Synthesis, Characterization and Luminescence of Poly[(*m*-phenylenevinylene)-*alt*-(1,4-dibutoxy-2,5-phenylenevinylene)] with Different Content of *cis*- and *trans*-Olefins

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Received February 8, 2001; Revised Manuscript Received June 22, 2001

ABSTRACT: Soluble poly[(*m*-phenylenevinylene)-*alt*-(1,4-dibutoxy-2,5-phenylenevinylene)]s were synthesized via Wittig and Wittig−Horner reactions. The contents of *trans*-CH═CH linkages in the polymers were estimated to be either ~35% or ~88%, depending on the polymerization method used. Due to the large difference in the *cis*-/*trans*-olefin ratio, polymers **3** (cis-enriched) and **8** (trans-enriched) exhibited noticeable difference in their UV−vis spectra ($\Delta\lambda_{max} \approx 19$ nm) in THF solution. Their emission spectra, however, were essentially the same with the fluorescence λ_{em} at ~445 nm and a shoulder at ~471 nm. The shoulder in the emission spectra was resolved into a pronounced peak at low temperature. The low temperature emission spectra were also slightly red-shifted (~7 nm) in comparison with their room-temperature spectra. Despite their comparable solution ϕ_{fl} values, a film of **3** emitted much stronger fluorescence than did its isomer **8**.

Introduction

π-Conjugated polymers with band gaps in the visible region such as poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted much 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 placing 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. Introducing *cis*-olefin linkages[8] in the PPV backbone interrupts conjugation length and is known to interfere with the packing in the solid state, thereby providing an amorphous PPV and enhancing its luminescence efficiency. The poor solubility of PPV, however, hampers an accurate estimation of the relative contents of *cis*-/*trans*-vinylene in this polymer.

Our recent study has shown that the presence of the *m*-phenylene unit[6b] along the PPV chain effectively interrupts π-conjugation, thereby tuning the emission color in a predictable manner. In addition, poly[(*m*-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)]s exhibit good solubility and high luminescence in both solution and solid states. To further improve the luminescent properties of the material, it appears necessary to systematically examine the effect of *cis*-/*trans*-vinylene. Synthesis via a Wittig reaction yields poly[(*m*-phenylenevinylene)-*alt*-(1,4-dibutoxy-2,5-phenylenevinylene)], **3**, with predominant *cis*-vinylene linkages. Although polymer **4** with *trans*-vinylene linkages can be obtained by refluxing the toluene solution of **3** in the presence of a catalytic amount of iodine, the polymer thus obtained may be contaminated by iodine, which is known to decrease the photoluminescence (PL) quantum yield[9] via the so-called “heavy-atom” effect. Thus, iodine-free polymers with different contents of the *cis*-/*trans*-vinylene are required to evaluate the effects of the *cis*-/*trans*-vinylene ratio on the physical properties. In this report, poly[(*m*-phenylenevinylene)-*alt*-(1,4-dibutoxy-2,5-phenylenevinylene)] **8** with *trans*-vinylene configuration was synthesized independently via the Wittig−Horner reaction, which provides iodine-free samples for PL and electroluminescence (EL) property studies.

Results and Discussion

Polymer Synthesis and Characterization. Polymers **3** and **4** were synthesized at room temperature according to the procedure[6b] reported previously (see Scheme 1). Polymer **8** (iodine-free) was obtained by using the Wittig−Horner reaction,[10] which is known to generate a *trans*-alkene structure. Thus, polymerization of 2,5-dibutoxy-1,4-xylene tetraethyl diphosphonate **7** with isophthaldehyde **2** in anhydrous tetrahydrofuran (THF) in the presence of potassium *tert*-butoxide provided polymer **8** in 63% yield. Polymers **3**, **4**, and **8** were yellow solids, which were quite soluble in common organic solvents such as toluene, THF, and chloroform. Thin films could be easily cast from their solutions. The molecular weight of **8** appeared to be higher than that of **3**, on the basis of ^{1}H NMR (fewer aldehyde end groups) and IR (carbonyl stretch at ~1700 cm^{-1}) analysis. The higher molecular weight could be partially attributed to the use of a better solvent system (higher THF content) in the Wittig−Horner reaction. Polymerization at room temperature occasionally led to partially soluble products. Lowering the polymerization temperature to about ~5 °C, however, gave reproducible results.

The high ratio of *trans*-CH═CH (~970 cm $^{-1}$) to *cis*-CH═CH (~873 cm^{-1}) in the IR spectrum of **8** (Figure 1) showed that the polymer contained predominantly

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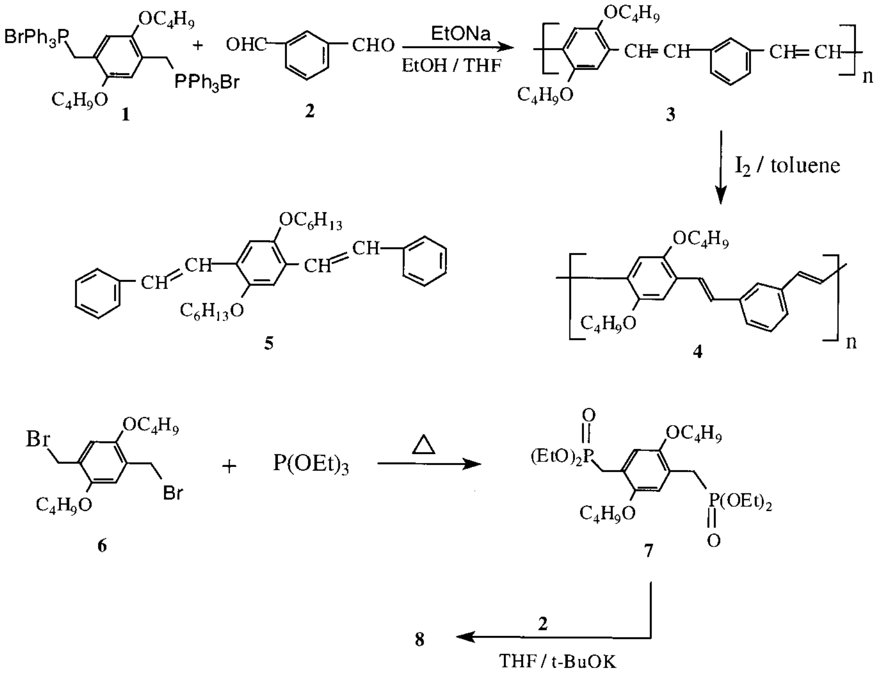
Scheme 1



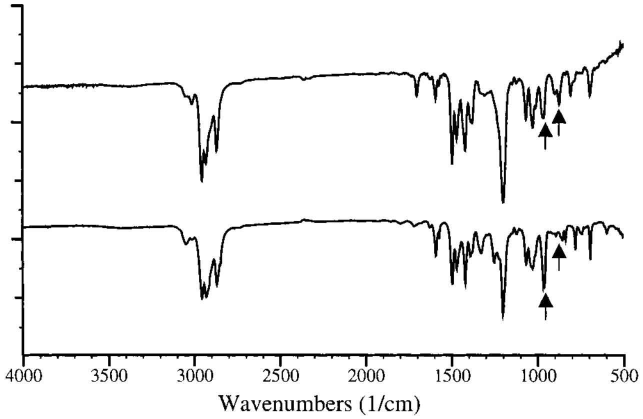


Figure 1. IR spectra of polymer films **8** (bottom, trans) and **3** (top, cis/trans) cast on NaCl disks. The vertical scale is transmittance in arbitrary units. The arrows mark the absorption of the olefinic C−H out-of-plane deformation (the *cis*-CH=CH at ~873 cm^{-1} and the *trans*-CH=CH at ~970 cm^{-1}).

trans-olefin groups. In comparison with **3**, polymer **8** showed a much simplified ^{1}H NMR spectrum (Figure 2), indicating a more regular structure for the latter. It was shown previously that the proton resonance signals of the −OCH$_2$− unit in alkoxy side chains[6b] were quite sensitive to the *cis*-CH=CH or *trans*-CH=CH configuration in poly[(*m*-phenylenevinylene)-*alt*-(1,4-dialkoxy-2,5-phenylenevinylene)]s. Clear separation between the two resonance signals near 4.0 and 3.5 ppm offered a convenient way to accurately estimate the relative *cis*-/*trans*-CH=CH contents in each polymer; these results are summarized in Table 1. Molecular weights of polymers were calculated from the integration of ^{1}H NMR signals for terminal groups (−CHO at ~9.9 ppm or Ar−CH$_2$−PO(OEt)$_2$ at ~3.2 ppm) and −OCH$_2$− units. The number-average degrees of polymerization were estimated to be $n \approx 42$ for **3** and $n \approx 73$ for **8**, respectively. The smaller amount of the end groups in **8** (both aldehyde and diethyl phosphonate) observed in the infrared spectra (Figure 1) was consistent with its higher molecular weight. Gel permeation chromatography (GPC) analysis results in THF showed monomodel distribution for both polymers, with Mw = 10 007 (PDI ≈ 2.5) for **3** and Mw = 11 589 (PDI ≈ 2.1) for **8**, respectively (relative to polystyrene standard).

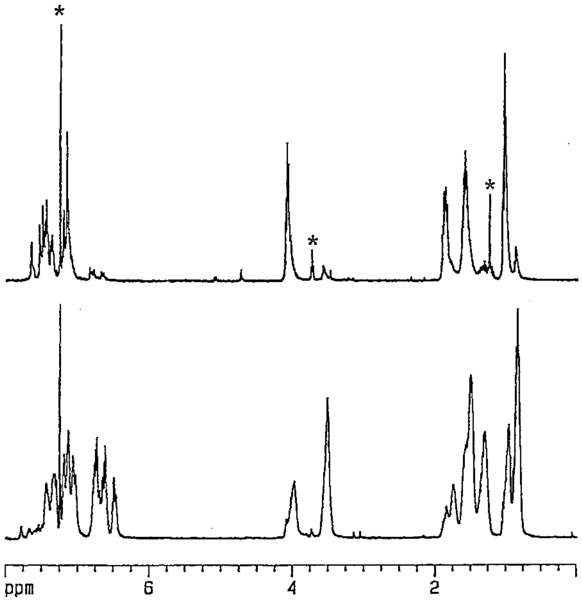


Figure 2. ^{1}H NMR of **8** (top) and **3** (bottom). The starred signals at 7.25, 3.74, and 1.25 ppm are attributed to trace CHCl$_3$, THF, and *tert*-butanol, respectively.

Photoabsorption and Photoluminescence of Solutions. UV−vis absorption and fluorescence spectra were acquired in THF dilute solution under equivalent conditions for comparison. Polymer **8** exhibited a slightly longer conjugation length than **3** (Figure 3), with the optical absorption λ_{max} equal to 404 nm for the former and 385 nm for the latter. Despite their noticeable difference (~19 nm) in the UV−vis absorption λ_{max}, polymers **3** and **8** showed nearly identical emission spectra with the emission peaks at $\lambda_{max} \approx 445$ and 471 nm. The remarkable similarity in their emission profiles indicated the possible existence of the same emitting

Table 1. Spectroscopic Data for *m*-Phenylene-Containing PPVs in THF

polymer or oligomer	content of *trans*-CH=CH[a] (%)	UV–vis λ_{max} (nm)	fluorescence λ_{em} (nm)	excitation λ_{max} (nm)	ϕ_{fl}[b]
3	35	325, 385	446, 474	398	0.63
4	91	328, 402	444, 469	398	0.64
5	99	325, 388	437	390	0.61
8	88	328, 404	445, 471	398	0.64

[a] The *trans*-CH=CH content was estimated from the integration of $-OCH_2-$ signals in the ^{1}H NMR. [b] The ϕ_{fl} values listed here were averaged from over three independent measurements. Both the sample and standard solutions were excited at 366 nm during the measurements.

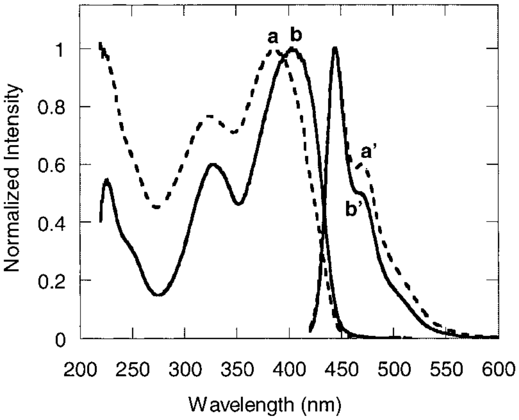


Figure 3. UV–vis (a and b) and PL (a′ and b′) spectra of polymers **3** and **8**, respectively, in THF solution. The spectra are normalized for comparison.

chromophore in **3** and **8**. This could be rationalized by considering an intramolecular energy migration from a higher (*cis*-olefin-containing chain fragment) to a lower (*trans*-olefin-containing fragment) band gap chromophore through the shared *m*-phenylene moiety.[6b] The emission peak width of **8** was narrower than that of **3**, partially attributed to the more uniform molecular structure along the polymer backbone in the former (predominantly *trans*-olefin). The fluorescence quantum efficiencies of **3**, **4**, **5**, and **8** were estimated, using the same experimental conditions. The results for **4** and **8** gave nearly the same ϕ_{fl} value, showing a negligible effect on the sample fluorescence intensity by iodine treatment. The ϕ_{fl} value of **8** was also comparable with that of **3**,[11] indicating a weak dependence of ϕ_{fl} on the relative content of *cis*-/*trans*-olefins along the polymer chains.

To examine the temperature effect on the emission characteristics of **3** and **8**, the polymer solutions were cooled by gradually pouring liquid nitrogen on the sample solutions and the spectra were acquired at the low temperature (−195 °C). As shown in Figure 4, the emission intensity was drastically increased at the low temperature, which is consistent[12] with its moderate ϕ_{fl} value at room temperature. The shoulder at $\lambda_{max} \approx 471$ nm was clearly resolved into a pronounced peak at low temperature, due to the reduced rotation in the frozen rigid media. In addition, the low-temperature emission spectra were slightly red-shifted with the emission maxima λ_{em} at 452 and 480 nm ($\sim$7 nm red-shifted). Emission at low temperature (about −195 °C) typically occurs from the Franck–Condon state,[13] which is the nonrelaxed excited state and permits a clearer correlation of fluorescence spectra with molecular structures.

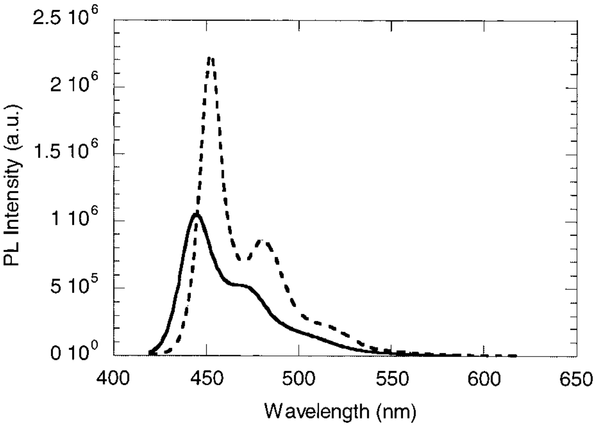


Figure 4. PL spectra of **8** in THF at room temperature (solid line) and at liquid nitrogen temperature (dotted line).

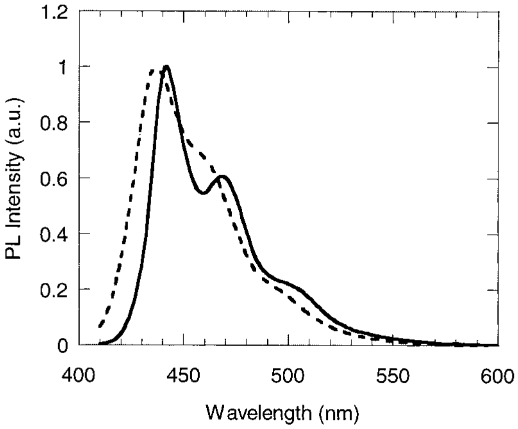


Figure 5. Normalized PL of **5** in THF at room temperature (dotted line) and low temperature (liquid nitrogen, solid line).

To confirm the trend observed in the polymers, the PL of the model compound **5** was measured at low temperature (Figure 5). In addition to the better resolved spectrum and higher emission intensity, a similar red-shift was observed at low temperature with the emission maxima λ_{em} at 443 and 470 nm ($\sim$7 nm red-shifted relative to the spectra at room temperature). This further revealed the structural similarity between **5** and **8**. A blue-shift[13,14] in the emission, however, would be typically expected from a Franck–Condon state, which had a higher energy than the solvent-relaxed state. The observed red-shifted emission spectra from **5** and **8** suggested that the molecules adopt a more planar conformation at the low temperature than that at room temperature. The spectroscopic red-shift[15] arising from the more planar conformation appeared to be larger than the blue-shift from the nonrelaxed excited state at the low temperature.

Thin Film Optical Properties. Polymer films **3** and **8** were prepared by spin-casting their solutions ($\sim$2 mg/mL concentration) onto quartz plates under the same experimental conditions. UV–vis spectra of the films (Figure 6) showed that both films had similar absorption characteristics. The absorption λ_{max} of **8** was slightly red-shifted ($\sim$28 nm) relative to that of **3**, due to the better conjugation permitted across *trans*-olefin bonds. In comparison with the corresponding solution spectra, film **3** showed nearly the same absorption λ_{max} at 324 and 384 nm, while polymer **8** exhibited about 8 nm red-shifted λ_{max} at 332 and 412 nm.

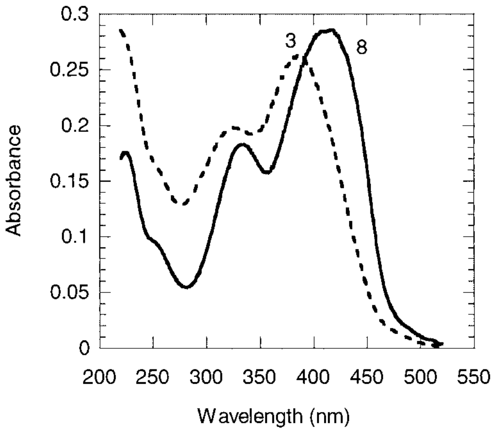


Figure 6. UV–vis spectra of polymer thin films **3** (dotted line, λ_{max} = 324 and 384 nm) and **8** (solid line, λ_{max} = 332 and 412 nm) on quartz plates.

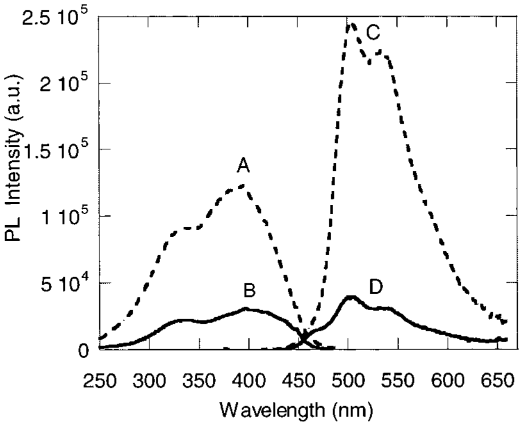


Figure 7. Excitation and emission spectra (monitored at 500 nm) of films **3** (curves A and C) and **8** (curves B and D) on quartz substrates. The emission spectra were acquired while the samples were excited at 366 nm.

The photoluminescence spectra of films **3** and **8** were very similar (Figure 7), despite the noticeable difference ($\Delta\lambda_{max} \approx$ 28 nm) in their UV–vis absorption spectra. This is likely to be due to the energy migration from a *cis*-olefin-containing fragment (high band gap chromophore) to an adjacent *trans*-olefin-containing fragment (low band gap chromopore), yielding only emission from the latter. Under the identical conditions, the PL intensity of **3** was found to be constantly higher than that of **8**, although the magnitude depended on the excitation wavelength used (about 4.4 and 5.3 times higher when both films were excited at 395 and 366 nm, respectively). The significant difference in the solid-state PL intensities is likely to be due to a higher degree of disorder in the solid-state packing of **3**, since both **3** and **8** had very similar fluorescence efficiencies in solutions. Polymers **3**, **4**, and **8** were EL active in single-layer devices (Figure 8). The emission peak width from **8** was slightly narrower than that of **3**, possibly due to the more uniform emission chromophores in the former. In comparison with that of **8**, the emission spectrum of **4** was not only broader but also slightly red-shifted, indicating the possible existence of some optical impurities introduced during the iodine-catalyzed isomerization step. A detailed study is in progress to correlate the EL characteristics with polymer chain microstructures (content of *cis*-/*trans*-olefins).

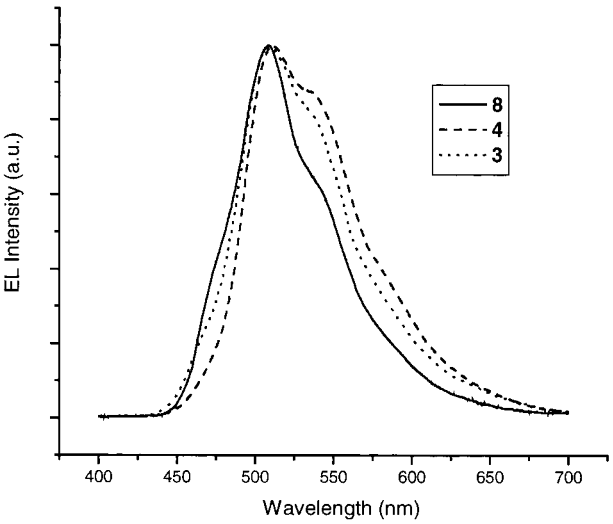


Figure 8. EL spectra of polymers **3** (cis/trans mixture), **4**, and **8** (trans) from a single-layer device (ITO/polym}er/Ca configuration).

Experimental Section

Materials and Instrumentation. Isophthalaldehyde (99%) and triethyl phosphite $P(OEt)_3$ (Acros Organics), and triphenylphosphine (PPh_3), potassium *tert*-butoxide (1.0 M in THF), and anhydrous ethanol (Aldrich Chemical Co.) were used without further purification. Sodium ethoxide was freshly prepared prior to use from sodium metal and anhydrous ethanol. 1,4-Bis(bromomethyl)-2,5-dibutoxybenzene (**6**) was synthesized according to the literature procedure.[16] 1,4-Distyryl-2,5-dihexyloxybenzene[6b] (**5**) was prepared as reported previously. 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 THF or from films spin-cast on quartz plates on a Beckman DU640 spectrophotometer at 23 °C. ^{1}H NMR spectra were acquired on a Bruker ARX400 spectrometer. Fluorescence spectra were recorded on a PTI steady-state fluorometer at 23 ± 1 °C. Fluorescence spectra of polymer films were recorded on quartz plates in air. The emission spectra were corrected.

Synthesis of 2,5-Dibutoxy-1,4-bis(diethoxyphosphorylmethyl)benzene (7).[17] A mixture of 1,4-bis(bromomethyl)-2,5-dibutoxybenzene (1.43 g, 3.50 mmol) and triethyl phosphite (1.32 mL, 1.28 g, 7.7 mmol) under an argon atmosphere was heated to 160–170 °C for 3 h. The excess triethyl phosphite and by-products were removed by vacuum (0.5 mmHg, at 100 °C for 0.5 h) to give product **7** as a colorless oil in quantitative yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (t, J = 7.4 Hz, 6H, $-CH_3$), 1.18–1.25 (m, 12 H, $-CH_3$), 1.40–1.50 (m, 4H, $-CH_2-$), 1.69–1.75 (m, 4H, $-CH_2-$), 3.21 (d, J = 20.2 Hz, 4 H, Ar$-CH_2-P$), 3.85–3.92 (t, J = 6.4 Hz, 4H, $-OCH_2-$), 3.97–4.03 (m, 8H, $-OCH_2-$), 6.89 (s, 2H, Ar–H). Anal. Calcd for $C_{24}H_{44}O_8P_2$: C, 55.16; H, 8.49. Found: C, 54.78; H, 8.46.

Poly[(2,5-dibutoxy-1,4-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] (8). 2,5-Dibutoxy-1,4-bis(diethoxyphosphorylmethyl)benzene **7** (0.523 g, 1.0 mmol) and isophthaldehyde **2** (0.1349, 1.0 mmol) were dissolved in dry THF (20 mL) in a 50 mL oven-dried round-bottomed flask, which was equipped with a magnetic stirring bar and capped with a rubber septum. After the solution was cooled to ~5 °C by an ice–water bath, potassium *tert*-butoxide (1.0 M in THF, 1 mL, 1 mmol) was added dropwise via a syringe under an argon atmosphere. When potassium *tert*-butoxide solution was added, a pink-red color formed locally and disappeared quickly as the reaction proceeded. At the end, no pink-red color was formed with addition of potassium *tert*-butoxide. The reaction mixture was stirred at ~5 °C for 1 h and at room temp for 2 h. The polymer was precipitated out by adding the product solution to methanol (150 mL). After drying under full vacuum (0.01 Torr), a yellow polymer was obtained (0.218 g) in 63% yield, mp 252−256 °C. Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.05; H, 8.00. UV (λ_{max}, THF): 336 nm, 412 nm. FT-IR (film on NaCl plate, cm^{-1}): 600 (w), 694 (m), 743 (w), 781 (m), 838 (w), 858 (w), 968 (s), 1032 (m), 1069 (m), 1204 (s), 1256 (m), 1333 (w), 1393 (m), 1422 (s), 1472 (m), 1499 (s), 1593 (m), 2872 (s), 2934 (s), 2957 (s), 3055 (w). ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.95−1.10 (6H, $-CH_3$), 1.51−1.68 (4H, CH_2), 1.81−1.93 (4H, CH_2), 3.43−3.52 (br, 0.49 H, $-OCH_2-$ (in *cis*-olefin fragment)), 3.98−4.14 (br, 3.51 H, $-OCH_2-$ (in *trans*-olefin fragment)), 7.06−7.25 (m, 3H, Ar−H), 7.27−7.60 (m, 3H, Ar−H).

Photoluminescence and Quantum Yield Measurements. The solution PL quantum yields were measured in dilute THF solution by using the literature procedure[18,19] as described previously. The solutions for the measurement were freshly prepared by dissolving the polymer into 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 their solutions. Measurements were performed at room temperature, while both sample and quinine sulfate solutions were excited at the same wavelength (366 nm) to avoid possible error caused by neglecting the difference between the excitation light intensities of different wavelengths. The quantum yield for quinine sulfate was assumed to be 0.53 when excited at 366 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 (∼1800 rpm). The relative PL quantum yields of 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 indices for the polymer films. Here, ϕ_r, A_r, and F_r are quantum efficiency, absorbance at excitation wavelength, and emission integration area for the reference while A_s and F_s are absorbance and emission integration for the sample film. The PL spectra for the reference and samples were taken with excitation at 366 nm. Emissions 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. The EL spectra were obtained from devices fabricated as previously described.[20]

Acknowledgment. Support of this work has been provided by AFOSR (Grant No. F49620-00-1-0090) and by NIH/NIGMS/MBRS/SCORE (Grant No. S06GM-08247). We thank a referee for helpful suggestions.

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MA010232Y