

# Synthesis and Characterization of an Efficiently Fluorescent Poly(phenylenevinylene) Possessing Pendant Dendritic Phenyl Groups

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**ABSTRACT:** We have synthesized a thermally stable and high molecular weight fluorescent poly(phenylenevinylene) (**PPV**) incorporating side-chain-tethered dendritic phenyl groups (**DENPPV**) through Gilch route; this **DENPPV** has a low abundance of tolane-bisbenzyl defects. Intramolecular energy transfer from the dendritic phenyl side group to the **PPV** backbone was evidenced from UV-vis and photoluminescence spectra of the **DENPPV** polymer and its model compound. Copolymers of **DENPPV** with 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (**MEHPPV**) display excellent photoluminescence both in solution and in the solid state; the highest quantum yield we observed was 82%. The electroluminescence of the copolymer **MEHPPV/DENPPV** (molar ratio: 25/75) was 70% higher than that of **MEHPPV** (0.12 lm/W vs 0.07).

## Introduction

Electroluminescence devices based on organic thin films are of great interest because of their potential applications as large-area light-emitting displays that require a low driving voltage and have good processability and a fast response time.<sup>1</sup> Although many poly(phenylenevinylene) (**PPV**) derivatives have been synthesized and applied in light-emitting diode (LED) applications, very few display high photoluminescence efficiencies.<sup>2</sup> There are a number of reasons for these low photoluminescence efficiencies: (a) Conjugated backbones tend to stack cofacially with one another as a result of favorable interchain  $\pi$ - $\pi$  interactions, which leads to a self-quenching of excitons. (b) An imbalance of hole/electron injection and transport occurs in the emission layer in devices because most emissive polymers conduct holes in preference to electrons.<sup>3</sup> (c) Trapping of excitons by defect sites in the polymer backbone causes nonradiative decay. These structural defects in the polymer not only reduce the photoluminescence quantum yield but also are responsible for the short operational lifetimes of LED devices.<sup>4</sup>

Various techniques have been proposed to improve the efficiency of **PPVs**, either by modifying their chemical structure with bulky side groups or by using a copolymerization approach to incorporate conjugated phenylenevinylene segments among nonconjugated spacers.<sup>5</sup> For example, soluble **PPV** derivative with bulky alkoxy side groups, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (**MEHPPV**) has been developed.<sup>6–9</sup> More recently, various bulky substituents, such as alkoxy, alkylsilyl, phenyl, and fluorenyl groups, have been substituted at the 2- or 2,5-positions of the **PPV** backbone to suppress the aggregation, caused by intermolecular interactions, that quench the formation of excimers.<sup>9,10</sup> Three new soluble **PPV** derivatives have been obtained through use of the Horner–Wittig–Emmons (HWE) reaction; these materials in the solid state display a photoluminescence quantum yields of 61%,<sup>10d</sup> which is higher than that of **MEHPPV**. One

weak feature of **PPV** derivatives that have flexible side chains is that they are sensitive to a combination of air and light.<sup>11</sup> In contrast, phenyl-substituted **PPVs** have higher resistance to photooxidation than do other substituted **PPVs**.<sup>12</sup> LEDs having longer lifetimes can be fabricated from a single phenyl group substituted **PPVs** that contain few head-to-head (HH) and tail-to-tail (TT) couplings,<sup>13,14</sup> such couplings referred to as tolane-bis(benzyl) (TBB) defects. It has also been demonstrated that polymers presenting fourth-generation dendrimers have a diminished amount of intermolecular  $\pi$ -stacking and, consequently aggregate formation is inhibited.<sup>15</sup> The photonic effects observed by the dendronization of polymers have been explored in recent years.<sup>16</sup> We have already demonstrated that higher luminescence efficiencies exist for polyfluorenes possessing side-chain tethered polyhedral oligomeric silsesquioxane (POSS).<sup>17a</sup> Moreover, Frechet-type dendrimers, a benzyl alcohol dendrimer, have been shown to have high photoluminescence.<sup>17b</sup> In contrast to the Frechet-type dendrimers, Mullen-type dendrimers,<sup>18,19</sup> which are polyphenylene dendrimers, are both shape-persistent and chemically stable. Therefore, their  $\pi$ -stacking is precluded at lower dendritic generations than it is for the Frechet type. Their three-dimensional shielding ability has been demonstrated by using perylene dyes as core units.<sup>18</sup> The Mullen type dendrimers do not interfere with the charge transport or emission properties of the polyfluorene. Dendrimer substitution has been performed to hinder excimer formation and exciton migration to oxidized ketonic sites, which thereby increases the color stability of the devices.<sup>19</sup> In the present study, we have employed the dendritic phenyl (Mullen-type) **PPV**, which offers the following advantages: (i) It permits spatial control of the polymer chain and shields it from interchain excimer formation; (ii) it is a fully conjugated **PPV**; (iii) it provides a very low abundance of TBB defects as a result of electronic (the stronger acidity of the bromomethyl moiety at the ortho position of the highly conjugated dendritic phenyl group) and steric effect of the substituent; (iv) its rigid aromatic structure provides higher stability to thermal oxidation; (v) its excitation energy is transferred to the polymer

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backbone, which leads to enhanced device performance and quantum efficiency. The preparation of this polymer is also a part of our effort to a production of fully conjugated PPVs possessing bulky pendants. To determine the minimal steric requirements necessary to prevent of aggregation and to enhance the solubility in organic solvents, we also prepared copolymers with MEHPPV. In this paper, we report the synthesis of a new PPV derivative containing dendritic phenyl groups on its side chains (DENPPV) as an example of highly thermally stable, and TBB defect-free phenyl-substituted PPV; in addition, we describe the performance of these polymers as emissive layers in LEDs.

## Experimental Section

**Materials and Characterization.** Bromoxylene, *n*-butyllithium, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetraphenylcyclopentadienone, and 4-bromophenylacetylene were purchased from Aldrich and were used as received. All other solvents were distilled before use.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-SX 102A spectrometer. Fourier transform infrared (FTIR) spectra were acquired using a Nicolet 360 FT-IR spectrometer. Gel permeation chromatographic analyses were performed on a Waters 410 differential refractometer and a Waters 600 controller (Waters Styragel Column). All GPC analyses of polymers were performed in THF solutions at a flow rate of 1 mL/min at 40 °C; the samples were calibrated using polystyrene standards. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at heating rates of 20 and 10 °C/min, respectively, using Du Pont TGA-2950 and TA-2000 instruments, respectively. UV-vis absorption and photoluminescence (PL) spectra were recorded on an HP 8453 spectrophotometer and a Hitachi F-4500 luminescence spectrometer, respectively. Before investigating the thermal stability of the synthesized polymers, their polymer films were annealed in air at 200 °C for 2 h.

**Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)xylene.** *n*-Butyllithium (1.6 M in hexane, 17.0 mL, 27.09 mmol) was added, by syringe, to a solution of bromoxylene (5.0 g, 28.7 mmol) in THF (100 mL) at -78 °C. The mixture was stirred at -78 °C, warmed to -10 °C for 15 min, and cooled again at -78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 g, 80.9 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ethyl acetate. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, hexane,  $R_f$  0.12) to provide 4.63 g (74%) of the title product.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (s, 1H), 7.06 (dd, 2H,  $J$  = 7.6 Hz), 2.41 (s, 3H), 2.22 (s, 3H), 1.19–1.37 (m, 12H). HRMS: calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_2\text{B}$ , 232.1634; found, 232.1636.

**Synthesis of 2,3,4,5-Tetraphenyl-4'-bromophenyl (DEN-Br).** A mixture of tetraphenylcyclopentadienone and 4-bromophenylacetylene was refluxed in xylene at 135 °C under nitrogen for 48 h. The reaction mixture was then slowly added into water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined extracts were dried ( $\text{MgSO}_4$ ), the solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate, 4:1) to afford **2** (3.23 g, 72%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (s, 1H), 7.35 (d,  $J$  = 8.1 Hz, 2H), 7.09–7.14 (m, 4H), 7.02 (d,  $J$  = 8.5 Hz, 2H), 6.87–7.00 (m, 16H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.22, 142.19, 142.00, 141.46, 141.26, 141.13, 140.82, 140.60, 140.45, 140.28, 140.18, 140.12, 139.95, 139.77, 139.67, 135.43, 132.53, 131.95, 131.89, 131.85, 131.67, 131.27, 130.75, 130.45, 130.38, 128.14, 128.09, 127.65, 127.43, 127.19, 127.14, 126.10, 121.12. Anal. Calcd for  $\text{C}_{36}\text{H}_{25}\text{Br}$ : C, 80.59; H, 4.66. Found: C, 80.81; H, 4.89. HRMS: calcd for  $\text{C}_{36}\text{H}_{25}\text{Br}$ , 536.1139; found, 536.1140.

**Synthesis of 2'-(2,3,4,5-Tetraphenyl-4'-phenyl)-1,4'-dimethylbenzene (D-CH<sub>3</sub>).** Suzuki Coupling Reaction. Carefully purified DENBr, (1.0 g 1.84 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)xylene (0.43 g 1.84 mmol), and  $(\text{PPh}_3)_4\text{Pd}^0$  (1 mol %) were dissolved in a mixture of toluene and 2 M aqueous  $\text{K}_2\text{CO}_3$  (1.5:1). The solution was placed under a nitrogen atmosphere and heated under reflux with vigorous stirring for 48 h. The mixture was poured into water and extracted with ethyl acetate. The organic extracts were washed with brine and then dried ( $\text{MgSO}_4$ ). The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel; 2% ethyl acetate in hexane,  $R_f$  0.3) to provide 650 mg (65%) of the title product.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (s, 1H), 7.25 (s, 1H), 7.10–7.18 (m, 10H), 7.02–7.09 (m, 2H), 6.81–6.90 (m, 14H), 2.33 (s, 3H), 2.16 (s, 3H).  $^{13}\text{C}$  NMR (300 MHz  $\text{CDCl}_3$ ):  $\delta$ : 142.08, 142.07, 142.06, 141.73, 141.12, 140.94, 140.70, 140.38, 140.33, 140.21, 140.12, 139.71, 139.61, 135.43, 132.53, 131.95, 131.89, 131.85, 131.67, 131.27, 130.75, 130.56, 130.33, 128.74, 128.16, 127.93, 127.43, 127.25, 126.97, 126.59, 125.93, 125.67, 21.38, 20.23. Anal. Calcd For  $\text{C}_{44}\text{H}_{34}$ : C, 93.91; H, 6.09. Found: C, 93.91; H, 6.01. HRMS: calcd for  $\text{C}_{44}\text{H}_{34}$ , 562.2661; found, 562.2662.

**Synthesis of 2-(2,3,4,5-Tetraphenyl-4'-phenyl)-1,4-dibromomethylbenzene (D-CH<sub>2</sub>Br).** A mixture of D-CH<sub>3</sub>, (1.0 g, 1.77 mmol) NBS (0.63 g, 3.55 mmol), and AIBN (0.04 g) was heated under reflux in carbon tetrachloride under nitrogen for 5 days. The reaction mixture was filtered to remove succinimide, the solvent was evaporated, and the residue was purified by column chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 7.62 (s, 1H), 7.46 (d,  $J$  = 7.92 Hz, 1H), 7.34 (d,  $J$  = 7.70 Hz, 1H) 7.24–7.15 (m, 10H), 6.94–6.88 (m, 15H), 4.46 (s, 2H), 4.35 (s, 2H).

$^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 142.27, 141.79, 141.66, 141.24, 140.87, 140.25, 139.91, 139.86, 139.51, 139.40, 137.96, 137.36, 135.50, 131.57, 131.52, 131.47, 131.21, 130.83, 129.95, 128.48, 128.15, 127.60, 126.99, 126.93, 126.65, 126.29, 125.74, 125.63, 125.38, 32.72, 31.44. Anal. Calcd for  $\text{C}_{44}\text{H}_{32}\text{Br}_2$ : C, 73.34; H, 4.48. Found: C, 73.05; H, 4.41. HRMS: calcd for  $\text{C}_{44}\text{H}_{32}\text{Br}_2$ , 720.0871; found, 720.0848.

### General Procedure for the Synthesis of Copolymers.

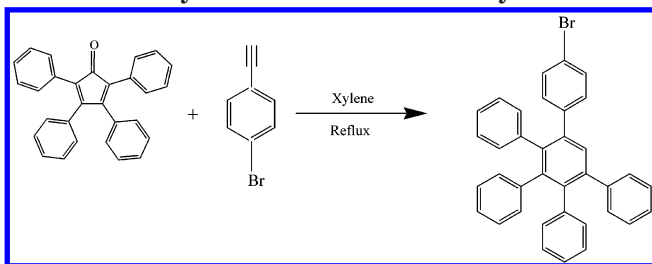
A 1 M solution of potassium *tert*-butoxide in THF was added to a solution of the monomer D-CH<sub>2</sub>Br in dry THF at room temperature, and then the mixture was stirred for 4 h. Addition of the THF solution to methanol precipitated the polymer, which was collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was again collected, stirred with a mixture of methanol and water (1/1) for 1 h, filtered, washed with methanol, and dried at 60 °C for 24 h.

**Device Fabrication and Testing.** The electroluminescent (EL) devices were fabricated on an ITO-coated glass substrate that was precleaned and then treated with oxygen plasma before use. A layer of poly(ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P from Bayer Co.; ca. 40 nm thick) was formed by spin-coating from its aqueous solution (1.3 wt %). The EL layer was spin-coated at 1500 rpm from the corresponding toluene solution (15 mg mL<sup>-1</sup>) on top of the vacuum-dried PEDOT:PSS layer. The nominal thickness of the EL layer was 65 nm. Using a base pressure below  $1 \times 10^{-6}$  Torr, a layer of Ca (30 nm) was vacuum deposited as the cathode and a thick layer of Al was deposited subsequently as the protecting layer. The current-voltage characteristics were measured using a Hewlett-Packard 4155B semiconductor parameter analyzer. The power of the EL emission was measured using a Newport 2835-C multifunction optical meter. The brightness was calculated using the forward output power and the EL spectra of the devices; a Lambertian distribution of the EL emission was assumed.

## Results and Discussion

The dendritic phenyl substitute, 2,3,4,5-tetraphenyl-4'-bromophenyl, was synthesized according to Scheme 1. Suzuki coupling of xylene boronic acid with 2,3,4,5-tetraphenyl-4'-bromophenyl in toluene, in the presence

## Scheme 1. Synthesis of Dendritic Phenyl Bromide

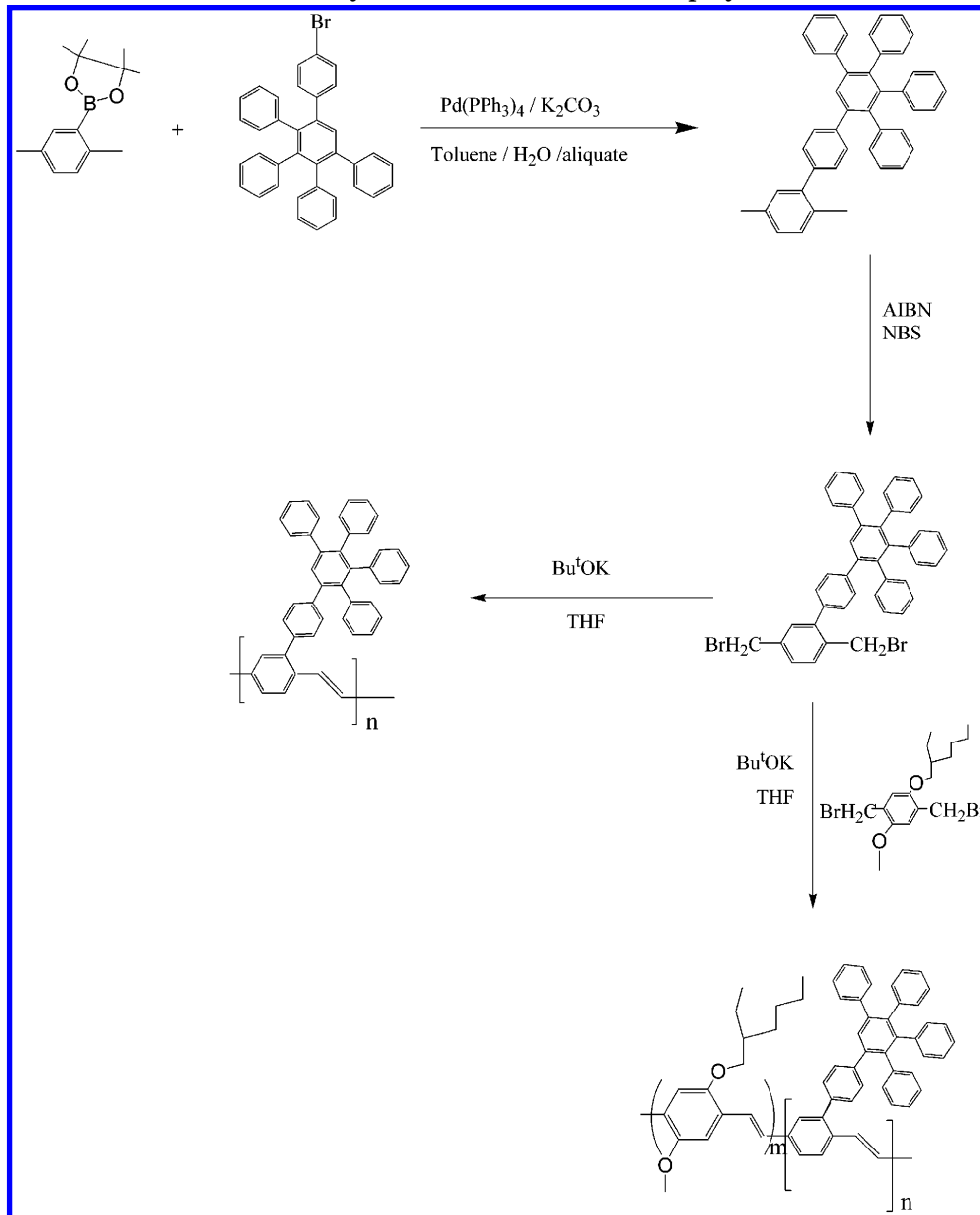


of tetrakis(triphenylphosphine)palladium(0) as catalyst, gave the dendritic phenyl-substituted xylene derivative. The dendritic phenyl-substituted dibromo monomer (**D-CH<sub>2</sub>Br**) was synthesized by bromination of 2'-(2,3,4,5-tetraphenyl-4'-phenyl)-1,4'-dimethylbenzene with NBS, using AIBN as the radical initiator. The polymers were prepared according to Scheme 2.

The copolymers were prepared using comonomer feed ratios of **D-CH<sub>2</sub>Br** and 2-methoxy-5-(2-ethyl)hexyloxy-1,4-bis(bromomethyl)benzene of 100:00, 88:12, 75:25, 63:37, 50:50, 25:75, and 0:100; we name the corresponding

copolymers **DENPPV**, **88DENPPV**, **75DENPPV**, **63DENPPV**, **50DENPPV**, **25DENPPV**, and **MEHPPV**, respectively. Figure 1 displays the FTIR spectra of **DENPPV** and **MEHPPV**. The absorption bands that appear at 1581–1596  $\text{cm}^{-1}$ , are characteristic of C=C bonds. The absorption bands at 3056 and 961  $\text{cm}^{-1}$  are due to stretching modes for the vinyne C=C bond and C–H out-of-plane bending, respectively, of the trans configuration. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **DENPPV** have been presented as Supporting Information. The aromatic and vinyl protons appear within the range of 7.60–6.84 ppm. **PPVs** containing TBB defect (head-to-head (H–H) or tail to tail (T–T) couplings, that are formed as the result of a side reactions<sup>4,20</sup> are responsible for the CH<sub>2</sub>–CH<sub>2</sub> groups that present the peaks at 2.5–2.9 ppm. We did not observe peaks for H–H couplings in the  $^1\text{H}$  NMR spectrum of the obtained polymer. It is clear that this side reaction is suppressed because of (i) the electronic effect arising from the stronger acidity of the bromomethyl moiety at the ortho position of the dendritic phenyl group and (ii) the steric effect of the substituting dendritic phenyl group. We

## Scheme 2. Synthesis of DEN PPV and Copolymers



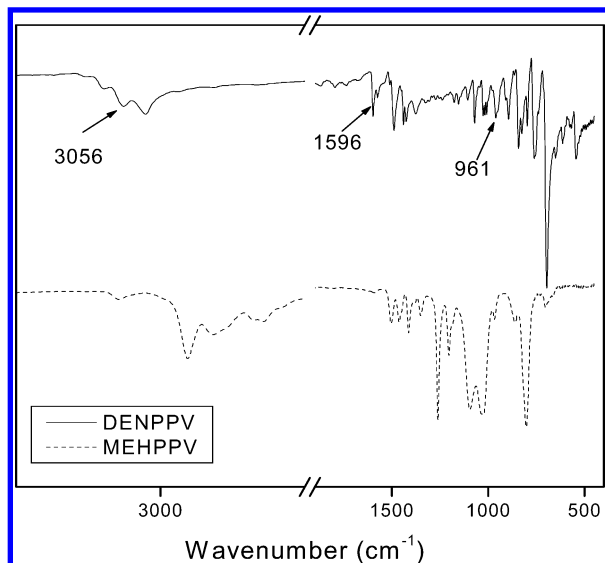


Figure 1. IR spectra of DENPPV and MEHPPV.

Table 1. Molecular Weights and Thermal Properties of DENPPV and Copolymers

polymer	mol wt <sup>c</sup>		PDI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	TGA 5 wt % loss temp (°C)
	$M_n$	$M_w$			
DENPPV	100 000	280 000	2.1	243	502
88DENPPV	120 000	173 000	1.5	226	468
75DENPPV	110 600	136 000	1.1	208	448
63DENPPV	98 000	188 000	1.9	198	427
50DENPPV	78 000	110 000	1.5	186	398
25DENPPV	95 000	238 000	2.0	145	389

<sup>a</sup> PDI = Polydispersity index. <sup>b</sup>  $T_g$  = Glass transition temperature. <sup>c</sup> Molecular weights were calculated with relative to polystyrene standard.

measured the molecular mass and polydispersity index (PDI) of each copolymer by GPC using THF as the eluent; the results are presented in Table 1. We determined the weight-average molecular weights of the polymers to be in the range  $(1.6\text{--}3) \times 10^5$  with polydispersities ranges from 1.1 to 2.1. The DENPPV polymer exhibits limited solubility in THF and in DMF, and it has very low solubility when its molecular weight reaches above  $3 \times 10^5$ . The glass transition temperature ( $T_g$ ) of DENPPV occurs at 243 °C, which is much higher than that of MEHPPV, that can extended device longevity.<sup>21,22</sup> TGA of the DENPPV copolymers displayed that their 5% weight losses occurred between 502 and 336 °C. These thermal stabilities and glass transition temperatures are higher than those of other phenylated PPVs reported previously. The higher glass transition and thermal stability are due to the restricted polymer chain mobility and resistant to thermal oxidation imparted by the rigid dendritic phenyl group.

The PL spectrum of the dendritic phenyl exhibits a peak maximum at 370 nm (Figure 2a), while the maximum absorption peak due to the  $\pi\text{--}\pi$  transition of the backbone of DENPPV appeared at 423 nm. A large overlapped area from the two respective peaks is present indicating the possible intramolecular energy transfer since it is known that energy transfer can occur readily when the PL of a chromophore having a wide band gap overlaps with the electronic absorption of the other chromophore possessing a narrow one. We measured the energy band gap of the polymers using the oxidation and reduction potentials obtained from cyclic voltammetry and the UV-vis absorption spectra. The

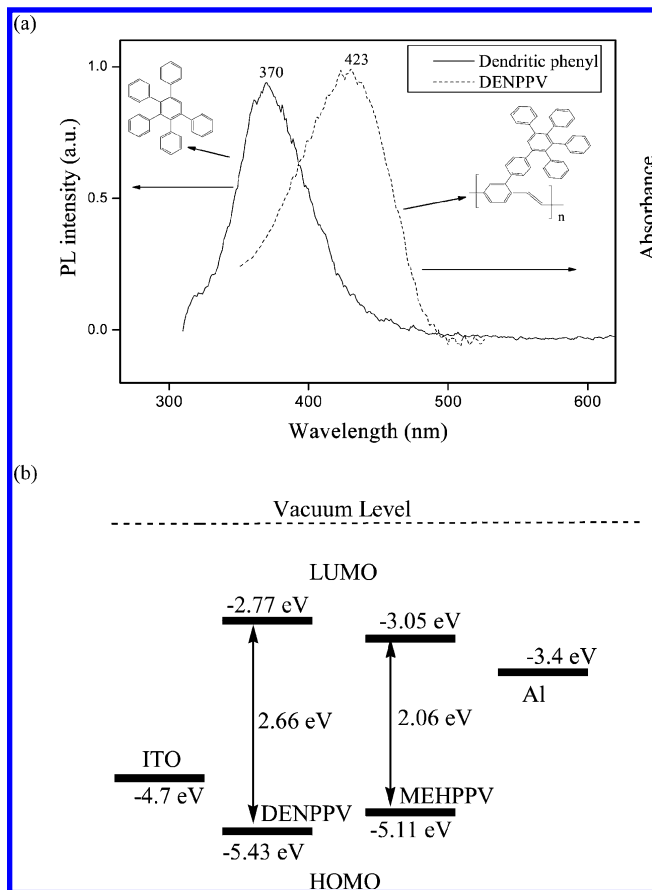


Figure 2. (a) UV and PL spectra of the DENPPV and a dendritic phenyl model compound and (b) energy level diagram of DENPPV and MEHPPV.<sup>26</sup>

reduction ( $E_{red}$ ) and oxidation ( $E_{ox}$ ) potentials for DENPPV were 1.63 and 1.13, respectively. The highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energies were estimated electrochemically to be  $-5.43$  and  $-2.77$  eV, respectively, with a band gap of 2.66 eV. Figure 2b presents the energy level diagram of DENPPV and MEHPPV. The LUMO of DENPPV is higher than that of MEHPPV, while the HOMO of DENPPV is lower than that of MEHPPV. From Figure 2, parts a and b, we conclude that intramolecular energy transfer can occur effectively from the phenylated dendrimer units to the polymer backbone.

The UV and PL spectra of the polymers in THF solution are presented in Figure 3. The absorption peak maximum of each polymer appears between 423 and 485 nm. The polymer solutions display intense blue-green emissions (peak maxima at 492–551 nm), which are blue-shifted as the concentration of the dendritic phenyl monomer in the copolymer increased. The DENPPV polymer displays an emission maximum at 492 nm and a shoulder peak in the range 520–550 nm. We attribute the shoulder peak that appears in the PL spectrum of DENPPV to the vibronic effect of the aromatic ring of the substituent phenylated dendrimer, because these two peaks differ by 1100–1200  $\text{cm}^{-1}$ , calculated using peak maximum values of PL spectrum.<sup>23</sup> Surprisingly, this shoulder peak was not prominent in the PL spectra of the copolymers. On the other hand, the emission at 598 nm, which is due to aggregation appeared in the spectra of MEHPPV and 25DENPPV. In Figure 3, we observe that excimer formation is suppressed significantly upon increasing the content of dendritic phenyl monomer in MEHPPV.

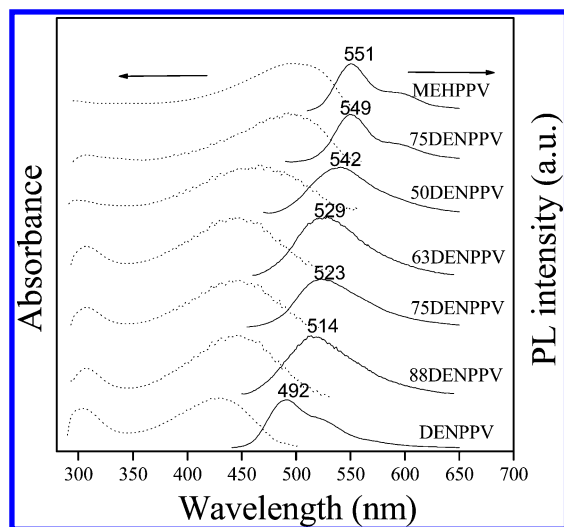


Figure 3. UV and PL spectra of DENPPV and copolymers.

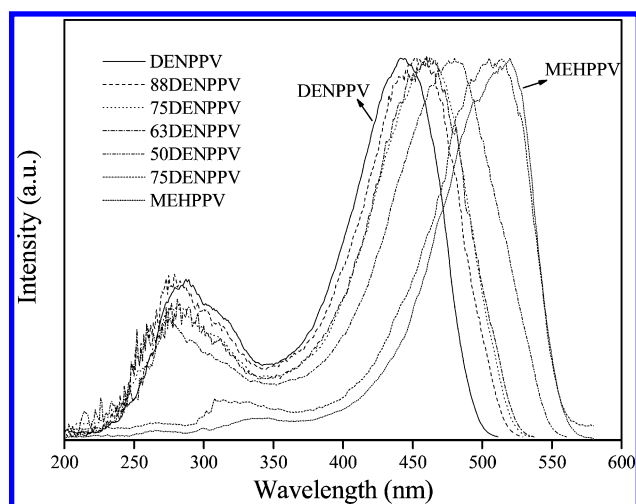


Figure 4. Excitation spectra of the copolymers in THF solution.

Figure 4 presents the excitation spectra of the polymers in solution; they indicate that the well-resolved small peak at 300 nm is due to the substituent dendritic phenyl group, which also confirms that energy transfer occurs from the side chain to the polymer backbone. We observe from Figure 4 that the excitation spectra are the same as the UV-vis spectra; this finding indicates the high purity of the emitting chromophores.

The thin film PL spectra was observed to be similar to those of the solutions, e.g., DENPPV undergoes no significant red shift in the film. In contrast, the MEHPPV, lacking dendron substituents exhibits a marked red shift in its solid state from its solution state absorption and emission spectra (551 vs 582 nm), which we believe can be attributed to interactions, such as  $\pi$ - $\pi$  stacking, between the chromophores. These spectra also suggest that the aggregation and migration of the chromophores are reduced in the dendrimers and indicate that even the first-generation dendrimers can effectively suppress  $\pi$ - $\pi$  stacking among polymer chains. Table 2 presents the quantum yields of polymers in the solid state and in solution, and their photoluminescence data. The decadic molar extinction coefficient ( $\epsilon$ ) was determined in THF using eq 1:

$$\epsilon = OD/cl \text{ (dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\text{)} \quad (1)$$

Table 2. Absorption and Photoluminescence Data of DENPPV and Copolymers

polymer	$\epsilon$ ( $\text{M}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	OD <sup>b</sup>	$L$ (nm) <sup>c</sup>	$M$ ( $\text{mol}/\text{cm}^3$ ) <sup>d</sup>	$\eta^s$ <sup>e</sup>	$\eta^{tf}$ <sup>f</sup>
DENPPV	72 900	0.241 47	65	5.04	0.67	0.65
88DENPPV	11 920	0.0855	45	3.09	0.66	0.68
75DENPPV	60 070	0.0862	52	2.75	0.55	0.82
63DENPPV	21 506	0.167 58	65	2.07	0.47	0.41
50DENPPV	52 185	0.169 08	60	5.33	0.50	0.42
25DENPPV	92 065	0.4284	45	1.33	0.33	0.30
MEHPPV	99 274	0.140 78	85	1.48	0.30	0.27

<sup>a</sup>  $\epsilon$  = Decadic molar extinction coefficient ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). <sup>b</sup> OD = Absorbance or optical density in the solid state. <sup>c</sup>  $L$  = Thickness of the thin film. <sup>d</sup>  $M$  = Fluorescent chromophore concentration in the film of each composite. <sup>e</sup>  $\eta^{tf}$  = Thin-film quantum yield estimated by using coumarin 6 dispersed in PMMA film at a concentration  $< 10^{-3} \text{ M}$ .<sup>25</sup> <sup>f</sup>  $\eta^s$  = Solution quantum yield estimated by using coumarin 6 in THF as the reference.

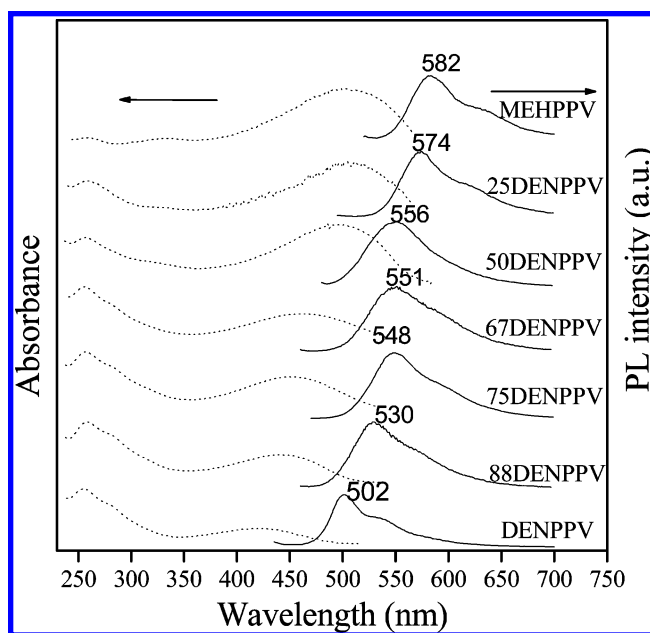


Figure 5. UV and PL spectra of DENPPV and copolymer thin films.

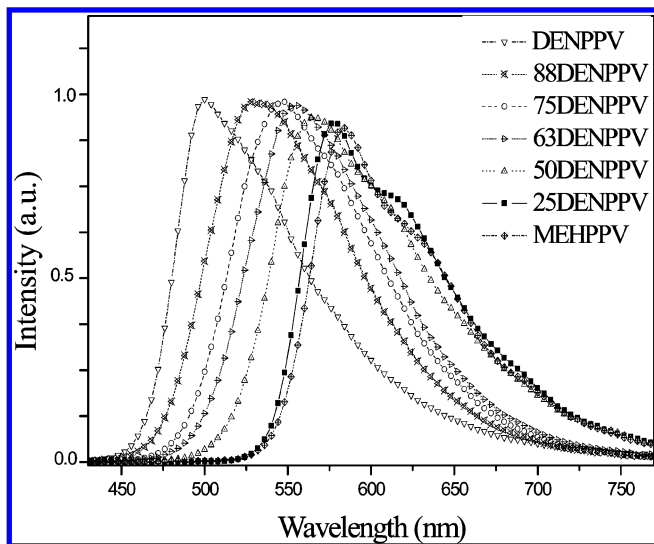
where OD is the optical density,  $c$  is the concentration of the polymer in solution, and  $l$  is the optical path length of the sample. We determined the fluorescent chromophore concentration ( $M$ ) in the thin film using eq 2:

$$M = OD/\epsilon L \text{ (mol}/\text{cm}^3\text{)} \quad (2)$$

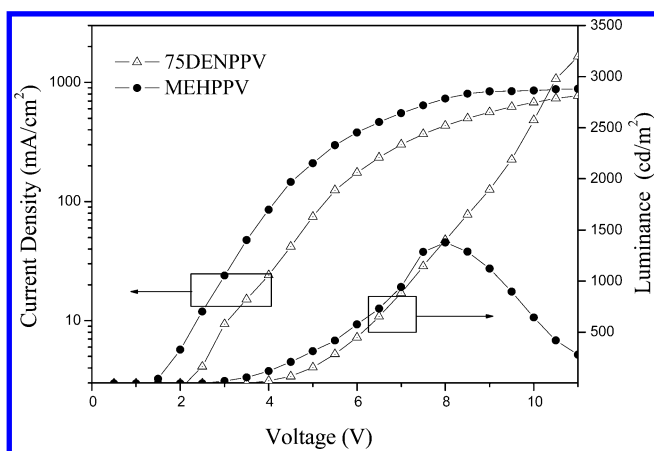
where  $L$  is the thickness of the film.

DENPPV displays a quantum yield of 0.67 in THF, calculated with reference to coumarin 6; this quantum yield is for about 2-fold higher than that of the well-established MEHPPV, in the solid state it is 0.65. The copolymer 75DENPPV displays a higher quantum yield (0.82) in the solid state than that of DENPPV, which can be explained by quantum confinement.<sup>24</sup> The higher quantum yields of copolymers 88DENPPV and 75DENPPV in their solid state than that of solution can be explained as being due to the steric effect of dendritic phenyls where the PPV backbone forces the pendant dendritic phenyl ring to point away (one up and one down) from the conjugated plane. Such a three-dimensional structure prevents PPV stacking in any dimension, providing higher quantum yields.<sup>10d</sup>

We fabricated double-layer LED devices having the configuration ITO/poly(3,4-ethylenedioxythiophene) (PE-



**Figure 6.** EL spectra of DENPPV and copolymers.



**Figure 7.** Plots of current density vs voltage and luminescence vs voltage of the devices prepared from 75DENPPV and MEHPPV.

DOT):poly(styrene sulfonic acid) (PSS)/DENPPV/Ca/Al. The EL spectrum of the DENPPV device was similar to its PL spectrum in that it displays an intense signal having a peak maximum at 499 nm (Figure 6.). The copolymer MEHPPV/DENPPV at a molar ratio of 25/75 exhibits an even more intense signal at 547 nm. Figure 7 presents the variations of the current density and brightness of the EL devices prepared from MEHPPV and 75DENPPV. The electroluminescence of copolymer 75DENPPV displays highest efficiency (0.12 lm/W), it is 70% higher than that of MEHPPV (0.07 lm/W) measured under similar conditions. All of these polymers shows better electroluminescence efficiency ( $\eta_{EL}$ ) providing that a minimization of the self-quenching has occurred by attaching the bulky dendrons on the polymer backbone and by preventing aggregation of the polymer chains without altering their electronic properties and better device structure.

## Conclusion

In this study, we synthesized a high molecular-weight poly(phenylenevinylene) (PPV) containing bulky dendritic phenyl groups (DENPPV) as PPV side chains. The dendritic phenyl-substituted monomer was synthesized through Suzuki coupling reaction and then polymerized using the Gilch route. The dendritic phenyl group is found to be involved in the intramolecular energy

transfer that occurs from the dendritic phenyl groups to the PPV backbone. The PL quantum yield of DENPPV (67%) is among the highest values reported for fully conjugated PPV. The copolymer DENPPV/MEHPPV molar ratio of 75/25 exhibited increased values of  $\eta_{EL}$  and  $\eta_{PL}$  that may make them useful as active layers in devices such as LEDs and photovoltaic diodes.

**Supporting Information Available:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of DENPPV and the monomer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## References and Notes

- (1) (a) Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* **1993**, *26*, 6570. (b) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M. *Science* **1995**, *267*, 1969. (c) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 3621. (d) Berggren, M.; Inganäs, O.; Gustafsson, G.; Carberg, J. C.; Rasmussen, J.; Anderson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444.
- (2) (a) Greenham, N. C.; Samuel, I. D. W.; Hayes, 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. (b) Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Crystall, B.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1996**, *76*, 15. (c) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. *J. Chem. Phys.* **1994**, *101*, 1673. (d) Hwang, D.-H.; Kim, S. T.; Li, X. C.; Chuah, B. S.; Demello, J. C.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Polym. Prepr.* **1997**, *38*, 319.
- (3) (a) Bao, Z.; Peng, Z.; Galvin, M. E.; Chandross, E. A. *Chem. Mater.* **1998**, *10*, 1201. (b) Chung, S. J.; Kwon, K. Y.; Lee, S. W.; Jin, J. I.; Lee, C. H.; Lee, C. E.; Park, Y. *Adv. Mater.* **1998**, *10*, 1112. (c) Chen, Z. K.; Meng, H.; Lai, Y. H.; Huang, W. *Macromolecules* **1999**, *32*, 4351. (d) Greenham, A. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1993**, *365*, 628.
- (4) Becker, H.; Spreitzer, H.; Kreuder, W.; Kluge, E.; Schenk, H.; Parker, I.; Cao, Y. *Adv. Mater.* **2000**, *12*, 42.
- (5) Sokolik, I.; Yang, Z.; Karasz, F. E.; Morton, D. C. *J. Appl. Phys.* **1993**, *74*, 3584. (b) Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* **1993**, *26*, 6570. (c) Pasco, S. T.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1999**, *32*, 6933. (d) Mikroyannidis, J. A. *Chem. Mater.* **2003**, *15*, 1865.
- (6) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
- (7) Aratani, S.; Zhang, C.; Pakbaz, K.; Hoger, S.; Wudl, F.; Heeger, A. J. *J. Elec. Mater.* **1993**, *22*, 745.
- (8) Yang, Y.; Heeger, A. J. *Appl. Phys. Lett.* **1994**, *64*, 1245.
- (9) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
- (10) (a) Chu, H. Y.; Hwang, D.-H.; Do, L.-M.; Chang, J.-H.; Shim, H.-K.; Holmes, A. B.; Zyung, T. *Synth. Met.* **1999**, *101*, 216. (b) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1993**, *115*, 231. (c) Lee, S. H.; Jang, B.-B.; Tsutsui, T. *Chem. Lett.* **2000**, 1184. (d) Peng, Z.; Zhang, J.; Xu, B. *Macromolecules* **1999**, *32*, 5162.
- (11) (a) Andersson, M. R.; Yu, G.; Heeger, A. J. *Synth. Met.* **1997**, *885*, 1275. (b) Wudl, F.; Srdanov, G.; US Patent No. 5 189 136, **1993**.
- (12) Johansson, D. M.; Xiangjun Wang; Tomas Johansson; Inganäs, O.; Yu, G.; Srdanov, G.; Andersson, M. R. *Macromolecules* **2002**, *35*, 4997.
- (13) Becker, H.; Spreitzer, H.; Kreuder, W.; Kluge, E.; Vestweber, H.; Schenk, H.; Treacher, K. *Synth. Met.* **2001**, *122*, 105.
- (14) Johansson, D. M.; Theander, M.; Srdanov, G.; Yu, G.; Inganäs, O.; Andersson, M. R. *Macromolecules* **2001**, *34*, 3716.
- (15) Klarner, G.; Miller, R. D.; Hawker, C. J. *Polym. Prepr.* **1998**, *39*, 1006.
- (16) Frauenrath, H. *Prog. Polym. Sci.* **2005**, *30* 325.

- (17) Chou, C.-H.; Hsu, S. L.; Dinakaran, K.; Chiu, M. Y.; Wei, K. H. *Macromolecules* **2005**, *38*, 745. (b) Chou, C.-H.; Shu, C.-F. *Macromolecules* **2002**, *35*, 9673.
- (18) Qu, J.; Zhang, J.; Grimsdale, A. C.; Mullen, K.; Jaiser, F.; Yang, X.; Neher, D. *Macromolecules* **2004**, *37*, 8297.
- (19) Pogantsch, A.; Wenzel, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Mullen, K. *Adv. Mater.* **2002**, *14*, 1061.
- (20) Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925.
- (21) Dogariu, A.; Gupta, R.; Heeger, A. J.; Wang, H. *Synth. Met.* **1999**, *100*, 95.
- (22) Shin, D. C.; Ahn, J. H.; Kim, Y. H.; Kwon, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3086.
- (23) Chen, S. H.; Su, A. C.; Chou, H. L.; Peng, K. Y.; Chen, S. A. *Macromolecules* **2004**, *37*, 167.
- (24) Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganas, O.; Andersson, M. R. *Macromolecules* **2000**, *33*, 2525.
- (25) Swanson, S. A.; Wallraff, G. M.; Chen, J. P.; Zhang, W.; Bozano, L. D.; Carter, K. R.; Salem, J. R.; Villa, R.; Scott, J. C. *Chem. Mater.* **2003**, *15*, 2305.
- (26) Jin, S. H.; Jang, M. S.; Suh, H. S.; Cho, H. N.; Lee, J. H.; Gal, Y. S. *Chem. Mater.* **2002**, *14*, 643.

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