

# Highly Substituted Poly(2,3-diphenyl-1,4-phenylenevinylene) Derivatives Having Bulky Phenyl and Fluorenyl Pendant Groups: Synthesis, Characterization, and Electro-Optical Properties

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**ABSTRACT:** Two series of poly(2,3-diphenyl-1,4-phenylenevinylene) (DP-PPV) derivatives containing multiple bulky substituents were synthesized. In the first series, two different groups were incorporated on C-5,6 positions of the phenylene moiety to increase steric hindrance and to obtain blue-shifted emissions. In the second series, bulky fluorenyl groups with two hexyl chains on the C-9 position were introduced on two phenyl pendants to increase the solubility as well as steric hindrance to prevent close packing of the main chain. Polymers with high molecular weights and fine-tuned electro-optical properties were obtained by controlling the feed ratio of different monomers during polymerization. The maximum photoluminescent emissions of the thin films are located between 384 and 541 nm. Cyclic voltammetric analysis reveals that the band gaps of these light-emitting materials are in the range from 2.4 to 3.3 eV. A double-layer EL device with the configuration of ITO/PEDOT/P4/Ca/Al emitted pure green light with CIE'1931 at (0.24, 0.5). Using copolymer P6 as the emissive layer, the maximum luminescence and current efficiency were both improved when compared with the homopolymer P4. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 6738–6749, 2006

**Keywords:** conjugated polymers; fluorescence; light-emitting diodes

## INTRODUCTION

Semiconducting polymers have been intensively investigated for their potential applications in light-emitting diodes,<sup>1</sup> thin film transistors,<sup>2</sup> organic laser,<sup>3</sup> and solar cells.<sup>4</sup> 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.<sup>5</sup> Long alkyl chains and/or

bulky substituents 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. Until 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.<sup>6</sup> Thin film of MEH-PPV can be obtained from a spin-coating process. Cyano-substituted poly(2,5-dialkoxy-1,4-phenylene vinylene) (CN-PPV) is a red emissive polymer with high electron affinities.<sup>7,8</sup> Silyl-substituted

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PPV is a greenish emissive material with a tendency to be easily charged by electrons rather than holes.<sup>9,10</sup>

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.<sup>11</sup> 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.<sup>12</sup> Long alkyl chains were incorporated to improve the solubility of the polymer.<sup>13</sup> Liquid crystalline side chains were also incorporated to achieve polarized emissions.<sup>14,15</sup> 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 above, low device performance by 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.<sup>16</sup>

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.<sup>17,18</sup> Hsieh et al. ever investigated 2,3,5,6-tetraphenyl PPV in their synthetic route. However, they met the problem of reducing sterically hindered ester groups, and the predictably insoluble chlorine precursor polymer discouraged further investigation.<sup>12</sup>

In this study, two series of DP-PPV derivatives were designed to modify luminescent properties. In the first series, asymmetrically bulky substituents were incorporated on C-5,6 positions of the phenylene moiety to further increase steric hindrance and to decrease the conjugation length of the main chain. The obtained DP-PPV derivatives were predicted to show blue-shifted emission. In the second series, a novel DP-PPV structure with two fluorenyl substituents on phenyl pendants was synthesized. This fluorenylphenyl group is essentially bulky to increase steric hindrance and to prevent close packing of polymer chains. Two

hexyl chains at C-9 position can also help to increase the solubility. The homopolymer and two copolymers derived from copolymerizing with 1,4-bis(chloromethyl)-2,5-dimethoxybenzene and 1,4-bis(chloromethyl)-2-[4'-(3,7-dimethyloxy)phenyl]-3-phenylbenzene<sup>16</sup> were also synthesized. The electrical and spectroscopic properties of these polymers were systematically investigated. In addition, double-layer light-emitting devices were also fabricated to study EL properties of the polymers.

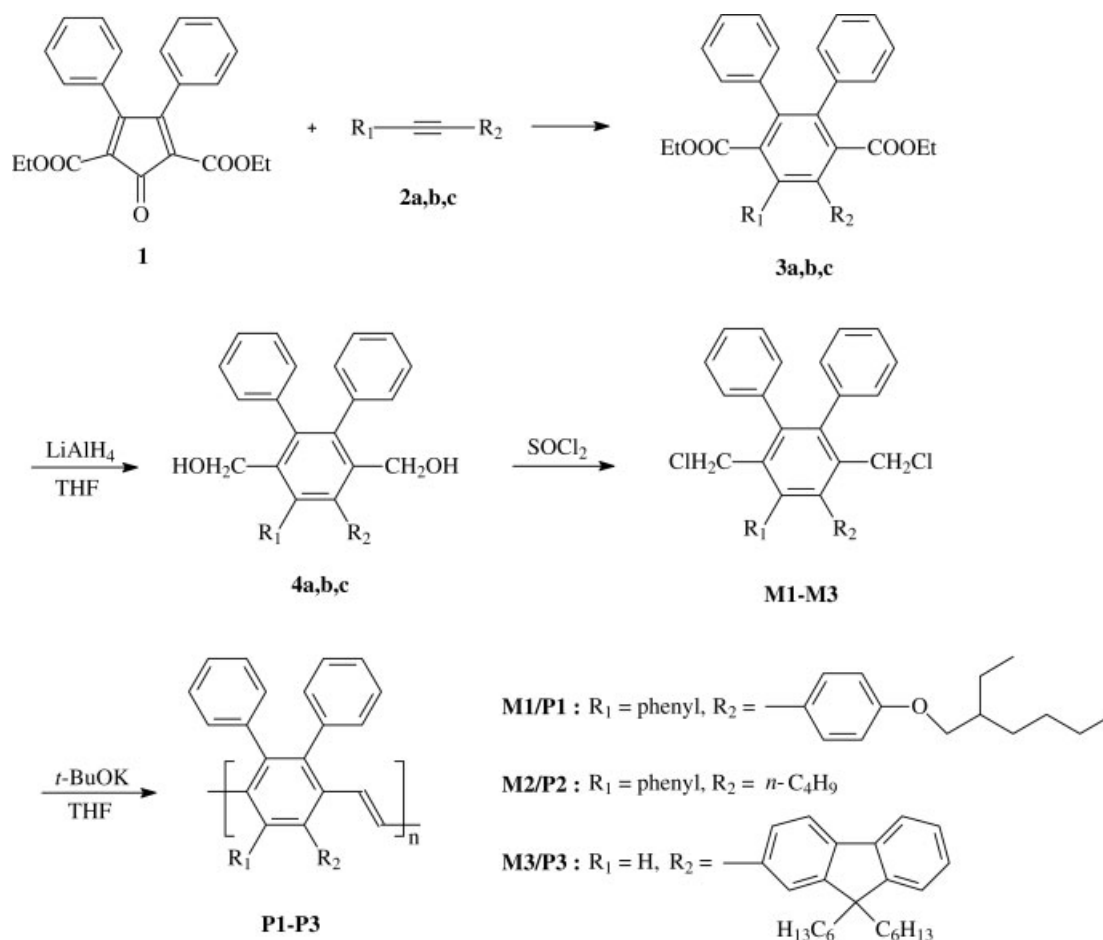
## EXPERIMENTAL

### Characterization Methods

<sup>1</sup>H NMR spectra were measured with a Varian 300 MHz spectrometer. Gel permeation chromatography 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 Perkin-Elmer Pyris Diamond DSC instrument at a scan rate of 10 °C min<sup>-1</sup>. Thermal gravimetric analysis (TGA) was undertaken on a Perkin-Elmer Pyris 1 TGA instrument with a heating rate of 10 °C min<sup>-1</sup>. 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<sub>3</sub>CN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) 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<sub>3</sub> solution, from Bioanalytical Systems, Inc.) 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 M1–M4

All reagents and chemicals were obtained from commercial sources (Aldrich, Merck, or TCI) and used without further purification. Tetrahydrofuran (THF) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were dried by distillation from sodium/benzophenone and calcium hydride, respectively. Schemes 1 and



**Scheme 1.** Synthesis of polymers **P1–P3**.

2 outline the synthetic routes for monomers **M1–M4**. The starting materials 2,5-dicarbethoxy-3,4-diphenylcyclopentadienone, (**1**) 1-phenyl-1-hexyne (**2b**), and 4,4'-dibromobenzil (**5**) were obtained from Aldrich Corp. The compound 2-(1-ethynyl)-9,9-dihexylfluorene (**2c**) was synthesized as described previously in the literature.<sup>19</sup>

#### 1-(2-Ethylhexoxy)-4-(2-phenyl-1-ethynyl)benzene (**2a**)

To a solution of phenylacetylene (7.3 g, 71.7 mmol) in triethylamine (350 mL) was added 1-(2-ethylhexoxy)-4-iodobenzene (22.6 g, 68.1 mmol), triphenylphosphine (1.43 g, 5.46 mmol), CuI (0.54 g, 2.87 mmol), and bis(triphenylphosphine) palladium(II) chloride (0.48 g, 0.68 mmol). The mixture was refluxed at 85 °C for 12 h. After cooling to room temperature, the crude product was filtered, washed with a large amount of *n*-hexane, and dried. It was purified by recrystallization

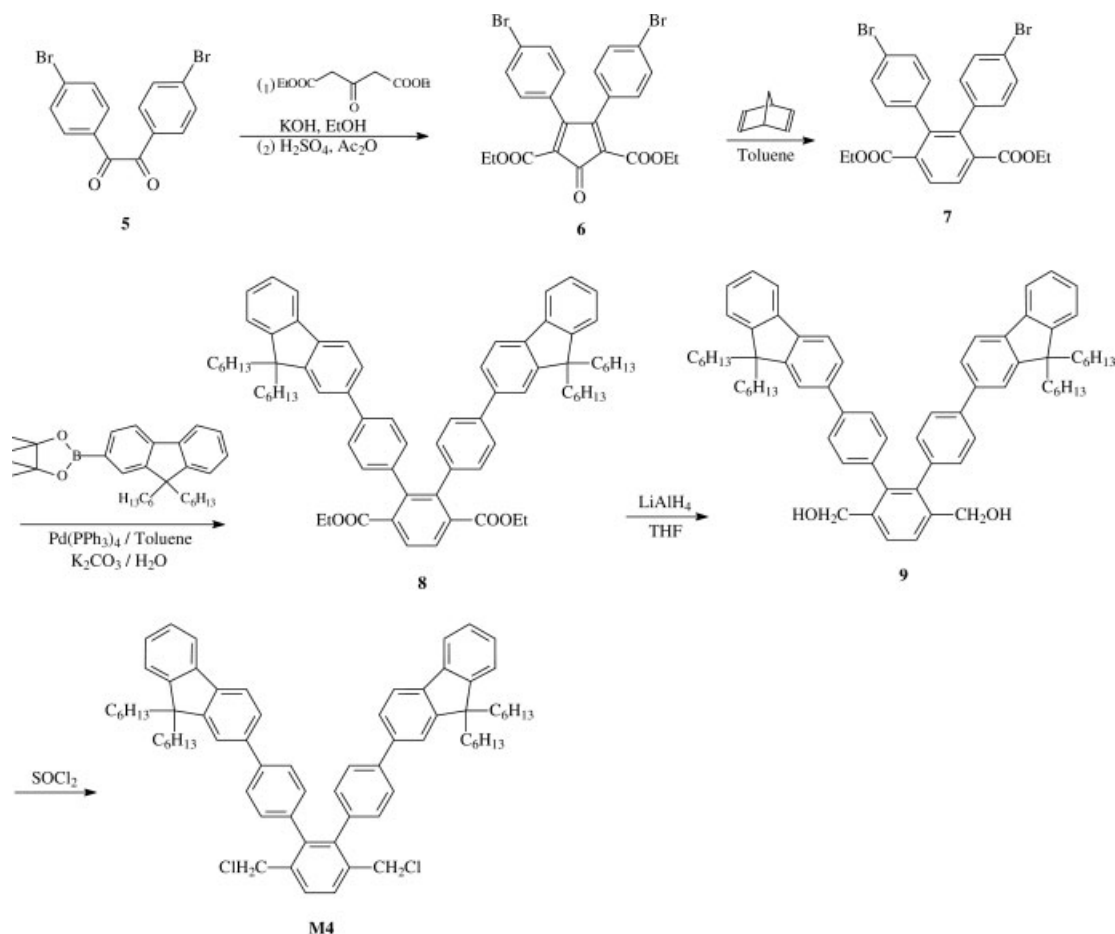
from methanol to yield 17.7 g (85%) of white crystals; mp 51 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.9–0.96 (t, *J* = 7 Hz, 6H, —OCH<sub>2</sub>—CH(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.28–1.52 (m, 8H, —OCH<sub>2</sub>—CH(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.69 (m, 1H, —O—CH<sub>2</sub>—CH—), 3.78 (d, *J* = 6.4 Hz, 2H, —OCH<sub>2</sub>—), 6.88 (d, *J* = 6.8 Hz, 4H, —C≡C—C<sub>6</sub>H<sub>4</sub>—O—), 7.33–7.57 (m, 5H, C<sub>6</sub>H<sub>5</sub>—C≡C—).

#### Diethyl 2-(4'-(2-ethylhexoxy)phenyl)-3,5,6-triphenylterephthalate (**3a**)

To a 100 mL round flask was added a mixture of **1** (9.72 g, 25.8 mmol) and **2a** (3.0 g, 10.3 mmol) and refluxed at 170 °C for 12 h. After cooling to room temperature, the crude product was purified by gel chromatography (silica gel, *n*-hexane as the eluent), following recrystallization from *n*-hexane to give 4.7 g (71%) of white crystals; mp 122 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.58–0.66 (m, 6H, —CO<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>), 0.81 (t, *J* = 7 Hz, 6H,



**Scheme 2.** Synthesis of monomer **M4**.

—OCH<sub>2</sub>—CH(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.2–1.66 (m, 9H, —OCH<sub>2</sub>—CH(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.55–3.61 (m, 4H, —CO<sub>2</sub>—CH<sub>2</sub>—), 3.72 (d, *J* = 6.4 Hz, 2H, —OCH<sub>2</sub>—), 6.57 (d, *J* = 7.2 Hz, 2H, aromatic-H), 6.91 (d, *J* = 7.2 Hz, 2H, aromatic-H), 7.03–7.08 (m, 15H, aromatic-H).

#### Diethyl 2-butyl-3,5,6-triphenyl terephthalate (**3b**)

By following the synthetic procedure for **3a** and using **2b** as starting material, the compound **3b** was obtained as white crystals (61% yield); mp 133 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.61–0.67 (t, *J* = 7 Hz, 3H, —(CH<sub>2</sub>)<sub>3</sub>—CH<sub>3</sub>), 0.87 (t, *J* = 7 Hz, 6H, —CO<sub>2</sub>—CH<sub>2</sub>CH<sub>3</sub>), 1.04 (m, 2H, phenyl-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33–1.42 (m, 2H, phenyl-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.43–2.45 (m, 2H, phenyl-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.51–3.94 (m, 4H, —CO<sub>2</sub>—CH<sub>2</sub>—), 7.01–7.12 (m, 10H, aromatic-H), 7.29–7.37 (m, 5H, aromatic-H).

#### Diethyl 2-(9,9-dihexylfluorene-2-yl)-5,6-diphenyl terephthalate (**3c**)

By following the synthetic procedure for **3a** and using **2c** as starting material, the compound **3c** was obtained as light-brown liquid (80% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 0.61–1.26 (m, 28H, fluorene—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>4</sub>—CH<sub>3</sub>), —CO<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>), 1.82 (t, *J* = 6.8 Hz, 4H, fluorene—CH<sub>2</sub>—), 6.99–7.14 (m, 10H, aromatic-H), 7.32–7.34 (m, 3H, aromatic-H), 7.44 (d, *J* = 7.4 Hz, 2H, aromatic-H), 7.73 (t, *J* = 7.8 Hz, 2H, aromatic-H), 7.86 (s, 1H, aromatic-H).

#### 1,4-Bis(hydroxymethyl)-2-(4'-(2-ethylhexoxy)-phenyl)-3,5,6-triphenylbenzene (**4a**)

A solution of **3a** (3.0 g, 4.7 mmol) in THF (30 mL) was added dropwise with stirring to a suspension of LiAlH<sub>4</sub> (1.02 g, 26.8 mol) in THF (40 mL) at 0 °C under nitrogen atmosphere. The solution was then refluxed at 70 °C for 4 h. After the solution was cooled in an ice-bath, a saturated

$\text{Na}_2\text{SO}_4$  aqueous solution was added dropwise until the solution became white. The white precipitate was removed by filtration. The crude product was isolated by evaporating the solvent and purified by recrystallization from *n*-hexane to yield 2.33 g (90%) of white crystals; mp 175 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.83 (t,  $J = 7$  Hz, 3H,  $-\text{OCH}_2-\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ), 1.22–1.32 (m, 9H,  $-\text{OCH}_2-\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ), 3.68 (t,  $J = 6.8$  Hz, 2H,  $-\text{OCH}_2-$ ), 4.11 (d,  $J = 6.4$  Hz, 2H,  $-\text{CH}_2\text{OH}$ ), 6.62 (d,  $J = 7.2$  Hz, 2H, aromatic-H), 6.95 (d,  $J = 7.2$  Hz, 2H, aromatic-H), 7.05–7.13 (m, 15H, aromatic-H).

#### 1,4-Bis(hydroxymethyl)-2-butyl-3,5,6-triphenylbenzene (4b)

By following the synthetic procedure for **4a** and using **3b** as starting material, the compound **4b** was obtained as white crystals (62% yield); mp 234 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.68 (t,  $J = 7$  Hz, 3H,  $-(\text{CH}_2)_3-\text{CH}_3$ ), 1.11–1.41 (m, 4H, phenyl- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.54 (m, 2H, phenyl- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.23 (d,  $J = 7.4$  Hz, 4H,  $-\text{CH}_2\text{OH}$ ), 7.02–7.15 (m, 10H, aromatic-H), 7.32–7.45 (m, 5H, aromatic-H).

#### 1,4-Bis(hydroxymethyl)-2-(9,9-dihexylfluoren-2-yl)-5,6-diphenylbenzene (4c)

By following the synthetic procedure for **4a** and using **3c** as starting material, the compound **4c** was obtained as white crystals (85% yield); mp 140 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.64–1.11 (m, 22H, fluorene- $\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$ ), 1.92 (t,  $J = 6.8$  Hz, 4H, fluorene- $\text{CH}_2-$ ), 4.41 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2\text{OH}$ ), 7.01–7.18 (m, 10H, aromatic-H), 7.28–7.35 (m, 3H, aromatic-H), 7.49–7.6 (m, 3H, aromatic-H), 7.7–7.78 (m, 2H, aromatic-H).

#### 1,4-Bis(chloromethyl)-2-(4'-(2-ethylhexoxy)phenyl)-3,5,6-triphenylbenzene (M1)

To a solution of **4a** (1.0 g, 1.56 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (30 mL) was slowly added 5 mL of thionyl chloride and stirred overnight under a nitrogen atmosphere. Water was then added dropwise into the solution to destroy excess thionyl chloride. The mixture was extracted with 10%  $\text{NaHCO}_3$  (aq) and organic phase was concentrated *in vacuo*. The crude product was purified by recrystallization from *n*-hexane to give 0.5 g (46%) of white crystals; mp 139 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.85 (t,  $J = 7$  Hz, 6H,  $-\text{OCH}_2-\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ), 1.1–1.32 (m, 9H,  $-\text{OCH}_2-\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ), 3.72 (t,  $J = 6.8$  Hz, 2H,  $-\text{OCH}_2-$ ), 4.1 (d,  $J = 6.4$  Hz, 2H,  $-\text{CH}_2\text{Cl}$ ), 6.66 (d,  $J = 7.2$  Hz, 2H, aromatic-H), 7.03 (d,  $J = 7.2$  Hz, 2H, aromatic-H), 7.05–7.13 (m, 15H, aromatic-H).

#### 1,4-Bis(chloromethyl)-2-butyl-3,5,6-triphenylbenzene (M2)

By following the synthetic procedure for **M1** and using **4b** as starting material, the compound **M2** was obtained as white crystals (42% yield); mp 184 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.69 (t,  $J = 7$  Hz, 3H,  $-(\text{CH}_2)_3-\text{CH}_3$ ), 1.13–1.45 (m, 4H, phenyl- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.54 (m, 2H, phenyl- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.02 (d,  $J = 7.4$  Hz, 4H,  $-\text{CH}_2\text{Cl}$ ), 7.03–7.17 (m, 10H, aromatic-H), 7.35–7.47 (m, 5H, aromatic-H).

#### 1,4-Bis(chloromethyl)-2-(9,9-dihexylfluoren-2-yl)-5,6-diphenylbenzene (M3)

By following the synthetic procedure for **M1** and using **4c** as starting material, the compound **M3** was obtained as white crystals (53% yield); mp 60 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.65–1.02 (m, 22H, fluorene- $\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$ ), 1.98 (t,  $J = 6.8$  Hz, 4H, fluorene- $\text{CH}_2-$ ), 4.29 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2\text{Cl}$ ), 7.04–7.16 (m, 10H, aromatic-H), 7.29–7.35 (m, 3H, aromatic-H), 7.43–7.64 (m, 3H, aromatic-H), 7.72–7.78 (m, 2H, aromatic-H).

#### Diethyl 4,5-bis(4'-bromophenyl)-2-oxo-3,5-cyclopentadiene-1,3-dicarboxylate (6)

To a mixture of **5** (10 g, 26.04 mmol) and diethyl 1,3-acetonedicarboxylate (5.26 g, 26.04 mmol) in ethanol (100 mL), a solution of KOH (1.46 g, 26.1 mmol) in ethanol (20 mL) was added and stirred at room temperature for 24 h. The resultant yellow precipitate was filtered off and dried.  $\text{H}_2\text{SO}_4$  was then added dropwise with stirring to slurry of the yellow precipitate in acetic anhydride (50 mL) until the solution became dark-red. After 30 min, 50 g of ice was added slowly to decompose excess acetic anhydride, and the crude product was collected and dried. It was purified by recrystallization from methanol to give 11.2 g (78%) of white crystals; mp 118 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.43–1.47 (t,  $J = 7$  Hz, 6H,  $-\text{CO}_2-\text{CH}_2\text{CH}_3$ ), 4.31–4.36 (q,  $J = 7$  Hz, 4H,  $-\text{CO}_2-\text{CH}_2-$ ), 7.58–7.62 (m, 4H, aromatic-H), 7.66–7.69 (m, 4H, aromatic-H).

#### Diethyl 2,3-bis(4'-bromophenyl)terephthalate (7)

A mixture of **6** (5 g, 9.1 mmol) and norbornadiene (4.4 g, 36.67 mmol) were dissolved in toluene (100 mL). The solution was refluxed at 120 °C for 12 h. After cooling to room temperature, the solution was concentrated *in vacuo* to remove the solvent and crude product was purified by recrystallization from methanol to give 3.9 g (78%) of white crystals; mp 127 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.28–1.32 (t,  $J = 7$  Hz, 6H,  $-\text{CO}_2-\text{CH}_2\text{CH}_3$ ), 4.21–4.27 (q,  $J = 7$  Hz, 4H,  $-\text{CO}_2-\text{CH}_2-$ ), 7.11–7.15 (m, 4H, aromatic-H), 7.28–7.31 (m, 4H, aromatic-H), 8.07 (s, 2H, aromatic-H).

#### Diethyl 2,3-bis(4'-(9,9-dihexylfluoren-2-yl)phenyl)terephthalate (8)

To a mixture of **7** (1.9 g, 3.57 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dihexylfluorene (3.4 g, 7.16 mmol),<sup>20</sup> tetrakis(triphenylphosphine)palladium (6.0 mg,  $5.3 \times 10^{-3}$  mmol),  $\text{K}_2\text{CO}_3$  (2.2 g, 15.92 mmol), and Aliquat 336 (0.4 g, 0.99 mmol) was added 15 mL of anhydrous toluene and 4 mL of de-ionized water. The resulting mixture was refluxed at 85 °C for 2 days under nitrogen atmosphere. After cooling to room temperature, the crude product was filtered, washed with a large amount of *n*-hexane, and dried. It was purified by gel chromatography (silica gel, *n*-hexane:ethyl acetate = 10:1 as the eluent) to give 1.1 g (53%) of pale-yellow liquid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.91–0.94 (t,  $J = 7$  Hz, 12H, fluorene- $(\text{CH}_2)_5-\text{CH}_3$ ), 1.28–1.32 (t,  $J = 7$  Hz, 6H,  $-\text{CO}_2-\text{CH}_2\text{CH}_3$ ), 1.33–1.44 (m, 32H, fluorene- $\text{CH}_2-(\text{CH}_2)_4-$ ), 2.56–2.84 (m, 8H, fluorene- $\text{CH}_2-$ ), 4.21–4.27 (q,  $J = 7$  Hz, 4H,  $-\text{CO}_2-\text{CH}_2-$ ), 6.78–6.8 (m, 4H, aromatic-H), 6.99–7.64 (m, 16H, aromatic-H), 7.91–7.92 (m, 2H, aromatic-H), 8.07 (s, 2H, aromatic-H).

#### 1,4-Bis(hydroxymethyl)-2,3-bis(4'-(9,9-dihexylfluoren-2-yl)phenyl)benzene (9)

By following the synthetic procedure for **4a** and using **8** as starting material, the compound **9** was obtained as white viscous liquid (90% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.91–0.94 (t,  $J = 7$  Hz, 12 H, fluorene- $(\text{CH}_2)_5-\text{CH}_3$ ), 1.23–1.44 (m, 32H, fluorene- $\text{CH}_2-(\text{CH}_2)_4-$ ), 2.56–2.84 (m, 8H, fluorene- $\text{CH}_2-$ ), 4.95 (d,  $J = 7.4$  Hz, 4H,  $-\text{CH}_2\text{OH}$ ), 6.81–6.84 (m, 4H, aromatic-H), 6.99–7.64 (m, 18H, aromatic-H), 7.9–7.91 (m, 2H, aromatic-H).

#### 1,4-Bis(chloromethyl)-2,3-bis(4'-(9,9-dihexylfluoren-2-yl)phenyl)benzene (M4)

By following the synthetic procedure for **M1** and using **9** as starting material, the compound **M4** was obtained as white viscous liquid (92% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.91–0.94 (t,  $J = 7$  Hz, 12 H, fluorene- $(\text{CH}_2)_5-\text{CH}_3$ ), 1.23–1.44 (m, 32H, fluorene- $\text{CH}_2-(\text{CH}_2)_4-$ ), 2.56–2.84 (m, 8H, fluorene- $\text{CH}_2-$ ), 5.07 (d,  $J = 7.2$  Hz, 4H,  $-\text{CH}_2\text{Cl}$ ), 6.81–6.84 (m, 4H, aromatic-H), 6.99–7.64 (m, 18H, aromatic-H), 7.9–7.91 (m, 2H, aromatic-H).

#### 1,4-Bis(chloromethyl)-2,5-dimethoxybenzene (M5) and 1,4-Bis(chloromethyl)-2-[4'-(3,7-dimethoxy)phenyl]-3-phenylbenzene (M6)

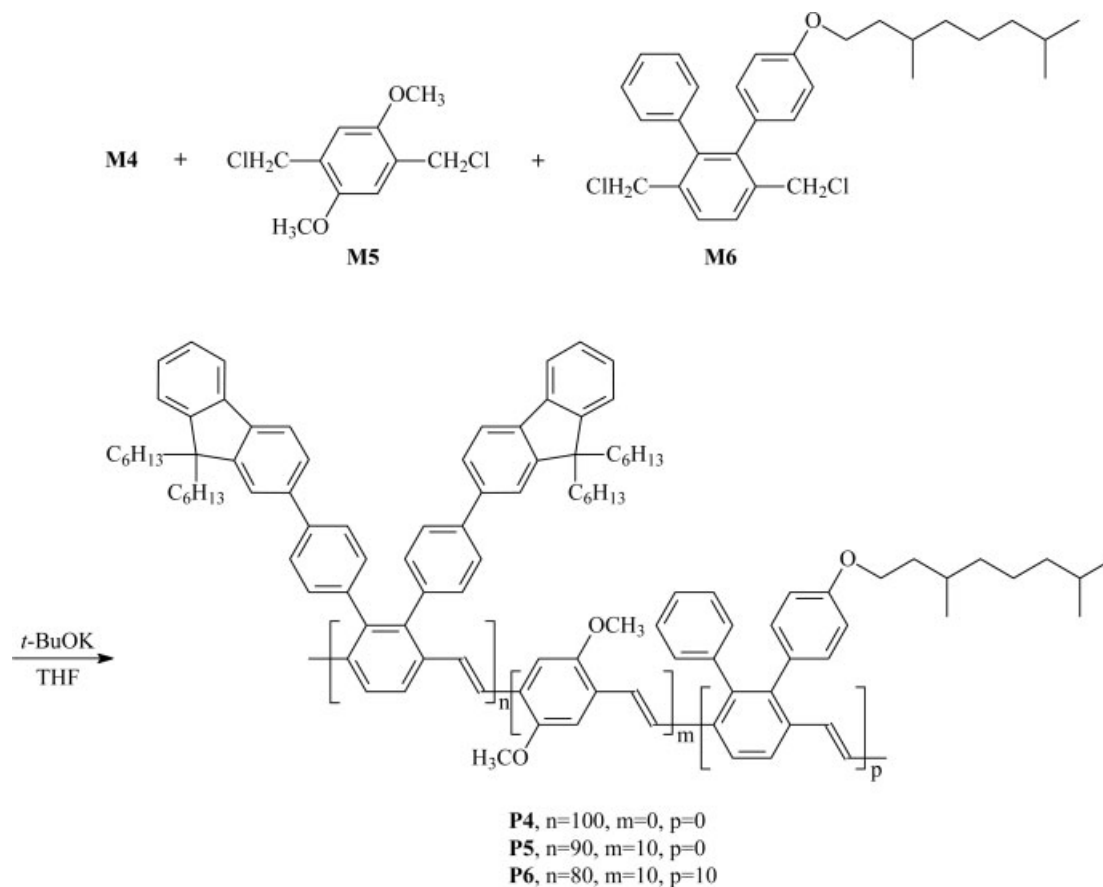
Monomers **M5** and **M6** were synthesized as described previously in the literatures.<sup>16,21</sup>

#### Synthesis of Polymers: General Procedure

Schemes 1 and 3 outline the syntheses of polymers **P1–P6**. An experimental procedure for the polymer **P1** is given below. To a solution of the monomer **M1** (2.0 g, 4.68 mmol) in THF (50 mL), a solution of potassium *tert*-butoxide (*tert*-BuOK, 12 equiv) in THF (15 mL) was added. 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 (20 mL) was then added and stirred for 6 h. The polymer was obtained by pouring the mixture into methanol and filtered. It was purified by dissolving in THF and reprecipitated from methanol twice. After drying under vacuum for 24 h, the polymer was obtained as brown solid (0.55 g, 41%).

#### 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, de-ionized water, and ace-



**Scheme 3.** Synthesis of polymers **P4–P6**.

tone. A 50 nm thick hole injection layer of poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (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 layer and dried at 50 °C overnight in a vacuum. The thickness of the active layer was ~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  $2 \times 10^{-6}$  torr. The active area of each EL device was 4 mm<sup>2</sup> and the device was characterized following a published protocol.<sup>22</sup>

## RESULTS AND DISCUSSION

### Synthesis of Polymers

Scheme 1 outlines the synthetic route for monomers **M1–M3**. Different substituents of R<sub>1</sub> and R<sub>2</sub>

were incorporated on the C5 and C6 positions of the phenylene moiety via the Diels–Alder reaction. The compound **4** with dihydroxy groups was obtained by the reduction of **3**, following the chlorination to give monomers **M1–M3**. Scheme 2 outlines the synthesis of monomer **M4**. The synthetic route is similar to the Scheme 1, except the incorporation of two bulky fluorenyl groups via the Suzuki coupling reaction. Schemes 1 and 3 outline the syntheses of polymers **P1–P6**. The polymerization was carried out via a modified Gilch route to obtain soluble DP-PPV derivatives. For a typical Gilch synthetic route,  $\alpha,\alpha'$ -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. The polymerization condition is mild and the molecular weights of obtained polymers are relatively large. In our experiments **P1–P4** are homopolymers, while **P5** and **P6** are copolymers obtained from copolymerizing **M4** with two different monomers **M5** and **M6**. It has been reported that incorporation of **M5** increased carrier mobility inside poly-

**Table 1.** Feed Ratio and Polymerization Results of Polymers **P1–P6**

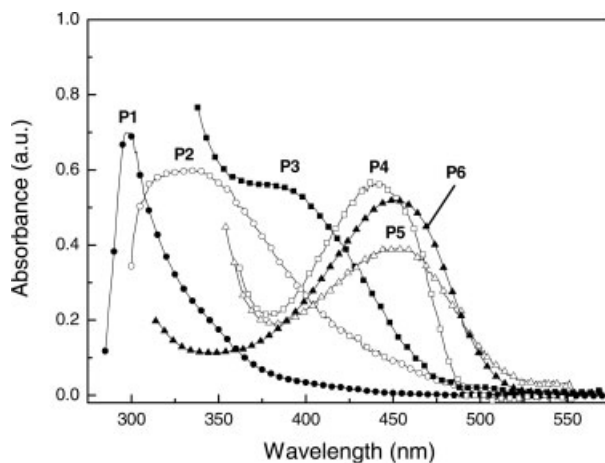
Polymer	<i>n</i>	<i>m</i>	<i>p</i>	Yield (%)	$\overline{M}_n$	$\overline{M}_w$	PDI
<b>P1</b>	100	–	–	33	1728	4888	2.59
<b>P2</b>	100	–	–	41	8882	41,025	4.61
<b>P3</b>	100	–	–	36	3695	6596	1.78
<b>P4</b>	100	–	–	55	580,800	557,000	1.15
<b>P5</b>	90	10	–	58	556,200	600,300	1.08
<b>P6</b>	80	10	10	54	332,900	360,000	1.08

mer layer.<sup>23</sup> **M6** was first synthesized and reported by our group. The syntheses, characterization, and electro-optical properties of several DP-PPV derivatives based on **M6** have been published previously.<sup>16</sup> We expect that incorporation of **M5** and **M6** can adjust the optical and electrical properties of the homopolymer **P4**.

Table 1 summarizes the feed ratio of monomers, molecular weights, and polydispersity index (PDI) of resulting polymers. The number-average molecular weight  $\overline{M}_n$  and weight-average molecular weights  $\overline{M}_w$  of **P1** and **P3** are below  $10^4$ , regarding as oligomers. The  $\overline{M}_n$  and  $\overline{M}_w$  of **P2** are 8882 and 41,025, respectively; however, its PDI value is large (4.61). The polymerization results for **P1–P3** are not quite satisfactory. For polymers **P4–P6**, the  $\overline{M}_n$  values are in the range from  $3.3 \times 10^5$  to  $5.8 \times 10^5$ , while the  $\overline{M}_w$  values are in the range from  $3.6 \times 10^5$  to  $6 \times 10^5$ . The molecular weight distribution is relatively narrow (PDI < 1.2). The obtained polymers **P4–P6** are soluble in common organic solvents, such as chloroform, toluene, and chlorobenzene. Transparent and self-standing films can be cast from their solutions. Although two fluorenyl substituents are bulky, polymers with high molecular weights can still be obtained. However, the molecular weights of polymers **P1–**

**Table 2.** Thermal and Optical Properties of Polymers **P1–P6**

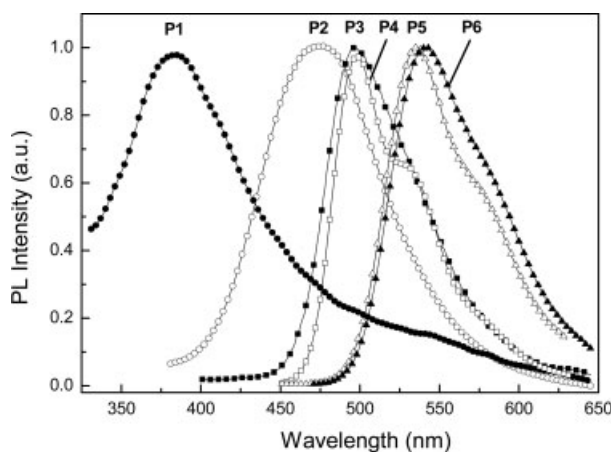
Polymer	$T_g$ (°C)	$T_d$ (°C)	UV-vis (nm)		PL (nm)	
			Solution	Film	Solution	Film
<b>P1</b>	166	330	297	303	407	384
<b>P2</b>	168	310	334	332	463	483
<b>P3</b>	160	433	389	390	500	506
<b>P4</b>	125	423	438	441	472	498
<b>P5</b>	144	421	449	452	505	535
<b>P6</b>	138	398	448	451	519	541

**Figure 1.** UV-vis absorption spectra of polymers **P1–P6** in thin film state.

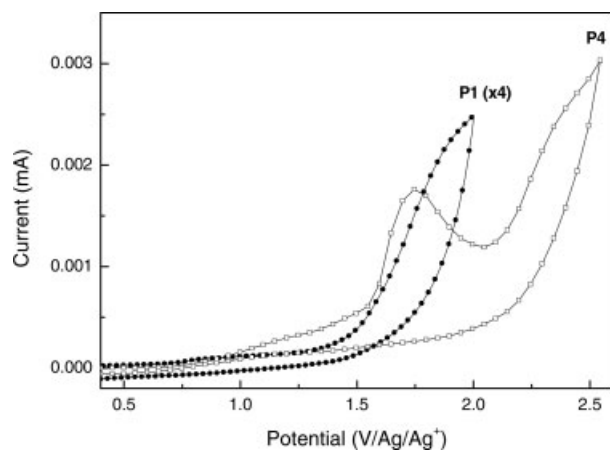
**P3** are much smaller. We explain this as a result of multiple substituents on the phenylene moiety. Monomers **M1–M3** belong to tri- or tetra-substituted bis(chloromethyl)benzene, resulting in large steric hindrance. They are hindered to react with each other and hence polymers with low molecular weights and wide distribution were obtained. These materials show insufficient film-forming property that limits their potential use in thin-film devices. In contrast, monomers **M4–M6** belong to disubstituted ones and the steric hindrance is smaller.

### Thermal Properties

Table 2 summarizes the thermal properties of polymers **P1–P6**. Most polymers show good thermal

**Figure 2.** PL emission spectra of polymers **P1–P6** in thin film state.





**Figure 3.** Cyclic voltammograms of homopolymers **P1** and **P4**.

stabilities with high glass-transition temperatures ( $T_g$ ) over 130 °C and high decomposition temperatures ( $T_d$ ) over 310 °C. Polymers **P3–P6** show even higher  $T_d$  than the others, which is attributed to high molecular weights and rigid fluorenyl group on the phenyl ring. On the other hand, **P1** and **P2** show lower  $T_d$  owing to low molecular weights; however, they show higher  $T_g$  as a result of tetra-substitution on the phenylene moiety, which hinders the segmental motion of the main chain.

### Optical Properties

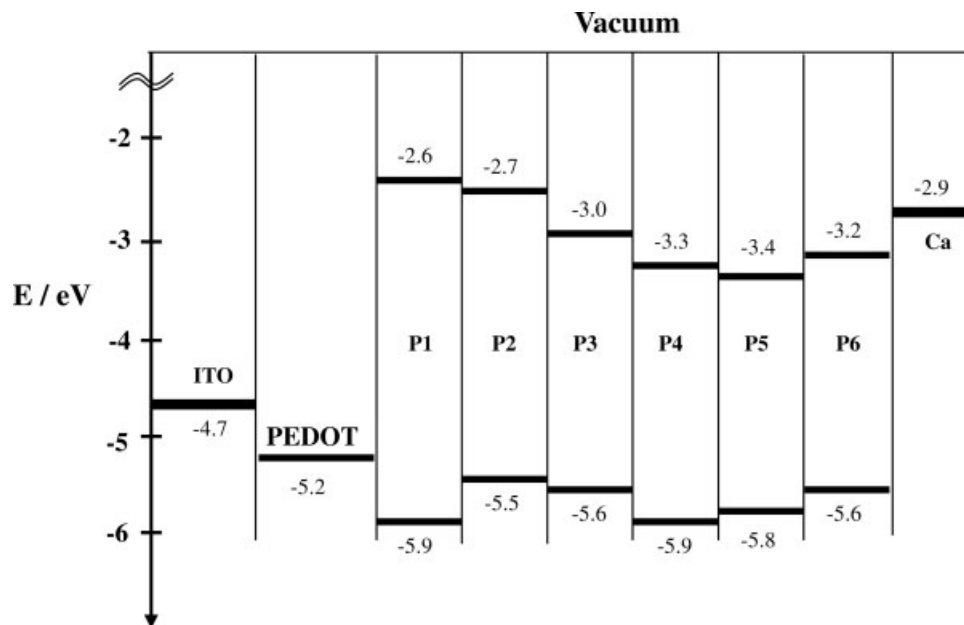
Figure 1 shows the UV–vis absorption spectra of polymers **P1–P6** in thin film state. Table 2 summarizes the UV–vis absorption maxima of all polymers in different states. The absorption maxima of synthesized polymers in toluene are located in the range from 297 to 449 nm, which is attributed to the  $\pi$ – $\pi^*$  transition along the conjugated backbone. A small red-shift of the absorption band in thin film state is observed, which is due to the effect of inter-

chain  $\pi$ -stacking. **P1** shows the most blue-shifted absorption band because of lowest molecular weight, referring to the shortest conjugation length among six polymers. **P3** shows more red-shifted absorption band than **P1** and **P2**, implying a longer conjugation length. This is attributable to the steric effect of less substituents on the phenylene moiety, and a smaller torsional angle between two repeating units is formed. In contrast, copolymers **P5** and **P6** show similar absorption bands and are red-shifted than **P4**, owing to two electron-donating alkoxy group on **M5**. It is also noted that incorporation of **M6** does not affect the conjugation length significantly.

Figure 2 reveals the PL emission spectra of polymers **P1–P6** in thin film state. The excitation wavelengths were based on their UV–vis absorption maxima in the same state. The PL emission maxima in different states are also summarized in Table 2. The maximum emission bands are located from 407 to 519 nm in solution state and from 384 to 541 nm in thin film state. Similar tendency of red-shift from solution to thin film state is observed, exclusive of **P1**. The emission maximum of **P1** is located at 407 nm in toluene, while it is blue-shifted to 384 nm in film state. It is generally thought that red-shift in one state means some close packing of the polymer chains to extend the conjugation length. It seems that **P1** in toluene has stronger  $\pi$ – $\pi$  interaction than in film state, may be due to similar structure of solvent and polymer structure. On the other hand, the shapes of PL spectra show some features. For **P1–P3**, no significant vibronic band is observed, indicating no or weak chain–chain interactions. The homopolymer **P4** shows a clear emission shoulder band at 530 nm, while the shoulder bands of copolymers **P5** and **P6** become less significant. This may be due to random structures of polymer main chains, which prevent close packing of neighboring polymers.

**Table 3.** Electrochemical Properties of Polymers **P1–P6** in Solid Films

Polymer	$E_{ox}$ (V)	HOMO (eV)	UV edge (nm)	EG (eV)	LUMO (eV)
<b>P1</b>	1.5	–5.9	376	3.3	–2.6
<b>P2</b>	1.1	–5.5	443	2.8	–2.7
<b>P3</b>	1.2	–5.6	461	2.7	–3.0
<b>P4</b>	1.5	–5.9	483	2.6	–3.3
<b>P5</b>	1.4	–5.8	517	2.4	–3.4
<b>P6</b>	1.2	–5.6	510	2.4	–3.2



**Figure 4.** Energy level diagrams of polymers **P1–P6**.

### Electrochemical Analysis

CV was employed to investigate the electrochemical behaviors of polymers synthesized 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 **P1** and **P4** in the oxidation process. The HOMO energy level is determined from the onset of the oxidation curve ( $E_{\text{ox}}$ ), which is given by

$$\text{HOMO(eV)} = -|E_{\text{ox}} + 4.4|$$

which is in the range from  $-5.9$  to  $-5.5$  eV. The energy gaps (EG) of materials are determined from the edge of their UV–vis absorption spectra ( $\lambda_{\text{onset}}$ ), which is given by

$$\text{EG(eV)} = 1240/\lambda_{\text{onset}}$$

which is in the range from 2.4 to 3.3 eV. Combining the electrochemical data and UV–vis charac-

teristics give an estimate of the LUMO energy levels. Table 3 summarizes the HOMO, LUMO, and EG values of polymers **P1–P6**. The energy level diagram of these materials is illustrated in Figure 4. The relatively small  $E_{\text{ox}}$  of **P2**, **P3**, and **P6** reveals that they are favored for *p*-doping process when compared with others. The smaller energy barrier between polymer **P2** (and **P3**, **P6**) and PEDOT layer also shows the benefit for hole injection. Turning to EA value, **P3** and **P6** show smaller energy barriers of 0.2 eV to the cathode Ca. This also implies that electron injection is favored for these two polymers.

### Device Performance

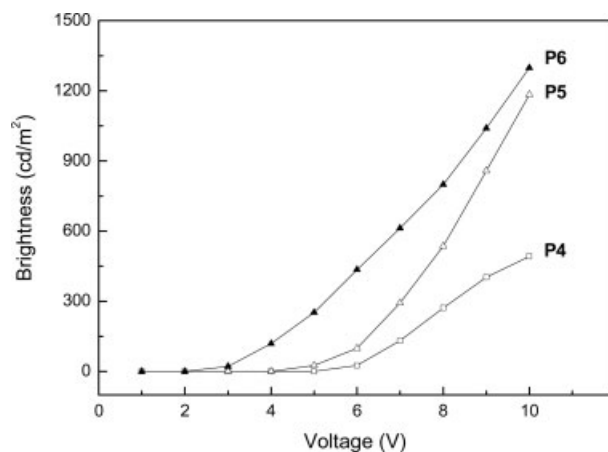
Double-layer light-emitting diodes with the configuration of ITO/PEDOT/Polymer/Ca/Al were fabricated to evaluate the potential use of synthesized DP-PPV derivatives. Among them, **P1–P3** has relatively low molecular weights and could

**Table 4.** Device Performance of Polymers **P4–P6** in ITO/PEDOT/Polymer/Ca/Al Devices

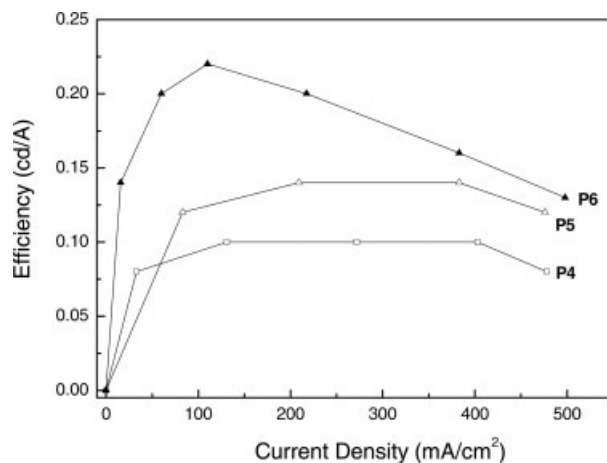
Polymer	EL (nm)	$V_{\text{turn-on}}$ (V)	Max. Brightness (cd/m <sup>2</sup> )	Max. Yield (cd/A)	CIE' 1931	
					<i>x</i>	<i>y</i>
<b>P4</b>	492	6	492	0.11	0.24	0.5
<b>P5</b>	530	5	1184	0.14	0.37	0.58
<b>P6</b>	524	3	1298	0.22	0.34	0.58

not provide sufficient film-forming properties. This may affect the device fabrication and performance evaluation. Hence, we fabricated three EL devices using **P4–P6** as the active layer. The maximum EL emission bands of **P4–P6** are listed in Table 4, which are located at 492, 530, and 524 nm, respectively. The CIE coordinates of the three polymers are also shown in Table 4, referring to pure green (**P4**) and yellowish green (**P5**, **P6**). Some extent of blue-shift of the EL emission with increasing the operation voltage is also observed. This phenomenon has been observed previously and explained as a result of charge-trapping/defect site from some head-to-head isomers.<sup>16</sup>

Figures 5 and 6 show the brightness-voltage and efficiency-current density characteristics, respectively, of the three devices fabricated using **P4–P6** as the active layer. The device using homopolymer **P4** as active layer showed a maximum brightness of 492 cd/m<sup>2</sup> at 10 V, and a maximum current efficiency of 0.11 cd/A at 8 V. Using copolymer **P5** as active layer, the device showed an improved brightness of 1184 cd/m<sup>2</sup> and current efficiency of 0.14 cd/A at 10 V. The luminescence is roughly improved by incorporating 2,5-dimethoxy-1,4-phenylene vinylene unit. The device of **P6** showed even higher brightness and current efficiency, which was 2-fold higher than the homopolymer **P4**. The better performance of devices using **P5** and **P6** as active layer is explained by the smaller energy barrier between metals and emissive layer. Holes/electrons are easier to be injected into copolymers **P5** and **P6** than the homopolymer **P4**, and thus higher opportunity of charge recombination occurs (Fig. 4). Moreover, the charge mobility may be somewhat improved



**Figure 5.** Brightness–voltage characteristics of polymers **P4–P6** in ITO/PEDOT/Polymer/Ca/Al devices.



**Figure 6.** Efficiency–current density characteristics of polymers **P4–P6** in ITO/PEDOT/Polymer/Ca/Al devices.

by incorporating **M5** and **M6**. The device performance of these DP-PPV derivatives is summarized in Table 4. Compared with previous reports, the materials synthesized in this work showed moderate EL properties. Better device performance was obtained when compared with previous trisubstituted DP-PPVs, but not as high as those with one fluorenyl ring as pendant group.<sup>15,16</sup> We consider that two bulky substituents on the main chain may also hinder carrier transport and movement inside polymer layer.

## CONCLUSIONS

In this work, six DP-PPV derivatives containing bulky substituents were synthesized. Highly phenylated DP-PPV derivatives with blue-shifted emission were obtained. However, the molecular weights are not very high. Bulky fluorenyl substituents with two hexyl chains were introduced on the pendant phenyl ring to increase steric hindrance and to prevent close packing of the main chains. The molecular weights of difluorenyl substituted DP-PPVs are sufficiently high. Double-layer devices with the configuration of ITO/PEDOT/polymer/Ca/Al were fabricated and characterized. Pure green light with CIE/1931 at (0.24, 0.5) was observed for **P4**. Using **P6** as the emissive layer, the maximum luminescence and current efficiency were both improved.

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