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Blue-Emitting Soluble Poly(*m*-phenylenevinylene) Derivatives

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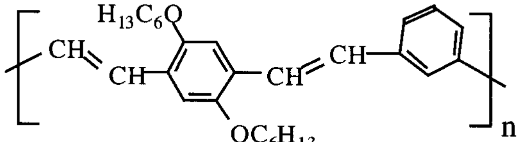
ABSTRACT: Soluble poly(*m*-phenylenevinylene) derivatives (**4**) were synthesized via Wittig−Horner reaction. The number-average degree of polymerization was estimated to be around 25−35. On the basis of FT-IR and ^{1}H NMR spectra, the olefins in the polymers were confirmed to be predominantly in the *trans*-configuration. A model compound, 3,5-distyryl-4-hexyloxytoluene (**5**), was also synthesized to aid the structural characterization. Comparison of photoabsorption and emission characteristics between **4** and **5** indicated that the *m*-phenylene effectively interrupted the conjugation, allowing predictable color control in the π-conjugated polymers. At low temperature, the fluorescence of **4** was readily resolved into two peaks, suggesting the predominant emissions were from 0−1 and 0−2 transitions. Polymers **4** were found to be highly luminescent in both solution and film states. LED devices using **4** gave blue EL output (emission λ_{max} at 445 and 462 nm).

Introduction

π-Conjugated polymers with band gaps in the visible region such as poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted significant attention over the past decade, due to their potential applications in light-emitting diodes (LEDs)[1,2] and lasers.[3,4] The emission color (or the band gap) of the materials can be tuned by attaching substituents[5] on the polymer backbone (through both steric and electronic influence), by introduction of kinked π-conjugated linkages,[6] or by inclusion of nonconjugated carbon bridges[7] along the polymer backbone. Soluble PPVs often require the attachment of long side chains. Among the known blue-emitting polymers are poly(*p*-phenylene)s,[8a] poly(9,9-dialkylfluorene),[9] and block *co*-polymers[7a] with well-defined and isolated chromophores. Although the blue-emitting polymers based on PPV-type materials can be obtained by randomly interrupting conjugation[7b] along the chain, the polymers thus prepared suffer from the drawback that the emission occurs usually from the more highly conjugated segments, and the emission spectrum therefore is usually broadened and red-shifted.

Our recent study has shown that the presence of *m*-phenylene units[6b] along PPV chain effectively interrupts π-conjugation, thereby tuning the emission color in a predictable manner. This is clearly shown by comparing absorption and emission λ_{max} values observed from the green-emitting polymer **1** and the model compound **2**. Poly[(*m*-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)]s also exhibit good solubility and high luminescence in both solution and solid states. Altering the green emission of **1** to a blue color requires decrease of the effective conjugation length of the emitting chromophore. Reasoning that a simultaneous enhancement in luminescence and solubility could also be achieved in blue-emitting polymers, we decide to explore the synthesis of **4**, in which all the benzene rings are linked at the *meta*-position.



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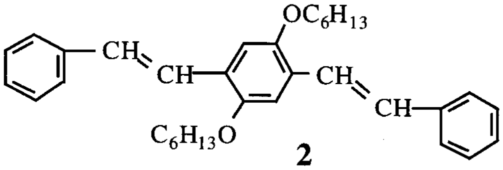

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Results and Discussion

Polymer **4** was synthesized by using the Wittig−Horner reaction,[10] which is known to produce *trans*-alkenes. In the polymer **4**, two different *m*-phenylene units were alternated along the backbone, thereby generating an emitting chromophore with a uniformly defined structure. Polymer **4** exhibited good solubility in common organic solvents such as THF, chloroform, and benzene. It appeared that only a short alkyl side chain on the substituted phenyl rings was necessary to keep the polymer soluble. The solubility of **4**, in general, was significantly higher than that of **1** in the same solvents, due to the increased content of *m*-phenylene linkage in the former. Uniform thin films could be cast from the polymer solutions. To aid the structural characterization, the model compound **5** was synthesized similarly by reacting **3** with benzaldehyde.

The high intensity of *trans*-CH═CH (~976 cm^{-1}) absorption in the IR spectrum of **4** (Figure 1) showed that the polymer contained predominantly *trans*-olefin

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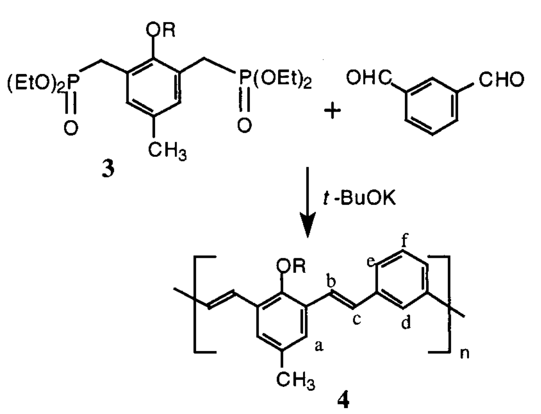
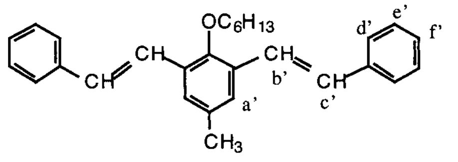


(**a**: R= n-Butyl; **b**: R= n-Hexyl; **c**: R= n-Octyl)



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groups. This was also supported by the ^{1}H NMR spectrum (Figure 2), since the proton resonance signals of $-OCH_2-$ unit in the alkoxy side chains[6b] were sensitive to the nearby *cis*-CH=CH or *trans*-CH=CH configuration in *m*-phenylene-containing PPVs. The sharp major resonance signal at ~3.84 ppm and the minor signal at ~3.93 ppm were attributed to the $-OCH_2-$ unit in the alkoxy side chains and were related to *trans*- and *cis*-olefins,[11] respectively. The assignment of ^{1}H NMR signals was confirmed by comparison with the spectrum of the model compound **5**. The *cis-/trans*-CH=CH ratios in **4**, which were conveniently estimated from the ^{1}H NMR signals at 3.84 and 3.93 ppm, are listed in Table 1. The signal at ~9.8 ppm ($-$CHO end group) was not detected in the ^{1}H NMR of **4**, which was in agreement with the disappearance of the C=O stretch band at ~1700 cm^{-1} in their IR spectra (Figure 1). The number-average degrees of polymerization of **4** were determined to be $n \approx 37$, 35, and 26 for **4a**, **4b**, and **4c**, respectively, using the ^{1}H NMR peaks for the terminal groups ($-CHO$ at ~9.9 ppm or $Ar-CH_2-PO(OEt)_2$ at ~3.2 ppm) and that for the $-OCH_2-$ unit in the side chains.

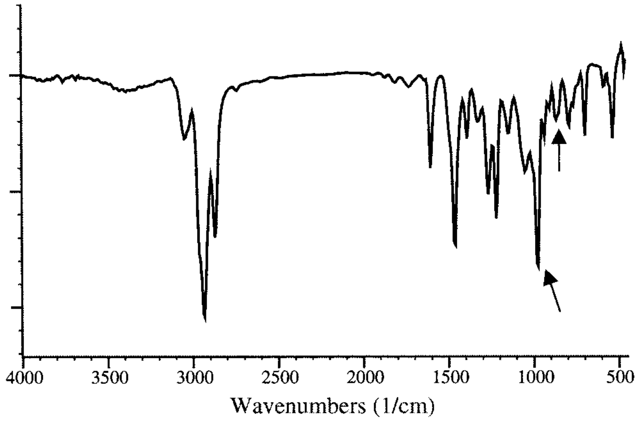

Figure 1. Infrared spectrum of **4b** in a KBr pellet. The vertical scale is transmittance in arbitrary units. The arrows mark the absorption for olefinic C$-$H out-of-plane deformation (*trans*-CH=CH at ~976 cm^{-1} and *cis*-CH=CH at ~872 cm^{-1}).

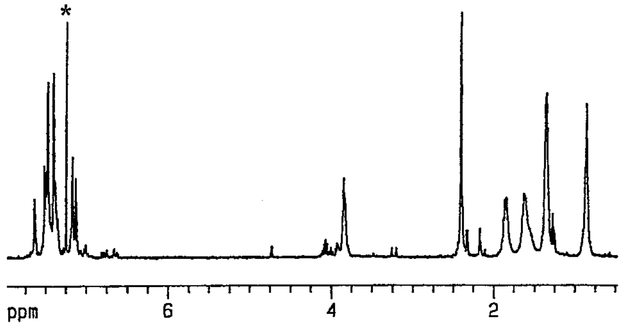

Figure 2. ^{1}H NMR of **4b**. The starred signal at 7.25 ppm is attributed to trace $CHCl_3$.

Table 1. Spectroscopic Data for Poly(*m*-Phenylenevinylene)s in THF

polymer	content (%) of *trans*-CH=CH[a]	UV–vis λ_{max} (nm)	fluor λ_{max} (nm)	peak width at half-height (nm)	ϕ_{fl}[b]
4a	87	306	421	73.9	0.40
4b	86	308	421	73.3	0.55
4c	91	307	408	71.3	0.53
5	87	299	402	61.4	0.68

[a] The *trans*-CH=CH content was estimated from the integration of $-OCH_2-$ signals in their ^{1}H NMR spectra. [b] The ϕ_{fl} values were averaged over three independent measurements. Both the sample and standard solutions were excited at 350 nm.

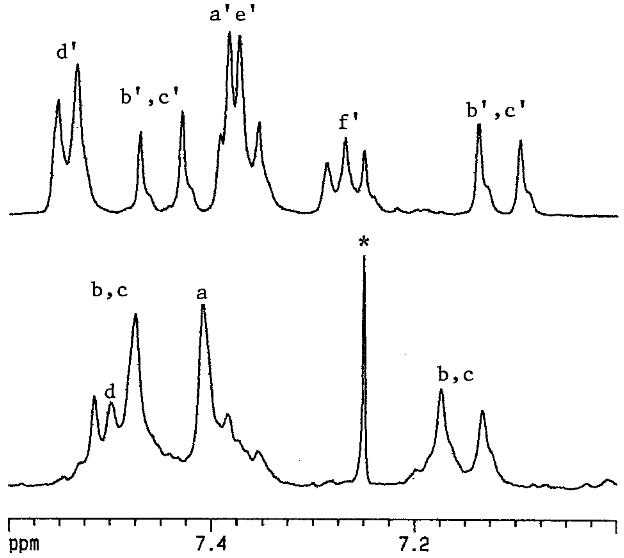

Figure 3. Comparison of ^{1}H NMR spectra for **4b** (bottom) and **5** (top). The starred signal at 7.25 ppm is attributed to trace $CHCl_3$. The peaks are assigned by using the same labels as in structures **4b** and **5** to indicate the positions for the corresponding protons.

The olefinic and aromatic region of the ^{1}H NMR spectra of **4** and **5** is shown in Figure 3 for comparison. The resonance signals were assigned by using the same labels as in the structures **4** and **5** to indicate the corresponding aromatic and olefinic protons. The presence of the doublet signals at about 7.11 and 7.45 ppm (marked b′ and c′ in Figure 3) with a large coupling constant (J = 16.5 Hz) further confirmed the *trans*-stereochemistry of CH=CH in **5**. This strong coupling pattern of *trans*-CH=CH was also observed in the polymer **4** as indicated by the doublet at about 7.15 ppm (marked b and c in Figure 3), although the other doublet at ~7.5 ppm was partially buried under the multiple signals. The relative signal intensity between the singlet

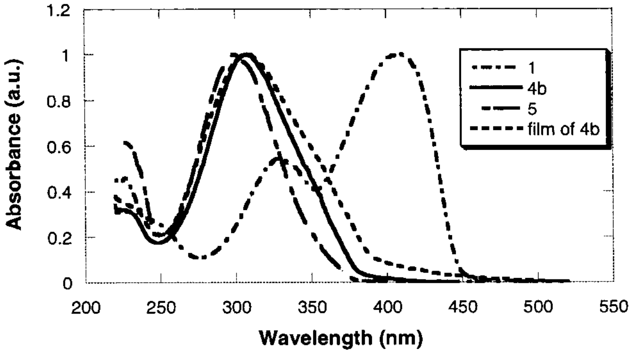

Figure 4. Normalized UV−vis absorption of **4b**, **5**, and **1** in THF solution. The curve marked “film of **4b**” was acquired from the film cast on a quartz plate.

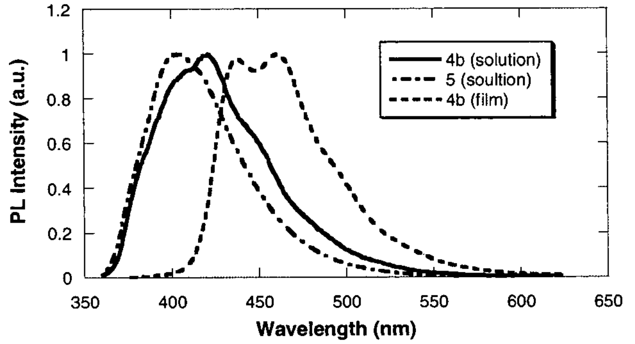

Figure 5. Photoluminescence (PL) spectra of **4b** and **5** in THF solution and **4b** film cast on a quartz substrate.

at ~7.41 ppm and the doublet at ~7.15 ppm was also consistent with the assumption that the majority of olefins in the polymer was in the *trans*-configuration.

Solution Photoabsorption and Photoluminescence (PL). The UV−vis absorption of **4** in dilute THF solutions (Figure 4) showed one major band with absorption $\lambda_{\max}$ at about 307 nm. The electronic band gap in **4** relative to **1** was significantly reduced (by about 97 nm), due to the replacement of the *p*-phenylene with an *m*-phenylene unit. In addition, the absorption band structure of **4** seemed to be simpler than that of **1**, with the latter exhibiting absorption maxima at about 328 and 404 nm. The absorption profiles and $\lambda_{\max}$ values of **4** were comparable to that of the model compound **5** (307 nm vs 299 nm), which had a similar *cis*/*trans*-olefin ratio as **4** (Table 1). The small difference (~8 nm) observed between the absorption $\lambda_{\max}$ values of **4b** and **5** is within the range of the expected substituent effect and indicates an effective conjugation interruption at *m*-phenylene.

The fluorescence spectra of **4** in THF solution are shown in Figure 5 with the emission $\lambda_{\max}$ centered near 410 nm. The emission peaks were quite narrow with a full width at half-maximum, fwhm, ≈ 70 nm, which was comparable to that of a block copolymer[5a] with an isolated emitting chromophore. The characteristic sharpness of the emission peak indicated that the emitting chromophore in **4** had a well-defined structure as a result of effective conjugation interruption at adjacent *m*-phenylene units. The very similar emission and absorption profiles of **4** and **5** further supported the assumption that the true chromophore in **4** had an electronic band structure as that in **5**. The fluorescence quantum efficiencies for **4** were estimated to be $\phi_{\mathrm{fl}} \approx 0.5$ (Table 1), and the length of the side chains showed a slight effect on the ϕ_{fl} values.

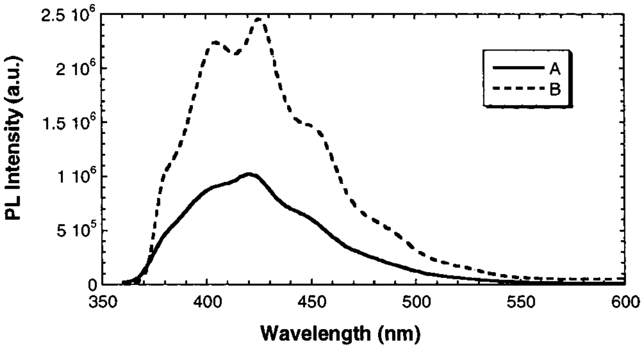

Figure 6. PL of **4b** at room temperature (A) and at −108 °C (B) in THF.

It was noted that the emission spectra of **4** in anhydrous THF solution at room temperature appeared to have some structures near the emission peak at 421 nm. By using liquid N_2, the polymer solutions were cooled to about −108 °C, at which temperature the polymer solution remained clear (at liquid state). The low-temperature fluorescence spectrum (Figure 6) showed that some shoulders in the room temperature spectrum were now resolved into peaks (emission $\lambda_{\max} = 405$ and 425 nm). These could be assigned to the 0−1 and 0−2 transitions if the shoulder near 385 nm was attributed to the 0−0 transition. In addition, the fluorescence intensity of **4** at low temperature[12] was significantly increased in comparison with that at room temperature, which was in agreement with its moderately high ϕ_{fl} values. The emission peaks were slightly red-shifted ($\Delta\lambda_{\max} \approx 4$ nm) at the low temperature. Emission at the low temperature typically occurs from a Franck−Condon state,[13] which is the nonrelaxed excited state. The observed red-shifted emission suggested that the polymer could adopt a more planar conformation at low temperature.

Thin-Film Optical Properties. Polymer films were prepared by spin-casting solutions onto quartz plates. UV−vis spectra of films of **4** were only slightly red-shifted relative to the solution spectra (~2 nm) with the absorption $\lambda_{\max} \approx 308$ nm. The solid-state PL spectra were acquired at room temperature with the films excited at 350 nm. As shown in Figure 5, the solid-state PL spectra of **4** were red-shifted (~30 nm) relative to the solution state spectra. In addition, the emission spectrum showed a vibrational structure with the emission $\lambda_{\max}$ at about 438 and 461 nm. This structured emission in the solid state could be an intrinsic property of the emitting chromophore in **4**, since the emission peak difference ($\Delta\lambda_{\max} \approx 23$ nm) of the film was very similar to that of the solution ($\Delta\lambda_{\max} \approx 20$ nm as measured at low temperature). Relative narrow peak widths in the solid-state PL spectrum, in comparison with its solution PL spectrum, were also in agreement with the confined emitting chromophore structure. The PL efficiency of **4b** was estimated to be about 0.29, by direct comparison with 9,10-diphenylanthracene[14] diluted in a PMMA film.

LED devices were fabricated using **4b** to examine the EL properties. The EL signal from a single layer device (ITO/**4b**/Ca) was weak. Therefore, poly(ethylene dioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) was sandwiched between ITO and the **4b** layers to improve hole injection and reduce turn-on voltage.[15] The double-layer device ITO/PEDOT/**4b**/Ca gives purple-blue emission at 445 and 462 nm with a turn-on voltage of ~5 V

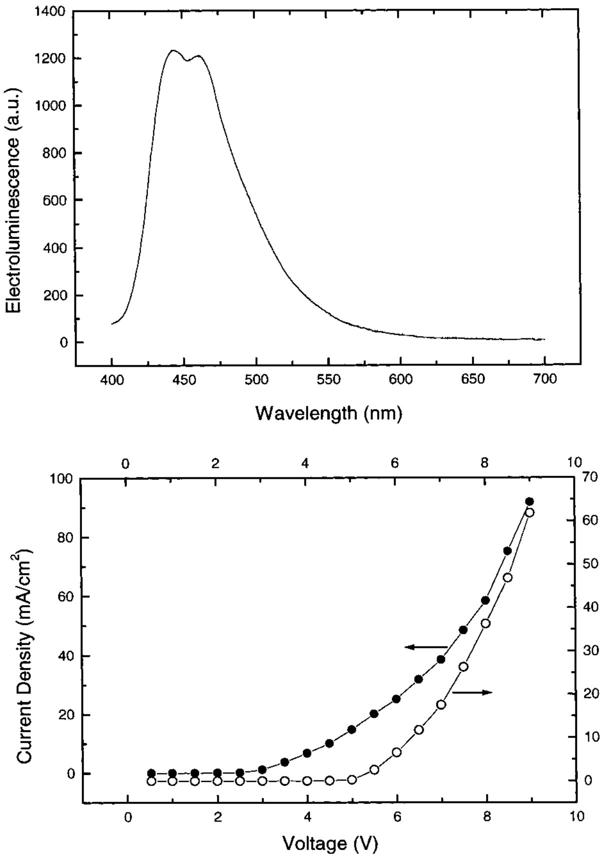

Figure 7. EL spectrum (top) and current density–voltage–brightness relationship (bottom) for the device ITO/PEDOT/**4b**/Ca.

(Figure 7). The external quantum efficiency of the device was estimated to be around 0.01%. The EL spectrum conforms very well with the PL spectrum, indicating that both EL and PL originate from the same radiative decay process of the singlet exciton.[16] Current studies are in progress to further improve the PL and EL properties of these polymers.

Experimental Section

Materials and Instrumentation. Isophthalaldehyde (99%), triethyl phosphite $P(OEt)_3$, 4-hydroxytoluene (Acros Organics), potassium *tert*-butoxide (1.0 M in THF), and hydrogen bromide (30 wt % solution in acetic acid) (Aldrich Chemical Co.) were used without further purification. Solvents were dried, distilled, and stored under nitrogen or argon. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer from films on NaCl plates. UV/vis spectra were recorded either in distilled dry tetrahydrofuran (THF) or from films spin-cast on quartz plates on a Beckman DU640 spectrophotometer at 23 °C. ^1H NMR spectra were acquired on a Bruker ARX400 spectrometer. Fluorescence spectra were recorded on a PTI steady-state fluorometer at 23 ± 1 °C. Corrected fluorescence spectra of the polymer films were recorded on quartz plates in air.

General Procedure for Preparation of 4-Alkoxytoluene. Williamson synthesis was used to prepare 4-alkyltoluene from 4-hydroxytoluene by a similar literature procedure.[17] Thus, a mixture of *p*-hydroxytoluene (100 mmol), 1-bromohexane (110 mmol), and potassium carbonate (110 mmol) in 2-butanone (75 mL) was heated to reflux under an argon atmosphere for 2 days. The K_2CO_3 residue was separated via filtration and then washed with two portions of acetone (50 mL each). The combined filtrate was evaporated under reduced pressure to give an oil residue. The residue was dissolved in hexanes (100 mL) and washed with six portions of 10 wt % NaOH aqueous solution (10 mL each). The organic layer was dried over $MgSO_4$. After removing solvent, the product, 4-hexyloxytoluene (**3b**), was obtained as a colorless oil in 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.90 (t, $J = 6.8$, 3H, $-CH_2CH_3$), 1.31–1.35 (m, 4H, $-CH_2-$), 1.43–1.47 (m, 2H, $-CH_2-$), 1.74–1.78 (m, 2H, $-CH_2-$), 2.28 (s, 3H, $Ar-CH_3$), 3.92 (t, $J = 6.6$, $-OCH_2-$), 6.79 (d, $J = 8.5$ Hz, 2H, $Ar-H$), 7.07 (d, $J = 8.5$ Hz, 2H, $Ar-H$).

Preparation of 3,5-Bis(bromomethyl)-4-alkoxytoluene. Bromomethylation of 4-alkoxytoluene was accomplished by using a literature procedure.[18] Thus, to a suspension of 4-hexyloxytoluene (7.69 g, 40 mmol) and paraformaldehyde (2.4 g, 80 mmol) in acetic acid (72 mL) was added hydrogen bromide (30 wt % in AcOH, 15.96 mL, 80 mmol) via a syringe under an argon atmosphere over a 15 min period. The mixture was then heated at 70–80 °C for 2 days. After cooling to room temperature, the reaction mixture was poured onto ice/water (100 mL) and extracted with four portions of hexanes (100 mL each). The combined organic layer was washed with water (twice, 30 mL each) and with 10% NaOH aqueous solution (four times, 4 mL each). The organic layer was then dried over $MgSO_4$. The solvents were removed under reduced pressure. After purification by column chromatography (silica gel, eluant: hexanes), 3,5-bis(bromomethyl)-4-hexyloxytoluene was obtained in 28% yield (4.23 g) as a white crystalline solid (mp 38–39 °C), which had the following spectral properties. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, $J = 7.1$, 3 H, $-CH_2CH_3$), 1.34–1.40 (m, 4H, CH_2), 1.52–1.57 (m, 2H, CH_2), 1.72–1.88 (m, 2H, CH_2), 2.28 (s, 3H, $ArCH_3$), 4.06 (t, $J = 6.6$, $-OCH_2$), 4.51 (s, 4H, $ArCH_2Br$), 7.16 (s, 2H, Ar–H). Anal. Calcd for $C_{15}H_{22}Br_2O$: C, 47.69; H, 5.86. Found: C, 48.67; H, 6.02.

3,5-Bis(bromomethyl)-4-butyloxytoluene was obtained as a white crystalline solid (mp 57–58 °C, yield 28%) and had the following spectral properties. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, $J = 7.4$ Hz, 3H, $-CH_2CH_3$), 1.55–1.63 (m, 2H, CH_2), 1.83–1.90 (m, 2H, CH_2), 2.29 (s, 3H, $Ar-CH_3$), 4.07 (t, $J = 6.6$ Hz, $-OCH_2-$), 4.51 (s, 4H, $ArCH_2Br$), 7.16 (s, 2H, Ar–H). Anal. Calcd for $C_{13}H_{18}Br_2O$: C, 44.60; H, 5.18. Found: C, 44.60; H, 5.22.

3,5-Bis(bromomethyl)-4-octyloxytoluene was obtained as a white crystalline solid (mp 34–35 °C, yield 27%). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, $J = 6.8$ Hz, 3H, $-CH_2CH_3$), 1.25–1.45 (m, 8H, CH_2), 1.45–1.59 (m, 2H, CH_2), 1.80–1.93 (m, 2H, CH_2), 2.29 (s, 3H, $Ar-CH_3$), 4.06 (t, $J = 6.6$ Hz, $-OCH_2-$), 4.51 (s, 4 H, $ArCH_2Br$), 7.16 (s, 2 H, Ar–H). Anal. Calcd for $C_{17}H_{26}Br_2O$: C, 50.27; H, 6.45. Found: C, 50.31; H, 6.53.

General Procedure for Synthesis of 4-Alkoxy-1-methyl-3,5-xylylene Tetraethyldiphosphonate (3). A mixture of 3,5-bis(bromomethyl)-4-hexyloxytoluene (0.756 g, 2.0 mmol) and triethyl phosphite (0.731 g, 4.40 mmol) was heated to 155–165 °C under an argon atmosphere for 3 h. The byproducts and excess triethyl phosphite were removed by vacuum (0.5 mmHg at 100 °C for 0.5–1 h) to give 4-hexyloxy-1-methyl-3,5-xylylene tetraethyldiphosphonate (**3b**) as a colorless oil (0.97 g, quantitative yield), which had the following spectral properties. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, $J = 3.5$ Hz, 3H, $-CH_3$), 1.23 (t, $J = 7.1$, 12H, $-OCH_2CH_3$), 1.29–1.35 (m, 4H, $-CH_2-$), 1.40–1.51 (m, 2H, CH_2), 1.70–1.81 (m, 2H, CH_2), 2.24 (s, 3H, $Ar-CH_3$), 3.15 (d, $J = 22.1$, 4H, $Ar-CH_2-P$), 3.80 (t, $J = 6.6$, 2H, $-OCH_2-$), 3.97–4.06 (quintet, $^3J_{HH} = {}^3J_{PH} = 7.2$ Hz, 8H, $-P-OCH_2CH_3$), 7.13 (s, 2H, Ar–H). IR (NaCl) ν_{max} (cm^{-1}): 2980 (m), 2957 (m), 2929 (m), 2862 (w), 1473 (m), 1391 (w), 1252 (s), 1163 (w), 1055 (s, ROP=O), 1028 (s, ROP=O), 959 (s, ROP=O), 779 (w).

4-Butyloxy-1-methyl-3,5-xylylene tetraethyldiphosphonate (**3a**) had the following spectral properties. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, $J = 7.4$ Hz, 3H, $-CH_2CH_3$), 1.15–1.27 (m, 12H, OCH_2CH_3), 1.45–1.57 (m, 2H, CH_2), 1.74–1.81 (m, 2H, CH_2), 2.25 (s, 3H, $ArCH_3$), 3.16 (d, $J = 22.1$ Hz, 4H, $ArCH_2P$), 3.82 (t, $J = 6.6$ Hz, 2H, OCH_2), 3.90–4.15 (quintet, $^3J_{HH} = {}^3J_{PH} = 7.2$ Hz, 8H, $-P-OCH_2CH_3$), 7.14 (s, 2H, Ar–H). IR (NaCl) ν_{max} (cm^{-1}): 2980 (m), 2932 (m), 2872 (w), 1474 (m), 1391 (w), 1250 (s), 1163 (w), 1055 (s, ROP=O), 1028 (s, ROP=O), 959 (s, ROP=O), 779 (w).

1-Methyl-4-Octyloxy-3,5-xylylene tetraethyldiphosphonate (**3c**) had the following spectral properties. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.87 (t, $J = 6.9$ Hz, 3H, $-CH_2CH_3$), 1.20−1.34 (m, 20H, CH_2, and $-CH_2CH_3$), 1.43−1.51 (m, 2H, CH_2), 1.72−1.82 (m, 2H, CH_2), 2.25 (s, 3H, ArCH_3), 3.16 (d, $J = 22.0$ Hz, 4H, ArCH_2P), 3.80 (t, $J = 6.6$ Hz, 2H, $-OCH_2CH_2-$), 3.97−4.25 (quintet, $^3J_{HH} = {^3J_{PH}} = 7.2$ Hz, 8H, $-P-OCH_2CH_3$), 7.13 (s, 2H, Ar−H). IR (NaCl) ν_{max} (cm^{-1}): 2980 (m), 2930 (m), 2858 (w), 1474 (m), 1393 (w), 1252 (s), 1163 (w), 1097 (w), 1057 (s, ROP═O), 1028 (s, ROP═O), 959 (s, ROP═O), 779 (w).

Synthesis of Poly[(1-hexyloxy-4-methyl-2,6-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] (4b). A mixture of 4-hexyloxy-1-methyl-3,5-xylylene tetraethyl diphosphonate (**3b**) (0.492 g, 1.0 mmol) and isophthaladehyde (0.134 g, 1.0 mmol) were dissolved in anhydrous THF (20 mL) in a round-bottomed oven-dried flask, which was equipped with a magnetic stirring bar and capped with a rubber septum. The reaction mixture was cooled to ~5 °C by an ice/water bath, and potassium *tert*-butoxide solution (1.0 M in THF, 2 mL, 2.0 mmol) was added dropwise via a syringe over a 15 min period under an argon atmosphere. The mixture was then stirred at ~5 °C for 2 h. The resulting polymer was precipitated out from MeOH (100 mL). The polymer precipitate was then subjected to Soxhlet extraction with methanol for 48 h. After drying under full vacuum (~0.01 Torr), a white polymer resin (**4b**) was obtained (0.21 g) in 66% yield. The integration and peak assignments of ^{1}H NMR (400 MHz, CDCl$_3$) of **4b** are listed as follows: δ 0.82−0.89 (3H, $-CH_3$), 1.31−1.39 (4H, $-CH_2-$), 1.50−1.70 (2H, $-CH_2-$), 1.72−1.90 (2H, $-CH_2-$), 2.41 (s, 3H, Ar−CH_3), 3.78−3.85 (1.73H, $-OCH_2-$ in *trans*-olefin fragment), 3.85−3.96 (0.27 H, $-OCH_2-$ in *cis*-olefin fragment), 7.13−7.64 (m, 10H, aromatic and olefinic). IR (NaCl, thin film) ν_{max} (cm^{-1}): 3040 (w), 2925 (s), 2863 (m), 1597 (m), 1450 (m), 1258 (m), 1212 (m), 972 (m). Based on the gel permeation chromatograph (GPC) analysis in THF solvent, the polymer exhibited a monomodel distribution with a weight-average molecular weight $M_w \approx 8453$ (PDI $\approx$ 2.1) in relative to polystyrene standard. This corresponds to a number-average degree of polymerization (DP), $n \approx 13$, which is smaller than that estimated from the end group analysis. The large difference between the DP values could be partially attributed to the integration error for the small ^{1}H NMR signals. Anal. Calcd for $C_{23}H_{26}O$: C, 86.75; H, 8.23. Found: C, 85.72; H, 8.24.

Poly[(1-butyloxy-4-methyl-2,6-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] (4a) was obtained as a white solid in 47% yield. ^{1}H NMR (CDCl$_3$) δ: 0.97−1.07 (m, 3H, $-CH_2CH_3$), 1.54−1.70 (m, 2H, $-CH_2-$), 1.81−1.88 (m, 2H, $-CH_2-$), 2.41 (s, 3H, Ar−CH_3), 3.77−3.90 (m, 1.73H, $-OCH_2-$ in *trans*-olefin fragment), 3.90−3.98 (m, 0.27H, $-OCH_2-$ in *cis*-olefin fragment), 7.03−7.70 (m, 10H, aromatic and olefinic). IR (NaCl, thin film) ν_{max} (cm^{-1}): 3033 (w), 2956 (s), 2925 (s), 2863 (m), 1698 (vw), 1598 (m), 1451 (s), 1381 (w), 1258 (m), 1212 (m), 1027 (w), 965 (s), 780 (w), 687 (w). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 85.84; H, 7.66.

Poly[(1-octyloxy-4-methyl-2,6-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] (4c) was obtained as a white solid in 60% yield. ^{1}H NMR (CDCl$_3$) δ: 0.77−0.86 (m, 3H, $-CH_2CH_3$), 1.11−1.34 (m, 6H, CH_2), 1.56−1.71 (m, 4H, $-CH_2-$), 1.82−1.86 (m, 2H, $-CH_2-$), 2.40 (s, 3H, Ar−CH_3), 3.85−3.95 (m, 1.82 H, $-OCH_2-$ in *trans*-olefin fragment), 3.85−3.95 (m, 0.18H, $-OCH_2-$ in *cis*-olefin fragment), 7.06−7.15 (m, 2H, $-CH{=}CH-$), 7.35−7.65 (m, 8H, aromatic and olefinic). IR (NaCl, thin film) ν_{max} (cm^{-1}): 3033 (vw), 2925 (s), 2855 (m), 1598 (w), 1458 (m), 1258 (m), 1212 (m), 1026 (w), 965 (m), 895 (vw), 856 (vw). Anal. Calcd for $C_{25}H_{30}O$: C, 86.66; H, 8.73. Found: C, 83.95; H, 8.80.

3,5-Distyryl-4-hexyloxytoluene (**5**) was synthesized from **3b** (0.493 g, 0.70 mmol) and benzaldehyde (1.40 g, 1.40 mmol) by using the same procedure for **4**. After purification on a column chromatography (silica gel, eluant: AcOEt:hexanes (3/97 v/v), **5** was obtained in 95% yield. ^{1}H NMR (CDCl$_3$) δ: 0.90 (t, $J = 6.8$ Hz, 3H, $-CH_2CH_3$), 1.34−1.38 (m, 4H, CH_2), 1.55−1.65 (m, 2H, $-CH_2-$), 1.80−1.87 (m, 2H, $-CH_2-$), 2.16 (s, 0.25H, Ar−CH_3, *cis/cis* and *cis/trans* olefin fragment), 2.39 (s, 2.75 H, Ar−CH_3, *trans/trans* olefin fragment), 3.82 (t, $J = 6.2$ Hz, 1.83H, OCH_2, *trans/trans* olefin fragment), 3.89 (t, $J = 6.2$ Hz, 0.166H, OCH_2, *cis/cis* olefin fragment), 7.11 (d, $J = 16.5$ Hz, 2H, *trans*-CH═CH), 7.27 (t, $J = 7.4$ Hz, 2H, Ar−H), 7.37 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.4$ Hz, 4H, Ar−H), 7.38 (s, 2H), 7.45 (d, $J = 16.5$ Hz, 2H, *trans*-CH═CH), 7.54 (d, $J = 7.6$ Hz, 4H, Ar−H). Anal. Calcd for $C_{29}H_{32}O$: C, 87.83; H, 8.13. Found: C, 87.95; H, 8.20.

Photoluminescence and Quantum Yield Measurements. The solution PL quantum yields were measured in dilute THF solution by using the literature procedure[19,20] as described previously. The solutions were freshly prepared by dissolving the polymer in anhydrous THF. Absorbance of the sample solutions was kept below 0.05 to avoid inner filter effect. The samples were deoxygenated by bubbling argon through the solutions. Measurements were performed at room temperature, while both sample and quinine sulfate solutions were excited at the same wavelength (350 nm) to avoid possible error caused by neglecting the difference between the excitation light intensities of different wavelengths. The quantum yield for quinine sulfate[19] was assumed to be 0.577 when excited at 350 nm.

The polymer films for solid-state PL measurement were prepared on quartz substrates by using a spin coater (model P6204) (Speciality Coating System, Inc). Film thickness was controlled by polymer solution concentration (~2 mg/mL in THF) and spinning rate (~1700 rpm). The reference film, 9,-10-diphenylanthracene in PMMA (~1 wt %), was obtained by dissolving them in toluene and then casting into film. The absorbance for polymer and reference films at 350 nm were 0.062 and 0.058, respectively. The PL efficiency[14] of the reference film was assumed to be 0.83. The PL spectra for the reference and sample films were taken with excitation at 350 nm. Emission were detected at 90° from the incident beam by the front face fluorescence method with the sample placed at an angle of about 45° to both incident beam and detector.

LED Fabrication and Measurement. PEDOT/PSS (Bayer Co.) was spin-cast onto ITO glass (OFC Co.) to be used as an anode. The polymer solutions (20 mg/mL in chloroform) were filtered through 0.2 μm Millex-FGS Filters (Millipore Co.) and were spin-cast onto ITO glass or dried PEDOT/ITO substrates under a nitrogen atmosphere. The polymer films were typically 75 nm thick. Calcium electrodes of 400 nm thickness were evaporated onto the polymer films at about 10^{-7} Torr, followed by a protective coating of aluminum. The devices were characterized using a system constructed in our laboratory described elsewhere.[21]

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