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Regiocontrolled Synthesis of Poly[(*p*-phenylene ethynylene)-*alt*-(2,5-thienylene ethynylene)]s: Regioregularity Effect on Photoluminescence and Solution Properties.

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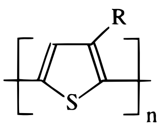
ABSTRACT: Regioregular poly[(*p*-phenylene ethynylene)-*alt*-(2,5-thienylene ethynylene)]s (PPETEs) have been synthesized to evaluate the pure regioregularity effect on the physical properties of π-conjugated polymers. Comparison of their UV−vis and ^{13}C NMR spectroscopy confirms the absence of steric interaction between the adjacent substituents on thiophene rings. Although both polymers emit at the same wavelength, PPETE **3** with a pure head-to-tail chain sequence exhibits a slightly stronger fluorescence from its solution than PPETE **4** with a head-to-head chain sequence ($\phi_{fl} = 0.59$ for **3** vs 0.53 for **4**). The Mark−Houwink constant α and radius of gyration R_g values have been determined for PPETEs **3** and **4**, both indicating that **3** has a more rigid conformation than **4**. The higher molecular rigidity for **3** might be partially responsible for its higher PL quantum efficiency. A significant enhancement in PL efficiency has been observed from PPETE films. Under identical experimental conditions, a film of **4** emits about 2.5 times stronger than **3** and 6 times stronger than the regiorandom PPETE, respectively.

Introduction

Regioregular structures of π-conjugated polymers can have a large impact on their physical properties as illustrated in poly(3-alkylthiophenes) (P3ATs), **1**.[1] The regioregular P3ATs with a head-to-tail chain sequence, for example, exhibit a remarkably longer conjugation length than the corresponding regiorandom P3ATs in their UV−vis λ_{max} (about 18−28 nm in solutions and 87−173 nm in films).[2] In addition, the PL efficiency[3] of P3ATs increases significantly with the content of head-to-tail chain sequence. Although different level of steric interaction between regioregular and regiorandom P3ATs could account for the difference in photoabsorbance λ_{max}, the enhancement in the PL efficiency could be due to both steric interaction and structural regioregularity in the polymer. To estimate the magnitude of regioregularity effect on the PL efficiency of the π-conjugated polymer, it is desired to isolate the regioregularity from the steric effect.



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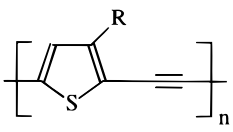

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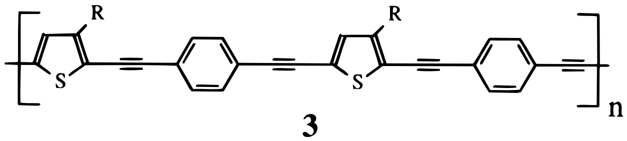
Recently regioregular poly(3-alkylthienyl ethynylene)s (P3ATEs), **2**, have been reported by this[4] and other[5] groups. Compared with that in P3AT, the steric interaction between the adjacent substituents in P3ATE is drastically reduced as a result of the increased distance between the adjacent alkyl substituents. Although the UV−vis absorption λ_{max} of the head-to-tail P3ATE is only slightly higher (4 nm) than that of the head-to-head P3ATE when the substituent is *n*-hexyl,[4] the PL efficiency for the head-to-tail P3ATE is about 10% higher in solution and 10 times higher in film than that of the corresponding head-to-head P3ATE. The structural regioregularity may therefore play an important role to enhance the PL efficiency of the π-conjugated polymers, especially in the solid state. To further investigate the long-range regioregularity effect, we have synthesized regioregular poly[(*p*-phenylene ethynylene)-*alt*-(3-hexylthienyl ethynylene)]s (PPETEs) **3** and **4**. The alkyl substituents in **3** and **4** (in comparison with **2**) are now further separated to eliminate the possible steric interaction between them. Such structural feature makes the overall steric interactions in **3** and **4** to be the same or very similar, thus allowing us to evaluate the PL enhancement solely originating from the structural regioregularity. Here we report their synthesis and characterization.



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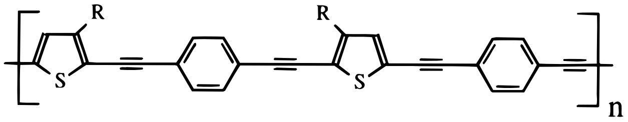

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Results and Discussions

The same synthetic methodology used for regioregular P3HTE (**2**) was adopted here to prepare regioregular PPETEs **3** and **4**. The correct chemical structure was ensured through the selective formation of carbon−carbon bonds at specific locations as shown below (Figures 1 and 2). All monomers were carefully purified and characterized to warrant a high content of regioregularity in the resulting polymers.

Synthesis of PPETE 3 with the Head-to-Tail Chain Sequence. The desired head-to-tail sequence was obtained via polymerizing monomer **7** at room temperature. In monomer **7** the phenylethynyl group

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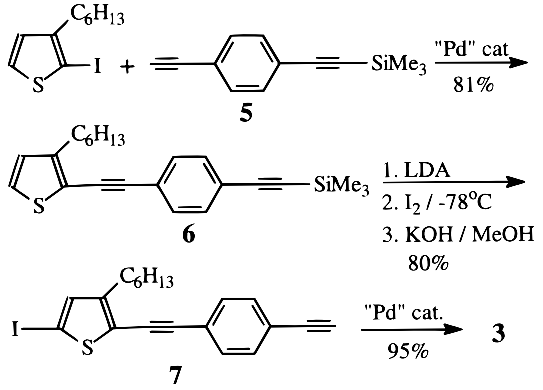

Figure 1. Regiocontrolled synthesis of PPETE with the head-to-tail chain sequence.

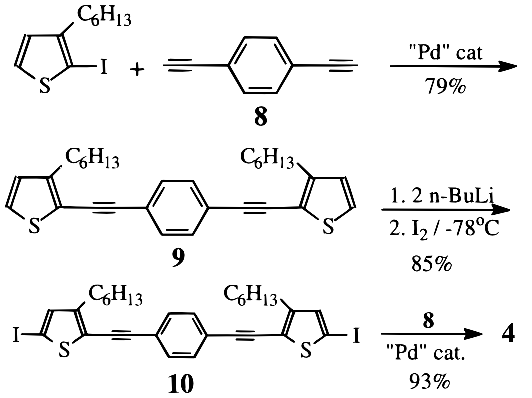

Figure 2. Regiocontrolled synthesis of PPETE with the head-to-head and tail-to-tail chain sequences.

had been selectively connected to the 2-position of the thiophene ring, thus leaving the formation of the head-to-tail linkage as the only choice during the polymerization. Synthesis of **7** was accomplished by coupling 2-iodo-3-hexylthiophene[3] with 1-ethynyl-4-(trimethylsilylethynyl)benzene (**5**)[6] and then iodination[7] at the 5-position of the thiophene ring (Figure 1).

Synthesis of PPETE 4 with the Head-to-Head and Tail-to-Tail chain Sequences. Synthesis of PPETE **4** was accomplished by separating the head-to-head and tail-to-tail linkage formation into the corresponding monomer and polymer synthesis steps. Thus direct coupling of 3-hexyl-2-iodothiophene with 1,4-diethynylbenzene conveniently afforded **9** with the desired head-to-head linkage in 79% isolation yield. Iodination[4] of **9** by using *n*-butyllithium followed by treatment with iodine at −78 °C proceeded in a combined yield of 85%. Coupling of **10** with **8** at room temperature eventually afforded PPETE **4** in 93% yield with formation of the tail-to-tail linkage.

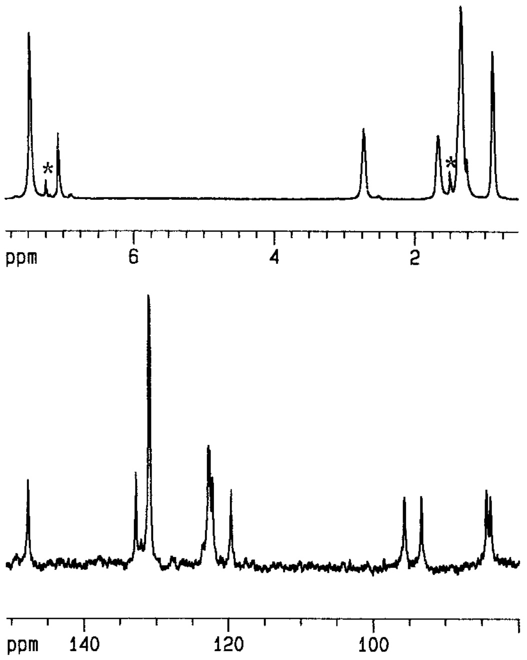

Figure 3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of PPETE **3** in CDCl$_3$. The stared signals at 1.5 and 7.25 ppm in the ^{1}H NMR spectrum are attributed to trace H$_2$O and CHCl$_3$.

Table 1. Molecular Weights and Chain Rigidity of PPETEs

PPETE	M_w[a] (PDI)	α[b]	R_g[c] (nm)	R_g/M_w (×10^4)
3 (HT)	37,900 (1.43)	1.06	9.24	2.438
4 (HH)	47,200 (1.98)	0.91	9.14	1.936
11[d]	31,100 (2.10)	0.94	6.93	2.228

[a] Weight-average molecular weight and polydispersity index. [b] Mark−Houwink constant. [c] Weight-average radius of gyration. [d] Random PPETE[9] with HT content about 50%.

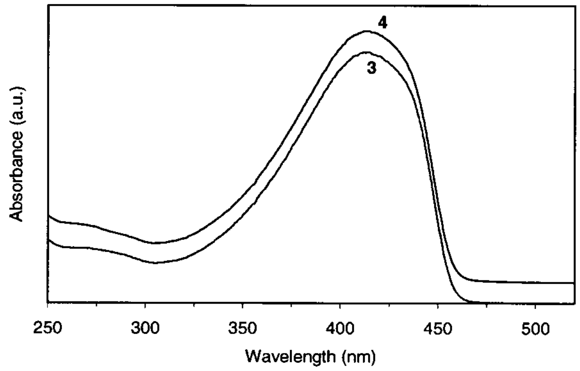

Figure 4. UV−vis spectra of PPETEs **3** (HT) and **4** (HH) (THF solvent) exhibit essentially the same absorption profile for both polymers. Spectra are offset for clarity.

Characterization of PPETEs. PPETEs **3** and **4** were yellow solids, which were soluble in nonpolar organic solvents such as THF, toluene, and chloroform. Uniform polymer films could be cast from their solutions. Polymer structures were characterized by UV−vis, and solution ^{1}H and ^{13}C NMR spectroscopy. No resonance signals near 3.15 ppm (acetylene protons) were detected in the ^{1}H NMR spectra of **3** and **4** (Figure 3), indicating the complete polymerization. Comparing with the regiorandom PPETE[8] synthesized at 60 °C, the ^{1}H NMR signals between 1 and 2 ppm in Figure 3 are quite simple and sharp. The sharper resonance signal is primarily due to the milder reaction used (not the structural regioregularity), since the ^{1}H NMR signals of the essentially same sharpness were also observed from the regiorandom PPETE of similar molecular weight (Table 1) prepared under the same experimental conditions. Figure 4 shows UV−vis absorption spectra of **3** and **4**, which are nearly identical and suggest essentially the same conjugation length along the π-conjugated polymer backbone in both polymers. Clearly the adjacent alkyl substituents on the thiophene rings in both **3** and **4** are now well separated so that they no longer interact with each other. Complete elimination of the steric interaction between the adjacent alkyl substituents in **3** and **4** is further evidenced by the nearly same ^{13}C chemical shift values observed

Table 2. Spectroscopical Data for PPETEs

PPETE polymer	^{13}C (C≡C)	λ_{max} (nm) absorption[a]	fluorescence[a]	excitation[b]	ϕ_{fl}[c]
3 (HT)	95.64, 93.27, 84.30, 83.77	414 (THF)	453, 479 (THF)	398, 410 (THF)	0.59 (THF)
4 (HH)	95.86, 93.44, 84.58, 83.92	415 (THF)	453, 478 (THF)	398, 410 (THF)	0.53 (THF)
11	95.71, 93.31, 84.38, 83.79	414 (THF)	451, 478 (THF)	398 (THF)	0.46 (THF)
		413 ($CHCl_3$)	455, 480 ($CHCl_3$)	398 ($CHCl_3$)	0.47 ($CHCl_3$)

[a] Solvent is shown in parentheses. [b] Fluorescence excitation λ_{max} observed while monitoring at fluorescence λ_{max}. [c] Quantum yields listed in the table were measuured in $CHCl_3$ and THF solvent while excited at 398 nm. When excitation $\lambda = 410$ nm was used, the ϕ_{fl} values were 0.52 for **3** and 0.46 for **4**.

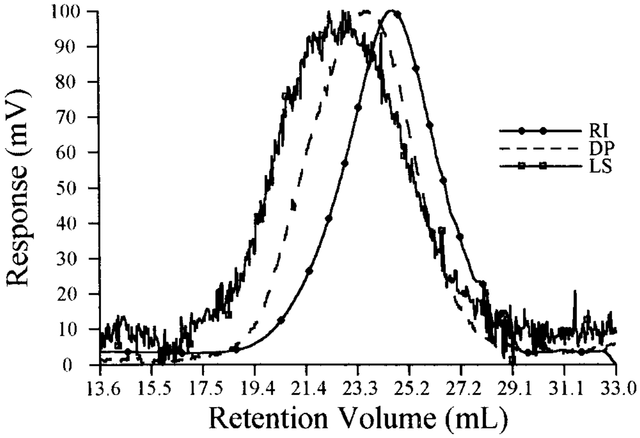

Figure 5. SEC^3 chromatogram for PPETE **4**.

for acetylene carbons (Table 2), which are quite sensitive to the substitution patterns in the π-conjugated polymers such as P3ATE (**2**).[4] The same number of acetylene ^{13}C NMR signals observed from both regiorandom[9] and regioregular PPETEs (**11**, **3**, and **4** in Table 2) confirms that the substituents are so well separated that their regioregular placement along the polymer chain has a negligible influence on the chemical shift environment of the acetylene nuclei. Combination of the nearly same ^{13}C NMR chemical shift values with the nearly identical UV−vis absorption profile indicates that the overall steric interactions in **3** and **4** are at the same level.

Molecular Weight and Chain Stiffness. The molecular weights of the polymers, which are listed in Table 1, 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). Comparable peak molecular weights were observed from refractive index (RI), viscosity (DP), and light-scattering (LS) detectors (Figure 5). The observed monomodel distribution and narrow polydispersity (PDI < 2) in molecular weights are consistent with the proposed linear structure[10] from the condensation polymerization. The relative lower polydispersity observed in regioregular than in regiorandom PPETE (**11**)[9] could be partially attributed to the larger monomers used in synthesizing **3** and **4**.

For π-conjugated polymers, a fundamental issue is how rigid these molecules are as a result of the extended $\pi-\pi$ conjugation. These valuable data can be accessed through evaluating their unperturbed molecular dimensions[11] in their corresponding solutions. Both the Mark−Houwink constant (α value) and the radius of gyration have been obtained for few conducting polymers such as poly(3-alkylthiophene)s[12] and poly(*p*-phenylene ethynylene)s.[13] No report has been found in the literature, however, to study the effect of regioregularity on the chain stiffness of π-conjugated polymers.

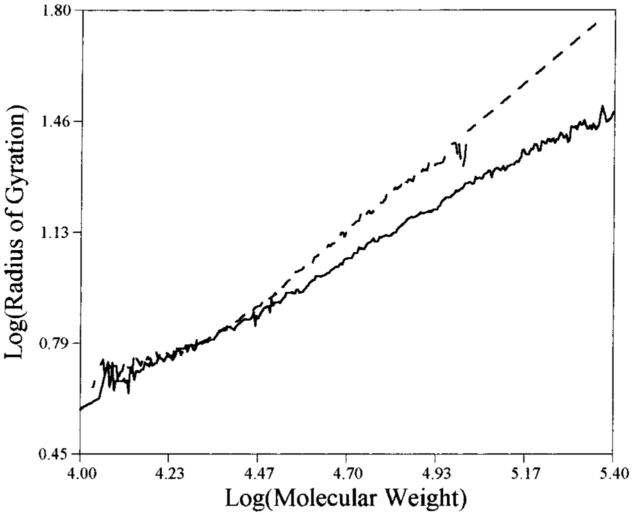

Figure 6. Radius gyration (in unit of nm) versus molecular weight plot for PPETE **4** (solid line) and **3** (dotted line). In the dotted line, the small negative peak at Log(M_w) ≈ 5 is due to the instrument noise from low concentration at the high M_w end. The dotted line with Log(M_w) > 5 is the extrapolation.

Thus obtaining the solution properties from the regioregular PPETEs **3** and **4** is highly desired since evaluation of their unperturbed molecular dimensions in dilute solutions could be a useful probe to gain an insight into the extended chain stiffness of these polymers. The α values in the Mark−Houwink equation, $[\eta] = K\ M^{\alpha}$, as measured by the on-line viscosity detector, were determined to be 1.06 for **3** and 0.91 for **4**. The higher a value for **3** indicated that the PPETE of a head-to-tail chain sequence had a slightly more rigid conformation in the dilute solution than the corresponding one of a head-to-head chain sequence.

The trend in molecular stiffness is further studied by comparing the radius of gyration (R_g),[14,15] which is another experimental quantity to measure the chain stiffness of the polymer. For the isomeric species **3** and **4**, the R_g/M_w quantity can be used conveniently for direct comparison of their relative chain stiffness. The measured R_g/M_w value for **3** is significantly higher than that for **4** (Table 1), confirming that the chain of the former is more rigid. As expected the chain stiffness of regiorandom PPETE **11** falls between the regioregular **3** and **4** (Table 1) from both the Mark−Houwink constant and the R_g/M_w value. An overlaying plot of radius gyration versus molecular weight is shown in Figure 6. The molecular sizes for **3** and **4** are about the same when their molecular weights are low. At a relative high molecular weight range ($M_w \geq 10^{4.4} \approx$ 25 120), however, the molecular size of **3** becomes relatively larger than the one of **4** for a given molecular weight. This result suggests that the local steric interaction in **3** is not responsible for its observed higher chain rigidity, which is consistent with the previously

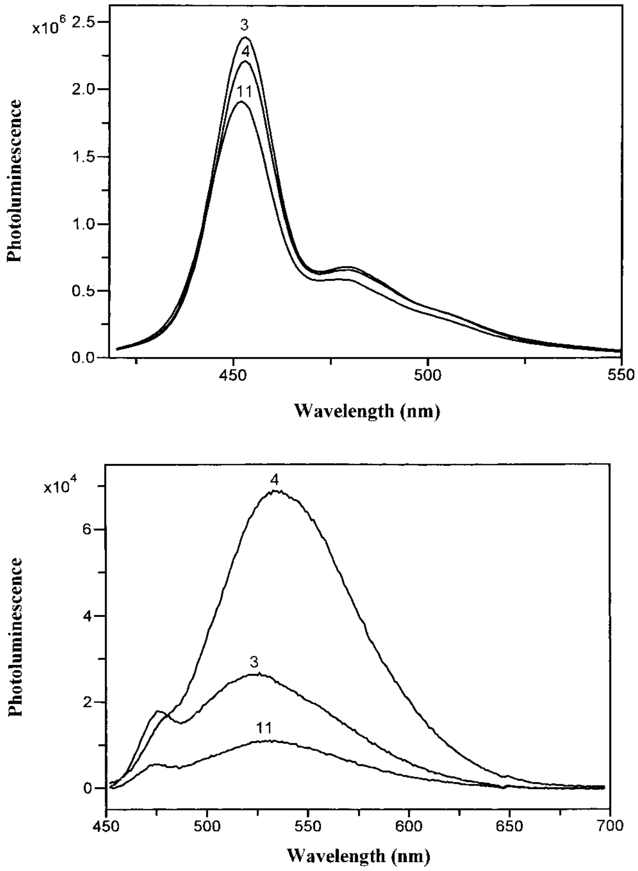

Figure 7. Photoluminescence spectra of PPETE **3**, **4**, and **11** acquired in THF (top) and film states (bottom).

observed UV–vis absorption data (both **3** and **4** have same absorption λ_{max}). Thus the molecular rigidity difference between **3** and **4** appears to originate from the long-range molecular interaction between chain segments.

Photoluminescence and Quantum Yields. As shown in Figure 7, both **3** and **4** exhibit the nearly identical photoluminescence (PL) profile with emission λ_{max} at about 453 and 478 nm, further confirming the existence of the essentially same energy band structure in both polymers. The quantum efficiency of **3** measured in THF in reference to quinine sulfate, however, is noticeably higher than that of **4** ($\phi_{fl} = 0.59$ for **3** vs 0.53 for **4**) in repeated measurements. The observed difference in the PL efficiency might be partially associated with their relative molecular stiffness of the polymers, since PPETE **3** has a more rigid molecular conformation in THF solution than **4**. It is noted that the quantum efficiencies of both regioregular PPETEs are significantly higher than that of regiorandom PPETE ($\phi_{fl} \approx 0.46$, Table 2),[9] which contains head-to-head and head-to-tail sequences in a ratio of about 50:50. This observation suggests that the PL efficiency of PPETE is affected not only by its relative content of head-to-tail sequences, which determines the chain rigidity, but also by its detailed linkages between the chain sequences. It should be pointed out that all PPETE solutions are excited at the same wavelength in the PL quantum efficiency measurement, and thus the above observed trend in PL quantum efficiencies is independent of the wavelength[15] of the excitation light used. The dependence of PL efficiency with the HT content in PPETE appears to be similar to the trend[3] reported for poly(3-hexylthiophene) (P3HT) whose PL efficiency consistently increases with the HT content (HT% ≥ 50%). Since no PL efficiency data are available from P3HT with HT content less than 50%, no comparison can be made between PPETE and P3HT for the dependence of PL efficiency with the HT content.

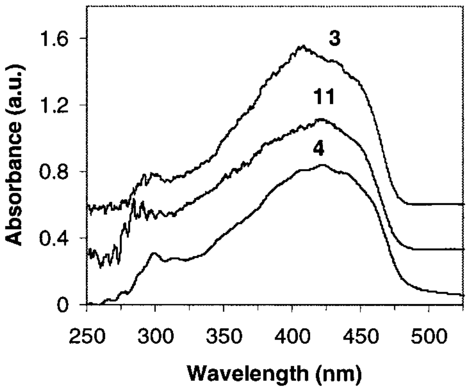

Figure 8. UV–vis absorption of PPETE films measured at room temperature on glass substrates. The spectra are offset for clarity.

Table 3. Photoabsorption and Fluorescence Characteristics of PPETE Films

PPETE	absorption λ_{max} (nm)	fluorescence $e\lambda_{max}$ (nm)	absorbance[a] of films at 368 nm	rel quantum efficiency[b]
3 (HT)	408	525	0.56	2.4
4 (HH)	431	534	0.53	6.0
11	421	530	0.54	1.0

[a] Absorbance of PPETE films at the excitation wavelength, which were used for their relative quantum efficiency measurements. [b] Relative quantum efficiencies were measured in relative to random PPETE **11** while the films were excited at 368 nm, which is one of the excitation λ_{max}.

Solid-state fluorescence spectra of PPETEs were measured from the corresponding polymer films on glass substrates under the identical conditions (Figure 7). The PPETE films for PL study were spin-cast from their solution with absorbance between 0.8 and 0.9 at their absorption λ_{max}. The absorption and fluorescence spectra from the film of **4** (Figures 7 and 8) are slightly red-shifted in comparison with the spectra from the film of **3**, whose absorption and fluorescence data are summarized in Table 3. It appears that the more symmetrical chain sequence (head-to-head and tail-to-tail) in **4** allows the better packing in the solid state, leading to a slightly longer effective conjugation length. Different from the trend observed in polymer solutions, fluorescence from the film **4** is about 2.5 times stronger than that from the film **3** (Table 3). It is noticed that the observed regioregularity effect on photoluminescence in PPETE films is significantly less than that observed in P3ATE films.[4] The difference may be partially rationalized by considering the fact that for a given effective conjugation length the number of substituents on PPETE is only about half of that on P3ATE. The relative quantum efficiencies in Table 3 also show that both **3** and **4** have significant stronger emission than the regiorandom PPETE **11**. Clearly the structural regioregularity plays an important role for PL enhancement, especially in the solid state.

Experimental Section

Materials and Instrumentation. 3-Hexyl-2-iodothiophene,[16] 1-ethynyl-4-(trimethylsilylethynyl)benzene,[5] and 1,4-

diethynylbenzene[5] were synthesized according to literature procedures. Solvents were dried, distilled, and stored under nitrogen or argon. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. UV/vis spectra were recorded in THF or $CHCl_3$ solvents on a Beckman DU640 spectrophotometer at 23 °C. UV/vis spectra of polymer films were recorded by using a Labsphere Reflectance Accessory on a Beckman DU640 spectrophotometer. 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. 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, a Model T60 dual detectors, a Model LR40 laser refractometer, and three mixed-bed columns (10 μm). Polymer concentrations for SEC experiments were prepared in a concentration of about 3 mg/mL. The SEC system was calibrated by using narrow and broad polystyrene standards prior to use.

Preparation of 1-Ethynyl-4-(trimethylsilylethynyl)-benzene (5). 1-Ethynyl-4-(trimethylsilylethynyl)benzene[5] was prepared by using a modified literature procedure. Thus methylmagnesium chloride (19.6 mL of a 3 M solution in THF) was added dropwise at 0 °C into a 250 mL oven-dried flask which contained 1,4-diethynylbenzene (7.4 g, 58.7 mmol) and 60 mL of anhydrous THF under an argon atmosphere. After the solution was stirred for 2 h at 0 °C (evolution of gas stopped), the reaction suspension was cooled to −78 °C and chlorotrimethylsilane (6.41 g, 59 mmol) was added dropwise via a syringe. Then the reaction mixture was gradually warmed to room temperature and stirred overnight. The crude product was washed with 50 mL of 0.1 M HCl aqueous solution. Purification on silica gel using hexanes gave pure 1-ethynyl-4-(trimethylsilylethynyl)benzene in 75% yield (lit.[6] yield 60%). ^{1}H NMR ($CDCl_3$): δ 7.40 (m, 4H), 3.14 (s, 1H), 0.24 (s, 9H).

Synthesis of 1-[(3′-Hexyl-2′-thienyl)ethynyl]-4-(trimethylsilylethynyl)benzene (6). 3-Hexyl-2-iodothiophene (6.9 g, 23.5 mmol), 1-ethynyl-4-(trimethylsilylethynyl)benzene (4.55 g, 23 mmol) and triethylamine (16 mL) were dissolved in 60 mL of anhydrous toluene in an oven-dried 250 mL round-bottomed flask which was equipped with a magnetic stirring bar and capped with a rubber septum. The solution was deoxygenated by freezing and evacuating, followed by filling with argon. Catalysts $PdCl_2(PPh_3)_2$ (39.5 mg, 0.05 mmol) and CuI (4.75 mg, 0.025 mmol) were added under an argon atmosphere at room temperature. The mixture was stirred at room-temperature overnight, and the product was purified as viscous oil on silica gel with hexanes. ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 4H), 7.18 (d, 1H, $J = 5.1$ Hz), 6.88 (d, 1H, $J = 5.1$ Hz), 2.75 (t, 2H, $J = 7.45$ Hz), 1.64 (t, 2H, $J = 7.22$ Hz), 1.32 (br, 6H), 0.87 (t, 3H, $J = 6.8$ Hz), 0.25 (s, 9H).

Synthesis of 1-[(3′-Hexyl-5′-iodo-2′-thienyl)ethynyl]-4-(trimethylsilylethynyl)benzene. 1-[(3′-Hexyl-2′-thienyl)-ethynyl]-4-(trimethylsilylethynyl)benzene (**6**) (2.206 g, 6.06 mmol) and anhydrous ether (10 mL) were placed in a 100 mL flask, which was fitted with a magnetic stirrer and capped with a rubber septum with an argon atmosphere. Lithium diisopropylamide (6.6 mmol in 20 mL of ether) was added into the reaction mixture while it was cooled to −78 °C. After addition, the temperature was gradually warmed to 0 °C for an hour and then cooled back to −78 °C. The formed thienyl anion solution was titrated at −78 °C with an iodine solution (1.67 g of I_2 in 10 mL of ether). Purification on a silica gel column with hexanes afforded 1-[(3′-hexyl-5′-iodo-2′-thienyl)ethynyl]-4-(trimethylsilylethynyl)benzene as a viscous oil in 85% yield. ^{1}H NMR ($CDCl_3$): δ 7.40 (m, 4H), 7.02 (s, 1H), 2.70 (t, 2H, $J = 7.4$ Hz), 1.61 (m, 2H), 1.31 (br, 6H), 0.88 (t, 3H, $J = 6.6$ Hz), 0.24 (s, 9H). Anal. Calcd for $C_{23}H_{27}ISiS$: C, 56.31; H, 5.55; S, 6.54. Found: C, 56.28; H, 5.60; S, 6.56.

Synthesis of Monomer 7. 1-[(3′-Hexyl-5′-iodo-2′-thienyl)-ethynyl]-4-(trimethylsilylethynyl)benzene (0.98 g, 2 mmol) and potassium hydroxide (10 mg) was placed in a 50 mL round-bottomed flask containing methanol (15 mL) and THF (5 mL). The solution was stirred at room temperature until the reaction was complete (in about 4 h). Purification on a silica gel column with hexanes gave monomer **7** as viscous oil (0.79 g, 95% yield). ^{1}H NMR ($CDCl_3$): δ 7.43 (m, 4H), 7.02 (s, 1H), 3.16 (s, 1H), 2.70 (t, 2H, $J = 7.4$ Hz), 1.60 (br, 2H), 1.31 (br, 6H), 0.86 (t, 3H, $J = 5.9$ Hz). Anal. Calcd for $C_{20}H_{19}IS$: C, 57.42; H, 4.58; S, 7.66. Found: C, 57.46; H, 4.60; S, 7.65.

Synthesis of 1,4-Bis[(3′-hexyl-2′-thienyl)ethynyl]benzene (9). 3-Hexyl-2-iodothiophene (0.9264 g, 3.13 mmol), 1,4-diethynylbenzene (0.189 g, 1.5 mmol), and triethylamine (2.1 mL) were reacted in 12 mL of anhydrous toluene under the same condition as in preparation of **6**. Purification on a silica gel column with hexanes afforded product **9** as a viscous oil (0.54 g, 79% yield). ^{1}H NMR ($CDCl_3$): δ 7.45 (s, 4H), 7.19 (d, 2H, $J = 5.1$ Hz), 6.88 (d, 2H, $J = 5.1$ Hz), 2.76 (t, 4H, $J = 7.6$ Hz), 1.66 (m, 4H), 1.32 (m, 12H), 0.88 (t, 6H, $J = 6.9$ Hz). Anal. Calcd for $C_{30}H_{34}S_2$: C, 78.55; H, 7.47; S, 13.98. Found: C, 78.63; H, 7.50; S, 13.99.

Synthesis of 1,4-Bis[(3′-hexyl-5′-iodo-2′-thienyl)ethynyl]benzene (10). 1,4-bis[(3′-hexyl-2′-thienyl)ethynyl]benzene (**9**) (0.33 g, 0.72 mmol) was dissolved in 10 mL of anhydrous ether in a 50 mL flask, which was fitted with a magnetic stirrer and capped with a rubber septum under an argon atmosphere. *n*-Butyllithium (1.58 mmol in hexanes) was added via a syringe at −78 °C. After the mixture was stirred at −78 °C for 20 min and then 0 °C for 30 min, the resulting solution gradually became a grayish suspension. The mixture was then cooled back to −78 °C, and the anion was titrated with iodine solution (0.40 g, 1.58 mmol in 10 mL of anhydrous ether). After being stirred at −78 °C for an hour, the reaction mixture was gradually warmed to room temperature and treated with 10 mL of saturated sodium bisulfite solution. Purification on a silica gel column with hexanes gave pure **10** (0.43 g, 85% yield) as yellowish crystals (mp 85−86 °C). ^{1}H NMR ($CDCl_3$): δ 7.43 (s, 4H), 7.03 (s, 2H), 2.71 (t, 4H, $J = 7.6$ Hz), 1.63 (m, 4H), 1.32 (m, 12 H), 0.88 (t, 6H, $J = 6.9$ Hz). Anal. Calcd for $C_{30}H_{32}I_2S_2$: C, 50.71; H, 4.54; S, 9.02; I, 35.72. Found: C, 50.77; H, 4.53; S, 9.01.

Synthesis of Regioregular PPETEs. Regioregular PPETEs **3** and **4** were prepared by polymerizing the corresponding monomers under the same experimental conditions used for regiorandom PPETE.[9] As an example, PPETE **4** had the following spectral characteristics. ^{1}H NMR ($CDCl_3$): δ 7.47 (s, 4H, phenyl H), 7.07 (s,1H, thiophene H), 2.73 (br, 2H, CH_2), 1.66 (br, 2H, CH_2), 1.33 (br, 6H, $(CH_2)_3$), 0.88 (br, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 147.8 (2C), 132.9 (2C), 131.1 (4C), 131.0 (4C), 122.9 (2C), 122.6 (2C), 119.8 (2C), 95.9 (2C), 93.4 (2C), 84.6 (2C), 83.9 (2C), 31.3 (2C), 29.7 (2C), 29.2 (2C), 28.6 (2C), 22.3 (2C), 13.8 (2C). Anal. Calcd for $(C_{20}H_{18}S)_n$: C, 82.71; H, 6.25. Found: C, 81.25; H, 6.09.

Photoluminescence and Quantum Yield Measurements. The solution PL quantum yields were measured by using the same procedure[9] as described previously. The relative PL quantum yields of PPETE films were estimated by using $\phi_s/\phi_r = (A_r/A_s)(F_s/F_r)\,(n_s^2/n_r^2) \approx (A_r/A_s)(F_s/F_r)$, assuming the same refractive index for PPETE films. Here ϕ_r, A_r, and F_r are the quantum efficiency, absorbance at excitation wavelength, and emission integration area for regiorandom PPETE. The films were spin-cast on glass substrates with photoabsorbance below 1.0 (typically between 0.8 and 0.9) at absorption λ_{max}. Absorbance at the excitation wavelength (368 nm) was at about 0.5 as listed in Table 3. Emission were detected at 90° from the incident beam by front face fluorescence method with the sample placed at an angle of about 45° to both incident beam and detector. It should be pointed out that the measurement on the films here is actually using "the optically dilute configuration" widely adopted for the dilute solution studies. It is therefore extremely important to keep the absorbance of the films well below 1.0 at the excitation wavelength. Our choice to control the film absorbance at about 0.5 (at the excitation wavelength) is based on the consideration that significant error might occur in measuring the low absorbance of the film.

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