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A Highly Luminescent Poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] with Defined Conjugation Length and Improved Solubility

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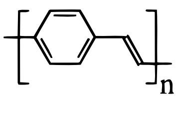
ABSTRACT: A derivative of poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (**7**) has been synthesized via the standard Wittig condensation to investigate the effects of *m*-phenylene on the physical properties of PPVs. The polymer synthesized has a molecular weight of about 20 000, corresponding to a number-average degree of polymerization of about 41. A model compound, 1,4-distyryl-2,5-dihexyloxybenzene (**9**), has also been synthesized to evaluate the effectiveness of π-conjugation interruption at *m*-phenylene. Comparison of photoabsorption and emission characteristics between **7** and **9** indicates that the presence of *m*-phenylene effectively interrupts the conjugation in PPV, allowing precise color control in the fully π-conjugated polymers. ^{1}H NMR is found to be a convenient tool to characterize the *cis/trans*-olefins in the polymer. The PL quantum yield of **7** is quite high in both solution and solid states (0.6−0.8), suggesting potential applications of the material in various electrooptical devices.

Introduction

Following the first report[1] to use poly(*p*-phenylenevinylene) (PPV, **1**) in light-emitting diodes (LEDs), a number of π-conjugated polymers[2] have been shown to exhibit electroluminescence and lasing properties. At present time, PPV and its derivatives remain the most popular and promising conjugated polymers for such applications. Current research efforts in conjugated PPV derivatives include (1) attachment of side substituents to improve the processibility, such as MEH−PPV (**2**); (2) color tuning via random introduction of saturated carbons[3] along the PPV backbone and via synthesis of block copolymers;[4] and (3) luminescence enhancement through polymer chain disorder[5] and attachment of bulk phenyl side groups.[6] The photoluminescence (PL) quantum efficiencies of PPV films, which are necessary for lasing and set an upper limit for the efficiencies of the corresponding LED devices, are estimated to be about 0.27 and 0.15 for **1** and **2**,[7] respectively. Although the PL efficiency[6] of a film of **3** is reported to be as high as 0.65, there is still ample space for further improvement in PL efficiencies of this class of materials.



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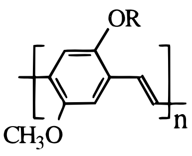

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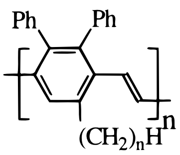

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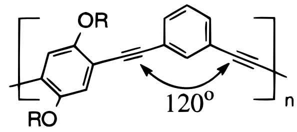
Our recent report[8] shows that the emission color of poly(phenyleneethynylene) (PPE) can be effectively controlled by the insertion of the *m*-phenylene unit. Although the solution PL efficiency of **4** is comparable to that of the structural isomer **5**, the film of the former exhibits a PL intensity about 5 times as strong as that of the latter. In addition, the solubility of **4** is significantly higher than that of **5**, attributed to the presence of *m*-phenylene which alters the linear rodlike chain conformation. Reasoning that the simultaneous enhancement in PL and solubility could also be observed in PPV,[9] we investigated poly[(*p*-phenylenevinylene)-*alt*-(*m*-phenylenevinylene) (**7**). Although an example of **7** with long alkyl chain (R = *n*-octyl)[11] has been briefly mentioned in the literature, it is desired to see whether the long alkyl chain is necessary to maintain the desired solubility of the material. Below we report the results on its synthesis and characterization.



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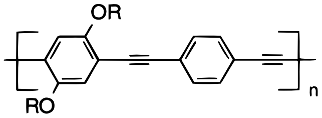

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Results and Discussion

Polymer Synthesis and Characterization. Monomer **6** was synthesized according to the literature procedure.[12] Wittig condensation[13] was used to polymerize **6** with isophthalaldehyde to afford **7** in 65−81% yield.[14] Both chloroform and THF were used as the cosolvent for the polymerization. The polymers obtained by using THF solvent had slightly higher molecular weights, attributed, perhaps, to the increased solubility of the products. A model compound **9** was similarly prepared to aid the structural characterization. Polymers **7a** and **7b** were yellowish transparent resins and had very good solubility in common organic solvents such as THF, chloroform, and toluene. Good solubility observed from **7b**, which bears relative short side chain

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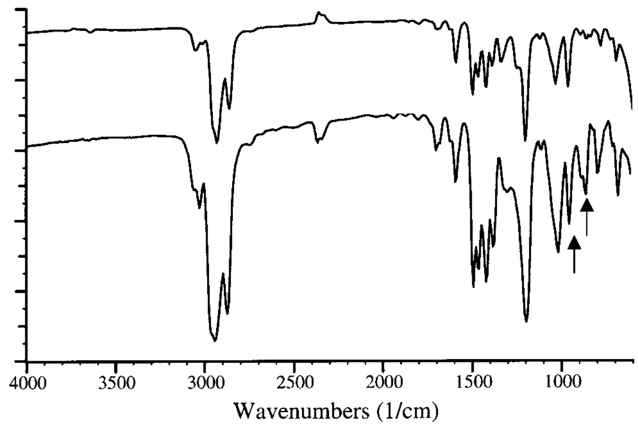


Figure 1. FT-IR of spectra of films **7a** (bottom) and **8a** (top) cast on NaCl plates. The vertical scale is transmittance in arbitrary units. The arrows mark the absorption for olefinic C−H out-of-plane defornmation (*cis*-CH=CH at ∼873 cm^{-1} and *trans*-CH=CH at ∼970 cm^{-1}).

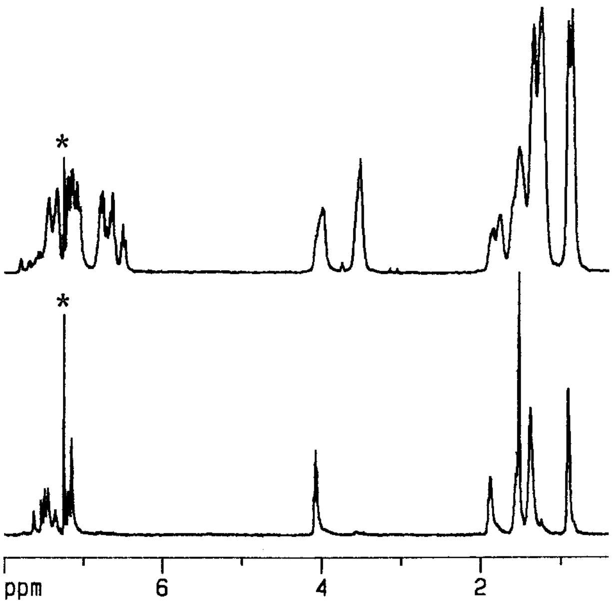


Figure 2. ^{1}H NMR of **7a** (top) and **8a** (bottom). The starred signals are attributed to $CHCl_3$.

(*n*-butyl), is apparently associated with the inclusion of *m*-phenylene along the polymer main chain.

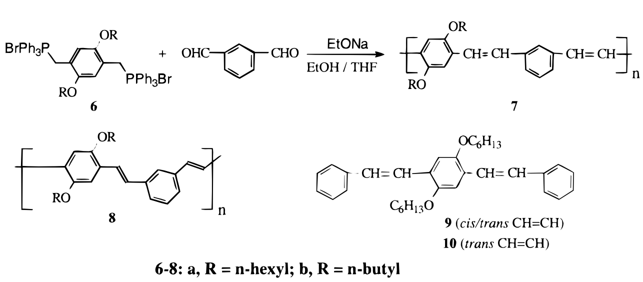


Table 1. Polymerization Results and Molecular Weights of Poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)]s

polymer	yield (%)	M_w[a]	PDI	α[b]
7a	81	24 900	1.5	0.84
7b	65	19 400	1.4	0.87
8a		25 000	1.6	1.0
8b		20 200	1.4	0.98

[a] M_w and PDI of the polymers were determined by using gel permeation chromatography equipped with light-scattering detector. [b] Mark−Houwink constant.

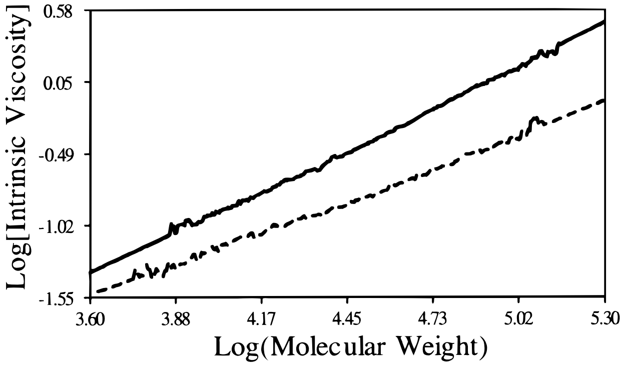


Figure 3. Overlay Mark−Houwink plot for **7a** (dotted line) and **8a** (solid line). The intrinsic viscosity in the plot is expressed in dL g^{-1}.

The IR spectrum of film **7** showed the presence of both *cis*-CH=CH (∼873 cm^{-1}) and *trans*-CH=CH (∼970 cm^{-1}) absorptions in medium intensity (Figure 1). ^{1}H NMR of **7** (Figure 2) showed the resonance signals at about 3.5 and 4.0 ppm (in a ratio of ∼3:2), which are attributed to the $-OCH_2^-$ unit and are related to *cis*- and *trans*-olefins, respectively. The assignment of ^{1}H NMR signals was confirmed by comparing with the spectrum of the pure *trans*-isomer **8**, which was obtained by refluxing[13] the toluene solution of **7** in the presence of a catalytic amount of iodine. To aid the spectroscopic assignment, the model compound **9** was also converted to the pure *trans*-isomer (**10**) by using the same condition. The pure *trans*-olefins in **8** were supported by both IR spectra (disappearance of the absorption band at ∼873 cm^{-1}) and ^{1}H NMR spectra (elimination of the resonance signal at ∼3.5 ppm).

Molecular Weight and Chain Stiffness. The molecular weights of **7** and **8**, which are listed in Table 1, were determined in THF by using size exclusion chromatography (SEC) equipped with on-line refractive index (RI), light-scattering (LS), and viscometer detectors. Combination of the high molecular weight, low polydispersity (PDI), and monomodel distribution, in addition to the high polymerization yield, suggested that cyclic products were not formed during the polymerization. The number-average degree of polymerization was estimated to be $n \approx 41$ for **7a** and $n \approx 39$ for **7b** by using M_n and the molecular weight of the repeating unit (400 for **7a** and 348 for **7b**). Comparable molecular weights and polydispersities between **7** and **8**, in addition to a large difference in *cis*/*trans*-CH=CH content between them, further indicate the linear polymer structure for them.

The solution property of the π-conjugated polymers can be studied by the SEC system equipped with RI−LS−viscometry detectors.[14] The Mark−Houwink α exponent in THF solvent at room temperature, which reflects the polymer chain conformation in the solution, was estimated to be ∼0.85 for **7** from the on-line viscometer detector, indicating some chain flexibility as a result of *m*-phenylene inclusion in **7**. Conversion of the olefins into an all-trans form slightly increases the chain rigidity as the Mark−Houwink α exponent for **8** was estimated to be about 1.0. An overlay Mark−Houwink plot displaying two representative curves is shown in Figure 3. For each polymer, a fairly good linearity was observed between log[η] and log(M_w)

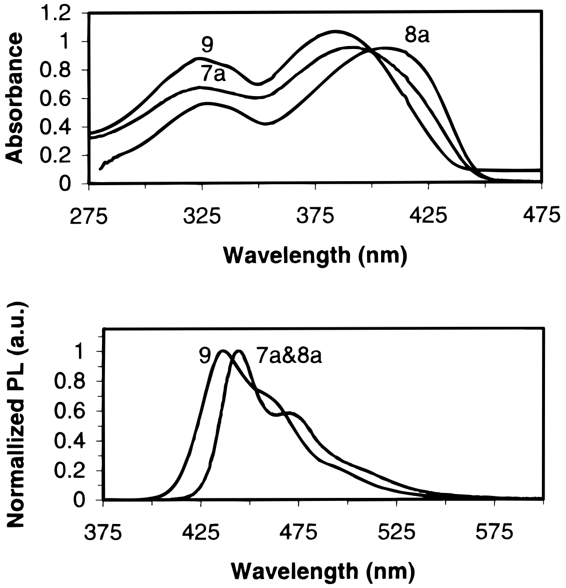


Figure 4. UV−vis (top) and PL (bottom) spectra of **7a**, **8a**, and **9** in their THF solution. The UV−vis spectrum of **9** (top) is slightly offset for clarity. The emission spectra for **7a** and **8a** are identical under the conditions used.

Table 2. Spectroscopic Data for *m*-Phenylene-Containing PPVs in THF

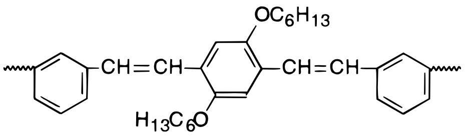
polymers	content of *trans*-CH=CH[a]	UV−vis λ_{max} (nm)	fluor λ_{em} (nm)	excitn λ_{max} (nm)	ϕ_{fl}[b]
7a	42	325, 391	444, 475	398	0.82
7b	32	326, 397	444, 470	398	0.81
8a	95	328, 406	444, 475	398	0.60
8b	91	328, 402	444, 469	398	0.65
9	41	324, 385	436	384	0.71
10	99	325, 388	437	390	0.61

[a] The content of *trans*-CH=CH content was estimated from the integration of −OCH$_2$− signals in their ^{1}H NMR. [b] The ϕ_{fl} values listed here were averaged from over three independent measurements.

within the molecular weight range of the sample, which is in agreement with the proposed linear polymer structure and indicates the absence of the chain branching.

Photoabsorption and Photoluminescence (PL). The UV−vis absorption and PL spectra were obtained from the dilute THF solutions of the polymers (Figure 4 and Table 2). Two major absorption bands of different intensity were observed from both **7** and **8** with the slightly red-shifted λ_{max} values for **8** (for example, 328 and 406 nm for **8a** versus 325 and 391 nm for **7a**). The absorption λ_{max} values of **7** were quite comparable to that of the model compound **9** (324 and 385 nm), which had a similar ratio of *cis*/*trans*-olefins as **7**. The small difference (∼6 nm) observed between the absorption λ_{max} values of **7a** and **9** is within the range of the expected substituent effect and indicates an effective conjugation interruption at *m*-phenylene. The similar absorption and emission profiles further suggest the nearly same electronic band structures exist between the model compound **9** and the polymer **7** of about 40 repeating units. Thus, incorporating *m*-phenylene into the fully conjugated PPV backbone has the advantage for the precise control of the π-conjugation length (or emission color), which is one of the essential material properties for electronic and optical applications. It should be pointed out that the conjugation length control via *m*-phenylene in **7** maintains the integrity of the fully conjugated polymer backbone. This is in contrast to the conventional color tuning approaches in PPVs, where saturated carbons[3] are randomly introduced to interrupt the π-conjugation. In comparison with other fully π-conjugated polymers, the *m*-phenylene approach appears to be superior to the conventional steric interaction approach illustrated, for example, in poly(fluorene)s[15] in which the optical absorption λ_{max} values continuously increase with the polymer chain length (up to ∼36 nm from the fluorene trimer to the decamer).

Despite the notable difference in their UV−vis spectra, *m*-phenylene-containing PPVs **7** and **8** exhibited an identical solution PL spectrum with the emission λ_{max} at about 444 and 475 nm (Figure 4). Clearly both **7** and **8** have the same emitting chromophore. This can be rationalized by analyzing the structure of **7**. Resulting from the effective π-conjugation interruption at *m*-phenylene linkages, the true chromophore in **7** can be simply represented as the molecular fragment **11**, where the two respective double bonds can be present in either the cis or trans form. It is anticipated that the molecular fragment **11** with the respective *cis*/*cis*-, *trans*/*cis*-, and *trans*/*trans*-olefin configurations will be randomly distributed along the polymer chain of **7**. Since a *trans*-olefin permits a longer conjugation than the corresponding isomeric *cis*-olefin,[16] the fragment **11** with the *trans*/*trans* configuration will have a lower band gap than the isomeric fragments with the *trans*/*cis* or *cis*/*cis* configurations. Thus, the fragment **11** with the *trans*/*trans* configuration is the true emitting chromophore in **7**, which gives the same emission spectrum as **8**. Emission only from the *trans*/*trans* fragment in **7** involves an intramolecular energy transfer[17] from a high (*trans*/*cis and cis*/*cis* configurations*)* to a low (*trans*/*trans* configuration) band gap chromophore through the shared *m*-phenylene moiety.



cis/cis:	*cis*	*cis*
trans/cis:	*trans*	*cis*
trans/trans:	*trans*	*trans*

11

The absorption spectra of the polymer films were slightly red-shifted from the solution to the film states, with λ_{max} values of about 395 and 415 nm for the films **7** and **8**, respectively (Figure 5). Both films of **7** and **8** exhibited very high luminescence in the solid state with comparable PL intensity. To evaluate the PL quantum efficiency, direct comparison was made between films of **8a** and PPV **1** under identical conditions. The PL efficiency of the former was estimated to be about 4.5 times as high as that of the latter. The unusually high PL efficiency of film **8a** was further confirmed by direct comparison with 9,10-diphenylanthracene[18] diluted in a PMMA film. The PL efficiency of film **8a** was estimated to be about 80%, the highest ever observed from any π-conjugated polymers. A single-layer LED device was fabricated from **8a**, and its EL spectrum was recorded (Figure 6). Under identical conditions, the EL efficiency of **8a** was higher than the regular PPV **1** by almost an order of magnitude (0.05% vs 0.006%).

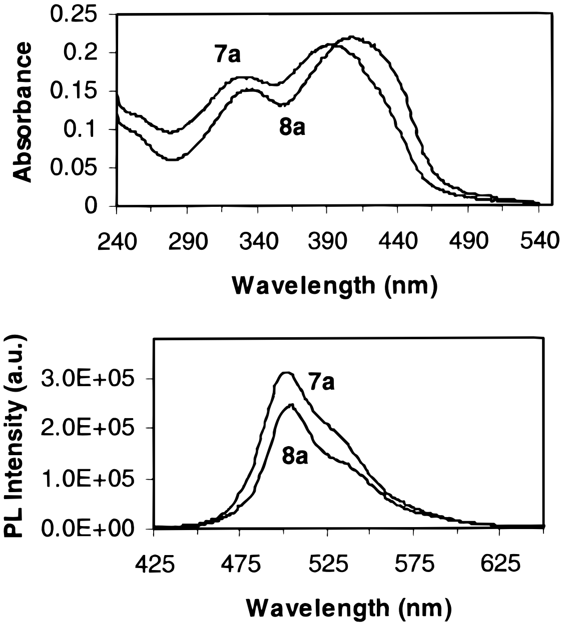


Figure 5. UV−vis (top) and photoluminescence (bottom) spectra of films **7a** and **8a** cast on quartz plates.

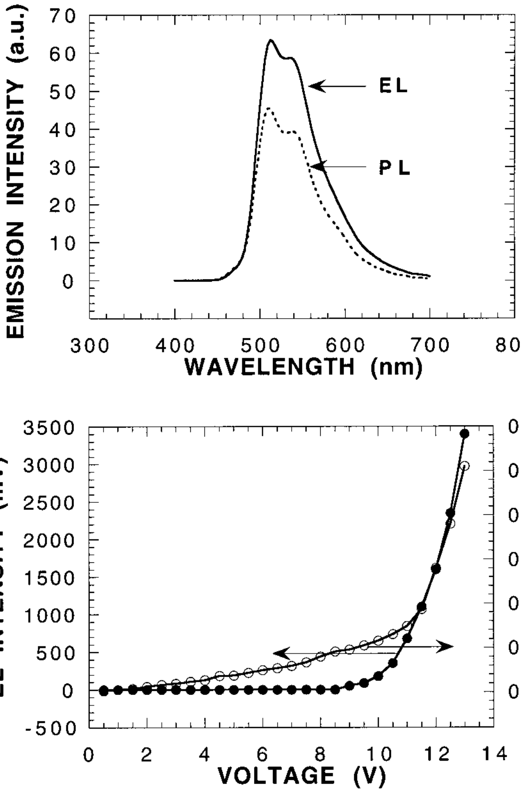


Figure 6. EL and PL spectra of **8a** with ITO and Ca electrodes (top) and its EL and current dependence on voltage (bottom).

Experimental Section

Materials and Instrumentation. Isophthalaldehyde (99%) of Acros Organics and triphenylphosphine (PPh_3) and anhydrous ethanol of 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-dialkoxybenzenes were synthesized according to the literature procedure.[12] 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. NMR spectra were acquired on a Bruker ARX400 spectrometer at 400 MHz for ^1H 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 quartz plates 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. The polystyrene standards were purchased from American Polymer Standards Corp.

1,4-Dihexyloxy-2,5-xylenebis(triphenylphosphonium bromide) (6a) was synthesized by using a literature procedure.[12] A mixture of 1,4-bis(bromomethyl)-2,5-dihexyloxybenzene (1.56 g, 3.35 mmol) and triphenylphosphine (2.64 g, 10 mmol) in 20 mL of anhydrous *N*,*N*-dimethylformide (DMF) was heated at reflux for 18 h. The resulting solution was added dropwise into 100 mL of ether to precipitate out the product. The white precipitates (3.25 g, 98% yield) were collected via filtration and dried under vacuum. ^1H NMR (400 MHz, $CDCl_3$): δ 7.5−7.8 (m, 30H, $-PPh_3$), 6.68 (s, 2H, Ar−H), 5.24 (d, $J = 11.62$ Hz, 4H, $-Ph-CH_2-PPh_3$), 3.01 (s, 4H, $-OCH_2-$), 1.23 (br, 4H), 1.10 (br, 12H), 0.87 (t, $J = 7.2$ Hz, 6H, $-CH_3$).

1,4-Dibutyloxy-2,5-xylenebis(triphenylphosphonium bromide) (6b) was synthesized by using the same procedure for **6a**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.70 (m, 30H, $-PPh_3$), 6.69 (s, 2H, Ar−H), 5.26 (d, $J = 12.7$ Hz, 4H, $-Ph-CH_2-PPh_3$), 3.00 (br, 4H), 1.06 (br, 8H), 0.75 (t, $J = 7.0$ Hz, 6H, $-CH_3$).

Synthesis of Poly[(2,5-dihexyloxy-1,4-phenylenevinylene)-*alt*-(1,3-phenylenevinylene) (7a). 1,4-Dihexyloxy-2,5-xylenebis(triphenylphosphonium bromide) (**6a**) (2.097 g, 2.12 mmol) and isophthalaldehyde (0.284 g, 2.12 mmol) were dissolved in a mixture of anhydrous ethanol (20 mL) and tetrahydrofuran (20 mL) in a 100 mL oven-dried round-bottomed flask, which was equipped with a magnetic stirring bar and capped with a rubber septum. A 5% sodium ethoxide in ethanol solution (2.93 g, 6.35 mmol), which was freshly prepared prior to use, was added dropwise to the reaction flask via a syringe at room temperature. The reaction mixture was stirred overnight at room temperature under an argon atmosphere. The resulting polymer was twice precipitated out from methanol. After drying under full vacuum (~0.01 Torr), a yellow polymer resin (**7a**) was obtained (0.65 g) in 81% yield. ^1H NMR spectrum of **7a** is shown in Figure 2. FT-IR (film on NaCl plate, cm^{-1}): 3050 (w), 2932 (s), 2865 (s), 1592 (w), 1500 (m), 1425 (m), 1205 (s), 1030 (m), 1070(m), 965 (m), 875 (m), 695 (m). Anal. Calcd for $C_{28}H_{36}O_2$: C, 83.12; H, 8.96. Found: C, 82.78; H, 9.01.

Poly[(2,5-dibutyloxy-1,4-phenylenevinylene)-*alt*-(1,3-phenylenevinylene) (7b) was synthesized in 65% yield by using the same procedure as for **7a.** The ^1H NMR spectrum of **7b** is very similar to that of **7a**. The integration and peak assignments of the ^1H NMR (400 MHz, $CDCl_3$) of **7b** are listed as follows: δ 6.4−7.6 (m, 6H, Ar−H), 3.95 (br, 1.28H, $-OCH_2-$ (in *trans*-olefin fragment)), 3.50 (br, 2.72H, $-OCH_2$- (in *cis*-olefin fragment)), 1.79 (br, 4H, $-CH_2-$), 1.27−1.63 (8H, $-CH_2-CH_2-$), 0.75−1.0 (6H, $-CH_3$). Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 83.04; H, 8.09.

Isomerization of the Carbon−Carbon Double Bonds To Synthesize 8a. A 0.65 g sample of poly[(2,5-dihexyloxy-1,4-phenylenevinylene)-*alt*-(1,3-phenylenevinylene) (**7a**) and 0.0017 g of iodine were dissolved in 20 mL of dry toluene in a 50 mL oven-dried round-bottomed flask, which was equipped with a magnetic stirrer and condenser. The solution was heated to reflux under an argon atmosphere for 4 h. The toluene and iodine were removed on a rotatory evaporator. The product was dissolved in chloroform and precipitated out with methanol. After drying under vacuum, 0.64 g of polymer **8a** was obtained as yellow resin. FT-IR (film on NaCl plate, cm^{-1}): 3050 (w), 2932 (s), 2863 (s), 1590 (w), 1496 (m), 1466 (w), 1425 (m), 1203 (s), 1035 (m), 965 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.62 (m, 3H, Ar−H), 7.19 (s, 1H), 7.15 (s, 2H), 4.08 (t, J = 6.10 Hz, 4H, $-OCH_2$-), 1.89 (m, 4H), 1.54 (br, 4H), 1.38 (m, 8H), 0.92 (t, J = 6.7 Hz, 6H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 137.7, 128.3, 126.4, 124.8, 123.2, 110.3, 69.1, 31.0, 28.9, 25.3, 22.0, 13.4. Anal. Calcd for $C_{28}H_{36}O_2$: C, 83.12; H, 8.96. Found: C, 82.58; H, 9.01.

Spectroscopic Properties of 8b. Polymer **8b** was prepared by using the same procedure for **8a** and has the following spectroscopic properties. FT-IR (film on NaCl plate, cm^{-1}): 3050 (w), 2953 (s), 2930 (s), 2870 (s), 1590 (w), 1494 (m), 1470 (w), 1423 (m), 1200 (s), 1067 (m), 1030 (m), 960 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.77 (m, 3H, Ar−H), 7.20 (s, 1H, Ar−H), 7.15 (s, 2H, Ar−H), 4.09 (t, J = 5.9 Hz, 4H, $-OCH_2-$), 1.88 (m, 4H, $-CH_2-$), 1.59 (m, 4H, $-CH_2-$), 1.04 (t, J = 7.2 Hz, 6H, $-CH_3$).

1,4-Bis(2′-phenylethenyl)-2,5-dihexyloxybenzene (9). The model compound **9** was prepared by reacting **6a** (0.987 g, 1 mmol) with benzaldehyde (0.223 g, 2 mmol) under the same conditions used for synthesizing **7a**. After purification on a silica gel column (hexanes/ethyl acetate = 100/1.5 by volume), **9** was obtained as a pale yellow solid (0.409 g) in 85% yield. The ^{1}H NMR spectrum of **9** in $CDCl_3$ showed the resonance signals for $-OCH_2-$ at 4.05 and 3.50 ppm, indicating the presence of both *trans*- and *cis*-olefins in a ratio of about 41:59.

To simplify the characterization, the double bonds in **9** were converted to **10** with pure *trans*-olefin configuration according to the same procedure used for **8a**. After purification on a silica gel column, the model compound **10** exhibited the following spectral properties. UV−vis (THF): λ_{max} 325 and 387 nm. FT-IR (in KBr pellet, cm^{-1}): 3049 (w), 2950 (s), 2925 9s), 2870 (m), 2857 (s), 1590 (w), 1510 9m), 1490 (m), 1465 (m), 1425 (m), 1253 (m), 1390 (m), 1340 (m), 1320 (m), 1210 (s), 955 (m), 690 (m), 750 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.4 Hz, 4H, Ar−H), 7.47 (d, J = 16.4 Hz, 2H, $-CH{=}CH-$), 7.29−7.49 (m, 6H, Ar−H), 7.13 (d, J = 16.5 Hz, 2H, $-CH{=}CH-$), 7.12 (s, 2H, Ar−H), 4.0 (t, J = 6.5 Hz, 4H, $-OCH_2-$), 1.87 (t, J = 7.4 Hz, 4H), 1.51 (m, 4H), 1.39 (m, 8H), 0.91 (t, J = 7.0 Hz, 6H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.9 (2C), 137.8 (2C), 128.6 (2C), 128.4 (4C), 127.2 (2C), 126.7 (2C), 126.3 (4C), 123.3 (2C), 110.5 (2C), 69.4 (2C), 31.4 (2C), 29.3 (2C), 25.7 (2C), 22.4 (2C), 13.8 (2C). Anal. Calcd for $C_{34}H_{42}O_2$: C, 84.60; H, 8.77. Found: C, 84.84; H, 8.75.

Photoluminescence and Quantum Yield Measurements. The solution PL quantum yields were measured by using the same procedure[19,20] as described previously. The polymer films for solid-state PL measurement were prepared by spin-cast on quartz substrates. The thickness of the films was controlled so that their absorbance at 366 nm was between 0.09 and 0.12. 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 index for 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 efficiency was calculated by assuming the efficiency[18] of the reference 9,10-diphenylanthracence in PMMA film to be 0.83. The PL spectra for reference and samples were taken with excitation at 366 nm. 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.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) For a recent review in electroluminescent conjugated polymers see: Kraft, A.; Grimsdale, A. C.; Holms, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(3) Some recent examples are: (a) Hay, M.; Klavetter, F. L. *J. Am. Chem. Soc.* **1995**, *117*, 7112. (b) Gowri, R.; Mandal, D.; Shivkumar, B.; Ramakrishnan, S. *Macromolecules* **1998**, *31*, 1819.

(4) Yang, Z.; Hu, B.; Karasz, F. E. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1998**, *35*, 233 and references therein.

(5) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.

(6) (a) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 231. (b) Hsieh, B. R.; Wan, W. C.; Yu, Y.; Gao, Y.; Gonzalez, S. A.; Feld, W. A. *Macromolecules* **1998**, *31*, 631.

(7) Greenham, N. C.; Samuel, I. D. W.; Hays, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.

(8) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1998**, *31*, 6730.

(9) Introducing *m*-phenylene in poly(9,9′-di-*n*-hexylfluorenediylvinylene-*alt*-1,3-phenylenevinylene)[10] and in PPV[11] has been briefly reported in recent literature. Quantitative characterization of *m*-phenylene on the conjugation length, PL efficiency, and chain rigidity of fully π-conjugated PPVs has not been reported.

(10) (a) Cho, H. N.; Kim, D. Y.; Kim, J. Y.; Kim, C. Y. *Synth. Met.* **1997**, *91*, 293. (b) Cho, H. N.; Kim, D. Y.; Kim, Y. C.; Lee, J. Y.; Kim, C. Y. *Adv. Mater.* **1997**, *9*, 326. (c) Kim, C. Y.; Hong, S. I.; Cho, H. N.; Kim, D. Y.; Kim, C. Y. *Polym. Bull.* **1997**, *38*, 169.

(11) (a) Ohnishi, T.; Doi, S.; Tsuchida, Y.; Noguchi, T. *IEEE Trans. Electron Devices* **1997**, *44* (8), 1253. (b) Doi, S.; Osada, T.; Tsuchida, Y.; Noguchi, T.; Ohnishi, T. *Synth. Met.* **1997**, *85*, 1281. (c) Ohnishi, T.; Doi, S.; Tsuchida, Y.; Noguchi, T. *Photonic and Optoelectronic Polymers*; ACS Symposium Series 672; American Chemical Society: Washington, DC, 1997; pp 345−357.

(12) Wang, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12.

(13) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.

(14) Yau, W. W.; Rementer, S. W. *J. Liq. Chromatogr.* **1990**, *13*, 627.

(15) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.

(16) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy;* Prentice-Hall: Upper Saddle River, NJ, 1998; p 289.

(17) Similar energy transfer from a high to low band gap chromophore has been observed recently in a PPV-related block copolymer. See: Hu, B.; Karasz, F. E. *Synth. Met.* **1998**, *92*, 157.

(18) Heinrich, G.; Schoof, S.; Gusten, H. *J. Photochem.* **1974/75**, *3*, 315.

(19) Li, J.; Pang, Y. *Macromolecules* **1998**, *31*, 5740.

(20) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

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