Synthesis and Opto-Electrical Properties of Dendron-Containing Poly(2,3-diphenyl-1,4-phenylenevinylene) Derivatives

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ABSTRACT: A new series of poly(2,3-diphenyl-1,4-phenylenevinylene) derivatives containing dendritic side groups were synthesized. Different generations of dendrons were integrated on the pendant phenyl ring to investigate their effect on optical and electrical properties of final polymers. Homopolymers can not be obtained via the Gilch polymerization because of sterically bulky dendrons. By controlling the feed ratio of different monomers during polymerization, dendron-containing copolymers with high molecular weights were obtained. The UV–vis absorption and photoluminescent spectra of the thin films are pretty close; however, quantum efficiency is significantly enhanced with increasing the generation of dendrons. The electrochemical analysis reveals that hole-injection is also improved by increasing dendritic generation. Double-layer light-emitting devices with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al were fabricated. High generation dendrons bring benefit of improved device performance. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 3440–3450, 2007
Keywords: conjugated polymers; light-emitting diodes (LED); luminescence

INTRODUCTION

Semiconducting polymers have been intensively investigated for their potential applications in light-emitting diodes,[1,2] thin film transitors,[3] organic laser,[4] and solar cells.[5] Among them, poly(1,4-phenylene vinylene) (PPV) has attracted a great deal of attention in recent years because of its unique structure and highly electroluminescent (EL) properties.[6] Long alkyl chains and/or bulky substitutents have been incorporated onto the PPV main chain to improve its solubility to cast thin films by solution process. Electron donating/withdrawing groups have also been introduced to adjust the optical and electrical properties. Till now many PPV derivatives have been synthesized to investigate their potential applications, for example, poly[2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV) is an orange–red emissive polymer and soluble in common organic solvents.[7] Thin film of MEH-PPV can be obtained from a spin-coating process. Cyano-substituted poly(2,5-dialkoxy-1,4-phenylene vinylene) is a red emissive polymer with high electron affinities.[8,9] Silyl-substituted PPV is a greenish emissive material with a tendency to be easily charged by electrons rather than holes.[10,11]

PPV, originally, is a yellow–green emissive polymer. Pure blue, green, and red emissions are not easy to achieve for fully conjugated PPV. It is generally thought that increase of steric hindrance can reduce the conjugation length of

the polymer chain and tune the emission to blue light region. For this reason, many bulky groups have been incorporated and blue-shifted emissions were obtained.[12,13] Hsieh et al. first proposed a synthetic route to poly(2,3-diphenyl-1, 4-phenylene vinylene) (DP-PPV), which exhibits high photoluminescence (PL) efficiency in the solid state.[14] Different substituents were introduced at C-5 position of the phenylene moiety to modify its properties. For example, highly phenylated DP-PPV was synthesized to further improve PL efficiency.[15] Long alkyl chains were incorporated to improve the solubility of the polymer.[16] Liquid crystalline side chains were also incorporated to achieve polarized emissions.[17,18] By following this synthetic route, monomers containing diverse functional groups are easily synthesized and therefore soluble DP-PPV derivatives with high molecular weights are also easily obtained. Despite the advantages mentioned earlier, low device performance using DP-PPVs as active layers is obtained and thus restricts their potential use for display applications. Recently we have reported two series of DP-PPV derivatives containing long branched alkoxy and fluorenyl substituents. Both the brightness and current efficiency are highly improved.[19]

For most of the conjugated polymers, their luminescent quantum efficiency is substantially lower in the solid state than that in the solution state because of intermolecular interactions, such as aggregation and excimer formation, which lead to a self-quenching process of excitons. To minimize such intermolecular interactions and increase the luminescent quantum efficiency in solid state, an effective strategy is introducing the bulky dendritic side groups to the conjugated polymer backbone. Many dendron-containing polymers and their self-assembled properties have been reported by Percec and cow-orkers.[20–29] Conjugated polymers with dendritic side groups have also been reported in the literatures, such as poly(*p*-phenylene vinylene),[30–22] polyfluorene,[33–35] and polythiophene.[36] In this study, we synthesized the first example of DP-PPV containing dendron side groups. Four copolymers derived from copolymerizing with 1,4-bis(chloromethyl)-2,5-dimethoxybenzene and 1,4-bis-(chloromethyl)-2-[4′-(3,7-dimethyloctoxy)phenyl]-3-phenylbenzene[19] were synthesized. The electrical and spectroscopic properties of theses polymers were systematically investigated. In addition, double-layer light-emitting devices were

also fabricated to study EL properties of the polymers.

EXPERIMENTAL

Characterization Methods

^{1}H NMR spectra were measured with a Varian 300 MHz spectrometer. Gel permeation chromatography (GPC) data assembled from a Viscotek T50A Differential Viscometer and a LR125 Laser Refractometer and three columns in series were used to measure the molecular weights of polymers relative to polystyrene standards at 35 °C. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris Diamond DSC instrument at a scan rate of 10 °C/min. Thermal gravimetric analysis (TGA) was undertaken on a PerkinElmer Pyris 1 TGA instrument with a heating rate of 10 °C/min. UV–vis absorption spectra were obtained with an HP 8453 diode array spectrophotometer. PL emission spectra were obtained using ARC SpectraPro-150 luminescence spectrometer. Cyclic voltammetric (CV) measurements were made in acetonitrile (CH_3CN) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scan rate of 50 mV/s. Platinum wires were used as both the counter and working electrodes, and silver/silver ions (Ag in 0.1 M $AgNO_3$ solution, from Bioanalytical Systems) as the reference electrode, and ferrocene was used as an internal standard. The corresponding highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels were estimated from the onset redox potentials.

Synthesis of Monomers and Polymers

All reagents and chemicals were purchased from commercial sources (Aldrich, Lancaster, or TCI) and used without further purification. Tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone. Scheme 1 outlines the synthetic routes for Dendrons **1**, **3**, and **5**.

(3,5-Bis(10-undecenyloxy)phenyl)methanol (1)

To a solution of 11-bromo-1-undecene (5.0 g, 21.44 mmol), potassium carbonate (3.22 g, 23.3 mmol), and potassium iodide (0.39 g, 2.33 mmol) in acetonitrile (50 mL) was added (3,5-dihydroxyphenyl)methanol (1.31 g, 9.32 mmol). The
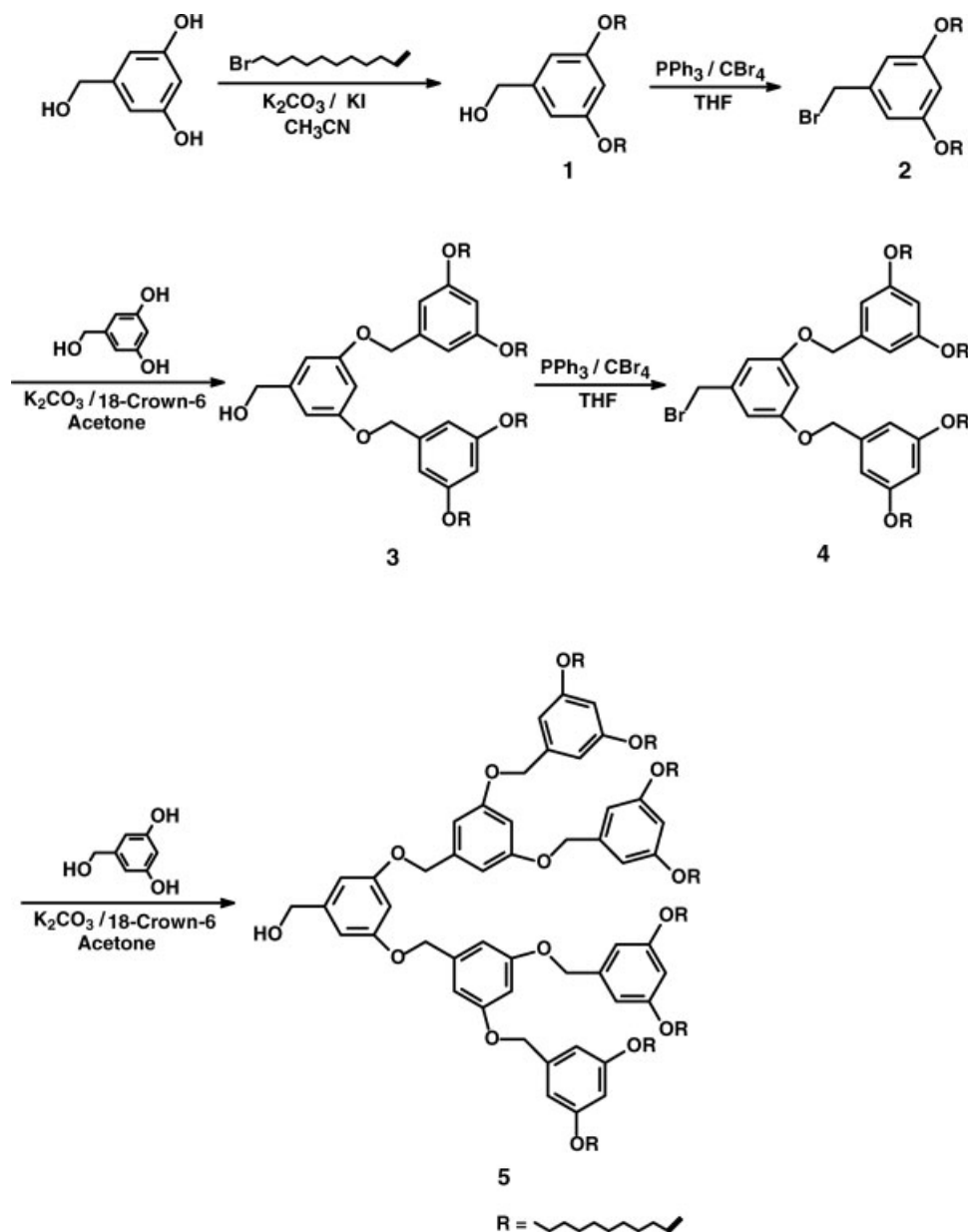
Scheme 1. Synthesis of Dendrons **1**, **3**, and **5**.

mixture was refluxed at 100 °C for 24 h. After cooling to room temperature, the solution was filtered and concentrated by evaporating the solvent. The crude product was dissolved in 50 mL of ethyl acetate and extracted with water (50 mL) twice. The organic phase was then dried over magnesium sulfate, isolated by evaporating the solvent, and purified by gel chromatography (silica gel, *n*-hexane:ethyl acetate = 5:1 as the eluent) to give 3.61 g (87%) of colorless liquid.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.28–1.52 (m, 24H, —(CH_2)$_6$—), 1.74 (m, 4H, —OCH$_2$—CH_2—), 2.01 (q, J = 6.4 Hz, 4H, —CH_2—CH=CH$_2$), 3.91 (t, J = 7 Hz, 4H, —OCH_2—), 4.59 (s, 2H, Ph—CH_2—OH), 4.94 (dd, J = 8.4 Hz, —CH=CH_2), 5.78 (m, 2H, —CH=CH$_2$), 6.35 (s, 1H, aromatic-H), 6.47 (s, 2H, aromatic-H).

(3,5-Bis(10-undecenyloxy)phenyl)methyl Bromide (2)

To a 50 mL two-necked round flask was added 1 (2.0 g, 4.5 mmol), carbon tetrabromide (2.23 g,

6.75 mmol), and THF (5 mL). A solution of triphenylphosphine (1.77 g, 6.75 mmol) in THF (5 mL) was then added dropwise at 0 °C. The mixture was stirred at room temperature for 30 min. After the reaction was completed, the solution was concentrated by evaporating the solvent. The crude product was dissolved in 30 mL of ethyl acetate and extracted with water (30 mL) twice. The organic phase was then dried over magnesium sulfate, isolated by evaporating the solvent, and purified by gel chromatography (silica gel, n-hexane:dichloromethane = 2:1 as the eluent) to give 2.12 g (93%) of colorless liquid.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.23–1.42 (m, 24H, —(CH$_2$)$_6$—), 1.74 (m, 4H, —OCH$_2$—CH$_2$—), 2.03 (q, J = 6.4 Hz, 4H, —CH$_2$—CH=CH$_2$), 3.9 (t, J = 7 Hz, 4H, —OCH$_2$—), 4.38 (s, 2H, Ph—CH$_2$—Br), 4.94 (dd, J = 8.4 Hz, —CH=CH$_2$), 5.78 (m, 2H, —CH=CH$_2$), 6.35 (s, 1H, aromatic-H), 6.48 (s, 2H, aromatic-H).

3,5-Bis(3,5-bis(10-undecenyloxy)benzyloxy)phenyl Methanol (3)

To a solution of 2 (2.0 g, 3.94 mmol), 18-crown-6 ether (0.12 g, 0.47 mmol), and potassium carbonate (0.65 g, 4.7 mmol) in acetone (20 mL) was added 3,5-dihydroxyphenylmethanol (0.26 g, 1.88 mmol). The mixture was refluxed at 80 °C for 24 h. After cooling to room temperature, the solution was filtered and concentrated by evaporating the solvent. The crude product was dissolved in 50 mL of ethyl acetate and extracted with water (50 mL) twice. The organic phase was then dried over magnesium sulfate, isolated by evaporating the solvent, and purified by gel chromatography (silica gel, n-hexane:ethyl acetate = 5:1 as the eluent) to give 1.59 g (85%) of pale-yellow liquid.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.24–1.41 (m, 48H, —(CH$_2$)$_6$—), 1.74 (m, 8H, —OCH$_2$—CH$_2$—), 2.03 (q, J = 6.4 Hz, 8H, —CH$_2$—CH=CH$_2$), 3.91 (t, J = 7 Hz, 8H, —OCH$_2$—), 4.61 (s, 2H, Ph—CH$_2$—OH), 4.93 (s, 4H, Ph—CH$_2$O—Ph), 4.94 (dd, J = 8.4 Hz, 8H, —CH=CH$_2$), 5.75 (m, 4H, —CH=CH$_2$), 6.37 (s, 2H, aromatic-H), 6.52 (s, 5H, aromatic-H), 6.58 (s, 2H, aromatic-H).

3,5-Bis-(3,5-bis(10-undecenyloxy)benzyloxy)benzyl Bromide (4)

By following the synthetic procedure for **2** and using **3** as starting material, the compound **4** was obtained as pale-yellow liquid (90% yield).

^{1}H NMR (CDCl$_3$, δ, ppm): 1.24–1.41 (m, 48H, —(CH$_2$)$_6$—), 1.74 (m, 8H, —OCH$_2$—CH$_2$—), 2.03 (q, J = 6.4 Hz, 8H, —CH$_2$—CH=CH$_2$), 3.91 (t, J = 7 Hz, 8H, —OCH$_2$—), 4.38 (s, 2H, Ph—CH$_2$—Br), 4.94 (s, 4H, Ph—CH$_2$O—Ph), 4.99 (dd, J = 8.4 Hz, 8H, —CH=CH$_2$), 5.78 (m, 4H, —CH=CH$_2$), 6.38 (s, 2H, aromatic-H), 6.52 (s, 5H, aromatic-H), 6.6 (s, 2H, aromatic-H).

3,5-Bis(3,5-bis(3,5-bis(10-undecenyloxy)benzyloxy)-benzyloxy)phenyl Methanol (5)

By following the synthetic procedure for **3** and using **4** as starting material, the compound **5** was obtained as yellow liquid (83% yield).

^{1}H NMR (CDCl$_3$, δ, ppm): 1.23–1.39 (m, 96H, —(CH$_2$)$_6$—), 1.73 (m, 16H, —OCH$_2$—CH$_2$—), 1.99 (q, J = 6.4 Hz, 16H, —CH$_2$—CH=CH$_2$), 3.9 (t, J = 7 Hz, 16H, —OCH$_2$—), 4.6 (s, 2H, Ph—CH$_2$—OH), 4.88 (s, 12H, Ph—CH$_2$O—Ph), 4.92 (dd, J = 8.4 Hz, 16H, —CH=CH$_2$), 5.78 (m, 8H, —CH=CH$_2$), 6.37 (s, 2H, aromatic-H), 6.47 (s, 5H, aromatic-H), 6.52 (s, 10H, aromatic-H), 6.63 (s, 4H, aromatic-H).

Synthesis of Monomers G1M-G3M: General Procedure

Scheme 2 shows the synthetic route for dendron-containing momomers **G1M–G3M** with different generations. An experimental procedure for **G1M** is given below. To a 50 mL round flask was added **1** (0.57 g, 1.28 mmol), **6** (0.5 g, 1.16 mmol), triphenylphosphine (PPh$_3$) (0.4 g, 1.51 mmol), and THF (10 mL). Diethyl azodicarboxylate (DIAD) (0.31 g, 1.51 mmol) was slowly added to the solution at 0 °C. The mixture was stirred at room temperature for 12 h. The crude product was isolated by evaporating the solvent and further purified by gel chromatography (silica gel, n-hexane:ethyl acetate = 5:1 as the eluent) to give the product of pale-yellow liquid.

1,4-Bis(bromomethyl)-2-(3,5-bis(10-undecenyloxy)-benzyloxy)phenyl-3-phenyl Benzene (G1M)

Yield 63%. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.28–1.4 (m, 24H, —(CH$_2$)$_6$—), 1.74 (m, 4H, —OCH$_2$—CH$_2$—), 2.01 (q, J = 6.4 Hz, 4H, —CH$_2$—CH=CH$_2$), 3.91 (t, J = 7 Hz, 8H, —OCH$_2$—), 4.24 (s, 4H, Ph—CH$_2$—Br), 4.89 (s, 2H, Ph—CH$_2$O—Ph), 4.94 (dd, J = 8.4 Hz, 4H, —CH=CH$_2$), 5.11 (s, 2H, diphenyl-OCH$_2$—), 5.78 (m, 2H, —CH=CH$_2$), 6.35 (s, 1H, aromatic-H),
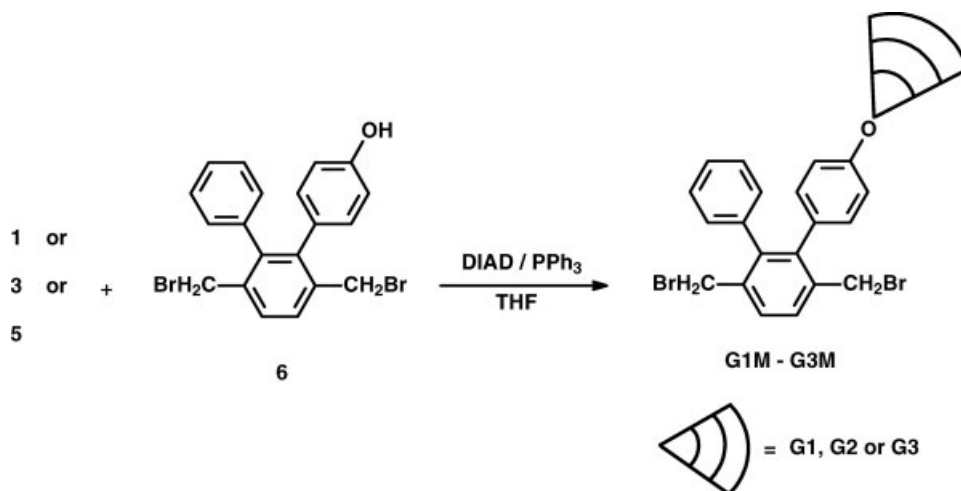
Scheme 2. Synthesis of dentron-containing monomers **G1M–G3M**.

6.47 (s, 2H, aromatic-H), 6.52 (s, 10H, aromatic-H), 6.87 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.02 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.12 (d, $J = 7.6$ Hz, 3H, aromatic-H), 7.17 (d, $J = 7.6$ Hz, 2H, aromatic-H), 7.41 (s, 2H, aromatic-H).

1,4-Bis(bromomethyl)-2-(3,5-bis(3,5-bis(10-undecenyloxy)benzyloxy)benzyloxy)phenyl-3-phenylbenzene (G2M)

Yield 61%. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.23–1.33 (m, 48H, —(CH_2)$_6$—), 1.74 (m, 8H, —OCH$_2$—CH_2—), 2.03 (q, $J = 6.4$ Hz, 8H, —CH_2—CH=CH$_2$), 3.91 (t, $J = 7$ Hz, 8H, —OCH_2—), 4.21 (s, 4H, Ph—CH_2—Br), 4.88 (s, 4H, Ph—CH_2O—Ph), 4.92 (dd, $J = 8.4$ Hz, 8H, —CH=CH_2), 5.22 (s, 2H, diphenyl-OCH_2—), 5.78 (m, 4H, —CH=CH$_2$), 6.38 (s, 2H, aromatic-H), 6.47 (s, 5H, aromatic-H), 6.52 (s, 2H, aromatic-H), 6.9 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.09 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.17 (d, $J = 7.6$ Hz, 3H, aromatic-H), 7.2 (d, $J = 7.6$ Hz, 2H, aromatic-H), 7.41 (s, 2H, aromatic-H).

1,4-Bis(bromomethyl)-2-(3,5-bis(3,5-bis(3,5-bis(10-undecenyloxy)benzyloxy)benzyloxy)benzyloxy)-phenyl-3-phenylbenzene (G3M)

Yield 59%. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.23–1.39 (m, 96H, —(CH_2)$_6$—), 1.73 (m, 16H, —OCH$_2$—CH_2—), 1.99 (q, $J = 6.4$ Hz, 16H, —CH_2—CH=CH$_2$), 3.9 (t, $J = 7$ Hz, 16H, —OCH_2—), 4.2 (s, 4H, Ph—CH_2—Br), 4.88 (s, 12H, Ph—CH_2O—Ph), 4.92 (dd, $J = 8.4$ Hz, 16H, —CH=CH_2), 5.22 (s, 2H, diphenyl-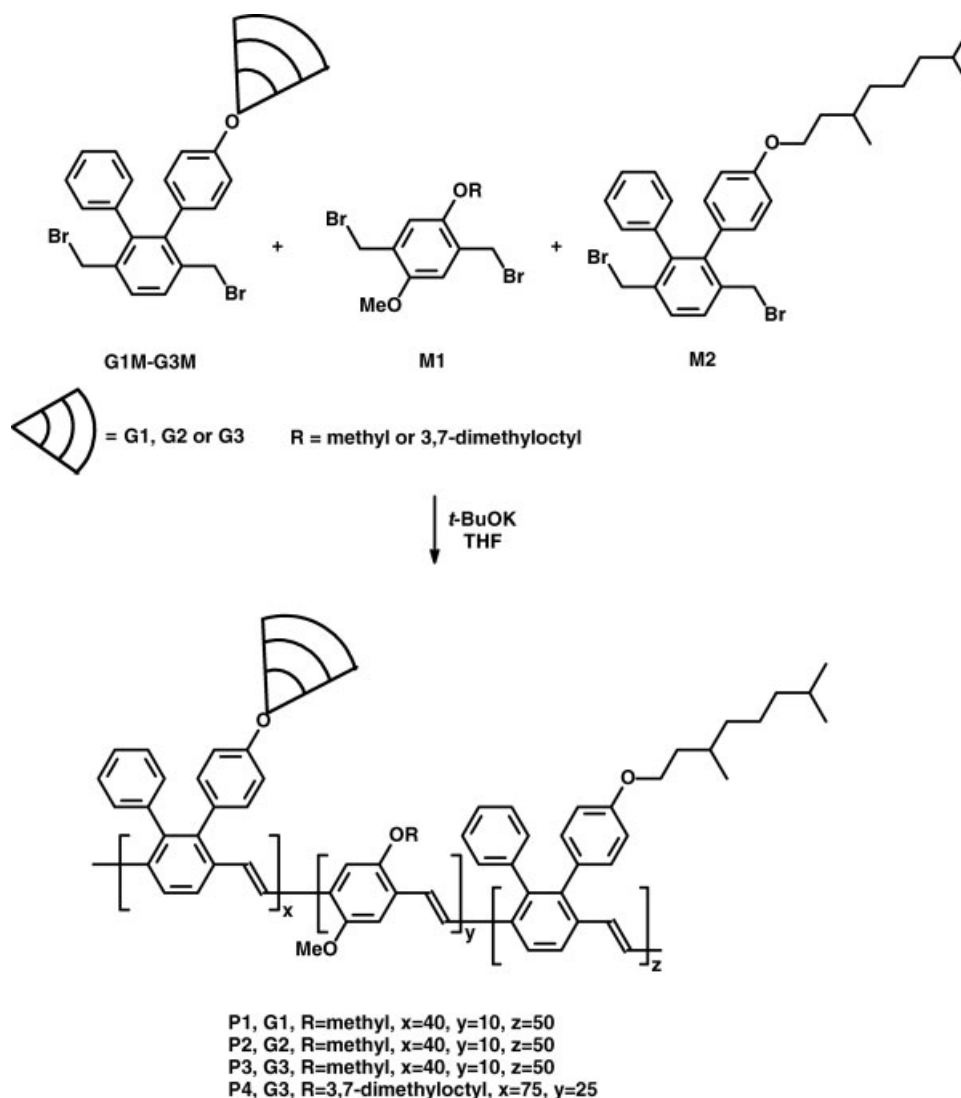OCH_2—), 5.78 (m, 8H, —CH=CH$_2$), 6.37 (s, 2H, aromatic-H), 6.47 (s, 5H, aromatic-H), 6.52 (s, 10H, aromatic-H), 6.63 (s, 4H, aromatic-H), 6.92 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.12 (d, $J = 7.4$ Hz, 2H, aromatic-H), 7.17 (d, $J = 7.6$ Hz, 3H, aromatic-H), 7.2 (d, $J = 7.6$ Hz, 2H, aromatic-H), 7.41 (s, 2H, aromatic-H).

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (M1) and 1,4-bis(bromomethyl)-2-[4′-(3,7-dimethyloctoxy)phenyl]-3-phenylbenzene (M2)

Monomers **M1** and **M2** were synthesized as described previously in the literatures.[19,37]

Synthesis of Polymers: General Procedure

Schemes 3 outlines the synthetic route for polymers **P1–P4**. An experimental procedure for polymer **P3** is given below. To a mixture of **G3M** (1.0 g, 0.4 mmol), **M1** (3.2×10^{-2} g, 0.1 mmol), **M2** (0.24 g, 0.5 mmol) in THF (25 mL) was added a solution of potassium *tert*-butoxide (*t*-BuOK, 12 equiv) in THF (15 mL). The resulting mixture was stirred at room temperature for 24 h under nitrogen atmosphere. A solution of 2,6-di-*tert*-butylphenol (6 equiv) as end-capping agent in THF (10 mL) was then added and stirred for additional 8 h. The polymer was obtained by pouring the mixture into methanol and filtered. It was purified by dialysis using Mw 50,000 membrane in THF. After drying under vacuum for 24 h, the polymer was obtained as bright-yellow solid (0.65 g, 51%).

P1, G1, R=methyl, x=40, y=10, z=50
P2, G2, R=methyl, x=40, y=10, z=50
P3, G3, R=methyl, x=40, y=10, z=50
P4, G3, R=3,7-dimethyloctyl, x=75, y=25

Scheme 3.   Synthesis of polymers **P1–P4**.

Device Fabrication and Measurements

Double-layer devices were fabricated as sandwich structures between calcium (Ca) cathodes and indium-tin oxide (ITO) anodes. ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water, and acetone. A 50 nm-thick hole-injection layer of poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate)

Table 1.   Feed Ratio and Polymerization Results of Polymers **P1–P4**

Polymer	G[a]	R	x	y	z	M_n $(\times 10^{-5})$	M_w $(\times 10^{-5})$	PDI[b]
P1	G1	Methyl	40	10	50	2.6	4.38	1.68
P2	G2	Methyl	40	10	50	2.47	4.09	1.66
P3	G3	Methyl	40	10	50	1.5	2.93	1.95
P4	G3	3,7-Dimethyloctyl	75	25		1.74	1.84	1.06

[a] Generation of dendrons.
[b] Polydispersity index = (M_w/M_n).

Table 2. Thermal and Optical Properties of Polymers **P1–P4**

Polymer	T_g (°C)	T_d (°C)	UV–vis (nm)		PL (nm)		Φ_{PL} (%)	
			Toluene	Film	Toluene	Film	Toluene	Film
P1	147	377	443	454	519	545	60	25
P2	145	364	447	453	517	540	68	37
P3	115	339	449	449	516	548	81	50
P4	119	378	454	453	533	552	75	46

(PSS) was spin-coated on top of ITO from a 0.7 wt % dispersion in water and dried at 150 °C for 1 h in a vacuum. Thin films of synthesized polymers were spin-coated from toluene solutions onto the PEDOT:PSS layer and dried at 50 °C overnight in a vacuum. The thickness of the active layer was about 50 nm. Finally, 35 nm Ca and 100 nm Al electrodes were made through a shadow mask onto the polymer films by thermal evaporation using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA). Evaporations were carried out typically at base pressures lower than 2×10^{-6} torr. The active area of each EL device was 4 mm^2 and the device was characterized following a published protocol.[38]

RESULTS AND DISCUSSION

Synthesis of Polymers

Scheme 1 outlines the synthetic route for dendrons with different generations. Long alkenyl chains were incorporated onto dendrons to increase solubility. Terminal vinyl bonds serve to identify intermediates and monomers, which shows characteristic peaks at 5–6 ppm in ^{1}H NMR spectra. Scheme 2 outlines the synthetic route for monomers **G1M–G3M**. Dendrons **1**, **3**, and **5** were reacted with Compound **6** via dehydration in the presence of DIAD/PPh$_3$ in THF to form monomers.

The polymerization was carried out via Gilch route to obtain soluble PPV derivatives. For a typical Gilch synthetic route, α,α'-dihalo-p-xylene is employed with excess amount of *tert*-BuOK in organic solvents. Alkyl or alkoxy chains are often incorporated on the aromatic rings to improve the solubility of the resulting polymers. It should be noted that only oligomers were obtained during homopolymerization of dendron-containing monomers; moreover, those oligomers could not provide sufficient thermal and film-forming properties. To effectively lower the steric hindrance during polymerization and

increase polymer molecular weights, copolymerization was carried out in this study. Scheme 3 outlines the syntheses of polymers **P1–P4**, from copolymerizing **G1M–G3M** with two different monomers **M1** and **M2**. It has been reported that incorporation of **M1** increases carrier mobility inside polymer layer.[39] **M2** is firstly synthesized and reported by our group, which shows electron-dominating property.[19] We expect that incorporation of **M1** and **M2** can adjust the optical and electrical properties of final polymers.

Table 1 summarizes the generation of dendrons, alkyl type on **M1**, feed ratio of monomers, molecular weights and polydispersity index (PDI) of resulting polymers. The number-average molecular weight (M_n) are in the range from 1.17×10^5 to 2.47×10^5, while the weight-average molecular weights (M_w) are in the range from 1.58×10^5 to 4.38×10^5. The molecular weight distribution is relatively narrow (PDI < 2). Polymers with high molecular weights can be obtained and soluble in common organic solvents, such as chloroform, toluene, and chlorobenzene. Transparent and self-standing films can be cast from their solutions.
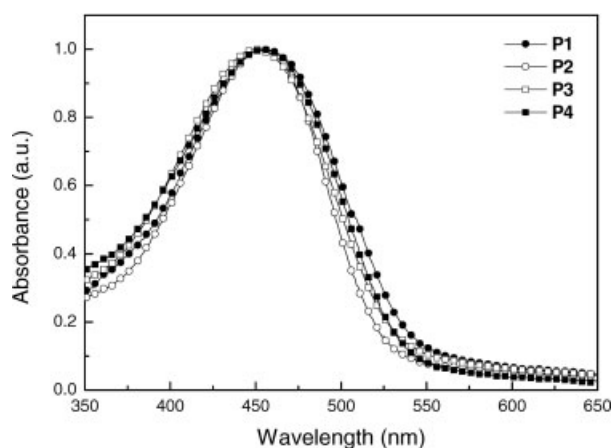

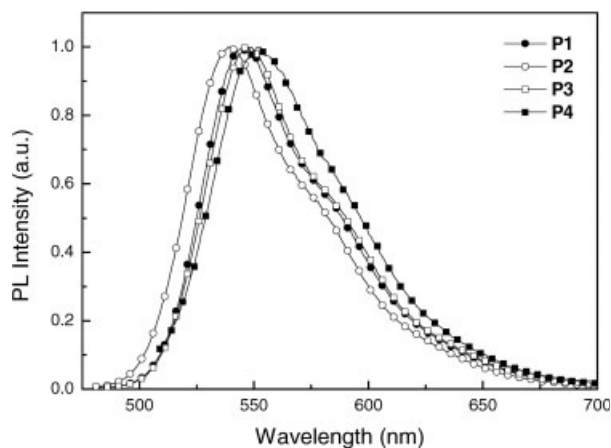**Figure 1.** UV–vis absorption spectra of polymers **P1–P4** in thin film state.

Figure 2. PL emission spectra of polymers **P1–P4** in thin film state.

From Table 1 some interesting tendencies are also noticed. By comparing polymers **P1–P3**, it is found that molecular weights were gradually decreased with increasing generation of dendrons. This is reasonable since bulky pendant groups result in large steric hindrance and hinder polymerization. Polymer **P4** has the smallest molecular weights and PDI value of 1.06.

Thermal Properties

Table 2 summarizes the thermal properties of polymers **P1–P4**. Most polymers show good thermal stabilities with high glass transition temperatures (T_g) over 115 °C and high decomposition temperatures (T_d) over 330 °C. Polymers **P1** and **P2** show even higher T_g (>140 °C), which can be attributed to their high molecular weights and low generation dendron.
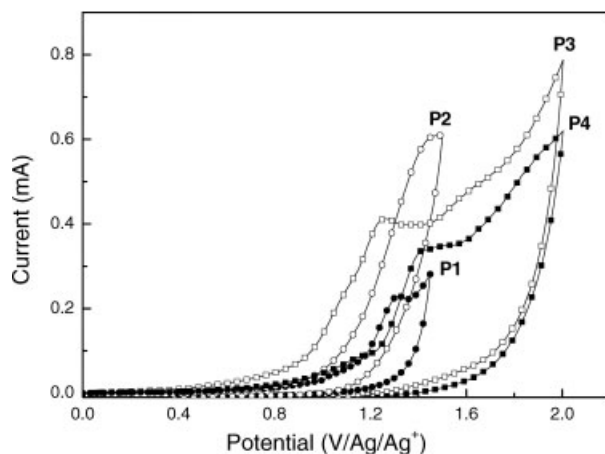
Table 3. Electrochemical Properties of Polymers **P1–P4** in Solid Films

Polymer	E_{ox} (V)	HOMO (eV)	UV Edge (nm)	EG (eV)	LUMO (eV)
P1	1.13	−5.53	546	2.27	−3.26
P2	1.08	−5.48	529	2.34	−3.14
P3	0.86	−5.26	535	2.32	−2.99
P4	1.18	−5.58	538	2.3	−3.28

For polymers **P1–P3**, it is seen that T_d value is gradually decreased with increasing generation of dendrons. It is clear that dendrons with higher generation own more alkyl groups. Polymers with long alkyl side chains are easier to decompose thermally than those with short chains.

Optical Properties

Figure 1 shows the UV–vis absorption spectra of polymers **P1–P4** in thin film state. Table 2 summarizes the UV–vis absorption maxima of all polymers in different states. The absorption maxima of synthesized polymers in toluene are located in the range from 443 to 454 nm, which is attributed to the $\pi–\pi^*$ transition along the conjugated backbone. The absorption maxima in thin film state show only small redshift (some are very close) compared with those in solution state. For these polymers dendritic groups play the role of preventing interchain interaction, which suggests no tendency toward aggregation in the solid state.

Figure 2 reveals the PL emission spectra of polymers **P1–P4** in thin film state. Similar to UV–vis spectra, the PL emission maxima is
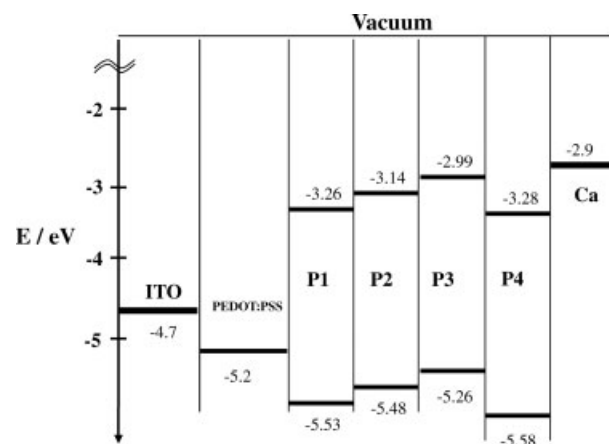

Figure 3. Cyclic voltammograms of polymers **P1–P4**.

Figure 4. Energy level diagrams of polymers **P1–P4**.
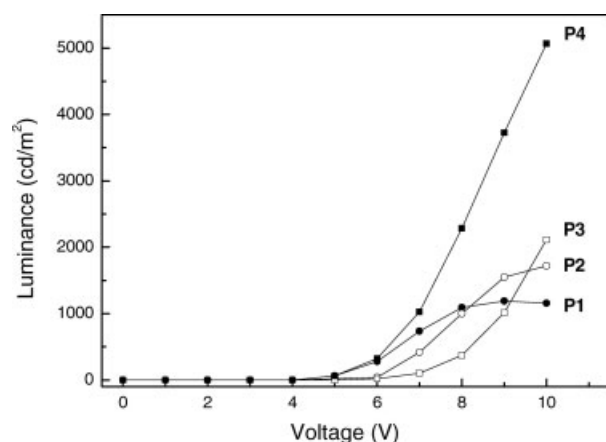
Table 4. Device Performance of Polymers **P1**–**P4** in ITO/PEDOT: PSS/Polymer/Ca/Al Devices

Polymer	EL (nm)	$V_{\text{turn-on}}$ (volt)	Max. Brightness (cd/m^2)	Max. Yield (cd/A)	CIE' 1931	
					x	y
P1	540	5	1190	0.68	0.39	0.58
P2	540	5	1721	0.88	0.39	0.58
P3	544	6	2114	4.53	0.43	0.56
P4	548	5	5068	0.64	0.43	0.55

somewhat close (within 12 nm). The PL emission maxima in different states are also summarized in Table 2. The PL quantum efficiency Φ_{PL} is increased with increasing the generation of dendrons, implying high generation dendrons can suppress the formation of aggregation. These results demonstrate that the incorporation of appropriate dendritic moieties into polymers can bring benefit of high quantum efficiency and less chain aggregation, without perturbing emission color.

Electrochemical Analysis

Cyclic voltammetry (CV) was employed to investigate the electrochemical behaviors of synthesized polymers and to estimate their energy levels. The oxidation process is clear and directly associated with the conjugation structure of the polymer. Figure 3 shows cyclic voltammograms of polymers **P1**–**P4** in the oxidation process. One can observe that the onset of oxidation potential is gradually decreased with increasing the generation of dendrons. It is known that lowering

oxidation potential favors hole-injection, which shows advantage for EL applications. The HOMO, LUMO, and energy gap of polymers **P1**–**P4** are estimated according to previous literature[19] and summarized in Table 3. The energy level diagram of these materials is illustrated in Figure 4. The smaller energy barrier between polymer **P3** and PEDOT:PSS layer shows the benefit for hole-injection. Turning to LUMO levels, **P3** has smallest energy barriers to the cathode Ca, implying good electron injection from cathode to polymer layer.

Device Performance

Double-layer light-emitting diodes with the configuration of ITO/PEDOT:PSS/Polymer/Ca/Al were fabricated to evaluate the potential use of synthesized DP-PPV derivatives. The device performance of these DP-PPV derivatives is summarized in Table 4. The maximum EL emission bands of these devices are located between 540 and 548 nm. The CIE coordinates demonstrate

Figure 5. Brightness–voltage characteristics of polymers **P1**–**P4** in ITO/PEDOT:PSS/Polymer/Ca/Al devices.
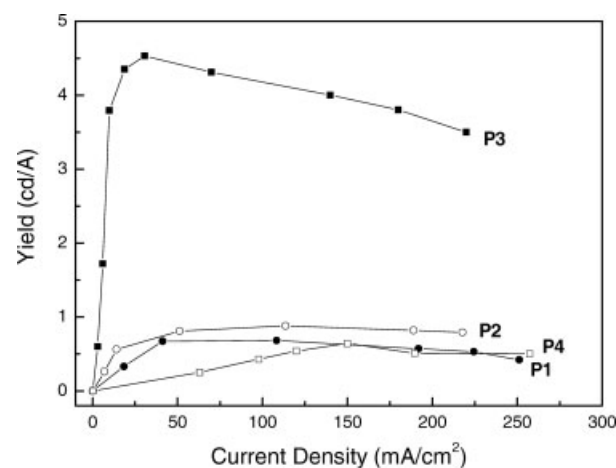
Figure 6. Efficiency–current density characteristics of polymers **P1**–**P4** in ITO/ PEDOT:PSS/Polymer/Ca/Al devices.

yellowish green color mostly. Figure 5 shows brightness–voltage characteristics of devices using polymers **P1–P4** as active layers. Figure 6 reveals efficiency-current density characteristics of same devices. The device of polymer **P1** showed maximum brightness of 1190 cd/m^2 and maximum luminescent efficiency of 0.68 cd/A at 10 V. With increasing generation of dendrons, the corresponding devices showed enhanced performance. The device of polymer **P2** showed improved brightness of 1721 cd/m^2 and maximum luminescent efficiency of 0.88 cd/A. Using polymer **P3** as active layer, its device showed even higher brightness of 2114 cd/m^2 and luminescent efficiency of 4.53 cd/A. Here again high generation dendrons bring benefit of improved device performance. Polymer **P4** showed an improved brightness of 5068 cd/m^2. However the luminescent efficiency dropped off.

CONCLUSIONS

In this work, four DP-PPV derivatives containing bulky dendritic side groups were synthesized. Homopolymerization of these dendron-containing monomers only gave oligomers, while high molecular weights of copolymers were obtained by controlling the feed ratio of different monomers. The luminescent quantum efficiency in solid state was gradually increased with increasing the generation of dendrons. The hole-injection ability, as well as device performance, were both improved with introducing high-generation dendritic groups.

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