

General Preparation of Regioregular P3HTEs. Preparation of HT Poly((3-hexylthiophene-ylene)ethynylene). 2-Ethynyl-3-hexyl-5-iodothiophene (1.0 g, 2.56 mmol) and triethylamine (2.6 g, 26 mmol) were dissolved in 35 mL of dry toluene in a 100 mL oven-dried, one-necked, round-bottomed flask equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by twice repeating a cycle of freezing and thawing under vacuum, followed by filling with an argon atmosphere. Catalysts $PdCl_2(PPh_3)_2$ (15.8 mg, 0.02 mmol) and CuI (4.8 mg, 0.01 mmol) were added at room temperature in a glovebag under a dry argon atmosphere. After the solution was stirred at room temperature for 4 h, the reaction mixture was heated to 40 °C overnight. The resulting orange-brown solution was twice precipitated from methanol to give a dark brown resin (0.44 g, 91% yield). Anal. Calcd for $(C_{12}H_{14}S)_n$: C, 75.74; H, 7.41. Found: C, 74.93; H, 7.38.

Photoluminescence Quantum Yield Measurements. All slits were kept at 2 nm for excitation and emission. Photoluminescence spectra were corrected for the spectral dispersion of the Xe lamp. All sample solutions were freshly prepared in dry THF, purged with high-purity argon, and used within 4 h. Absorbances of all sample solutions were kept between 0.05 and 0.08. Quantum yields of fluorescence were determined relative to quinine sulfate[24,25] in 1 N H_2SO_4 at 23 ± 1 °C, assuming a quantum yield of 0.546 when excited at 365 nm. Refractive indices[26] of pure 1 N H_2SO_4 and THF were used for the standard and sample solutions during the calculation of quantum yield. The quantum yields reported here are averaged over at least three measurements, with a standard deviation below 0.02.

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