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Synthesis of Poly[2-decyloxy-5-(4'-*tert*-butylphenyl)-1,4-phenylenevinylene] as a Light Emitting Material

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In this study, a new electroluminescent poly(2-decyloxy-5-(4'-*tert*-butylphenyl)-1,4-phenylene-vinylene) (designated as DBP-PPV) with no tolane-bis-benzyl (TBB) structure defect was prepared by dehydrohalogenation of 1,4-bisbromomethyl-2-decyloxy-5-(4'-*tert*-butylphenyl) benzene (as monomer). The monomer bearing decyloxy and 4'-*tert*-butylphenyl substituents was synthesized via alkylation, bromination and Suzuki coupling reactions. The two asymmetric substituents of the monomer can suppress the formation of TBB defect during polymerization process and make the resultant polymer be soluble in common organic solvents. The structure and properties of DBP-PPV were examined by ¹H-NMR, FT-IR, UV/Vis, TGA and photoluminescence (PL) analyses. Moreover, with the DBP-PPV acting as a light-emitting polymer, a device with sequential lamination of ITO/PEDOT/DBP-PPV/Ca/Ag was fabricated. The electroluminescence (EL) spectrum of the device showed a maximum emission at around 546 nm, corresponding to a yellowish-green light. The device showed a turn-on voltage of about 8.4 V and a maximum luminescence efficiency of 0.11 cd/A at an applied voltage of 12 V.

Keywords: yellowish-green; electroluminescence; poly(phenylenevinylene) derivatives; photoluminescence

1 Introduction

Great research interest has been focused on the electro-optical properties of poly(*p*-phenylenevinylene) (PPV) derivatives by incorporating appropriate substituents to the polymer backbone (1–8), since the report of PPV as a light emitting material for light emitting diodes (LED) in 1990 (9). Owing to the rigid main-chains, PPV exhibits poor solubility in common organic solvents and limited processibility. These problems can be solved by two approaches, i.e., the precursor approach and the incorporation of side chains to polymer backbones. The former approach involves preparing a soluble precursor polymer and then casting it to obtain a film. For this approach, there are two generally-used routes, i.e., the Wessling (10) and chlorine precursor routes (CPR) (11). The preparation of poly(*p*-phenylenevinylene) (PPV) from the *p*-phenylenedimethylene bis-(tetramethylene sulfonium chloride) (12) through a sulfonium precursor is one

example of the Wessling precursor route. The CPR method is illustrated by first reacting the 1,4-bischloromethyl-2,3-diphenyl benzene with about one equivalent of *tert*-butyl potassium oxide to obtain a soluble chlorine precursor polymer, then heating the precursor polymer under vacuum to obtain poly(2,3-diphenyl-1,4-phenylenevinylene) (DP-PPV) (13).

The other approach of incorporating side chains to polymer backbones is achieved by preparing a soluble polymer from a monomer having multiple substituents. For this approach, the Gilch procedure is a typical polymerization method (14). The synthesis of poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene) from 2-methoxy-5-dodecyloxy-*p*-xylene dichloride (15) by using large excess of *tert*-butyl potassium oxide is one example of the Gilch procedure. However, Becker et al. (16, 17) discovered the presence of structure defects located in polymer main-chains of the PPV derivatives prepared by the Gilch procedure. The structure defects are named tolane-bis-benzyl (TBB) defects. These defects result from the happening of head-to-head (or tail-to-tail) coupling reaction, instead of regular head-to-tail one, during the polymerization reaction. The increase of TBB content would significantly decrease the lifetime of the resulting LED device (17). The TBB content could be reduced by introducing asymmetric substituents to the phenyl rings of PPV

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monomer, ex. with two halomethyl groups in the respective *ortho* and *meta* positions of an alkoxy group. Because the alkoxy group is strongly electron-donative, the halomethyl group in *ortho* position would be more acidic than that in *meta* position (18). The difference in acidity or reactivity of these two halomethyl groups makes the polymerization reaction of the monomers proceed in a regular head-to-tail way.

We synthesized a new soluble fluorescent PPV derivative with no TBB defect, poly(2-decyloxy-5-(4'-*tert*-butylphenyl)-1,4-phenylenevinylene) (DBP-PPV), by a method similar to the Gilch procedure. The DBP-PPV contains *tert*-butylphenyl and decyloxy groups on the respective 5-position and 2-position of the phenylene rings in the polymer main-chains. The incorporation of decyloxy substituents on the polymer main-chains would be expected to make the polymer soluble in common solvents and to suppress the presence of TBB defects. The rigid *tert*-butylphenyl substituents would be expected to enhance thermal stability of the polymer. The electro-optical and thermal properties of the DBP-PPV were also examined in this work.

2 Experimental

2.1 Materials

Benzoyl peroxide (BPO), 2,5-dimethylphenol, 1-bromodecane, N-bromosuccinimide (NBS), bromine, potassium hydroxide, potassium carbonate, tetra-butyl ammonium bromide (TBAB), magnesium sulfate, carbon tetrachloride and acetic acid were purchased from Fluka Chemical (Ronkonkoma, NY). The *n*-butyl lithium (*n*-BuLi, 2.5 M in hexane) was purchased from Chemetall (Chang Bin Industrial Park, Hsien-si, Chang-Hua County, Taiwan, ROC). Potassium *tert*-butoxide (*t*-BuOK) and iron (III) bromide (FeBr_3) were purchased from Sigma-Aldrich (Steinheim, Germany). Tetrakis(triphenylphosphine) palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) and 4-*tert*-butylbenzene boronic acid were purchased from ACROS (Geel, Belgium). All the above reagents were synthetic grade and used as received. Tetrahydrofuran (THF) and 1,4-dioxane were synthetic grade and purchased from Tokyo Chemical Industry Co. (Tokyo, Japan), which were dehydrated with sodium and distilled prior to use.

2.2 Instrument

Melting points of compounds were determined on a Buchi B-540 apparatus. The ^1H and ^{13}C -NMR spectra of the specimen solutions in CDCl_3 were measured by a Bruker Avance 300 spectrometer (300 MHz). Elemental analyses were performed with a Heraeus CHN-O-Rapid Analyzer. FT-IR spectra were recorded by a Perkin-Elmer Spectrum One spectrometer. UV-VIS spectra of the samples in THF were measured by a Shimadzu UV-160 spectrophotometer. The mass spectra were measured by a Bruker APEX

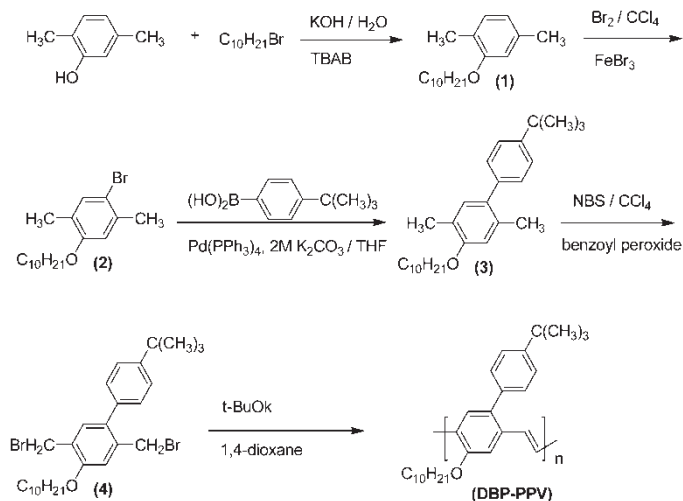
spectrometer. The fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. The thickness of DBP-PPV ultra-thin film was measured by a Kosaka Laboratory ET-4000 M photometer. The weight and number average molecular weights of DBP-PPV were measured by a gel permeation chromatographer (GPC) of the Analytical Scientific Instrument Model 500 system. Polystyrene standards were used for molecular weight calibration and tetrahydrofuran was used as carrier solvent. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer Model TGA-7 thermogravimetric analyzer under a nitrogen stream in the range of 50–600°C and with a heating rate of 10°C/min. The current–voltage (*I*-*V*) characteristics and luminance of the devices were measured by a Keithly 2400 current/voltage source and a Topcon BM-8 meter, respectively.

2.3 Synthesis Process

The process for preparing the monomer and polymer is illustrated in Scheme 1. The monomer was prepared via various chemical reactions as alkylation, bromination and Suzuki coupling reactions. The DBP-PPV was obtained by a method similar to the Gilch procedure.

2.4 Synthesis of 2-(Decyloxy)-1,4-dimethylbenzene (1)

A solution mixture of 2,5-dimethylphenol (12.2 g, 100 mmol), potassium hydroxide (8.4 g, 150 mmol), 50 ml H_2O and tetra-butyl ammonium bromide (3.4 g, 105 mmol) was stirred for 15 min. Then, 1-bromodecane (22.1 g, 100 mmol) was added to the solution mixture. The reaction proceeded with stirring and reflux heating at 80°C for 22 h. After the completion of the reaction, the solution was cooled to room temperature. 100 ml H_2O was added to the resultant solution and the organic layer was collected. Subsequently, the organic layer was washed with aqueous sodium hydroxide solution



Sch. 1. Synthesis process for the monomer and polymer.

(10%, 2 × 50 ml) and 100 ml H₂O successively. The resultant organic layer was dewatered with anhydrous MgSO₄, and filtered. The solvent was distilled off under reduced pressure with a rotary evaporator. Finally, 2-(decyloxy)-1,4-dimethylbenzene (1) was obtained as pale brown oil with a yield of 93% (24.62 g).

¹H-NMR (CDCl₃) δ: 7.01(d, *J* = 7.36 Hz, 1H, aromatic H), 6.69 (d, *J* = 7.72 Hz, 1H, aromatic H), 6.65 (s, 1H, aromatic H), 3.95 (t, *J* = 6.44 Hz, 2H, -OCH₂), 2.33 (s, 3H, aromatic CH₃), 2.20 (s, 3H, aromatic CH₃), 1.84–1.30 (m, 16H, aliphatic C-H), 0.91 (t, *J* = 6.52 Hz, 3H, aliphatic CH₃). FTIR (KBr pellet, cm⁻¹): 3072, 2924, 2856, 1615, 1586, 1509, 1463, 1415, 1378, 1265, 1158, 1131, 1040, 842, 802. ¹³C NMR (CDCl₃) δ: aromatic (C) 157.1, 136.4, 130.2, 123.6, 120.5, 111.9, aliphatic (C) 67.9, 31.9, 30.0, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 21.4, 15.7, 14.1. FABMS⁺: *m/z*; 263 (M⁺ + H, 50%), 262 (M⁺, 74%), 122 (M⁺ + H-C₁₀H₂₁, 100%), 121 (M⁺-C₁₀H₂₁, 47%).

2.5 Synthesis of 1-Bromo-4-(decyloxy)-2,5-dimethylbenzene (2)

A solution mixture of compound (1) (13.1 g, 50 mmol), 35 ml carbon tetrachloride and iron (III) bromide (1 g, 3 mmol) was stirred in an iced bath. Bromine (8 g, 50 mmol) was slowly dropped into the mixture through a condenser and stirred for 24 h. After the completion of the reaction, the solution was washed with aqueous sodium hydroxide solution (10%, 2 × 50 ml) and 100 ml H₂O successively. Then, the organic phase was dewatered with anhydrous MgSO₄. After the removal of MgSO₄, the solvent was distilled off under reduced pressure with a rotary evaporator. Subsequently, a pale yellow crude product was obtained. The crude product was washed with methyl alcohol and dried under dynamic vacuum. Finally, 1-bromo-4-(decyloxy)-2,5-dimethylbenzene (2) was obtained as colorless solids with a yield of 79% (13.58 g).

M.p.: 52–53°C, ¹H-NMR (CDCl₃) δ: 7.23(s, 1H, aromatic H), 6.65 (s, 1H, aromatic H), 3.90 (t, *J* = 6.4 Hz, 2H, -OCH₂), 2.32 (s, 3H, aromatic CH₃), 2.13 (s, 3H, aromatic CH₃), 1.79–1.26 (m, 16H, aliphatic C-H), 0.86 (t, *J* = 6.6 Hz, 3H, aliphatic CH₃). FTIR (KBr pellet, cm⁻¹): 3072, 2924, 2847, 1731, 1606, 1567, 1496, 1462, 1383, 1363, 1163, 1034, 958, 879, 835. ¹³C NMR (CDCl₃) δ: aromatic (C) 156.4, 135.5, 133.6, 126.3, 114.4, 113.5, aliphatic (C) 68.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.9, 22.7, 15.5, 14.1. FABMS⁺: *m/z*; 343 (M⁺ + 2 + H, 25%), 341 (M⁺ + H, 32%), 202 (M⁺ + 2 + H-C₁₀H₂₁, 95%), 200 (M⁺ + H-C₁₀H₂₁, 100%).

2.6 Synthesis of 2-(Decyloxy)-5-(4'-tert-butylphenyl)-1,4-dimethylbenzene (3)

A solution mixture of compound (2) (3.41 g, 10 mmol), 4-tert-butylbenzene boronic acid (ACROS, 1.95 g, 10.9 mmol), 25 ml 2M K₂CO₃ solution, 35 ml THF and Pd

(PPh₃)₄ (0.07 g) was reflux-heated for 24 h under a nitrogen atmosphere. Then the reaction was terminated by pouring with 25 ml water. The resultant solution was extracted with diethyl ether. Subsequently, the organic phase was dewatered with anhydrous MgSO₄ and filtered through a filter paper. After the solvent of organic phase was distilled off under reduced pressure with a rotary evaporator, a greenish-yellow viscous oil was obtained. The viscous oil was purified by column chromatography (silica gel, n-hexane/ethyl acetate (20/1) as an eluent) to give the 2-(decyloxy)-5-(4'-tert-butylphenyl)-1,4-dimethylbenzene (3) with a yield of 67% (2.66 g).

¹H-NMR (CDCl₃) δ: 7.47 (d, *J* = 7.93 Hz, 2H, aromatic H), 7.31 (d, *J* = 7.98 Hz, 2H, aromatic H), 7.09 (s, 1H, aromatic H), 6.77 (s, 1H, aromatic H), 4.04 (t, *J* = 6.26 Hz, 2H, -OCH₂), 2.28 (s, 3H, aromatic CH₃), 2.24 (s, 3H, aromatic CH₃), 1.90–1.26 (m, 25H, aliphatic C-H), 0.95 (t, *J* = 6.59 Hz, 3H, aliphatic CH₃). FTIR (KBr pellet, cm⁻¹): 3076, 2925, 2856, 1613, 1503, 1468, 1386, 1234, 1137, 1042, 837. FABMS⁺: *m/z*; 395 (M⁺ + H, 31%), 394 (M⁺, 85%), 254 (M⁺ + H-C₁₀H₂₁, 29%) 253 (M⁺-C₁₀H₂₁, 22%).

2.7 Synthesis of 1,4-Bis(bromomethyl)-2-decyloxy-5-(4'-tert-butylphenyl) benzene (4)

Benzoyl peroxide (0.03 g, 0.12 mmol) and N-bromosuccinimide (0.8 g, 4.4 mmol) were added to a solution of compound (3) (0.81 g, 2 mmol) in 50 ml carbon tetrachloride. After reflux heating for 24 h, the mixture was cooled to room temperature. The floating succinimide in the mixture was filtered away and the solvent was distilled off under reduced pressure with a rotary evaporator. The obtained yellowish viscous oil is 1,4-bis(bromomethyl)-2-decyloxy-5-(4'-tert-butylphenyl) benzene (4) that with a yield of 54% (0.62 g).

¹H-NMR (CDCl₃) δ: 7.46 (d, *J* = 8.15 Hz, 2H, aromatic H), 7.36 (d, *J* = 8.18 Hz, 2H, aromatic H), 7.23 (s, 1H, aromatic H), 6.99 (s, 1H, aromatic H), 4.54 (s, 2H, -CH₂Br), 4.45 (s, 2H, -CH₂Br), 4.08 (t, *J* = 6.25 Hz, 2H, -OCH₂), 1.96–1.20 (m, 25H, aliphatic C-H), 0.88 (t, *J* = 6.4 Hz, 3H, aliphatic CH₃). FTIR (KBr pellet, cm⁻¹): 3066, 2922, 2855, 1610, 1568, 1495, 1469, 1391, 1322, 1240, 1213, 1149, 839. FABMS⁺: *m/z*; 555 (M⁺ + 4 + H, 20%), 553 (M⁺ + 2 + H, 66%), 551 (M⁺ + H, 88%).

2.8 Polymerization of Compound (4)

The 0.55 g compound (4) (1 mmol) was dissolved in 60 ml dry 1,4-dioxane. Subsequently, the solution was heated at 96°C for 15 min under nitrogen atmosphere, then a fresh solution of t-BuOK (0.291 g, 2.6 equiv) in 1,4-dioxane (2.6 ml) was added drop by drop. The solution was further stirred for about 5 min at 96°C and excess t-BuOK (0.224 g, 2.0 equiv) in 1,4-dioxane (2 ml) was added by a syringe. The solution was cooled to 50°C after stirring for

an additional 3 h at 96°C. The obtained viscous yellow/orange solution was mixed with 0.39 ml solution of acetic acid in 1,4-dioxane where the equivalent ratio of acetic acid to the base was 1.5 : 1. After stirring for 20 min, the mixture was poured into 70 ml water under stirring and was further stirred for 10 min. Subsequently, DBP-PPV was precipitated from the mixture by adding 200 ml methyl alcohol. The DBP-PPV was filtered, washed with methyl alcohol and dried under dynamic vacuum. The DBP-PPV was obtained as dark orange solids with a yield of 39% (0.15 g).

$^1\text{H-NMR}$ (CDCl_3) δ : 7.8–6.6 (m, 8H, aromatic and vinyl H), 4.2–3.8 (m, 2H, $-\text{OCH}_2$), 1.9–0.3 (m, 28H, aliphatic C-H). FTIR (KBr pellet, cm^{-1}): 3029, 2924, 2849, 1600, 1495, 1385, 1228, 1137, 1031, 970, 838. Elem. Anal. Calcd. for $\text{C}_{28}\text{H}_{38}\text{O}$: C, 86.09%; H, 9.81%. Found: C, 84.84%; H, 10.04%. GPC (0.8 mg cm^{-3} , 22.6°C), weight-average molecular weight (M_w): 31,606 g/mole, number-average molecular weight (M_n): 7,394 g/mole, polydispersity (M_w/M_n): 4.27, and degree of polymerization: 19.

2.9 Fabrication of a LED Device

A glass substrate with a 170 nm thin film of indium-tin oxide (ITO) on one side was successively washed with water, acetone and isopropyl alcohol under ultrasonic wave. The surface electrical resistance of the ITO film is 7 Ohm/cm^2 . The poly(3,4-ethylenedioxythiophene) (PEDOT) doped by aqueous polystyrenesulfonate solution was spin-coated on the ITO film to act as a hole-injection layer. The PEDOT layer is 50 nm in thickness. Then, a DBP-PPV film of 96 nm thickness was spin-coated on the PEDOT layer at 800 rpm for 15 s. Prior to the above-mentioned spin coating, the 0.98 wt% DBP-PPV solution in *p*-xylene was filtered through a $0.45 \mu\text{m}$ pore size filter. For the fabrication of a cathode, a 10 nm layer of calcium (Ca) was deposited on the DBP-PPV layer under a high vacuum of 5×10^{-6} Torr. Finally, a protecting layer of 100 nm silver (Ag) was deposited on the Ca layer under vacuum. All measurements of the device characteristics were conducted in air at room temperature. The active area of the device is about 0.24 cm^2 .

3 Results and Discussion

3.1 Structure Analysis of the DBP-PPV

The $^1\text{H-NMR}$ spectrum of DBP-PPV solution in CDCl_3 is shown in Figure 1. The peak of CDCl_3 is at 7.26 ppm. Figure 1 shows that the two proton peaks of 1,4-bisbromomethyl groups of the monomers (compound (4)) at 4.54 and 4.45 ppm have disappeared and a new broad peak has appeared in the range of 6.6–7.8 ppm. This new broad peak results from the protons of aromatic rings and the conjugated vinylene double bonds. It also shows the oxymethylene and alkyl proton peaks in the ranges of 3.8–4.2 and 0.3–1.9 ppm, respectively.

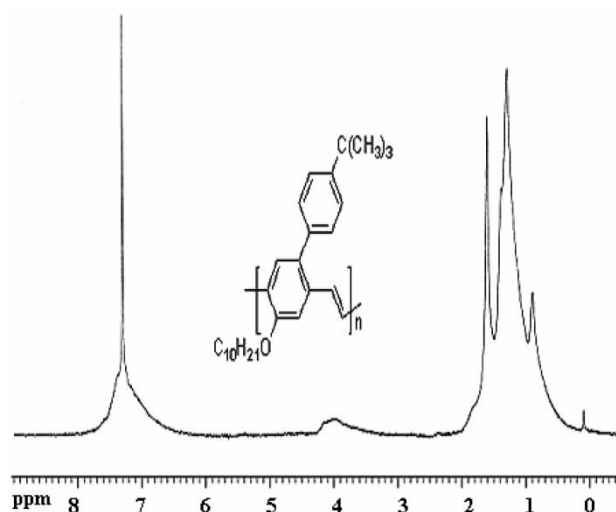


Fig. 1. $^1\text{H-NMR}$ spectrum of the DBP-PPV in CDCl_3 .

The formation of TBB defects in the PPV derivatives prepared through the ordinary Gilch procedure can be ascribed to the occurrence of side reaction, i.e., the head-to-head (or tail-to-tail) coupling, during the polymerization process (16). The $^1\text{H-NMR}$ signal of $\text{CH}_2\text{-CH}_2$ groups, resulting from the head-to-head coupling, should be at around 2.7–2.9 ppm (16). However, there is no such signal in Figure 1. This indicates that the polymerization process for DBP-PPV proceeded mainly in a regular head-to-tail way. One of the two reasons for a regular head-to-tail coupling is the steric hindrance effect of 5-(4'-*tert*-butylphenyl) substituent on the phenylene ring of compound (4). The other reason is that the bromomethyl group in the ortho position relative to 2-decyloxy substituent on the phenylene ring of compound (4) is more acidic than the other bromomethyl group in the meta position. The difference in acidity or reactivity of these two bromomethyl groups can be attributed to the strong electron-donating property of the 2-decyloxy substituent of compound (4).

Figure 2 shows FT-IR spectrum of the DBP-PPV. The absorption peak at 3029 cm^{-1} is due to the C-H stretching

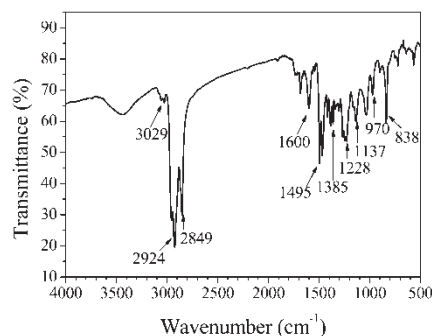


Fig. 2. FT-IR spectrum of the DBP-PPV film on KBr.

of trans-vinylenes and aromatic rings. The peaks at 2924 and 2849 cm^{-1} are due to C-H stretching of the alkyl side chains, and that at 1600 cm^{-1} is due to the aromatic ring stretching. Those absorption peaks at 1495 and 1385 cm^{-1} are due to -CH₂- segmental bending of the alkyl side chains and that at 1228 cm^{-1} is due to C-H in plane bending of vinylene units. The peak at 1137 cm^{-1} is due to symmetric C-O-C bond stretching and that at 970 cm^{-1} is due to C-H out-of-plane bending of trans-vinylene units. The peak at 838 cm^{-1} is due to C-H out-of-plane bending of *p*-phenylene units. In addition to the ¹H NMR spectrum, this IR spectrum also confirms the formation of DBP-PPV.

3.2 Optical Properties of the DBP-PPV

Figure 3 shows UV/Vis spectra of the DBP-PPV and *tert*-butylbenzene in THF (0.031 wt%) separately. The *tert*-butylbenzene, one substituent of DBP-PPV, was prepared by the Friedel-Crafts alkylation of benzene with *tert*-butyl chloride. Figure 3a shows two strong absorption peaks of DBP-PPV at 298 and 427 nm. Figure 3b shows one absorption peak of *tert*-butylbenzene at 294 nm. The comparison of Figure 3a and 3b reveals that the absorption peak of DBP-PPV at 298 nm is in close vicinity to that of *tert*-butylbenzene at 294 nm. This leads to the conclusion that the $\pi \rightarrow \pi^*$ transition of *tert*-butylbenzene substituent causes the absorption peak of DBP-PPV at 298 nm. On the other hand, it is reported in literature (19) that the poly(2,5-didecyloxy-*p*-phenylenevinylene) (decyloxy-PPV) film has only one absorption peak at 470 nm due to the $\pi \rightarrow \pi^*$ transition of PPV conjugated segments. The decyloxy-PPV and DBP-PPV have a similar structure except that the former is without the *tert*-butylbenzene substituent. It is therefore concluded that the other absorption peak of DBP-PPV at 427 nm is due to the $\pi \rightarrow \pi^*$ transition of PPV conjugated segments.

The optical energy (E , in eV) is described by the following equations, (1) and (2):

$$E = \frac{hc}{\lambda} \quad (1)$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ Joule} \quad (2)$$

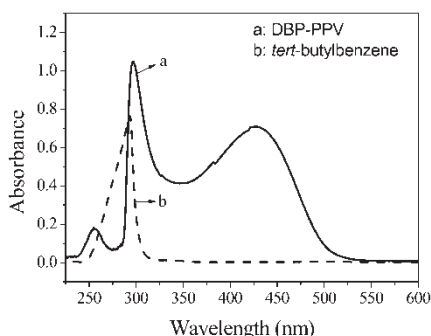


Fig. 3. UV/Vis spectra of the DBP-PPV (a) and *tert*-butylbenzene (b) in THF.

where E (in eV) represents the optical energy, h is the Planck constant (6.63×10^{-34} Joule-s), c (3×10^8 m/s) is the light velocity, and λ is wavelength of the absorption threshold. Using the value of absorption threshold of DBP-PPV solution, 520 nm, we deduce that the energy band gap of DBP-PPV in THF is 2.38 eV.

3.3 Thermal Stability of the DBP-PPV

Figure 4 shows the results of TGA measurement of DBP-PPV. There is no appreciable weight loss when heating DBP-PPV below 160°C. The weight loss begins to increase pronouncedly when heating DBP-PPV above 175°C. This is due to the decomposition of alkoxy substituents. The weight loss is 5% when heating the polymer to 250°C. While heating DBP-PPV above 450°C, the appreciable weight loss is due to the decomposition of rigid conjugated main-chains as polyaniline does (20).

3.4 Performance of LED Application

Figure 5 shows photoluminescence (PL) spectra of the solutions and film of DBP-PPV. The wavelength of excitation light is 390 nm. PL emission peaks of the DBP-PPV solutions in THF of concentrations 0.031 wt%, 0.062 wt% and 0.125 wt% are at 504, 523 and 531 nm, respectively. Meanwhile, PL emission peak of the DBP-PPV film is at 561 nm. The wavelength of the emission peak increases with increasing DBP-PPV concentration. The PL emission has a red shift of about 57 nm from a dilute solution state of 0.031 wt% to a film state. The red shift may be attributed to the more aggregated conformation of the polymer main-chains in a film state than in a solution state. The more aggregated conformation makes the energy band gap for the $\pi \rightarrow \pi^*$ transition of the conjugated segments smaller. Thus, the energy transfer takes place more easily in a film state than in a solution state (19).

Owing to the presence of asymmetric substituents on the aromatic rings, DBP-PPV is easily soluble in common organic solvents. Therefore, DBP-PPV is easily spin-coated on various substrates as smooth thin films for fabricating

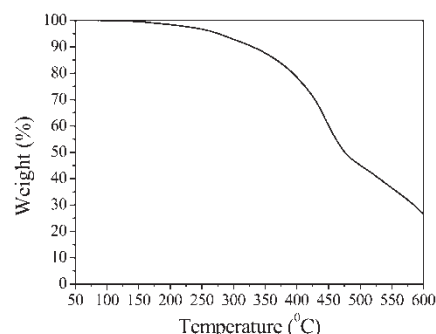


Fig. 4. TGA thermogram of the DBP-PPV under a nitrogen stream.

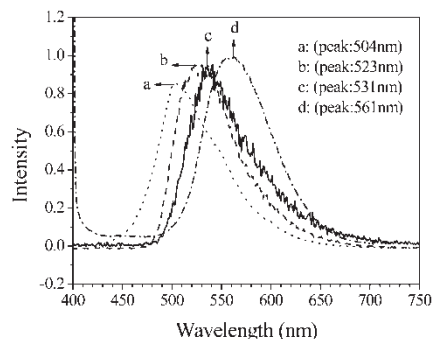


Fig. 5. PL spectra of the DBP-PPV solution in THF ((a) 0.031 wt%, (b) 0.062 wt%, (c) 0.125 wt%), and of the DBP-PPV film (d).

light-emitting devices. Figure 6 shows both film photoluminescence (PL) and electroluminescence (EL) spectra of a DBP-PPV film. The EL spectrum of DBP-PPV was obtained from an ITO/PEDOT/DBP-PPV/Ca/Ag device. The EL spectrum shows a maximum emission band at around 546 nm, corresponding to a yellowish-green light. According to the Commission Internationale de l'Éclairage, the chromaticity coordinates of the yellowish-green are $x = 0.369$ and $y = 0.495$. On the other hand, the PL spectrum of the DBP-PPV film shows an emission maximum at 561 nm. Generally, PL and EL spectra of a polymer with conjugated segments would be nearly identical. However, there is a small shift of about 15 nm between these two spectra in our result. The possible interpretation of the shift is that the vibronic peak intensity is transferred to lower energy in photoluminescence than in electroluminescence (21).

Figure 7 shows the current density-voltage-luminescence efficiency characteristics of the device. The turn-on voltage of the device is about 8.4 V. The maximum luminescence efficiency of the device is 0.11 cd/A at an applied voltage of 12 V. We hope that higher EL performance of the device could be obtained by further purifying DBP-PPV and optimizing the device structure in our future work.

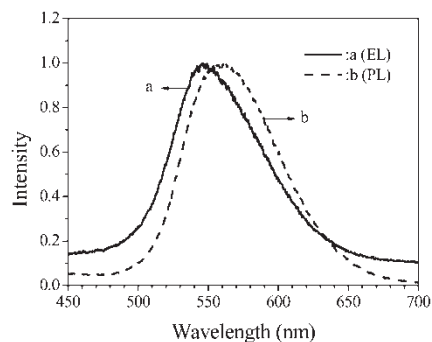


Fig. 6. EL (a) and PL (b) spectra of the DBP-PPV film.

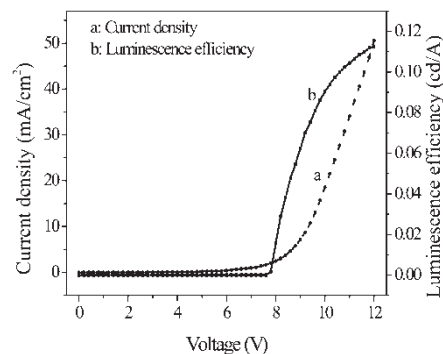


Fig. 7. Current density-Voltage-Luminescence efficiency curves of the ITO/PEDOT/DBP-PPV/Ca/Ag device.

4 Conclusions

The 1,4-bisbromomethyl-2-decyloxy-5-(4'-*tert*-butylphenyl) benzene, as a monomer, was successfully synthesized via various chemical reactions from the starting material of 2,5-dimethylphenol. Then, a new electroluminescent material, DBP-PPV, was synthesized from this monomer by a method similar to the Gilch procedure. The incorporation of decyloxy substituents in the 2-position of phenylene rings makes DBP-PPV soluble in common organic solvents and suppresses the presence of TBB defects. The energy band gap of DBP-PPV in THF is 2.38 eV. The PL emission of DBP-PPV has a red shift of about 57 nm from a dilute solution state of 0.031 wt% to a film state. The red shift may be attributed to the more aggregated conformation of the polymer main-chains in a film state than in a solution state. Moreover, with DBP-PPV acting as a light emitting material, EL spectrum of the device shows an emission peak at 546 nm, corresponding to a yellowish-green light. In addition, the turn-on voltage of the device was at about 8.4 V. The maximum luminescence efficiency of the device is 0.11 cd/A at an applied voltage of 12 V.

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