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Synthesis and characterization of the soluble luminescent poly[2-decyloxy-5-(4'-ethoxyphenyl)-1,4-phenylenevinylene]

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Summary

A new soluble luminescent poly[2-decyloxy-5-(4'-ethoxyphenyl)-1,4-phenylene-vinylene] (DEP-PPV) is prepared by the dehydrohalogenation of 1,4-bis(bromo-methyl)-2-decyloxy-5-(4'-ethoxyphenyl) benzene in this study. The structure and properties of the DEP-PPV are examined by ^{1}H NMR, FT-IR, UV/VIS, TGA, photoluminescence (PL), and electroluminescence (EL) analyses. The incorporation of a decyloxy substituent in the 2-position of phenylene ring makes the DEP-PPV soluble in organic solvents and eliminates tolan-bis-benzyl structure defects. The energy band gap of DEP-PPV in tetrahydrofuran is 2.36 eV. The PL peak of DEP-PPV solution shifts to higher wavelength as the solution concentration increases. The PL spectrum of the DEP-PPV film shows a peak at 546 nm and the one of the pristine PPV film does at 540 nm. This red shift of PL peak for the DEP-PPV as compared with that for the PPV indicates that the incorporation of a conjugated ethoxyphenyl group on the phenylene ring can increase the conjugation length of phenylenevinylene units in the DEP-PPV. With the DEP-PPV acting as a light-emitting polymer, a device is fabricated with a sequential lamination of ITO/PEDOT/DEP-PPV/Ca/Ag. The EL spectrum of the device shows a maximum emission at 530 nm, which corresponds to the yellowish-green light. The turn-on voltage of the device is about 16 V. Its maximum brightness is 46 cd/m^2 at a voltage of 18 V.

Introduction

Poly(*p*-phenylenevinylene) (PPV) was discovered as a light-emitting material for light-emitting diodes (LEDs) in 1990 [1]. Since then, there have been a lot of studies on the development of appropriate conjugated polymers for LEDs [2-9]. Of all conjugated polymers, PPV and its derivatives are still the most popular for the fabrication of LEDs today. This is because of their high luminescence efficiency in the LED application. PPV exhibits poor solubility in common organic solvents and

limited processibility. This is mainly due to the rigid main chain of repetitive phenylenevinylene units. There are two approaches to solve these difficulties. The first involves preparing a soluble precursor polymer and then casting it to obtain a film. For this approach, there are two generally used routs, i.e., the Wessling [10, 11] and chlorine precursor routes (CPR) [12, 13]. The second is through the incorporation of side chains to a polymer backbone. The incorporation of side chains is achieved by preparing a soluble polymer from a monomer having multiple substituents. For this second approach, the Gilch procedure [14] is the most frequently used polymerization method. The synthesis of the poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene) from the dehydrohalogenation of 1,4-bis(chloromethyl)-2-methoxy-5-dodecyloxy-benzene [15] is one of examples for the Gilch procedure. The Gilch procedure normally leads to the PPV derivatives with high molecular weight and a good film-forming property.

Recently, 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 tolan-bis-benzyl (TBB) defects. The increase in TBB content decreases the lifetime of the resultant LED device significantly [17]. However, Becker et al. [18] also found that the introduction of an alkoxy group with a strong electron-donating property decreases the TBB content in the polymer main chains of the PPV derivatives. This is due to the fact that the halomethyl group in the ortho position of the alkoxy group is more acidic than the other halomethyl group in the meta position. 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 [19].

In this paper, the synthesis and characterization of the poly[2-decyloxy-5-(4'-ethoxy-phenyl)-1,4-phenylenevinylene] (DEP-PPV) are reported. A decyloxy group and an ethoxyphenyl group are respectively incorporated in the 2-position and 5-position of a phenylene ring in the DEP-PPV. The incorporation of a decyloxy group is expected to make the DEP-PPV soluble in organic solvents and to suppress the presence of TBB defects in the polymer main chains. On the other hand, the incorporation of a conjugated ethoxyphenyl group is anticipated to lengthen the conjugation length of phenylenevinylene units. The electro-optical and thermal properties of the DEP-PPV are also examined in this study.

Experimental

Materials

Benzoyl peroxide, 2,5-dimethylphenol, potassium hydroxide, 1-bromodecane, diethyl ether, N-bromosuccinimide (NBS), bromine, acetic acid, potassium carbonate, tetrabutylammonium bromide (TBAB), anhydrous magnesium sulfate, and carbon tetrachloride were purchased from Fluka Chemicals (Ronkonkoma, NY). Tetrakis (triphenylphosphine) palladium (0) (Pd(PPh$_3$)$_4$) and 4-ethoxyphenyl boronic acid were purchased from ACROS (Geel, Belgium). Potassium tert-butoxide (t-BuOK), and iron (Ⅲ) bromide were purchased from Sigma-Aldrich (Steinheim, Germany). All the above reagents were synthetic grade and used as received. Tetrahydrofuran (THF) and 1,4-dioxane were synthetic grade and obtained from Tokyo Chemical Industry Co. (Tokyo, Japan), which were dried over sodium and distilled prior to use.

Instrument

Melting points of compounds at different synthesis stages were determined on a Buchi B-540 apparatus. The NMR spectra of the specimen solutions in CDCl$_3$ were measured by a Bruker Avance 300 spectrometer (300 MHz). FT-IR spectra were recorded by a Perkin Elmer Model Spectrum One spectrometer. The UV-VIS spectra of the samples in THF were measured by a Shimadzu Model UV-160 spectro-photometer. The mass spectra were measured by a Bruker APEX Π spectrometer. Elemental analyses were taken with a Heraeus CHN-O-Rapid Analyzer. The fluorescence spectra were recorded by a Hitach F-4500 fluorescence spectrometer. The thickness of DEP-PPV ultrathin film was measured by a Kosaka Laboratory ET-4000M photometer. The weight and number average molecular weights of the DEP-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 THF was used as carrier solvent. Thermal gravimetric analyses were performed on a Perkin Elmer Model TGA-7 thermo-gravimetric analyzer under a nitrogen stream and with a heating rate of 10 ^{o}C/min. The current–voltage (I-V) characteristics and luminance of the LED device were measured by a Keithely 2400 current/voltage source and a Topcon BM-8 meter, respectively.

Preparation of the monomer and polymer

The synthesis route for the monomer and polymer is illustrated in Scheme 1. The monomer was prepared via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions from the starting material 2,5-dimethylphenol. The DEP-PPV was obtained by a method similar to the Gilch procedure.

Synthesis of 2-decyloxy-p-xylene (1)

Compound (1) was prepared by the alkylation of 2,5-dimethylphenol with 1-bromodecane.

A solution of 2,5-dimethylphenol (12.20 g, 100 mmol), potassium hydroxide (8.40 g, 150 mmol), and tetrabutylammonium bromide (3.40 g, 105 mmol) in 50 ml H$_2$O was stirred at room temperature for 15 min. Then 1-bromodecane (22.10 g, 100 mmol) was added to the solution mixture. The reaction proceeded with stirring and heating for 22 h at reflux. After the reaction was completed, the reaction mixture was extracted with 30 ml diethyl ether. The organic diethyl ether layer was washed with aqueous sodium hydroxide solution (10 %, 2×50 ml) and 100 ml H$_2$O successively. The resultant organic layer was dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure to give the 2-decyloxy-*p*-xylene (**1**) as pale brown oil (24.62 g) in 93 % yield (yield = (moles of product obtained actually / moles of product obtained theoretically) × 100 %). ^{1}H NMR (CDCl$_3$): δ 7.01 (d, J = 7.36 Hz, 1H, aromatic C-H), 6.69 (d, J = 7.72 Hz, 1H, aromatic C-H), 6.65 (s, 1H, aromatic C-H), 3.95 (t, J = 6.44 Hz, 2H, -OCH$_2$), 2.33 (s, 3H, aromatic CH$_3$), 2.20 (s, 3H, aromatic CH$_3$), 1.84-1.30 (m, 16H, aliphatic C-H), 0.91 (t, J = 6.52 Hz, 3H, aliphatic CH$_3$). FTIR (KBr pellet, cm^{-1}): 3072, 2924, 2856, 1615, 1586, 1509, 1463, 1415, 1378, 1265, 1158, 1131, 1040, 842, 802. FABMS$^+$: m/z; 262 (M+1, 74), 121 (47), 105 (27).

Synthesis of 2-bromo-5-decyloxy-p-xylene (2)

Compound (2) was prepared by the bromination of 2-decyloxy-p-xylene (1) with bromine.

A solution of compound (1) (13.10 g, 50 mmol) and iron (III) bromide (1.01 g, 3 mmol) in 35 ml CCl_4 was stirred in an iced bath. Bromine (8.01 g, 50.1 mmol) was slowly added to the solution through a condenser and stirred for 24 h. After the completion of reaction, the reaction mixture was washed with aqueous sodium hydroxide solution (10 %, 2×50 ml) and 100 ml H_2O successively. Then the organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was distilled off under reduced pressure to give a pale yellow crude product. The crude product was washed with methyl alcohol, filtered, and dried under dynamic vacuum to give 2-bromo-5-decyloxy-*p*-xylene (2) as a colorless solid (13.58 g) in 79 % yield. Melting point: 52-53 °C, ^{1}H NMR ($CDCl_3$): δ 7.23 (s, 1H, aromatic C-H), 6.65 (s, 1H, aromatic C-H), 3.90 (t, J = 4.24 Hz, 2H, -OCH_2), 2.32 (s, 3H, aromatic CH_3), 2.13 (s, 3H, aromatic CH_3), 1.79-1.26 (m, 16H, aliphatic C-H), 0.86 (t, J = 6.6 Hz, 3H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3072, 2924, 2847, 1631, 1606, 1567, 1496, 1462, 1383, 1363, 1163, 1034, 985, 879, 835. FABMS$^+$: m/z; 341 (M+1, 32), 200 (100), 184 (5), 154 (37). Elem. Anal. Calcd. for $C_{18}H_{29}BrO$: C, 63.34%; H, 8.56%. Found: C, 63.36%; H, 8.56%.

Synthesis of 2-decyloxy-5-(4´-ethoxyphenyl)-p-xylene (3)

Compound (3) was prepared by the Suzuki coupling reaction of 2-bromo-5-decyloxy-p-xylene (2) with 4-ethoxyphenol boronic acid. Suzuki coupling is the palladium-catalyzed cross coupling between organoboronic acids and halides.

A mixture of compound (2) (3.41 g, 10 mmol), 4-ethoxyphenyl boronic acid (ACROS, 1.82 g, 10.9 mmol), 25 ml of 2M K_2CO_3 solution, 35 ml of THF, and Pd (PPh$_3$)$_4$ (0.07 g) was stirred at room temperature under a nitrogen atmosphere for 10 min. After heating at reflux for 24 h, the reaction was terminated by adding 25 ml water. The resultant mixture was extracted with diethyl ether. The organic phase was dried with anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. After 30 ml methyl alcohol was added to the residue, the desired product precipitated. The precipitate was washed with methyl alcohol, filtered, and dried under dynamic vacuum to afford the 2-decyloxy-5-(4′-ethoxyphenyl)-*p*-xylene (3) as a pale yellow solid (2.05 g) in 53 % yield. Melting point: 45-47 °C, ^{1}H NMR ($CDCl_3$): δ 7.19 (d, J = 4.84 Hz, 2H, aromatic C-H), 6.97 (s, 1H, aromatic C-H), 6.88 (d, J = 4.76 Hz, 2H, aromatic C-H), 6.68 (s, 1H, aromatic C-H), 4.04 (t, J = 6.96 Hz, 2H, -OCH_2), 3.96 (t, J = 6.44 Hz, 2H, -OCH_2), 2.22 (s, 3H, aromatic CH_3), 2.18 (s, 3H, aromatic CH_3), 1.80-1.26 (m, 19H, aliphatic C-H), 0.86 (t, J = 6.52 Hz, 3H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3076, 2925, 2856, 1610, 1568, 1501, 1476, 1388, 1303, 1283, 1232, 1175, 1133, 1050, 923, 890, 837. FABMS$^+$: m/z; 383 (M+1, 35), 242 (30), 213 (33), 181 (22). Elem. Anal. Calcd. for $C_{26}H_{38}O_2$: C, 81.62%; H, 10.01%. Found: C, 80.10%; H, 9.87%.

Synthesis of 1,4-bis(bromomethyl)-2-decyloxy-5-(4´-ethoxyphenyl) benzene (4)

Compound (4) was prepared by the bromination of 2-decyloxy-5-(4´-ethoxyphenyl)-p-xylene (3) with N-bromosuccinimide.

A solution of compound (3) (1.62 g, 4.2 mmol), benzoyl peroxide (0.06 g, 0.2 mmol), and N-bromosuccinimide (1.62 g, 9.1 mmol) in 30 ml CCl_4 was stirred at room

temperature for 10 min. After heating at reflux for 16 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 to give a gray crude product. The crude product was washed with methyl alcohol, filtered, and dried under dynamic vacuum to give 1,4-bis(bromomethyl)-2-decyloxy-5-(4′-ethoxyphenyl) benzene **(4)** as a gray white solid (1.33 g) in 58 % yield. Melting point: 72-73 °C, ^{1}H NMR (CDCl$_3$): δ 7.36 (d, J = 8.56 Hz, 2H, aromatic C-H), 7.31 (s, 1H, aromatic C-H), 7.02 (d, J = 3Hz, 2H, aromatic C-H), 6.99 (s, 1H, aromatic C-H), 4.60 (s, 2H, -CH$_2$Br), 4.48 (s, 2H, -CH$_2$Br), 4.23 (m, 4H, 2×-OCH$_2$), 1.96-1.34 (m, 19H, aliphatic C-H), 0.94 (t, J = 5.47 Hz, 3H, aliphatic CH$_3$). FTIR (KBr pellet, cm^{-1}): 3066, 2921, 2853, 1613, 1568, 1499, 1473, 1391, 1291, 1240, 1208, 1178, 1147, 1050, 922, 839. FABMS$^+$: m/z; 540 (M+1, 15), 239 (100), 211 (95), 195 (67). Elem. Anal. Calcd. for C$_{26}$H$_{36}$Br$_2$O$_2$: C, 57.79%; H, 6.71%. Found: C, 57.53%; H, 6.64%.

Preparation of poly[2-decyloxy-5-(4′-ethoxyphenyl)-1,4-phenylenevinylene] (DEP-PPV)

A solution of compound **(4)** (0.54 g, 1.0 mmol) in 60 ml of dry 1,4-dioxane was stirred and heated at reflux under nitrogen atmosphere for 15 min. A fresh solution of potassium tert-butoxide (0.291 g, 2.6 equiv) in 1,4-dioxane (2.6 ml) was added drop by drop to the solution. The solution was further heated at 96 °C for about 5 min and excess potassium tert-butoxide (0.224 g, 2.0 equiv) in 1,4-dioxane (2 ml) was syringed into the reaction mixture. After stirring for additional 3 h at 96 °C, a viscose yellow/orange solution was obtained. This viscose solution was then cooled to 50 °C and mixed with 0.39 ml solution of acetic acid in 1,4-dioxane where the equivalent of acetic acid was 1.5 times that of the base. After stirring for 20 min, the mixture was poured into 70 ml water with stirring and was further stirred for 10 min. Finally, the DEP-PPV was precipitated from the mixture by adding 200 ml methyl alcohol. The DEP-PPV was filtered, washed with some methyl alcohol, and dried under dynamic vacuum. The DEP-PPV was obtained as an orange solid (0.28 g) in 88 % yield. GPC (0.8 mg cm^{-3}, 22.6 °C), weight-average molecular weight (Mw): 254,418 g/mole, number-average molecular weight (Mn): 17,581 g/mole, polydispersity (Mw/Mn) index: 14, and the degree of polymerization of DEP-PPV: 46. ^{1}H NMR (CDCl$_3$): δ 7.5-6.8 (m, 8H, aromatic and vinyl C-H), 4.2-3.8 (m, 4H, 2×-OCH$_2$), 1.8-0.6 (m, 22H, aliphatic C-H). FTIR (KBr pellet, cm^{-1}): 3043, 2918, 2849, 1594, 1496, 1389, 1200, 1138, 1086, 1019, 960, 800.

Fabrication of the 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 with a thickness of 50 nm. A thin DEP-PPV film (110 nm) was then spin-coated on the PEDOT layer with a spin rate of 1000 rpm and duration of 15 s. Prior to the spin coating, the 1.8 wt% DEP-PPV solution in *p*-xylene was filtered through a 0.45 μm pore size filter. For the fabrication of a cathode, a layer of calcium (10 nm) was deposited on the DEP-PPV layer under a high vacuum of 5x10^{-6} torr. Finally, a protecting layer of
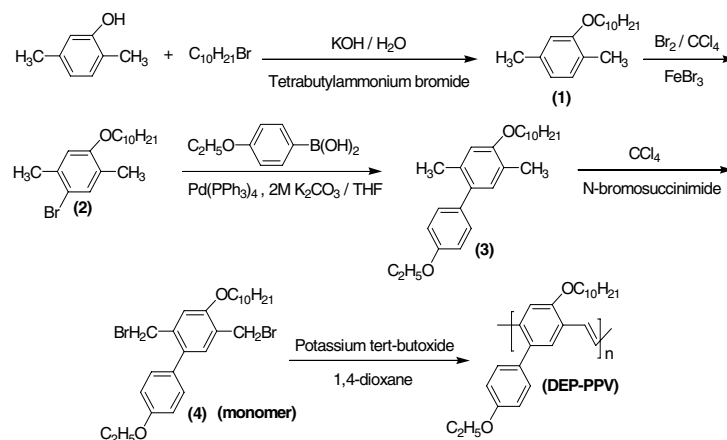
Scheme 1. Synthesis route for the monomer and polymer.

silver (100 nm) was deposited on calcium 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.

Results and discussion

Structure of the DEP-PPV

Figure 1(a) shows ^{1}H NMR spectrum of the compound (**4**) in CDCl$_3$. The peak of CDCl$_3$ is at 7.26 ppm. Two proton peaks of the bromomethyl groups are at 4.48 and 4.60 ppm. The results of Figure 1(a) confirm the formation of compound (**4**). The ^{1}H NMR spectrum of the DEP-PPV solution in CDCl$_3$ is shown in Figure 1(b). It shows that the two proton peaks of the bromomethyl groups have disappeared and a new bimodal broad peak has appeared in the range of 6.8-7.5 ppm. The new bimodal peak results from the protons of aromatic rings and the conjugated vinylene double bonds. It also shows oxymethylene and alkyl proton peaks in the range of 3.8-4.2 and 0.6-1.8 ppm, respectively.

The formation of TBB defects in the PPV derivatives prepared by the Gilch procedure can be ascribed to the side reaction, i.e., the head to head (or tail to tail) coupling during the polymerization process [16]. The ^{1}H NMR signals of CH$_2$-CH$_2$ groups resulting from the head to head coupling should appear at 2.7-2.9 ppm [16]. However, there are no such signals around 2.7-2.9 ppm in Figure 1(b). This indicates that the polymerization process for the DEP-PPV in this study proceeded mainly in a regular head-to-tail way. There are two reasons for this regular head-to-tail coupling. One is the steric hindrance effect of the 5-ethoxyphenyl substituent on the phenylene ring of compound (**4**). The other is that the bromomethyl group in the ortho position relative to 2-decyloxy group 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 group of compound (**4**).

Figure 2 shows FT-IR spectrum of the DEP-PPV. The absorption peak at 3043 cm^{-1} is due to the C-H stretching of aromatic ring. The peaks at 2918 and 2849 cm^{-1} are due to the C-H stretching of alkyl side chains and one at 1594 cm^{-1} is due to the stretching of

aromatic ring. The absorption peaks at 1496 and 1389 cm^{-1} are due to the –CH$_2$-segmental bending of alkyl side chains and one at 1200 cm^{-1} is due to the C-H in plane bending of aromatic ring. The peak at 1086 cm^{-1} is due to the symmetric C-O-C bond stretching and one at 960 cm^{-1} is due to the C-H out-of-plane bending of trans-vinylene unit. The results of Figure 2 also confirm the formation of the DEP-PPV.
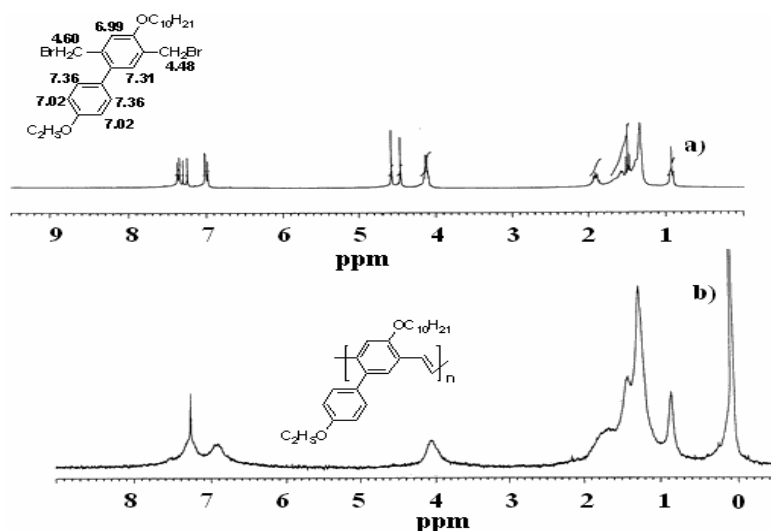

Figure 1. ^{1}H NMR spectra of the 1,4-bis(bromomethyl)-2-decyloxy-5-(4′-ethoxyphenyl) benzene (a) and DEP-PPV (b) in CDCl$_3$.
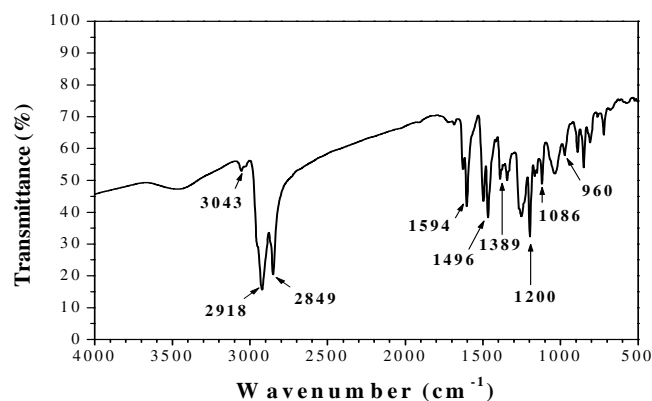

Figure 2. FT-IR spectrum of the DEP-PPV film on KBr.

Optical properties of the DEP-PPV

Figure 3 is UV/VIS spectra of the DEP-PPV and ethoxybenzene in THF. The ethoxybenzene, one substituent of the DEP-PPV, was prepared by the alkylation reaction of phenol with bromoethane. Figure 3(a) shows two absorption peaks of the
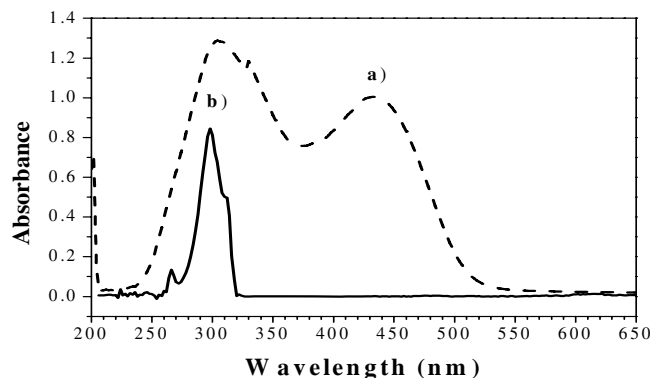
Figure 3. UV/VIS spectra of the DEP-PPV (a) and ethoxybenzene (b) in THF.

DEP-PPV at 302 and 440 nm. Figure 3(b) shows one absorption peak of the ethoxybenzene at 298 nm. The comparison of Figure 3(a) and 3(b) reveals that the absorption peak of DEP-PPV at 302 nm is in close vicinity to that of the ethoxybenzene at 298 nm. This leads to the conclusion that the $\pi \rightarrow \pi^*$ transition of ethoxyphenyl substituent causes the absorption peak of DEP-PPV at 302 nm. On the other hand, it is reported in literature [20] 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 DEP-PPV have a similar structure except that the former is without the ethoxyphenyl substituent. It is therefore concluded that the other absorption peak of DEP-PPV at 440 nm is due to the $\pi \rightarrow \pi^*$ transition of PPV conjugated segments.

The optical energy (E, in eV) is described by the following equation **(i)**:

$$E = h \times c / \lambda \qquad \qquad \textbf{(i)}$$

where h is the Planck constant, c is the light velocity, and λ is the wavelength of absorption threshold. Using the value of absorption threshold λ (525 nm), we deduce that the energy band gap of DEP-PPV in THF is 2.36 eV.

Figure 4 shows the photoluminescence (PL) spectra of the DEP-PPV film and solutions (the excited wavelength, 390 nm). PL emission peaks of the DEP-PPV in
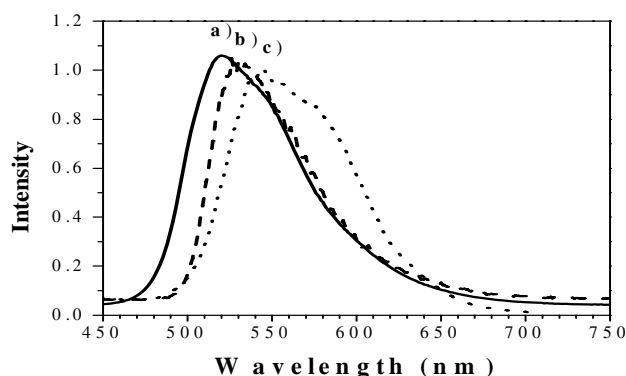
Figure 4. PL spectra of the DEP-PPV in THF ((a) 0.02 %, (b) 0.16 %), and (c) DEP-PPV film.

THF at the concentrations of 0.02 wt% and 0.16 wt% are 520 nm and 530 nm, respectively. On the other hand, the emission peak of the DEP-PPV film is at 546 nm. The wavelength of the emission peak increases as the concentration of the DEP-PPV goes up. The PL emission has a red shift of about 26 nm from a dilute solution state (0.02 wt%) to a film state. The shift is probably due 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 process takes place more easily in a film state than in a solution state [20].

Comparison of the optical properties between DEP-PPV and DO-PPV solutions

The poly(2-decyloxy-1,4-phenylenevinylene) (DO-PPV) was also prepared by the same procedure as used for the synthesis of DEP-PPV in this study. Both DO-PPV and DEP-PPV were prepared from the same starting material, i.e. 2,5-dimethylphenol. The structure of DO-PPV is similar to that of the DEP-PPV except that the former doesn't have the ethoxyphenyl substituent. Both DEP-PPV and DO-PPV are soluble in THF and $CHCl_3$ owing to the presence of decyloxy substituent. The wavelengths of the photoluminescence emission peaks (PL_{max}'s) and UV/VIS absorption ones (abs_{max}'s) for DEP-PPV and DO-PPV in THF as well as $CHCl_3$ are given in Table 1. Incidentally, the pristine PPV is insoluble in organic solvents. The PL_{max}'s and abs_{max}'s for DEP-PPV and DO-PPV in $CHCl_3$ have a slight red shift of 2-6 nm as compared with those of DEP-PPV and DO-PPV in THF. This shift may be attributed to the fact that there is a more aggregated conformation of polymer main chains in $CHCl_3$ than in THF. As shown in Table 1, the more aggregated conformation of polymer main chains in $CHCl_3$ also makes the energy band gap (E_g) for the $\pi \rightarrow \pi^*$ transition of the conjugated segments smaller. The

Table 1. Photoluminescence maxima (PL_{max}), UV/VIS absorption maxima (abs_{max}), and Energy band gaps (E_g) of the DEP-PPV and DO-PPV solutions at a concentration of 0.02 wt%.

		Solvents	
		THF	$CHCl_3$
DEP-PPV	PL_{max} (nm)	520	526
	abs_{max} (nm)	440	443
	E_g (eV)	2.36	2.32
DO-PPV[a]	PL_{max} (nm)	501	506
	abs_{max} (nm)	422	424
	E_g (eV)	2.40	2.38

[a]: DO-PPV was obtained as an orange solid in 73 % yield by the dehydrohalogenation of 1,4-bis(bromomethyl)-2-decyloxy-benzene (0.42g, 1mmol). ^{1}H NMR ($CDCl_3$): δ 7.6-6.9 (m, 5H, aromatic and vinyl C-H), 4.1-3.8 (m, 2H, $-OCH_2$), 1.8-0.6 (m, 19H, aliphatic C-H). FTIR (KBr pellet, cm^{-1}): 3037, 2918, 2850, 1600, 1523, 1421, 1356, 1250, 1138, 1075, 1003, 967, 800. The aforementioned 1,4-bis(bromomethyl)-2-decyloxybenzene was obtained as an yellowish solid in 52 % yield from the bromination of compound (**1**) (2.62 g, 10mmol) with NBS (3.63 g, 20.4 mmol). ^{1}H NMR ($CDCl_3$): δ 7.30 (d, J = 7.80 Hz, 1H, aromatic C-H), 6.93 (d, J = 7.50 Hz, 1H, aromatic C-H), 6.88 (s, 1H, aromatic C-H) 4.53 (s, 2H, $-CH_2Br$), 4.45 (s, 2H, $-CH_2Br$), 4.06 (t, J = 6.39 Hz, 2H, $-OCH_2$), 1.84-1.30 (m, 16H, aliphatic C-H), 0.91 (t, J = 5.41 Hz, 3H, aliphatic CH_3).

PL$_{max}$'s and abs$_{max}$'s for DEP-PPV in THF and CHCl3 have a red shift of 18-20 nm compared to those of the DO-PPV in the same solvents. One possible explanation is that the ethoxyphenyl substituent lengthens the conjugation length of DEP-PPV, thus causing the aforementioned red shift phenomena. That the DEP-PPV has longer conjugation length than the DO-PPV would also make the former exhibit lower E$_g$ than the latter.

Thermal stability of the DEP-PPV

Figure 5 shows the results of TGA measurement of the DEP-PPV. There is no appreciable weight loss before 200 ^{o}C. The weight loss begins to increase pronouncedly at 250 ^{o}C, at which the decomposition of alkoxy substituent starts to take place. The weight loss reaches 5 % as the temperature increases to 350 ^{o}C. The weight loss above 400 ^{o}C is due to the decomposition of the rigid conjugated main chains as is observed with polyaniline [21]. The high thermal resistance property of the DEP-PPV is significant to its application in LEDs.
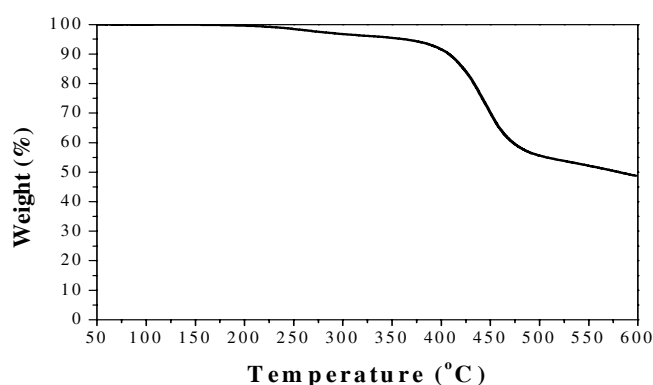

Figure 5. TGA curve of the DEP-PPV under a nitrogen stream.

Performance in LED application

Figure 6 shows the PL and electroluminescence (EL) spectra of the DEP-PPV film. The EL spectrum of the ITO/PEDOT/DEP-PPV/Ca/Ag device shows a maximum emission band at around 530 nm, which corresponds to the yellowish-green light. According to Commission International de l'Eclairage, the chromaticity coordinates of the yellowish-green are x = 0.28 and y = 0.45. On the other hand, the PL spectrum of DEP-PPV film shows an emission maximum at 546 nm. Generally, PL and EL spectra of the polymer with conjugated segments are nearly the same. However, a small shift of about 16 nm has developed for PL and EL spectra of the DEP-PPV in this study. A possible interpretation of the shift is that the vibronic peak intensity is transferred to lower energy in PL compared to EL [22]. Moreover, the PL spectrum of the DEP-PPV film shows a peak at 546 nm and the one of the pristine PPV film does at 540 nm [23]. This red shift of PL peak for the DEP-PPV as compared with that for the PPV indicates that the incorporation of a conjugated ethoxyphenyl group on the phenylene ring lowers the energy band gap (E$_g$) for the $\pi \rightarrow \pi^{*}$ transition of the conjugated

segments. In other words, the incorporation of a conjugated ethoxyphenyl group increases the conjugation length of phenylenevinylene units in the DEP-PPV.

Figure 7 shows the luminescence efficiency-voltage-brightness characteristics of the device. The turn-on voltage of the device is about 16 V. The maximum brightness and luminance efficiency of the device are 46 cd/m^2 and 0.0522 cd/A, respectively, both at a voltage of 18 V. We hope that a higher EL performance of the device could be obtained by optimizing the device structure in our future work.
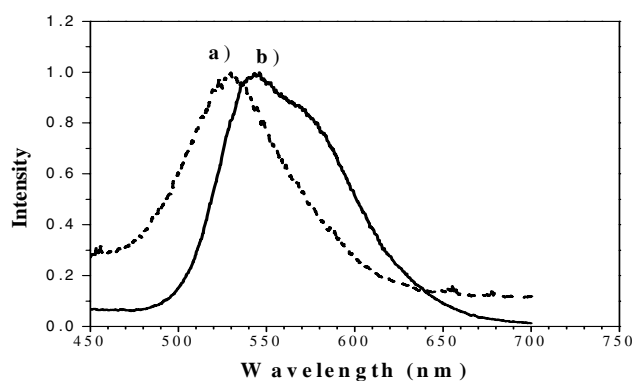

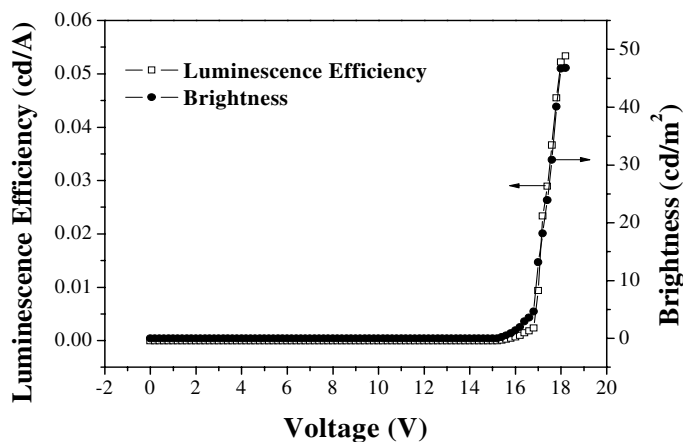**Figure 6.** EL (a) and PL (b) spectra of the DEP-PPV film.

Figure 7. Efficiency-Voltage-Brightness curves of the ITO/PEDOT/DEP-PPV/Ca/Ag device.

Conclusion

A new soluble luminescent DEP-PPV without TBB defects was prepared in this study by a method similar to the Gilch procedure. The incorporation of a decyloxy substituent in the 2-position of the phenylene ring makes the DEP-PPV soluble in organic solvents and suppresses the presence of TBB defects. The energy band gap of DEP-PPV in THF is 2.36 eV. The PL emission of DEP-PPV has a red shift of about 26 nm from a dilute solution state (0.02 wt%) to a film state. The shift is probably due

to a more aggregated conformation of polymer main chains in a film state than in a solution state. The PL spectrum of the DEP-PPV film shows a peak at 546 nm and the one of the pristine PPV film does at 540 nm. This red shift of PL peak for the DEP-PPV as compared with that for the PPV indicates that the incorporation of a conjugated ethoxyphenyl group on the phenylene ring can increase the conjugation length of phenylenevinylene units in the DEP-PPV. With the DEP-PPV acting as a light emitting material, the EL spectrum of the device shows an emission peak at 530 nm, which corresponds to the yellowish-green light. The maximum brightness of the device is 46 cd/m^2 at a voltage of 18 V.

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