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Synthesis, electroluminescence, and photovoltaic properties of dendronized poly(*p*-phenylene vinylene) derivatives

Rupei Tang[a], Zhan'ao Tan[b], Caixia Cheng[a], Yongfang Li[b,*], Fu Xi[a,*]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b]*CAS Key Laboratory of Organic Solids, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

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Abstract

Two dendronized poly(*p*-phenylene vinylene) (PPV) derivatives, **ED-PPV** and **BB-PPV**, have been successfully synthesized according to the Gilch route. The obtained polymers possess excellent solubility in common solvents, good thermal stability with 5% weight loss temperature of more than 340 °C. The weight-average molecular weight (M_w) and polydispersity index (PDI) of **ED-PPV** and **BB-PPV** are in the range of $(1.26–2.34)\times10^5$ and 1.37–1.45, respectively. Polymer light-emitting diodes (PLEDs) with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al devices were fabricated, and the PLEDs emitted green–yellow light. The turn-on voltages of the PLEDs based on **ED-PPV** and **BB-PPV** were approximately 4.3, and 4.5 V, respectively. The PLED devices of **ED-PPV** exhibited the maximum luminance of about 157 cd/m^2 at 10.5 V. Photovoltaic cells with the configuration of ITO/PEDOT:PSS/polymer:C_{60} (1:1)/Al were also fabricated, and the energy conversion efficiency of the devices based on **ED-PPV** and **BB-PPV** was measured to be 0.58, and 0.014%, respectively, under the white light at 75 mW/cm^2.

Keywords: Poly(*p*-phenylene vinylene); Polymer light-emitting diodes; Photovoltaic cells

1. Introduction

Conjugated polymers have attracted much attention during the past decades for their potential applications in polymer optoelectronic devices, such as polymer light-emitting diodes (PLEDs) [1,2], photovoltaic cells [3], and transistors [4]. PLEDs, where these conjugated polymers are used as emitting layers, possess many advantages over inorganic and organic small molecule-based light-emitting diodes (LEDs), such as easy fabrication, low cost, good processability, and film-forming properties of the conjugated polymers [5–7]. Another important application of the conjugated polymers is their use in photovoltaic cells, which is developing rapidly, and presents a new renewable, alternative source of electrical energy, compared to the relative expensive inorganic photovoltaic cells.

Among the vast kinds of conjugated polymers, PPV and its derivatives are one of the most extensively investigated polymers employed as active layers in PLEDs and photovoltaic cells [8,9]. As that of many other conjugated polymers, the luminescent quantum efficiency of PPVs is substantially lower in the solid state than their inorganic counterparts due to intermolecular interaction, such as aggregation and excimers formation, which will lead to a self-quenching process of excitons [10–12]. Branching of π-conjugated systems, such as conjugated dendrimers, can be designed to minimize their tendency to aggregate, and also define the color of the light emission [13–15]. But it is very difficult for the branched systems to obtain because of their complex synthetic route and low yield. Another effective strategy to suppress this drawback is to introduce bulky substituents to the PPV backbones to prevent close packing of the polymer chains with each other through relatively easier synthetic methods. Whereas such bulky side groups as alkoxy, alkylsilyl, phenyl, fluorenyl groups are known [10–12], the dendritic pendants have been

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* Corresponding authors. Tel.: +86 10 6255 7907; fax: +86 10 6255 9373.

E-mail addresses: liyf@iccas.ac.cn (Y. Li), xifu@iccas.ac.cn (F. Xi).

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explored to a much lesser extent. Among the examples are dendronized PPV alternative copolymers with a low molecular weight via Heck/Witting reaction, and there are no reports on their photovoltaic properties [16,17].

In the present article, we report the syntheses, electroluminescence, and photovoltaic properties of two dendronized PPV derivatives by the Gilch route [18]. The obtained polymers in this paper, **ED-PPV**, and **BB-PPV**, have a high molecular weight, high thermal stability, and easy applicability for PLEDs and photovoltaic cells. The different dialkoxy-branched long chains in the side chain were introduced to improve solubility in common organic solvents, and tune the luminescent and photovoltaic properties. To the best of our knowledge, this is the first paper reporting the syntheses of dendrimer-substituted PPV homopolymers via Gilch polymerization method, and characterization of their electroluminescence and photovoltaic properties.

2. Experimental section

2.1. Measurements

^1H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Molecular weights and polydispersities of polymers were determined by Gel permeation chromatography (GPC) analysis relative to polystyrene calibration (waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF as eluent at a flow rate of 1.0 ml/min at 35 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin–Elmer 7 thermogravimetric analyzer with a heating rate of 20 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on 2920 MDSC (TA instruments) under a nitrogen atmosphere with a heating rate of 10 °C/min. The UV-vis spectra were recorded on a Hitachi UV-3010 spectrometer. The photoluminescence (PL) and EL spectra were obtained with a Hitachi F-4500 Fluorescence Spectrophotometer. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Luminance units (cd/m^2) were calculated using the forward output power and the EL spectra devices, assuming Lambertian distribution of the devices. The Commission International de L'Eclairage coordinates were measured using a PR-650 SpectraScan SpectraColorimeter. Current–voltage characteristics of the PLED devices were measured with a Hewlett Packard 4140B semiconductor parameter analyzer. The current–voltage (I–V) measurements of photovoltaic devices were conducted on a computer-controlled Keithley 236 source measure unit. A tungsten lamp simulated a white-light source; the optical power at the sample was 75 mW/cm^2. All the measurements were performed under ambient atmosphere at room temperature.

2.2. Materials

THF was distilled over sodium and benzophenone. Chloroform and methanol was dried by distillation over CaH_2. Dimethyl hydroxyterephthalate was prepared from dimethyl aminoterephthalate according to literature procedures [19]. 3,5-Bis(2′-ethylhexyloxy)benzyl bromide and 3,7-dimethyloctyl bromide were prepared according to literature procedures [20]. All other solvents and reagents were analytic-grade quality, purchased commercially, and used without further purification.

2.3. Synthesis

*2.3.1. 3-(2′-Ethylhexyloxy)-5-hydroxybenzoaic methyl ester (**1a**)*

To a stirred mixture of methyl 3,5-dihydroxybenzoate (6.20 g, 36.90 mmol), 2-ethylhexylbromide (7.47 g, 38.73 mmol), tetrabutylammonium bromide (2.38 g, 7.38 mmol), and acetone (180 ml) under argon was added K_2CO_3 (5.09 g, 36.90 mmol). The reaction mixture was refluxed for 72 h, and cooled to room temperature. Then the solid residue was removed by filtration, and acetone in filtrate was removed by evaporation. The chloroform and water were added, and two phases were separated, and the water phase was extracted twice with chloroform. The resulting organic phases were combined and washed three times with water. The organic extracts were dried over magnesium sulfate, evaporated, and purified with column chromatography (silica gel, petroleum ether/chloroform (5/1) as eluent) to yield 4.34 g (42%) of 3-(2′-ethylhexyloxy)-5-hydroxybenzoaic methyl ester as a light yellow oil. ^1H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 6H, CH_3), 1.31–1.51 (m, 8H, CH_2), 1.71–1.73 (m, 1H, $\mathit{CH}CH_2$), 3.83–3.85 (d, 2H, OCH_2), 3.91 (s, 3H, OCH_3), 6.63 (s, 1H, ArH), 7.17 (s, 2H, ArH). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.44; H, 8.60.

*2.3.2. 3-(2′-Ethylhexyloxy)-5-(3′,7′-dimethyloctyl)benzoaic methyl ester (**2a**)*

Compound **2a** was synthesized according to the procedure described for **1a** using **1a** (4.15 g, 14.82 mmol), 3,7-dimethyloctylbromide (3.60 g, 16.30 mmol), tetrabutylammonium bromide (0.96 g, 2.98 mmol), and K_2CO_3 (4.26 g, 30.87 mmol). A light yellow oil (5.29 g) of 3-(2′-ethylhexyloxy)-5-(3′,7′-dimethyloctyl)benzoaic methyl ester was obtained in 85% yield. ^1H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.95 (m, 15H, CH_3), 1.15–1.53 (m, 17H, $\mathit{CH}(CH_3)_2$, CH_2), 1.72–1.82 (m, 2H, $\mathit{CH}CH_2$), 3.85–3.86 (d, 2H, OCH_2), 3.90 (s, 3H, OCH_3), 3.94–4.06 (m, 2H, OCH_2), 6.64 (s, 1H, ArH), 7.17 (s, 2H, ArH). Anal. Calcd for $C_{26}H_{44}O_4$: C, 74.24; H, 10.54. Found: C, 74.06; H, 10.50.

2.3.3. 3-(2′-Ethylhexyloxy)-5-(3′,7′-dimethyloctyl)benzyl alcohol (**3a**)

To a stirred mixture of $LiAlH_4$ (0.54 g, 13.47 mmol) in dried THF (30 ml) was added dropwise a solution of **2a** (5.20 g, 12.82 mmol) in dried THF (10 ml), and the mixture was refluxed overnight. The reaction mixture was cooled to room temperature, and 1.0 M HCl, water, and chloroform were added successively. The two phases were separated, and the water phase was extracted twice with chloroform. The combined organic extracts were washed three times with water, dried over magnesium sulfate, evaporated to yield 4.55 g (94%) of 3-(2′-ethylhexyloxy)-5-(3′,7′-dimethyloctyl)benzyl alcohol as a colorless oil, which was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 15H, CH_3), 1.14–1.47 (m, 17H, *CH*$(CH_3)_2$, CH_2), 1.69–1.73 (m, 2H, *CH*CH_2), 3.81–3.83 (d, 2H, OCH_2), 3.95–4.00 (m, 2H, OCH_2), 4.61 (s, *CH*$_2$OH), 6.38 (s, 1H, ArH), 6.50 (s, 2H, ArH). Anal. Calcd for $C_{25}H_{44}O_3$: C, 76.48; H, 11.30. Found: C, 76.36; H, 11.24.

2.3.4. 3-(2′-Ethylhexyloxy)-5-(3′,7′-dimethyloctyl)benzyl bromide (**4a**)

To a stirred solution of **3a** (4.50 g, 11.48 mmol) and triphenyl phosphine (3.76 g, 14.34 mmol) in dried THF (60 ml) under argon at 0 °C was added carbon tetrabromide (4.76 g, 14.34 mmol) in portions. The reaction mixture was kept stirring overnight at room temperature, then chloroform and water were added after the most THF was evaporated. The two phases were separated, and the water phase was extracted twice with chloroform. The combined organic extracts were dried over magnesium sulfate, evaporated, purified with column chromatography (silica gel, petroleum ester as eluent) to yield 3.66 g (70%) of 3-(2′-ethylhexyloxy)-5-(3′,7′-dimethyloctyl)-benzyl bromide as a light yellow oil. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 15H, CH_3), 1.14–1.46 (m, 17H, *CH*$(CH_3)_2$, CH_2), 1.72–1.82 (m, 2H, *CH*CH_2), 3.78–3.84 (q, 2H, OCH_2), 3.95–3.99 (m, 2H, OCH_2), 4.42 (s, CH_2Br), 6.39 (s, 1H, ArH), 6.51 (s, 2H, ArH). Anal. Calcd for $C_{25}H_{43}BrO_2$: C, 65.92; H, 9.51. Found: C, 65.81; H, 9.48.

2.3.5. 2-(3′-(2″-Ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)terephthalic acid dimethyl ester (**5a**)

To a stirred mixture of dimethyl hydroxyterephthalate (1.51 g, 7.19 mmol), **4a** (3.60 g, 7.91 mmol), tetrabutylammonium bromide (0.46 g, 1.44 mmol), and acetone (40 ml) under argon was added K_2CO_3 (1.98 g, 14.38 mmol). The reaction mixture was refluxed for 42 h, and cooled to room temperature. Then the solid residue was removed by filtration, and acetone in filtrate was removed by evaporation. The chloroform and water were added, and two phases were separated, and the water phase was extracted twice with chloroform. The resulting organic phases were combined and washed three times with water. The organic extracts were dried over magnesium sulfate, evaporated, and purified with column chromatography (silica gel, petroleum ether/chloroform (1/3) as eluent) to yield 3.32 g (79%) of 2-(3′-(2″-ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)terephthalic acid dimethyl ester as a light yellow oil. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 m, 15H, CH_3), 1.14–1.46 (m, 17H, *CH*$(CH_3)_2$, CH_2), 1.73–1.85 (m, 2H, *CH*CH_2), 3.82–3.84 (d, 2H, OCH_2), 3.92 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 3.95–4.01 (m, 2H, OCH_2), 5.15 (s, 2H, OCH_2), 6.39 (s, 1H, ArH), 6.65 (s, 2H, ArH), 7.64–7.66 (d, 1H, ArH), 7.67 (s, 1H, ArH), 7.81–7.83 (d, 1H, ArH). Anal. Calcd for $C_{35}H_{52}O_7$: C, 71.89; H, 8.96. Found: C, 71.72; H, 8.91.

2.3.6. 2-(3′-(2″-Ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-bis(hydroxymethyl)benzene (**6a**)

Compound **6a** was synthesized according to the procedure described for **3a** using **5a** (3.25 g, 5.57 mmol), and $LiAlH_4$ (0.44 g, 11.71 mmol). A colorless oil (2.79 g) of 2-(3′-(2″-ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-bis(hydroxymethyl)benzene was obtained in 95% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.93 (m, 15H, CH_3), 1.15–1.46 (m, 17H, *CH*$(CH_3)_2$, CH_2), 1.72–1.83 (m, 2H, *CH*CH_2), 3.80–3.83 (m, 2H, OCH_2), 3.95–4.02 (m, 2H, OCH_2), 4.65–4.68 (d, 2H, *CH*$_2$OH), 4.72–4.75 (d, 2H, *CH*$_2$OH), 5.05 (s, 2H, OCH_2), 6.42–6.45 (t, 1H, ArH), 6.54–6.56 (d, 2H, ArH), 6.94–6.96 (d, 1H, ArH), 7.00 (s, 1H, ArH), 7.28–7.29 (d, 1H, ArH). Anal. Calcd for $C_{33}H_{52}O_5$: C, 74.96; H, 9.91. Found: C, 74.88; H, 9.90.

2.3.7. 2-(3′-(2″-Ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-bis(bromomethyl)benzene (**7a**)

Compound **7a** was synthesized according to the procedure described for **4a** using **6a** (2.70 g, 5.11 mmol), triphenyl phosphine (3.75 g, 14.31 mmol), and carbon tetrabromide (4.75 g, 14.31 mmol). A light yellow oil (2.24 g) of 2-(3′-(2″-ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-bis(bromomethyl)benzene was obtained in 67% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 15H, CH_3), 1.14–1.57 (m, 17H, *CH*$(CH_3)_2$, CH_2), 1.81–1.88 (m, 2H, *CH*CH_2), 3.83–3.86 (q, 2H, OCH_2), 3.98–4.02 (q, 2H, OCH_2), 4.45 (s, 2H, CH_2Br), 4.59 (s, 2H, CH_2Br), 5.09 (s, 2H, OCH_2), 6.42 (s, 1H, ArH), 6.66 (s, 2H, ArH), 6.95 (s, 1H, ArH), 6.97 (s, 1H, ArH), 7.30–7.33 (d, 1H, ArH). ^{13}C NMR (300 MHz, $CDCH_3$): δ (ppm) 11.07, 14.09, 19.65, 22.70, 23.04, 23.81, 24.64, 27.96, 28.66, 29.02, 30.47, 33.21, 36.17, 37.25, 39.29, 66.46, 70.03, 70.67, 101.07, 105.09, 105.26, 112.72, 121.43, 126.70, 131.11, 138.57, 139.87, 156.64, 160.48, 160.74. Anal. Calcd for $C_{33}H_{50}Br_2O_3$: C, 60.55; H, 7.70. Found: C, 60.40; H, 7.65.

*2.3.8. Poly(2-(3′-(2″-ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-phenylenevinylene) (**ED-PPV**)*

To a stirred solution of **7a** (0.42 g, 0.65 mmol) in dried THF (40 ml) under argon at room temperature was added dropwise potassium *tert*-butoxide (3.90 ml, 1.0 M in THF, 3.90 mmol). The mixture was stirred overnight at room temperature. The viscous mixture was added dropwise to stirred methanol. The crude polymer was collected by filtration, and washed with methanol, and stirred with two portions of a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, dried under high vacuum, and dissolved in chloroform. The solution was filtered, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under high vacuum. Then the polymer was again dissolved in chloroform, filtered, precipitated with methanol, and dried under high vacuum to yield 199 mg (62%) of poly(2-(3′-(2″-ethylhexyloxy)-5′-(3″,7″-dimethyloctyl)benzyloxy)-1,4-phenylenevinylene) as a orange-red solid. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (br, 15H, CH_3), 1.13–1.58 (br, 17H, $CH(CH_3)_2$, CH_2), 1.67–1.69 (br, 2H, $CHCH_2$), 3.81–3.89 (br, 4H, OCH_2), 5.12 (br, 2H, OCH_2), 6.44 (br, 1H, ArH), 6.67 (br, 2H, ArH), 7.05–7.23 (br, 4H, ArH, $CH{=}CH$), 7.56 (br, 1H, ArH). Anal. Calcd for $(C_{33}H_{48}O_3)_n$: C, 80.44; H, 9.82. Found: C, 80.27; H, 9.77.

*2.3.9. 3-(3′,5′-Bis(2″-ethylhexyloxy)benzyloxy)-5-hydroxybenzoaic methyl ester (**1b**)*

Compound **1b** was synthesized according to the procedure described for **1a** using methyl 3,5-dihydroxybenzoate (8.36 g, 49.77 mmol), 3,5-bis(2′-ethylhexyloxy)-benzyl bromide (17.00 g, 39.81 mmol), tetrabutylammonium bromide (4.01 g, 12.44 mmol), and K_2CO_3 (27.51 g, 199.35 mmol). A light yellow oil (7.98 g) of 3-(3′,5′-bis(2″-ethylhexyloxy)benzyloxy)-5-hydroxybenzoaic methyl ester was obtained in 39% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.88–0.94 (m, 12H, CH_3), 1.27–1.50 (m, 16H, CH_2), 1.69–1.71 (m, 2H, $CHCH_2$), 3.82–3.90 (m, 4H, OCH_2), 3.91 (s, 3H, CH_3), 4.98 (s, 2H, OCH_2), 6.42–6.43 (t, 1H, ArH), 6.56 (d, 2H, ArH), 6.68–6.70 (t, 1H, ArH), 7.17 (d, 1H, ArH), 7.24 (t, 1H, ArH). Anal. Calcd for $C_{31}H_{46}O_6$: C, 72.34; H, 9.01. Found: C, 72.26; H, 8.99.

*2.3.10. 3-(3′,5′-Bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzoaic methyl ester (**2b**)*

Compound **2b** was synthesized according to the procedure described for **1a** using **1b** (7.90 g, 15.36 mmol), 3,7-dimethyloctylbromide (8.16 g, 16.91 mmol), tetrabutylammonium bromide (0.99 g, 3.07 mmol), and K_2CO_3 (4.24 g, 30.74 mmol). A light yellow oil (9.71 g) of 3-(3′,5′-bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzoaic methyl ester was obtained in 69% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 30H, CH_3), 1.14–1.56 (m, 34H, $CH(CH_3)_2$, CH_2), 1.70–1.81 (m, 4H, $CHCH_2$), 3.82–3.84 (d, 4H, OCH_2), 3.90 (s, 3H, CH_3), 3.95–4.00 (q, 4H, OCH_2), 4.98–4.99 (d, 4H, OCH_2), 6.42 (s, 2H, ArH), 6.56 (s, 4H, ArH), 6.81 (s, 1H, ArH), 7.29 (s, 2H, ArH). Anal. Calcd for $C_{58}H_{92}O_8$: C, 75.94; H, 10.11. Found: C, 75.86; H, 10.05.

*2.3.11. 3-(3′,5′-Bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzyl alcohol (**3b**)*

Compound **3b** was synthesized according to the procedure described for **3a** using **2b** (9.50 g, 10.37 mmol), and $LiAlH_4$ (0.42 g, 10.89 mmol). A colorless oil (8.56 g) of 3-(3′,5′-bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzyl alcohol was obtained in 93% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 30H, CH_3), 1.14–1.54 (m, 34H, $CH(CH_3)_2$, CH_2), 1.71–1.80 (m, 4H, $CHCH_2$), 3.82–3.83 (q, 4H, OCH_2), 3.94–3.99 (m, 4H, OCH_2), 4.61–4.63 (d, 2H, CH_2OH), 4.95 (d, 4H, OCH_2), 6.41–6.42 (t, 2H, ArH), 6.55–6.56 (d, 5H, ArH), 6.62 (s, 2H, ArH). Anal. Calcd for $C_{57}H_{92}O_7$: C, 76.98; H, 10.43. Found: C, 76.88; H, 10.36.

*2.3.12. 3-(3′,5′-Bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzyl bromide (**4b**)*

Compound **4b** was synthesized according to the procedure described for **4a** using **3b** (8.50 g, 9.57 mmol), triphenyl phosphine (3.14 g, 11.97 mmol), and carbon tetrabromide (3.97 g, 11.97 mmol). A light yellow oil (6.74 g) of 3-(3′,5′-bis(2″-ethylhexyloxy)benzyloxy)-5-(3′,5′-bis(3″,7″-dimethyloctyloxy)benzyloxy)benzyl bromide was obtained in 74% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 30H, CH_3), 1.15–1.53 (m, 34H, $CH(CH_3)_2$, CH_2), 1.70–1.82 (m, 4H, $CHCH_2$), 3.82–3.83 (m, 4H, OCH_2), 3.97–3.98 (m, 4H, OCH_2), 4.41 (s, 2H, CH_2Br), 4.94–4.95 (d, 4H, OCH_2), 6.41–6.42 (d, 2H, ArH), 6.55 (d, 5H, ArH), 6.64 (s, 2H, ArH). Anal. Calcd for $C_{57}H_{91}BrO_6$: C, 71.90; H, 9.63. Found: C, 71.73; H, 9.55.

*2.3.13. 2-(3′-(3″,5″-Bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy) terephthalic acid dimethyl ester (**5b**)*

Compound **5b** was synthesized according to the procedure described for **5a** using dimethyl hydroxyterephthalate (0.88 g, 4.21 mmol), **4b** (4.00 g, 4.21 mmol), tetrabutylammonium bromide (0.27 g, 0.08 mmol), and K_2CO_3 (1.16 g, 8.41 mmol). A colorless oil (4.36 g) of 2-(3′-(3″,5″-bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy)terephthalic acid dimethyl ester was obtained in 96% yield. ^{1}H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.95 (m, 30H, CH_3), 1.14–1.56 (m, 34H, $CH(CH_3)_2$, CH_2), 1.70–1.80 (m, 4H, $CHCH_2$), 3.80–3.86 (q, 4H, OCH_2), 3.92–3.94 (d, 6H, CH_3), 3.96–4.01 (m, 4H, OCH_2), 4.97–4.98 (d, 4H, OCH_2), 5.17–5.18 (d, 2H, OCH_2), 6.41 (d, 2H, ArH), 6.57 (s, 5H, ArH), 6.80 (s, 2H, ArH), 7.65–7.68 (t, 2H, ArH), 7.83–7.86

(q, 1H, ArH). Anal. Calcd for $C_{67}H_{100}O_{11}$: C, 74.41; H, 9.32. Found: C, 74.38; H, 9.28.

*2.3.14. 2-(3′-(3″,5″-Bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy)-1,4-bis(hydroxymethyl)benzene (**6b**)*

Compound **6b** was synthesized according to the procedure described for **3a** using **5b** (4.33 g, 4.01 mmol), and $LiAlH_4$ (0.32 g, 8.42 mmol). A colorless oil (3.91 g) of 2-(3′-(3″,5″-bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy)-1,4-bis(hydroxymethyl)benzene was obtained in 95% yield. ^1H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 30H, CH_3), 1.14–1.56 (m, 34H, $\mathit{CH}(CH_3)_2$, CH_2), 1.71–1.82 (m, 4H, $\mathit{CH}CH_2$), 3.82–3.84 (d, 4H, OCH_2), 3.95–3.99 (q, 4H, OCH_2), 4.66 (s, 2H, $\mathit{CH_2}OH$), 4.70 (s, 2H, $\mathit{CH_2}OH$), 4.95–4.96 (d, 4H, OCH_2), 5.05 (s, 2H, OCH_2), 6.41–6.42 (t, 2H, ArH), 6.56 (s, 5H, ArH), 6.59–6.64 (d, 2H, ArH), 6.92–6.95 (d, 2H, ArH), 7.28–7.30 (d, 1H, ArH). Anal. Calcd for $C_{65}H_{100}O_9$: C, 76.13; H, 9.83. Found: C, 76.04; H, 9.82.

*2.3.15. 2-(3′-(3″,5″-Bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy)-1,4-bis(bromomethyl)benzene (**7b**)*

Compound **7b** was synthesized according to the procedure described for **4a** using **6b** (3.85 g, 3.56 mmol), triphenyl phosphine (2.62 g, 9.98 mmol), and carbon tetrabromide (3.31 g, 9.98 mmol). A light yellow oil (2.76 g) of 2-(3′-(3″,5″-bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy)benzyloxy)-1,4-bis(bromomethyl)benzene was obtained in 64% yield. ^1H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.86–0.94 (m, 30H, CH_3), 1.14–1.55 (m, 34H, $\mathit{CH}(CH_3)_2$, CH_2), 1.70–1.79 (m, 4H, $\mathit{CH}CH_2$), 3.83–3.84 (d, 4H, OCH_2), 3.95–4.00 (m, 4H, OCH_2), 4.42(s, 2H, CH_2Br), 4.56 (s, 2H, CH_2Br), 4.97–4.98 (d, 4H, OCH_2), 5.10 (s, 2H, OCH_2), 6.40–6.41 (t, 2H, ArH), 6.55–6.56 (d, 4H, ArH), 6.60 (s, 1H, ArH), 6.75 (s, 2H, ArH), 6.93–6.94 (d, 2H, ArH), 7.28–7.30 (d, 1H, ArH). ^{13}C NMR (300 MHz, $CDCH_3$): δ (ppm) 11.14, 14.11, 19.66, 22.62, 22.72, 23.06, 23.89, 24.66, 27.99, 29.10, 29.86, 30.55, 33.19, 36.19, 37.30, 39.26, 39.42, 66.40, 66.54, 69.95, 70.24, 70.32, 70.52, 100.86, 101.93, 105.75, 105.90, 112.78, 121.52, 126.76, 131.14, 131.99, 132.17, 138.84, 139.91, 156.58, 160.11, 160.19, 160.23, 160.53, 160.78. Anal. Calcd for $C_{65}H_{98}Br_2O_7$: C, 67.81; H, 8.58. Found: C, 67.57; H, 8.49.

*2.3.16. Poly(2-(3′-(3″,5″-bis(2‴-ethylhexyloxy)benzyloxy)-5′-(3″,5″-bis(3‴,7‴-dimethyloctyloxy)benzyloxy) benzyloxy)-1,4-phenylenevinylene) (**BB-PPV**)*

Compound **BBD-PPV** was synthesized according to the procedure described for **ED-PPV** using **7b** (0.40 g, 0.35 mmol), potassium *tert*-butoxide (2.1 ml, 1.0 M in THF, 2.10 mmol), and THF (30 ml). A orange solid (158 mg) of poly(2-(3′,5′-bis(3″,5″-bis(2‴-ethylhexyloxy)-benzyloxy)benzyloxy)-1,4-phenylenevinylene) was obtained in 46% yield. ^1H NMR (300 MHz, $CDCH_3$): δ (ppm) 0.85–0.94 (br, 30H, CH_3), 1.14–1.55 (br, 34H, $\mathit{CH}(CH_3)_2$, CH_2), 1.72–1.78 (br, 4H, $\mathit{CH}CH_2$), 3.76 (br, 4H, OCH_2), 3.90 (br, 4H, OCH_2), 4.91 (br, 4H, OCH_2), 5.13 (br, 2H, OCH_2), 6.38–6.79 (br, 9H, ArH), 7.04–7.20 (br, 4H, ArH, $\mathit{CH{=}CH}$), 7.48 (br, 1H, ArH). Anal. Calcd for $(C_{65}H_{96}O_7)_n$: C, 78.90; H, 9.78. Found: C, 78.77; H, 9.69.

3. Results and discussion

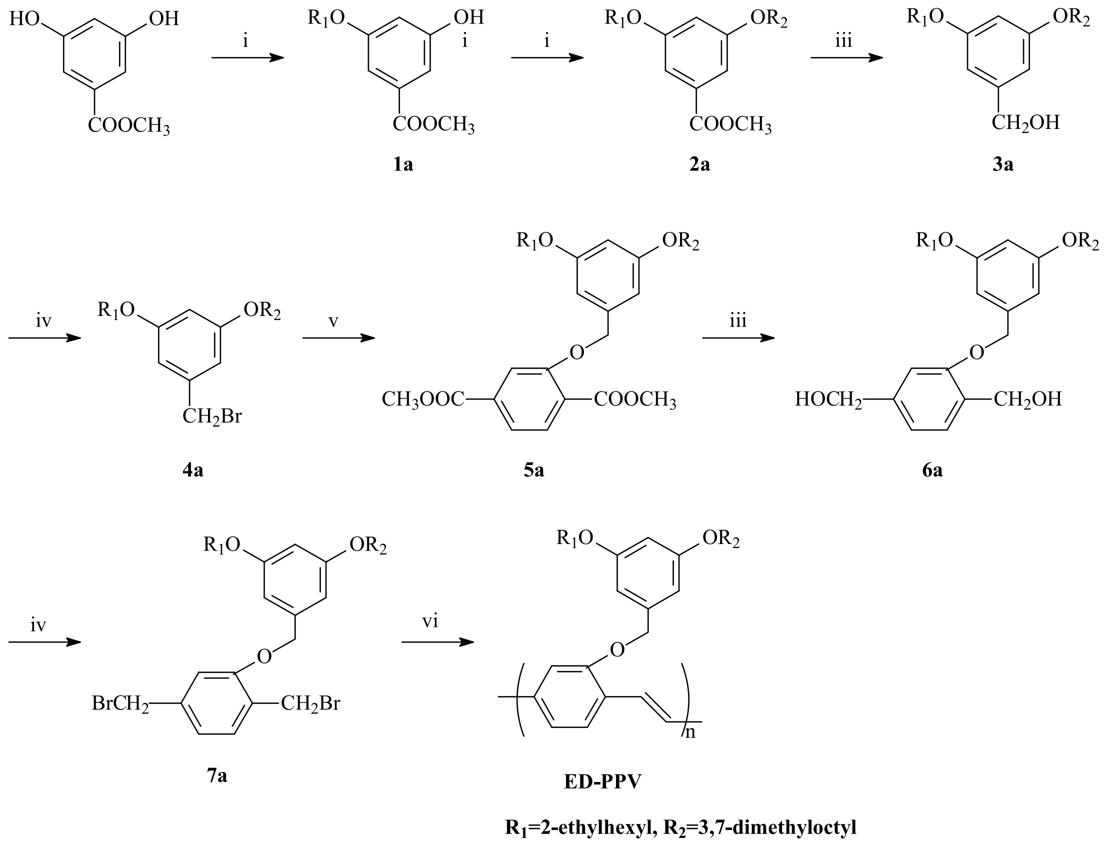
3.1. Synthesis and characterization

The syntheses of the monomers and the corresponding polymers are outlined in Schemes 1 and 2. The key intermediate, substituted 1,4-bis(bromomethyl)benzene, **7a**, was prepared with the reduction of its corresponding 1,4-bis(hydroxymethyl)benzene, **6a**, which was synthesized in an easy six-step reaction. The alkylation of methyl 3,5-dihydroxybenzoate with 2-ethylhexylbromide in the presence of K_2CO_3 gave **1a**, which was then alkylated to yield **2a** using 3,7-dimethyloctylbromide by the same procedure as **1a**. The reduction of **2a** with $LiAlH_4$ gave **3a**. **6a** was easily obtained via the reaction of **3a**, first with bromination to yield the benzyl bromides **4a**, and subsequent conversion using the procedure described for **1a** to the substituted terephthalic acid ester **5a**, which was in turn reduced using $LiAlH_4$ to give the corresponding substituted benzyl alcohol. The another key intermediate, substituted 1,4-bis(bromomethyl)benzene, **7b**, was prepared according to the procedure described for **7a**.

The structures of the monomers were confirmed by ^1H and ^{13}C NMR spectroscopy, and elemental analysis. The resulting polymers, **ED-PPV**, and **BB-PPV**, were easily prepared by using the Gilch polymerization method. During the polymerization, the reaction mixture became progressively viscous, and remained homogeneous without any formation of gel portions, showing a strong fluorescent light. The synthesized polymers were easily soluble in common organic solvents, such as chloroform, toluene, and xylene at room temperature.

The structures of the obtained polymers were identified by ^1H NMR spectroscopy, and elemental analysis. The benzyl proton peaks at about 4.50 ppm for monomers disappeared during the polymerization and the new vinylic proton peaks at about 7.0–7.2 ppm together with the phenyl protons, which confirmed the polymerization reaction. In addition, all other peaks showed good correspondence with the resulting polymers.

Fig. 1 shows GPC traces of the resulting polymers. The GPC traces are almost symmetrical and monomodal, indicating good polymerization results. The weight-average molecular weight (M_w) and polydispersity index (PDI) of **ED-PPV**, and **BB-PPV** were in the range of $(1.26–2.34)\times 10^5$ and 1.37–1.45, respectively. Table 1 summarizes the polymerization results, molecular weights, and thermal data



Scheme 1. Reagents and conditions: (i), K_2CO_3/aceton, tetrabutylammonium bromide, R_1Br; (ii), K_2CO_3/aceton, tetrabutylammonium bromide, R_2Br; (iii), $LiAlH_4$/THF; (iv), CBr_4/THF, PPh_3; (v), K_2CO_3/aceton, tetrabutylammonium bromide, dimethyl hydroxyterephthalate; (vi), *t*-BuOK/THF.

of the present polymers. The TGA curves of the polymers reveal a relatively high thermal stability, and are shown in Fig. 2. Initial weight loss (5%) temperatures of **ED-PPV** and **BB-PPV** were found to be 340, and 358 °C, respectively. DSC curves display glass transitions temperature (T_g) of **ED-PPV** and **BB-PPV** at 227, 223 °C. The high thermal stability of the EL polymers is closely related to the performance of the LEDs, which prevents morphological change, deformation, and degradation of the active layers during the operation of EL and photovoltaic cells devices [21,22].

3.2. Optical and photoluminescence properties

Fig. 3 shows the optical absorption (Abs) and photoluminescence (PL) spectra of **ED-PPV**, and **BB-PPV** in dilute chloroform solution. Both polymers have almost identical absorption maximum at about 453 nm, which is corresponding to π–π^* transition. The two polymers emit green light in dilute chloroform solution. As shown in Fig. 3, the maximum emission of **ED-PPV**, and **BB-PPV** in dilute chloroform solution is observed at about 505, and 506 nm, respectively. The PL quantum yield (Φ_f) of the polymers was determined in dilute chloroform (1×10^{-6} M) according to the literature procedure [23], to be 0.42, and 0.67 for **ED-PPV**, and **BB-PPV**, respectively. There is clear correlation between the Φ_f and the polymer structure. The more well-separated the polymer chain, the higher the Φ_f. As a result, the PL quantum yield of **BB-PPV** with larger dendritic pendant was observed to be obviously higher than **ED-PPV** with smaller dendritic side group, which is in accordance to the results obtained previously [24,25].

Fig. 4 shows the optical absorption (Abs) and photoluminescence (PL) spectra of **ED-PPV**, and **BB-PPV** films.

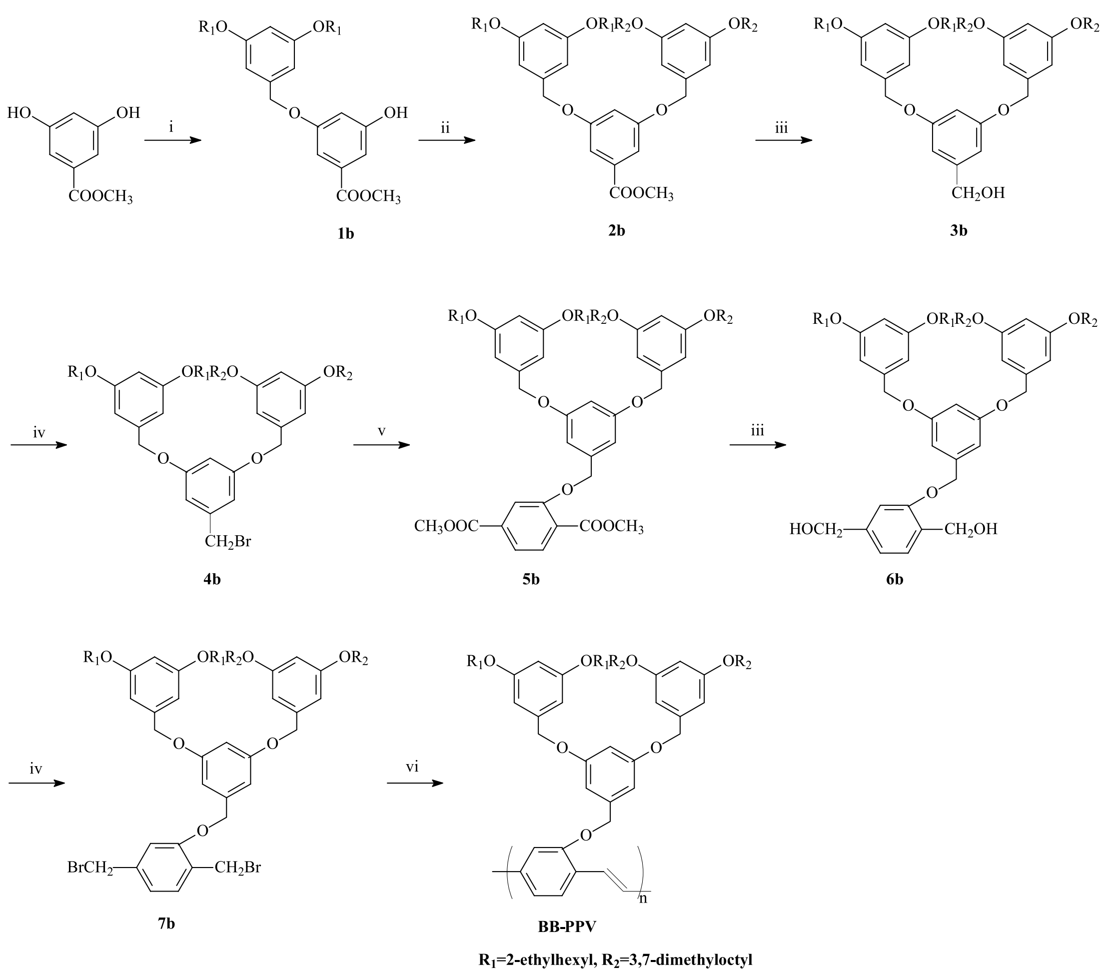
Table 1
Polymerization results, molecular weights, and thermal data of polymers

Polymer	Yield (%)	M_n ($\times 10^{-5}$)[a]	M_w ($\times 10^{-5}$)[a]	PDI	TGA (°C)[b]	T_g (°C)[c]
ED-PPV	62	1.71	2.34	1.37	340	227
BB-PPV	46	0.86	1.26	1.45	358	223

[a] Determined by GPC in THF based on polystyrene standards.

[b] Temperature at 5% weight loss under nitrogen.

[c] Determined by DSC at a heating rate of 10 °C/min under nitrogen.



Scheme 2. Reagents and conditions: (i), K_2CO_3/aceton, tetrabutylammonium bromide, 3,5-bis(2′-ethylhexyloxy)benzylbromide; (ii), K_2CO_3/aceton, tetrabutylammonium bromide, 3,7-dimethyloctylbromide; (iii), $LiAlH_4$/THF; (iv), CBr_4/THF, PPh_3; (v), K_2CO_3/aceton, tetrabutylammonium bromide, dimethyl hydroxyterephthalate; (vi), *t*-BuOK/THF.

The absorption bands of the polymers in solid state are similar to those in chloroform solution. The solid-state absorption bands of the polymers are, however, broader and red-shifted by about 50 nm, compared to the solution spectra. The results suggest a significant increase in conjugation length in the solid state, which is mostly due to the more planar conformation resulted from π-stacking/aggregation in solid state. The maximum absorption peaks of **ED-PPV**, and **BB-PPV** corresponding to π–π^* transition are observed at 466, and 468 nm. Optical band gaps (E_g)

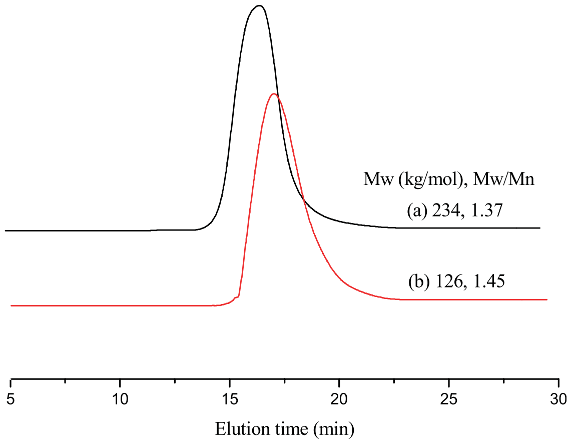


Fig. 1. GPC traces of the resulting polymers: (a) **DE-PPV**; (b) **BB-PPV**.

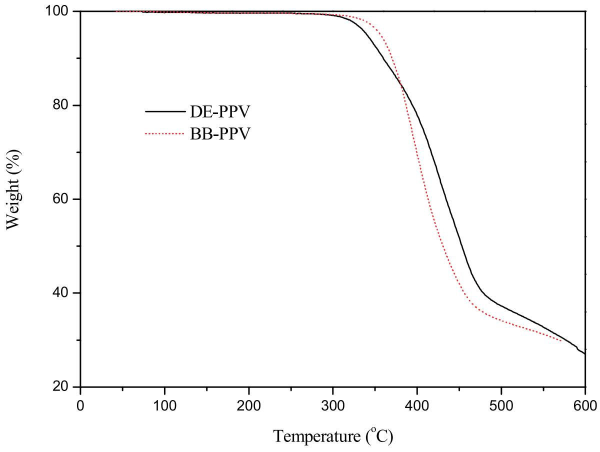


Fig. 2. TGA thermograms of the resulting polymers.

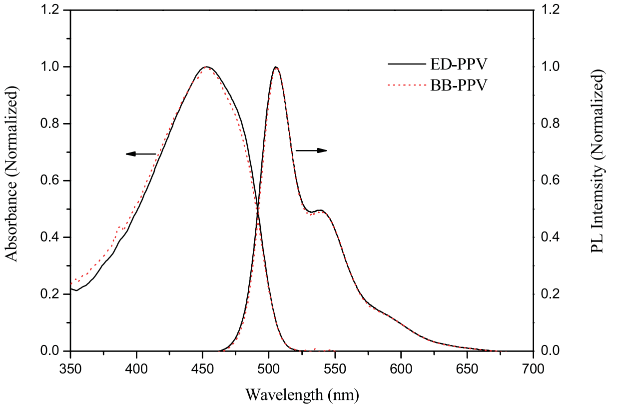


Fig. 3. UV–vis absorption and PL spectra of the resulting polymers in dilute chloroform solution.

determined from the absorption edge of the spectra of the polymer films are shown in Table 2. The PL bands of the polymers in solid state are almost similar to those in chloroform solution. In addition, compared to the solution PL spectra, the thin film PL spectra of the polymers are red-shifted by about 30 nm. The maximum emission peaks of **ED-PPV**, and **BB-PPV** films are observed at about 536, and 540 nm, respectively. The absorption and PL properties of the polymers are summarized in Table 2.

3.3. Electroluminescence properties of LED devices

PLED devices based on the two polymers with the configuration of ITO/PEDOT:PSS(40 nm)/polymer(100 nm)/Ca(4 nm)/Al(100 nm) were fabricated. The polymer film was spin-coated from its chloroform solution (10 wt%) onto the ITO/PEDOT:PSS film, and dried at 50 °C in a vacuum overnight. After that, the Ca cathode was thermally evaporated under a vacuum of lower than 2×10^{-6} Torr. The cathode layer was coated with an Al layer for improving the stability of the devices in air. The EL spectra of the devices are displayed in Fig. 5. It was observed that the PLEDs of the dendronized PPV derivatives emitted green–yellow light. The EL spectrum peaks of **ED-PPV**, and **BB-PPV**, were almost identical to those of their PL spectra as shown in Fig. 4. The results indicated that the PL and EL processes experienced the same excited state.

Fig. 6 shows current density–voltage (*I*–*V*) and luminance–voltage (*L*–*V*) characteristics of the PLED devices. The current density increased exponentially with the increasing forward bias voltage, which was a typical diode

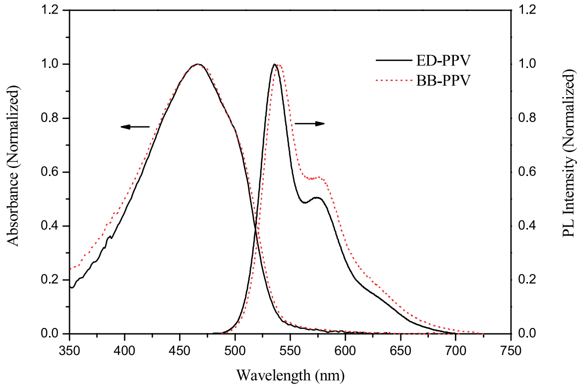


Fig. 4. UV–vis absorption and PL spectra of the polymers films.

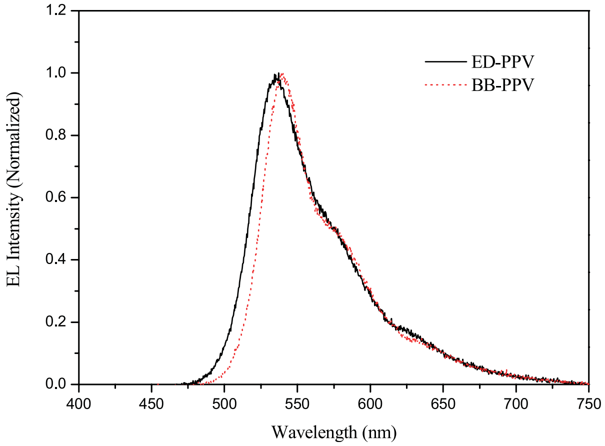


Fig. 5. EL spectra of the ITO/PEDOT:PSS/polymer/Ca/Al devices.

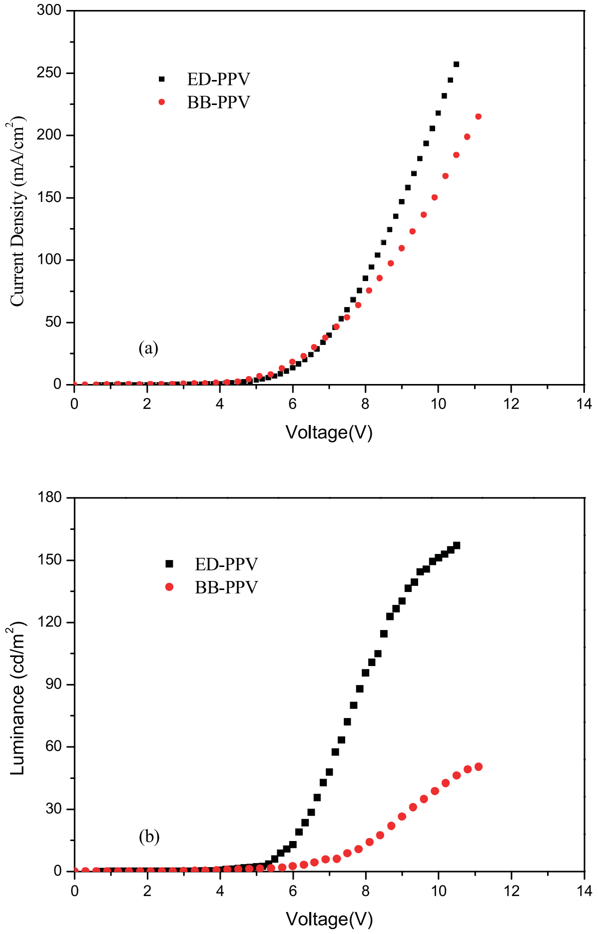


Fig. 6. Current density–voltage (*I*–*V*) (a) and luminance–voltage (*L*–*V*) (b) characteristics of the ITO/PEDOT:PSS/polymer/Ca/Al devices.

Table 2
Optical and photoluminescence properties of the polymers

Polymer	Soln λ_{max} (nm)[a]		Film λ_{max} (nm)[b]		Φ_f (soln)	E_g (eV)[c]
	Abs	PL	Abs	PL		
ED-PPV	453	505	466	536	0.42	2.20
BB-PPV	453	506	468	540	0.67	2.27

[a] Measured in chloroform solution.
[b] Polymer cast from chloroform solution.
[c] Band gap estimated from the onset wavelength of the optical absorption.

characteristic (Fig. 6(a)). The turn-on voltage of the PLEDs based on **ED-PPV**, and **BB-PPV** was approximately 4.3, and 4.5 V, respectively, which was very low compared with that of other PPV dendrimers [13–15]. As shown in Fig. 6(b), the maximum luminance of **BB-PPV** was about 50 cd/m^2 with a maximum luminescence efficiency of about 0.04 cd/A. While the maximum luminance of **ED-PPV** increased greatly, and reached about 157 cd/m^2 with a maximum luminescence efficiency of about 0.06 cd/A, in comparison of **BB-PPV** with **ED-PPV**, the PL efficiency of **BB-PPV** is ca. 50% higher than **ED-PPV**, as shown in Table 2. However, the EL efficiency of **BB-PPV** is 50% lower than that of **ED-PPV**. The lower EL efficiency of **BB-PPV** is probably due to the poor electron injection and transportation of the polymer because of its larger side-groups. The electroluminescent properties of the PLEDs based on the polymers are summarized in Table 3.

3.4. Photovoltaic properties

Photovoltaic cells were fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:C_{60} (1:1, 80 nm)/Al (100 nm) where the polymer/C_{60} composite was used as the active layer. Fig. 7 shows the *I*–*V* characteristics in the dark and under the illumination of a tungsten lamp. The relevant data of the *I*–*V* characteristics of the photovoltaic devices are summarized in Table 4. The device of **BB-PPV** has an open-circuit voltage (V_{oc}) of 0.30 V, short-circuit current density (I_{sc}) of 0.15 mA/cm^2 and the filling factor (FF) of 24%; the energy conversion efficiency (η) of the device is calculated to be 0.014%. Interestingly, the device of **ED-PPV** demonstrates higher sensitivity under illumination, as shown in Fig. 7. The **ED-PPV** has a V_{oc} of 0.69 V, I_{sc} of 1.98 mA/cm^2 and FF of 32%; the energy conversion efficiency (η) of the device is calculated to be 0.58%, which is about 30 times greater than that of **BB-PPV**. The improvement of the energy conversion efficiency may be mostly due to the relatively higher mobility of charge carriers resulted from the more planar conformation of **ED-PPV** main chains with smaller dendritic group, and due to the more conjugated chains extisted in **ED-PPV** with the smaller side groups. The efficiency of 0.58% of the device based on **ED-PPV**/C_{60} with a weight ratio of 1:1 is a relatively higher value for the photovoltaic cells with common conjugated polymer/C_{60} composite (typically 0.10%) [26].

Table 3
Electroluminescent device properties of the polymers

Polymer	EL λ_{ma} (nm)	V_{on}[a] (V)	L_{max}[b] (Voltage) (cd/m^2)	Efficiency[c] (cd/A)
ED-PPV	537	4.3	157 (10.5)	0.06
BB-PPV	540	4.5	50 (11.1)	0.04

[a] Turn-on voltage.
[b] Luminance at maximum bias voltage.
[c] Maximum luminescence efficiency.

4. Conclusions

We reported the synthesis, electroluminescence, and photovoltaic properties of the dendronized PPV derivatives by the Gilch route. The resulting polymers possess excellent solubility in common organic solvents, good thermal stability, and high molecular weights. In soluton, the polymers emit green light with a relatively high PL quantum yields. The PLEDs with the configuration of the ITO/PEDOT:PSS/polymer/Ca/Al were fabricated, and emitted green–yellow light. The turn-on voltages of the PLEDs based on the polymers are lower than that of other PPV dendrimers. Photovoltaic cells with the configuration of ITO/PEDOT:PSS/polymer:C_{60} (1:1)/Al were fabricated, and demonstrated a distinct photovoltaic effect under illumination. The device based on **ED-PPV** showed the

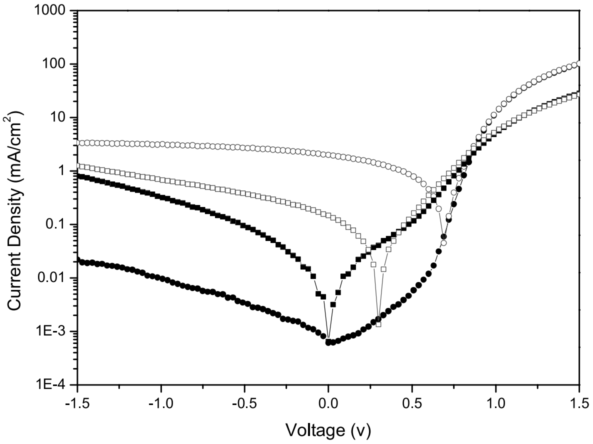


Fig. 7. Dark current (● for **ED-PPV** and ■ for **BB-PPV**), and photocurrent (○ for **ED-PPV**:C_{60} and □ for **BB-PPV**:C_{60}).

Table 4
Photovoltaic device properties of the polymers

Polymer	I_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
ED-PPV	1.98	0.69	32	0.58
BB-PPV	0.15	0.30	24	0.014

relatively higher energy conversion efficiency of 0.58%, compared to that of the devices based on common conjugated polymer/C_{60} composite. From the results, the synthesized dendronized PPV derivatives may have potential application for photovoltaic cells.

Acknowledgements

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