

Poly(*p*-phenylenevinylene) Presenting Pendent Pentaphenylene Dendron Groups for Light-Emitting Diodes

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ABSTRACT: We have synthesized, using the Gilch method, a novel poly(*p*-phenylenevinylene) derivative (PPV-PP) containing two pendent pentaphenylene dendritic wedges, and have characterized its structure and properties. The incorporated side chain pentaphenylene dendrons serve as solubilizing groups, prevent π -stacking interactions from occurring between the polymer main chains, and suppress the formation of excimers in the solid state. Photoluminescence studies indicate that efficient intramolecular energy transfer occurred from the photoexcited pentaphenylene groups to the poly(*p*-phenylenevinylene) backbone. The polymer film exhibits a maximum emission at 510 nm and had a photoluminescence efficiency of 46%, which is similar to that measured in dilute solution. The photoluminescence spectra remained almost unchanged after thermal annealing at 150 °C for 20 h, and displayed inhibited excimer formation. Polymer light-emitting diodes that we fabricated in the configuration ITO/PEDOT/PPV-PP/Mg:Ag/Ag exhibited a maximum emission peak at 513 nm, corresponding to the green region [$x = 0.30$ and $y = 0.62$ in the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates]. The maximum brightness and maximum luminance efficiency were 1562 cd/m² and 1.93 cd/A, respectively. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 5147–5155, 2005

Keywords: conjugated polymer; dendrimer; LED; photoluminescence; poly(*p*-phenylenevinylene)

INTRODUCTION

Ever since poly(phenylenevinylene) (PPV) was first employed in a polymer-based light-emitting diode (PLED) in 1990,¹ organic light-emitting polymers have been subject to an intense amount of academic and industrial research because of their potential applications in flat-panel displays.^{2–5} Organic luminescent polymers are attractive because of (a) the ability to fine-tune the luminescence properties of polymers by manipulating their chemical structure and (b)

the feasibility of using spin-coating and ink-jet printing processes for preparing large-area display devices. PPV and its derivatives are among the leading candidates for light-emitting materials,^{6–10} because they offer several advantages associated with their good mechanical properties, solution processability, thermal stability, and structural diversity; they have already been used in PLED applications. An ideal LED polymer, however, must possess a high photoluminescence (PL) quantum efficiency and the relatively low quantum efficiencies of PPVs in the solid state remains an issue that needs to be resolved.¹¹ The major cause of the PPVs' low PL quantum efficiencies is mutual cofacial stacking of their conjugated backbones through favorable

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interchain π - π interactions, especially in the solid state, which leads to self-quenching arising from the formation of excimers.^{12,13} To overcome this problem, various bulky substituents, such as alkoxy, alkylsilyl, phenyl (aryl), and fluorenyl groups, have been attached to the PPV backbone to prevent its close packing and suppress the intermolecular interactions that lead to the formation of excimers.¹⁴⁻²⁷

Dendronized polymers, which consist of a linear, polymeric core appended with dendrons or dendrimers,²⁸⁻³⁰ are another class of macromolecules that presently is receiving a considerable degree of attention.³¹⁻³³ This dendronized polymer approach has been applied to polymers having conjugated backbones, such as poly(*p*-phenylene),^{34,35} poly(*p*-phenylenevinylene),³⁶⁻³⁸ poly(*p*-phenyleneethynylene),³⁹ poly(thiophene),⁴⁰ and poly(fluorene).⁴¹⁻⁴³ Recently, Müllen et al. reported polyfluorenes appended with pentaphenylene dendrons, anticipating that the incorporation of the three-dimensional dendritic side chain to the light-emitting polymer would improve its luminescence activity.⁴¹ They demonstrated that the shielding effect provided by the dendritic side chains on the conjugated polyfluorene backbone prevents π -stacking and suppresses the formation of aggregates/excimers. In this article, we report the synthesis of a new PPV derivative, PPV-PP, possessing pentaphenylene dendrons incorporated as pendent units at the 2nd and 5th positions of the PPV backbone. The introduction of sterically hindered pentaphenylene groups in PPV not only enhances the thermal stability but also minimizes interchain interactions, and thus, high PL quantum yields are achieved. In addition, the side substituents present two flexible 2-ethylhexyloxy chains that improve the solubility of the polymer. We prepared PPV-PP through the macromonomer route, using the Gilch method to polymerize dendronized 1,4-bis(bromomethyl)benzene, and also investigated its thermal, photo-physical, and electroluminescence (EL) properties.

EXPERIMENTAL

General Directions

1,2-Bis(4-hydroxyphenyl)-1,2-ethanedione (**2**)⁴⁴ and 1,4-diethynyl-2,5-dimethylbenzene⁴⁵ were prepared according to reported procedures. Solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated. ¹H and ¹³C NMR spectra were recorded on either a Varian Unity

Yinova 500 MHz or a Bruker DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-SX/SX 110 mass spectrometer. IR spectra were obtained on a Nicolet 360 FT-IR spectrometer. Size exclusion chromatography (SEC) was performed using a Waters chromatography unit interfaced to a Waters 410 differential refractometer. Three 5- μ m Waters styragel columns (300 \times 7.8 mm²) connected in series in decreasing order of pore size (10⁴, 10³, and 10² Å) were used in conjunction with THF as the eluent. Standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a SEIKO EXSTAR 6000DSC unit, at a heating rate of 10 °C min⁻¹ and a cooling rate of 40 °C min⁻¹. Samples were scanned from 30 to 300 °C, cooled to 0 °C, and scanned again from 30 to 300 °C. Thermogravimetric analysis (TGA) was done on a DuPont TGA 2950 instrument. The thermal stability of each sample under a nitrogen atmosphere was determined by measuring its weight loss while heating at a rate of 20 °C min⁻¹. UV-vis spectra were measured using an HP 8453 diode-array spectrophotometer. PL spectra were obtained on a Hitachi F-4500 luminescence spectrometer.

1,2-Bis[4-(2-ethylhexyloxy)phenyl]-1,2-ethanedione (**3**)

A stirred mixture of **2** (6.50 g, 26.83 mmol), 2-ethylhexyl bromide (13.68 g, 69.77 mmol), K₂CO₃ (9.62 g, 69.76 mmol), and DMF (65 mL) was heated at 120 °C for 48 h under nitrogen. The resulting mixture was poured into water (250 mL) and extracted with EtOAc (3 \times 100 mL). The combined extracts were dried using MgSO₄, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography using hexane to afford **3** (9.42 g, 75.3%) as a yellow oil. ¹H NMR (CDCl₃): δ 7.90 (dt, *J* = 9.5, 2.4 Hz, 4H), 6.93 (dt, *J* = 9.5, 2.4 Hz, 4H), 3.89 (d, *J* = 5.7 Hz, 4H), 1.76–1.67 (m, 2H), 1.50–1.23 (m, 16H), 0.92–0.85 (m, 12H). ¹³C NMR (CDCl₃): 193.6, 164.7, 132.3, 126.0, 114.7, 70.8, 39.2, 30.4, 29.0, 23.7, 23.0, 14.0, 11.0. HRFAB-MS (*m/z*): [M + H]⁺ calcd for C₃₀H₄₃O₄, 467.3161; found 467.3161. Anal. Calcd (%) for (C₃₀H₄₂O₄): C, 77.21; H, 9.07. Found: C, 77.04; H, 9.11.

3,4-Bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (**4**)

Tetrabutylammonium hydroxide (Bu₄NOH, 35 mL) was added dropwise to a stirred solution of

3 (8.00 g, 17.14 mmol) and 1,3-diphenyl-2-propanone (3.96 g, 18.85 mmol) in 1,4-dioxane (36 mL) at 80 °C. The mixture was heated at 80 °C for 1 h before being poured into water (300 mL) and extracted with EtOAc (3 × 100 mL). The combined extracts were dried using MgSO₄, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (EtOAc/hexane, 1:100) to yield **4** (6.08 g, 55.3%) as a brown syrup. ¹H NMR (CDCl₃): δ 7.27–7.22 (m, 10H), 6.86 (dt, *J* = 9.2, 2.3 Hz, 4H), 6.72 (dt, *J* = 9.2, 2.3 Hz, 4H), 3.82 (d, *J* = 5.8 Hz, 4H), 1.72–1.58 (m, 2H), 1.49–1.30 (m, 16H), 0.97–0.90 (m, 12H). ¹³C NMR (CDCl₃): 200.4, 159.7, 154.2, 131.4, 131.2, 130.2, 128.1, 127.2, 125.0, 124.7, 114.0, 70.6, 39.4, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. HRFAB-MS (*m/z*): [M + H]⁺ calcd for C₄₅H₅₃O₃, 641.3995; found 641.3994. Anal. Calcd (%) for (C₄₅H₅₂O₃): C, 84.33; H, 8.18. Found: C, 84.38; H, 8.42.

1,4-Dimethyl-2,5-bis{3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylphenyl}benzene (**5**)

A solution of **4** (10.30 g, 16.07 mmol) and 1,4-diethynyl-2,5-dimethyl-benzene (0.86 g, 5.6 mmol) in *o*-xylene (80 mL) was heated under reflux for 12 h. The reaction mixture was concentrated, and the residue was recrystallized from acetone to give **5** (6.20 g, 80.3%, mp 190–192 °C) as a white solid. ¹H NMR (CDCl₃): δ 7.33 (s, 2H), 7.20–7.11 (m, 10H), 6.89–6.57 (m, 20H), 6.48–6.38 (m, 8H), 3.66 (d, *J* = 6.1 Hz, 4H), 3.63 (d, *J* = 6.3 Hz, 4H), 1.90 (s, 6H), 1.63–1.55 (m, 4H), 1.45–1.26 (m, 32H), 0.86 (t, *J* = 7.4 Hz, 12H), 0.85 (t, *J* = 7.1 Hz, 12H). ¹³C NMR (CDCl₃): 157.1, 156.8, 142.3, 142.2, 141.1, 140.4, 140.3, 140.2, 140.1, 139.9, 139.7, 138.7, 132.8, 132.6, 132.44, 132.37, 132.1, 131.9, 131.7, 131.4, 131.2, 130.8, 130.0, 127.5, 126.6, 125.9, 125.2, 125.1, 113.2, 113.0, 70.5, 39.3, 39.27, 30.5, 29.1, 23.8, 23.0, 19.8, 14.1, 11.1. HRFAB-MS (*m/z*): [M + H]⁺ calcd for C₁₀₀H₁₁₅O₄, 1379.8796; found 1379.8793. Anal. Calcd (%) for (C₁₀₀H₁₁₄O₄): C, 87.04; H, 8.33. Found: C, 87.13; H, 8.50.

1,4-Dibromomethyl-2,5-bis{3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylphenyl}benzene (**6**)

N-Bromosuccinimide (NBS, 180 mg, 1.02 mmol) and azobis(isobutyronitrile) (AIBN, 10 mg) were added to a solution of **5** (700 mg, 507 μmol) in CCl₄ (20 mL). The mixture was heated under

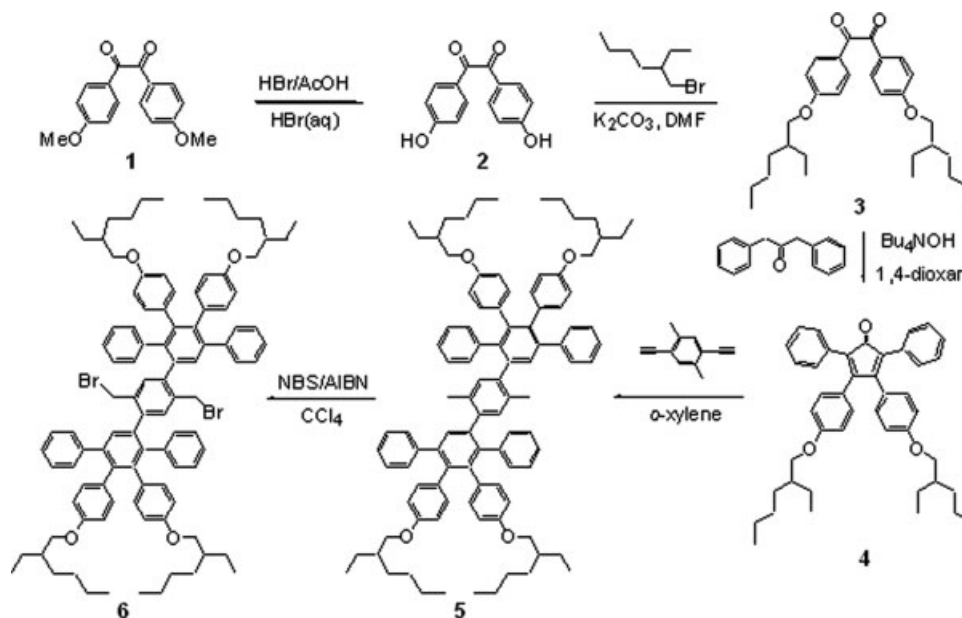
reflux for 8 h before being cooled and filtered. The filtrate was concentrated and purified by column chromatography (EtOAc/hexane, 1:200) to yield **6** (200 mg, 25.5%, mp 89–92 °C) as a white solid. ¹H NMR (CDCl₃): δ 7.39 (s, 2H), 7.30 (s, 2H), 7.17–7.08 (m, 10H), 6.89–6.59 (m, 18H), 6.47 (d, *J* = 8.4 Hz, 4H), 6.39 (d, *J* = 8.5 Hz, 4H), 4.27 (d, *J* = 10.1 Hz, 1H), 4.21 (d, *J* = 10.3 Hz, 1H), 4.17 (d, *J* = 10.2 Hz, 1H), 4.11 (d, *J* = 10.4 Hz, 1H), 3.66 (d, *J* = 6.0 Hz, 4H), 3.62 (d, *J* = 5.7 Hz, 4H), 1.63–1.55 (m, 4H), 1.44–1.23 (m, 32H), 0.85 (t, *J* = 7.6 Hz, 12H), 0.83 (t, *J* = 7.6 Hz, 12H). ¹³C NMR (CDCl₃): 157.9, 157.6, 142.7, 142.5, 142.3, 142.1, 141.14, 141.07, 140.93, 140.87, 140.5, 140.4, 140.1, 138.3, 138.1, 135.3, 134.3, 134.1, 133.2, 133.1, 133.05, 132.7, 132.3, 132.0, 131.4, 131.2, 130.7, 128.2, 127.6, 126.8, 126.3, 126.2, 114.0, 113.7, 71.2, 40.0, 39.96, 32.6, 32.5, 31.2, 31.1, 29.8, 24.5, 23.7, 14.8, 11.8. [M + H]⁺ calcd for C₁₀₀H₁₁₃Br₂O₄, 1535.7005; found 1535.7008. Anal. Calcd (%) for (C₁₀₀H₁₁₂Br₂O₄): C, 78.19; H, 7.35. Found: C, 78.40; H, 7.51.

PPV-PP

A solution of *t*-BuOK (86 mg, 0.78 mmol) in anhydrous THF (1.6 mL) was added dropwise to a stirred solution of monomer **6** (100 mg, 65.1 μmol) in anhydrous THF (1.0 mL) at 55 °C. The mixture was then heated at 55 °C for 12 h. The end groups were capped by heating with benzyl bromide (11 mg, 60 μmol) at 55 °C for another 2 h. The reaction mixture was cooled to room temperature and precipitated into a mixture of MeOH and H₂O (1:1 v/v). The crude polymer was collected and washed with excess MeOH. The resulting polymer was dissolved in chloroform and reprecipitated into MeOH. The precipitate was then washed for 48 h with acetone, using a Soxhlet apparatus before being dried under vacuum to give PPV-PP (70 mg, 77%). ¹H NMR (CDCl₃): δ 7.45–6.60 (m, 42H), 3.61 (br, 8H), 1.57 (br, 4H), 1.26 (br, 32H), 0.86 (br, 24H).

Light-Emitting Devices

Polymer LED devices were fabricated in the configuration ITO/poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) (35 nm)/light-emitting layer (160 nm)/Mg:Ag (100 nm)/Ag (100 nm). To improve hole injection and substrate smoothness, the PEDOT was spin-coated onto the ITO glass and dried at 80 °C for 12 h under vac-



Scheme 1. Synthesis of macromonomer containing polyphenylene dendrons.

uum. The light-emitting layer was spin-coated on top of the PEDOT layer, using chlorobenzene as the solvent and then dried for 3 h under vacuum at 60 °C. Before film casting, the polymer solution was filtered through a Teflon filter (0.45 μm). Subsequently, the cathodic Mg:Ag (10:1, 100 nm) alloy was deposited by coevaporation onto the emitting layer; an additional layer of Ag (100 nm) deposited onto top of the device to act as a protection layer. The current–voltage–luminance characteristics were measured under ambient conditions, using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with an 818ST silicon photodiode.

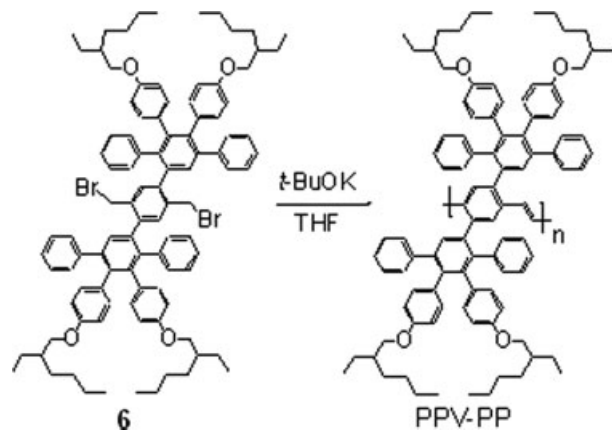
RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Scheme 1 presents the synthesis of the macromonomer containing pentaphenylene pendent groups. The dendritic side chains used here are similar to those developed by Müllen et al.⁴¹ 4,4'-Dimethoxybenzil¹ was demethylated in HBr/AcOH and then treated with 2-ethylhexyl bromide in the presence of K_2CO_3 to yield the alkoxy derivative **3**. Subsequent Knoevenagel condensation of the dialkoxybenzil **3** with 1,3-diphenyl-2-propanone in 1,4-dioxane, using Bu_4NOH as base, afforded 3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylcyclopenta-2,4-dien-

one.⁴ The Diels-Alder reaction of **4** with 1,4-diethynyl-2,5-dimethylbenzene in refluxing *o*-xylene gave the pentaphenylene dendrimer **5** possessing a *p*-xylene core, which was then brominated with NBS to furnish the corresponding 1,4-bis(bromomethyl)benzene **6**.

As indicated in Scheme 2, we performed the homopolymerization of monomer **6** to the poly(*p*-phenylenevinylene) bearing pentaphenylene dendron side chains in THF, according to the Gilch method, using excess potassium *tert*-butoxide as both a condensing agent and a dehydrobrominating agent. During the polymerization, the viscosity of the reaction mixture increased without precipitation, and we observed an in-



Scheme 2. Synthesis of PPV with polyphenylene pendants.

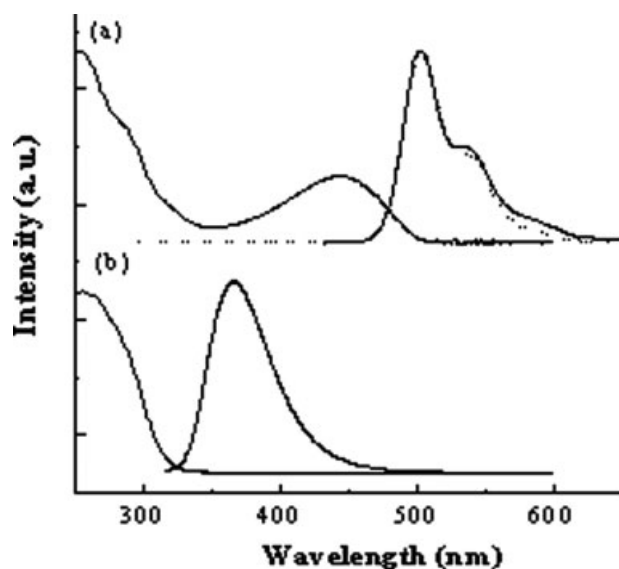


Figure 1. (a) UV-vis absorption (solid line) and PL (solid and dotted lines: excited at 444 and 260 nm, respectively) spectra of PPV-PP in THF solution. (b) UV-vis absorption and PL (excited at 260 nm) spectra of compound **5** in THF.

tense fluorescence. In the ^1H NMR spectrum of the PPV-PP obtained, the characteristic signal of the benzylic protons of monomer **6** (at ~ 4.20 ppm) disappeared entirely, which confirmed that complete polymerization had occurred. We also compared the IR spectrum of PPV-PP with that of compound **5**. PPV-PP displayed an additional absorption at $\sim 970\text{ cm}^{-1}$, which we assign to the out-of-plane deformations of the trans vinylene moieties, but we observed no signal at $\sim 873\text{ cm}^{-1}$ corresponding to any cis vinylene groups. These results indicate that the vinylene group formed under Gilch conditions existed predominantly in the trans configuration.

We determined the molecular weights of the PPV-PP by using gel permeation chromatography (GPC), with THF as the eluent, calibrated against polystyrene standards. GPC analysis indicated that the weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of this polymer are 3.6×10^5 g/mol and 2.4, respectively; these values are merely indicative because the rigid structure of this rod-type poly(*p*-phenylenevinylene) may deviate strongly from that of the coil-like polystyrene standards. The GPC data do reveal, however, that the poly(*p*-phenylenevinylene) prepared using the Gilch method possesses a relatively high molecular weight. PPV-PP is readily soluble in common organic solvents, such as THF, toluene, chloroform, and chlorobenzene. We attribute the high solubility of this polymer to the presence of the highly branched dendrons, along with the two flexible 2-ethylhexyloxy chains attached to the side substituents. We investigated the thermal properties of PPV-PP through TGA and DSC. As revealed by TGA, the polymer exhibited good thermal stability, with its 5% weight loss occurring at $327\text{ }^\circ\text{C}$. DSC was performed in the temperature range from 30 to $300\text{ }^\circ\text{C}$. We did not detect any possible phase transition signals for PPV-PP when we repeated the heating/cooling cycles during DSC. This finding occurs probably as a result of the rigidity of the dendronized polyphenyl substituents and the stiffness of this polymer chain; we believe that practically no segmental motion of the polymer backbone is possible, even at an elevated temperature.

Photophysical Properties

Figure 1 displays the UV-vis absorption and PL spectra of a dilute PPV-PP solution; Table 1

Table 1. Optical Properties and Quantum Yields of PPV-PP, **5**, and DO-PPV

	Solution ^a			Film ^b		
	Abs (nm)	PL (nm)	Φ_f^c	Abs (nm)	PL (nm)	Φ_f^d
PPV-PP	256,444	503,532 (sh)	0.51	257,450	510,545 (sh)	0.46
5	260	366				
DO-PPV ^e	445	507	0.32	435	546	0.10

^a Evaluated in THF.

^b Prepared by spin-coating from a CHCl_3 solution.

^c Relative to quinine sulfate in $0.1\text{ N H}_2\text{SO}_4$ ($\Phi_f = 0.53$).

^d Relative to 9,10-diphenylanthracene dispersed in poly(methyl methacrylate) (PMMA) film ($\Phi_f = 0.83$).

^e Data from 19.

summarizes the spectral data. The absorption and PL spectra of compound **5**, which serves as a model compound for studying the optical properties of the dendritic pentaphenylene moieties, are also presented in Figure 1. In THF solution, PPV-PP exhibits two major absorptions: one below 350 nm and the other over a longer wavelength region with λ_{max} at 444 nm. By comparing with the absorption spectrum of compound **5**, the first absorption of PPV-PP (in the short-wavelength region) was ascribed to π -electron transitions that originate predominately from the pentaphenylene dendritic pendent units and the second was assigned to a π - π^* transition derived from the conjugated poly(*p*-phenylenevinylene) (PPV) backbone. On excitation of the PPV main chain at 444 nm, the PL displays an emission band at 503 nm combined with a shoulder at 532 nm. When the PL of PPV-PP was compared with that of MEH-PPV, the PL spectrum of PPV-PP was relatively blue-shifted.²⁷ This was attributed to the presence of bulky pendent groups, which may disrupt the coplanarity of the main chain and cause a partial destruction of the π -delocalization along the polymer backbone. We measured the PL quantum yield (Φ_f) of PPV-PP in THF to be 0.51, relative to a quinine sulfate standard ($\Phi_f = 0.53$ in 0.1 N H₂SO₄ at 365 nm excitation).⁴⁶

Moreover, on irradiation at 260 nm—a wavelength we attribute to the absorptions of the pendent pentaphenylene units—the PL spectrum remains almost identical to that obtained under excitation of the PPV backbone at 444 nm. We did not detect any luminescence arising from the dendritic polypenylene side chains at ~ 366 nm. This result suggests that efficient Förster energy transfer occurred as a consequence of the moderate spectral overlap between the emission spectrum of the dendritic PP side chains and the absorption spectrum of the PPV polymer backbone (Fig. 1).⁴⁷ Most of the excitons formed in the PP pendent groups on direct photoexcitation are more likely to migrate to the lower PPV backbone, from which the emission occurs. The fact that we observed complete quenching of the dendritic pentaphenylene emission even in a very dilute solution (10^{-6} M) indicates that efficient intramolecular energy transfer takes place in the PPV-PP polymer and may contribute significantly to the emission intensity of the PPV chain.

To investigate the effects of the dendritic side chains on the packing of the polymer chains, we

investigated the photophysical properties of PPV-PP in the solid state. Figure 2 displays the absorption and PL spectra of PPV-PP films spin-coated from CHCl₃ solution onto quartz plates. In comparison with the PL spectrum of the corresponding dilute solutions, the signals of the polymer film are only slightly red-shifted (~ 7 nm) and do not provide any signs of aggregate or excimer formation. The PL quantum efficiency of the film was 0.46; we determined this value by comparing it with the PL of 9,10-diphenylanthracene dispersed in poly(methyl methacrylate) (PMMA) film ($\Phi_f = 0.83$).⁴⁸ We believe that both the PL spectrum and quantum efficiency in the film state are nearly identical to those obtained from dilute solution because of the presence of the bulky pentaphenylene dendrimer substituents. Generally, the luminescence efficiency of PPV in the solid state is substantially lower than that measured for isolated molecules because of interchain interactions that produce lower-energy excited states that are not strongly radiatively coupled to the ground state.^{11–13} The large dendritic frameworks are more likely to encapsulate the conjugated backbone and prevent π -stacking interactions between the polymer main chains, which has the effect of suppressing the formation of aggregates/excimers in the solid state.^{41–43} In contrast, the film of a PPV polymer [poly(2,5-dioctyloxy-1,4-phenylenevinylene) (DO-PPV)] that possesses two flexible alkoxy substituents per monomer unit, but does not present dendritic side chains, exhibits a nearly 40-nm red-

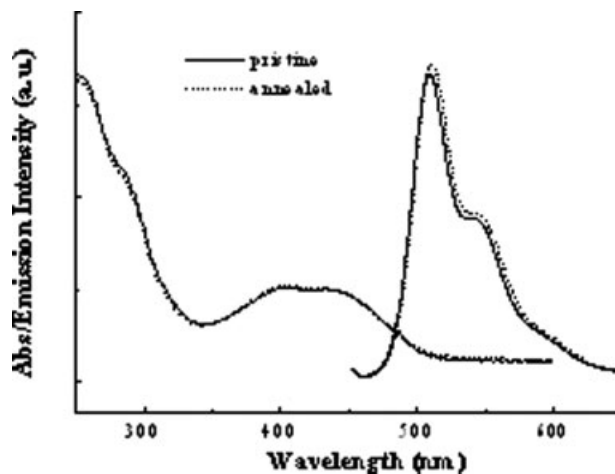


Figure 2. UV-vis absorption and PL (excited at 450 nm) spectra of PPV-PP film before and after annealing at 150 °C for 20 h under a nitrogen atmosphere.

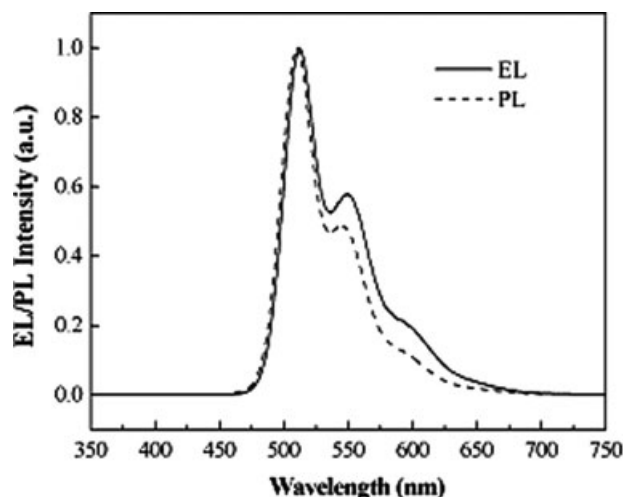


Figure 3. PL spectrum of PPV-PP film and EL spectrum of ITO/PEDOT/PPV-PP/Mg:Ag/Ag device.

shift in its PL spectrum and a much lower quantum efficiency than it does in dilute solution.¹⁹

Conjugated polymers generally are rigid-chain molecules that possess relatively planar geometries and have a great tendency to pack cofacially in the solid state through molecular chain diffusion.¹² The reduced emission intensity that occurs on prolonged heating could arise from enhanced interchromophoric interactions, which result in a long tail appearing in the emission spectrum and quenching through the formation of nonemissive excimers. We heated the polymer film on a hot plate at 150 °C under a nitrogen atmosphere for 20 h to examine the effect that incorporating the PP pendent groups has on the thermal stability of PPV-PP; we recorded the PL spectrum once the film had cooled to room temperature. After this thermal treatment, the PL spectra remained almost unchanged, as indicated in Figure 2, and we did not observe a long-wavelength emission band caused by excimer formation. Because of the presence of the bulky dendrimer pendent groups, the steric demand of which restricts the close packing of the polymer chains and reduces the probability of interchain interactions, the tendency for formation of aggregates and excimers, even on thermal treatment, is suppressed.

Electroluminescence Properties of LED Device

To evaluate the potential of using PPV-PP as an emissive material in polymer LED applications, we fabricated a double-layer LED having the configuration ITO/PEDOT/PPV-PP/Mg:Ag/Ag for

our preliminary investigations. We used PEDOT as a hole-injection layer and deposited a thick layer of Ag on the top of the device to act as a protection layer. As indicated in Figure 3, the EL spectrum exhibits a maximum at ~ 513 nm with a shoulder at ~ 549 nm, which corresponds to a green light having Commission Internationale de L'Eclairage (CIE) color coordinates of (0.30, 0.62). In addition, the EL spectrum is quite similar to the PL spectrum. This result indicates that both the EL and PL originate from the same radiative decay process of the singlet exciton. Figure 4 presents plots of the luminance efficiency and brightness vs. current density for the nonoptimized device. The luminance reached 1562 cd/m^2 at a current density of 89.3 mA/cm^2 , corresponding to an efficiency of 1.75 cd/A . The maximum luminance efficiency was 1.93 cd/A at 824 cd/m^2 , with a current density of 42.6 mA/cm^2 . Further improvements in the EL performance may be possible by optimizing the device structure.

CONCLUSIONS

Using the macromonomer approach, we have synthesized a dendronized polymer, PPV-PP, which consists of a conjugated poly(*p*-phenylenevinylene) backbone on which are appended pentaphenylene dendritic wedges. The dendritic monomer **6** was prepared through Diels–Alder cycloaddition of 1,4-diethynyl-2,5-dimethylbenzene with tetraphenylcyclopentadienone derivative **4**; it was polymerized using the Gilch

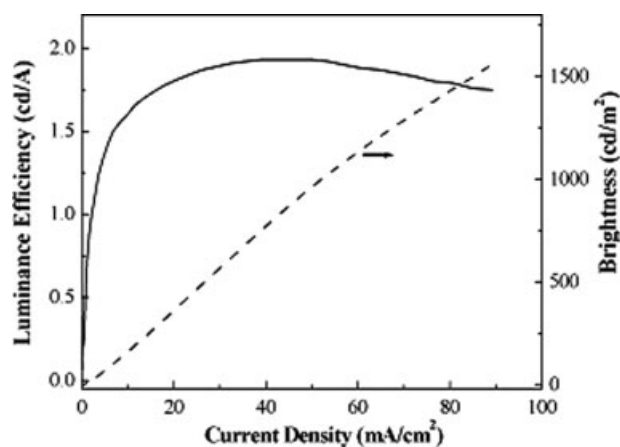


Figure 4. Plots of the luminance efficiency and brightness versus current density of the PPV-PP-based device.

method to afford PPV-PP. As a result of incorporating the dendritic pentaphenylene pendent groups, which reduce interchain interactions and suppress the formation of excimers, this PPV-PP is soluble in common organic solvents and it exhibits a high PL efficiency in the solid state. Even after being annealed at 150 °C for 20 h, the PL spectra of the polymer film remained almost unchanged with no excimer being formed. Using this dendritic polymer, we fabricated a double-layer LED device having the configuration ITO/PEDOT/PPV-PP/Mg:Ag/Ag. The EL of the device exhibited a green light having CIE color coordinates of (0.30, 0.62). The maximum luminance efficiency was 1.93 cd/A at 824 cd/m², with a current density 42.6 mA/cm².

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