Synthesis and Characterization of the Soluble Fluorescent Poly[2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)-1,4-phenylenevinylene]

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ABSTRACT: A new soluble fluorescent polymer, poly[2-decyloxy-5-(2′-(6′-dodecyl-oxy)naphthyl)-1,4-phenylenevinylene] (DDN-PPV), with no tolane-bisbenzyl (TBB) structure defects is prepared by the dehydrohalogenation of 1,4-bis(bromomethyl)-2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)benzene (as monomer) in this study. The aforementioned monomer is synthesized via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions. The structure and properties of the DDN-PPV are examined by ^{1}H NMR, FTIR, UV/vis, TGA, photoluminescence (PL), and electroluminescence (EL) analyses. The two asymmetric decyloxy and 6′-dodecyloxynaphthyl substitu-ents on the phenylene ring make the DDN-PPV soluble in organic solvents and eliminate the TBB structure defects. With the DDN-PPV acting as a light-emitting polymer, a device is fabricated with a sequential lamination of ITO/PEDOT/DDN-PPV/Ca/Ag. The EL spectrum of the device shows a maximum emission at 538 nm. The turn on voltage of the device is about 16.6 V. Its maximum brightness is 14 cd/m^2 at a voltage of 18.2 V. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2734–2741, 2007

Key words: fluorescent; poly(*p*-phenylenevinylene) derivatives; photoluminescence; FTIR; electroluminescence

INTRODUCTION

Since the report of PPV as a light emitting material for light emitting diodes (LEDs) in 1990,[1] extensive research interest was focused on the electro-optical properties of poly(*p*-phenylenevinylene) (PPV) derivatives by incorporating appropriate substituents to the polymer backbone.[2–9] The category of PPV and its derivatives is still the most popular kind of conjugated polymers used for fabricating LEDs today. This is because of their high luminescence efficiency in the LED application. Owing to the rigid main chains of repetitive phenylenevinylene units, 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 a polymer backbone. 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(2-methoxy-5-hexylthio-1,4-phenylenevinylene) (PMHPV) from the 2-methoxy-5-hexylthio-1,4-phenylenedi-methylene bis(tetrahydrothiophenium

chloride)[12] through a sulfonium precursor is one example of the Wessling precursor route. The CPR method is illustrated by first reacting the 2-phenoxy-1,4-bischloromethyl benzene with about 1 equiv. of potassium *tert*-butoxide to obtain a soluble chlorine precursor polymer, then heating the precursor polymer under an inert atmosphere to obtain the poly (2-phenoxy-*p*-phenylenevinylene) (PO-PPV).[13]

The other approach of incorporating side chains to a polymer backbone is achieved by preparing a soluble polymer from a monomer having multiple substituents. For this approach, the Gilch procedure[14] is the most frequently used polymerization method. The synthesis of spirobifluorenyl-substituted poly(*p*-phenylenevinylene)[15] by the dehydrohalogenation of 1,4-bis(bromomethyl)-2-(2′-ethylhexyloxy)-5-(2″-((2‴, 7‴-di-*tert*-butyl)-9″,9‴-spirobifluorenyl)) benzene using large excess of potassium *tert*-butoxide is one example of the Gilch procedure.

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 tolane-bisbenzyl (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 head-to-head (or tail-to-tail) coupling reaction leads to nonconjugated segments in the polymer chains, i.e., conjugation

breaks in a conjugated polymer chain. This leads to a lower charge mobility in the polymer at an applied voltage. With this PPV derivative containing TBB defects used in a LED device, the lower charge mobility will result in a higher probability of additional conjugation breaks by the collapse of *trans*-vinylene double bonds. This causes the performance degradation of the LED. Therefore, the increase in TBB content decreases the lifetime of the resultant LED device significantly.[17] However, the TBB content of polymer main chains can be reduced by the incorporation of asymmetric substituents on the phenyl rings of the monomers. The dehydrohalogenation of 1,4-bis(chloromethyl)-2-methoxy-5-(3′-decyloxyphenyl) benzene gives the poly(2-methoxy-5-(3′-decyloxyphenyl)-1,4-phenylenevinylene)[17] with almost no TBB defects. This is due to the fact that the halomethyl group in the ortho position of the methoxy substituent, a strong electron-donating 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 to proceed in a regular head-to-tail way.[18] Moreover, the steric hindrance of the bulky decyloxyphenyl substitute is also conducive to the regular head-to-tail coupling reaction of the monomers.

In this article, the synthesis and characterization of the poly[2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)-1,4-phenylenevinylene] (DDN-PPV) are reported. A decyloxy group and a 6′-dodecyloxynaphthyl group are respectively, incorporated in the 2-position and 5-position of a phenylene ring in the DDN-PPV. The incorporation of a decyloxy group is expected to make the polymer soluble in organic solvents and to suppress the presence of TBB defects in the polymer main chains. Moreover, the incorporation of a rigid and bulky 6′-dodecyloxynaphthyl group is anticipated to enhance the thermal stability of the polymer and to make the polymerization reaction of the monomers to proceed in a regular head-to-tail way. The electro-optical and thermal properties of the DDN-PPV are also examined in this work.

EXPERIMENTAL

Materials

Benzoyl peroxide, 2,5-dimethylphenol, 1-bromodecane, 1-bromododecane, *N*-bromosuccinimide (NBS), bromine, potassium hydroxide, potassium carbonate, tetrabutylammonium bromide (TBAB), magnesium sulfate ($MgSO_4$), sulfuric acid, carbon tetrachloride, and acetic acid were purchased from Fluka Chemical (Ronkonkoma, NY). The *n*-butyl lithium (*n*-BuLi, 2.5M in hexane) was purchased from Chemetall (Chang Bin Industrial park Hsien-Si, Chang-Hua

County, Taiwan, Republic of China). Trimethyl borate, potassium *tert*-butoxide (*t*-BuOK), and iron (III) bromide were purchased from Sigma–Aldrich (Steinheim, Germany). Tetrakis(triphenylphosphine)-palladium(0) ($Pd(PPh_3)_4$) and 6-bromo-2-naphthol were purchased from ACROS (Geel, Belgium). All the above reagents were of synthetic grade and were used as received. Tetrahydrofuran (THF) and 1,4-dioxane were of synthetic grade and were purchased from Tokyo Chemical Industry (Tokyo, Japan), which were dried over sodium and distilled prior to use.

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 tetrabutylammonium bromide (3.4 g, 105 mmol) was stirred at room temperature 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 reaction, the solution was cooled to room temperature. 100-mL H_2O was added to the resultant solution and the organic layer was separated. The organic layer was washed with aqueous sodium hydroxide solution (10%, 2× 50 mL) and 100-mL H_2O successively. The resultant organic layer was dried over anhydrous $MgSO_4$, and filtered. The solvent was distilled off under reduced pressure with a rotary evaporator. 2-Decyloxy-1,4-dimethylbenzene (1) was obtained as pale brown oil with a yield of 93% (24.62 g). ^{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 (C—H stretching of aromatic ring), 2924, 2856 (C—H stretching of alkyl side chains), 1615, 1586, 1509 (C=C stretching of aromatic ring), 1463, 1415, 1378 (—CH$_2$— segmental bending of alkyl side chains), 1265 (C—O—C asymmetric stretching), 1158, 1131 (C—H in plane bending of aromatic ring), 1040 (C—O—C symmetric stretching), 842, 802 (C—H out-of-plane bending of aromatic ring). ^{13}C NMR (CDCl$_3$) (ppm): 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: 262 (M$^+$ + 1, 74%), 121 (M$^+$ + 1 − C$_{10}$H$_{21}$, 47%), 105 (M$^+$ + 1 − OC$_{10}$H$_{21}$, 27%).

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

A solution mixture of Compound (**1**) (13.1 g, 50 mmol), 35 mL of 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 solution through a condenser and stirred for 24 h. After the completion of reaction, the solution 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 $MgSO_4$. After the removal of $MgSO_4$, the solvent was distilled off under reduced pressure with a rotary evaporator and a pale yellow crude product was obtained. The crude product was washed with methyl alcohol, filtered, and dried under dynamic vacuum to give 1-bromo-4-decyloxy-2,5-dimethylbenzene (2) as a colorless solid (13.58 g) in 79% yield. Melting point: 52–53°C, ^1H 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 (C—H stretching of aromatic ring), 2924, 2847 (C—H stretching of alkyl side chains), 1631, 1606, 1567, 1496 (C=C stretching of aromatic ring), 1462, 1383, 1363 (—CH$_2$— segmental bending of alkyl side chains), 1163 (C—H in plane bending of aromatic ring), 1034 (C—O—C symmetric stretching), 958, 879, 835 (C—H out-of-plane bending of aromatic ring). ^{13}C NMR (CDCl$_3$) (ppm): 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: 341 (M$^+$ + 1, 32%), 200 (M$^+$ + 1 − C$_{10}$H$_{21}$, 100%), 184 (M$^+$ + 1 − OC$_{10}$H$_{21}$, 5%), 154 (M$^+$ + 1 − (C$_{10}$H$_{21}$ and 2CH$_3$), 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-bromo-6-(dodecyloxy)naphthalene (3)

A solution mixture of 6-bromo-2-naphthol (9.32 g, 41 mmol), potassium hydroxide (3.37 g, 60 mmol), 15-mL H_2O, and tetrabutylammonium bromide (1.36 g, 4.2 mmol) was stirred for 15 min. Then 1-bromododecane (10.2 g, 41 mmol) was added into the solution mixture. The reaction proceeded with stirring and reflux heating at 85°C for 22 h. After the completion of reaction, the solution was cooled to room temperature and then filtered to obtain a solid product. The obtained crude product was successively washed with 100-mL H_2O and 100-mL methyl alcohol. After the product was dried under vacuum, 2-bromo-6-(dodecyloxy)naphthalene (3) was obtained as yellowish solids with a yield of 85% (13.94 g). Melting point: 64.7–65.2°C, ^1H NMR (CDCl$_3$): δ 7.88 (s, 1H, aromatic C—H), 7.62 (d, J = 8.0 Hz, 1H, aromatic C—H), 7.57 (d, J = 8.76 Hz, 1H, aromatic C—H), 7.48 (d, J = 8.72 Hz, 1H, aromatic C—H),

7.15 (d, J = 8.96 Hz, 1H, aromatic C—H), 7.05 (s, 1H, aromatic C—H), 4.03 (t, J = 6.56 Hz, 2H, —OCH$_2$), 1.86–1.34 (m, 20H, aliphatic C—H), 0.87 (t, J = 6.12 Hz, 3H, aliphatic CH$_3$). FTIR (KBr pellet, cm^{-1}): 3046 (C—H stretching of aromatic ring), 2900, 2851 (C—H stretching of alkyl side chains), 1615, 1588 (C=C stretching of aromatic ring), 1464, 1385 (—CH$_2$— segmental bending of alkyl side chains), 1262 (C—O—C asymmetric stretching), 1211, 1165 (C—H in plane bending of aromatic ring), 851 (C—H out-of-plane bending of aromatic ring). ^{13}C NMR (CDCl$_3$) (ppm): aromatic (C) 157.4, 133.1, 129.9, 129.6, 129.4, 128.4, 128.3, 120.1, 116.8106.5, aliphatic (C) 68.1, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. FABMS$^+$ m/z: 391 (M$^+$ + 1, 29%), 222 (M$^+$ + 1 − C$_{12}$H$_{25}$, 100%), 142 (M$^+$ + 1 − (C$_{12}$H$_{25}$ and Br), 10%), 126 (M$^+$ + 1, − (OC$_{12}$H$_{25}$ and Br), 24%). Elem. Anal. Calcd. for C$_{22}$H$_{31}$BrO: C, 67.51%; H, 7.98%. Found: C, 67.70%; H, 8.04%.

Synthesis of 6-(dodecyloxy)naphthalene-2-boronic acid (4)

A 12-mL solution of n-BuLi in hexane (2.5M) was added drop by drop to a solution of 7.82 g (20 mmol) of Compound (3) in 40 mL of dry THF at −78°C. The temperature of −78°C was maintained by a mixture of dry ice and acetone outside of the reactor. The solution mixture was stirred at −78°C, then warmed up to 0°C, and cooled back to −78°C. To the above mixture, 5.2 g (50 mmol) trimethyl borate was added in one shot and the resulting solution was warmed up to room temperature and stirred for 48 h. The above solution was then poured into a mixture of 150-g crushed ice and 140-mL sulfuric acid (10%) under stirring. The resultant precipitates were filtered and washed successively with water and n-hexane several times. Finally, the 6-(dodecyloxy)naphthalene-2-boronic acid (4) was obtained as white solids with a yield of 47% (3.37 g). Melting point: 97.1–97.8°C, ^1H NMR (DMSO-d_6): δ 8.25 (s, 1H, aromatic C—H), 7.79 (d, J = 3.63 Hz, 2H, aromatic C—H), 7.71 (d, J = 8.24 Hz, 1H, aromatic C—H), 7.24 (s, 1H, aromatic C—H), 7.11 (d, J = 8.95 Hz, 1H, aromatic C—H), 4.04 (t, J = 5.98 Hz, 2H, —OCH$_2$), 1.21–1.76 (m, 20H, aliphatic C—H), 0.82 (t, J = 6.61 Hz, 3H, aliphatic CH3). FTIR (KBr pellet, cm^{-1}): 3417 (O—H stretching), 3096 (C—H stretching of aromatic ring), 2919, 2851 (C—H stretching of alkyl side chains), 1628 (C=C stretching of aromatic ring), 1472, 1347 (—CH$_2$— segmental bending of alkyl side chains), 1215, 1107 (C—H in plane bending of aromatic ring), 1022 (C—O—C symmetric stretching), 858 (C—H out-of-plane bending of aromatic ring). Elem. Anal. Calcd. for C$_{22}$H$_{33}$BO$_3$: C, 74.16%; H, 9.34%. Found: C, 73.93%; H, 9.44%.

Synthesis of 2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)-1,4-dimethylbenzene (5)

A solution mixture of Compound (2) (2.73 g, 8 mmol), Compound (4) (3 g, 8.4 mmol), 20 mL of $2M$ K_2CO_3 solution, 28 mL of THF, and Pd $(PPh_3)_4$ (0.06 g) was stirred at room temperature under a nitrogen atmosphere for 10 min. After reflux heating at 70°C under a nitrogen atmosphere for 24 h, the reaction was terminated by adding 20-mL water. The resultant solution was extracted with diethyl ether. The organic phase was dried with anhydrous $MgSO_4$ and filtered through a filter paper. After the solvent of the organic phase was distilled off under reduced pressure with a rotary evaporator, pale yellow solids were obtained. The pale yellow solids were washed with methyl alcohol twice, filtered, and dried under dynamic vacuum to give the 2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)-1,4-dimethyl-benzene (5) as yellowish solids (2.95 g) in 63% yield. Melting point: 45.4–45.9°C, ^{1}H NMR (CDCl$_3$): δ 7.80 (d, J = 2.74 Hz, 1H, aromatic C—H), 7.76 (s, 1H, aromatic C—H), 7.71 (s, 1H, aromatic C—H), 7.47 (d, J = 8.2 Hz, 1H, aromatic C—H), 7.20 (d, J = 6.16 Hz, 2H, aromatic C—H), 7.15 (s, 1H, aromatic C—H), 6.80 (s, 1H, aromatic C—H), 4.14 (t, J = 6.54 Hz, 2H, —OCH$_2$), 4.06 (t, J = 6.41 Hz, 2H, —OCH$_2$), 2.34 (s, 3H, aromatic CH$_3$), 2.29 (s, 3H, aromatic CH$_3$), 1.96–1.33 (m, 36H, aliphatic C—H), 0.95 (m, 6H, aliphatic 2× CH$_3$). FTIR (KBr pellet, cm^{-1}): 3062 (C—H stretching of aromatic ring), 2920, 2851 (C—H stretching of alkyl side chains), 1604, 1510 (C=C stretching of aromatic ring), 1469, 1378 (—CH$_2$— segmental bending of alkyl side chains), 1256 (C—O—C asymmetric stretching), 1203, 1166 (C—H in plane bending of aromatic ring), 1067 (C—O—C symmetric stretching), 856 (C—H out-of-plane bending of aromatic ring). FABMS$^+$ m/z: 573 (M$^+$ + 1, 50%), 263 (M$^+$ + 1 − (C$_{12}$H$_{25}$ and C$_{10}$H$_{21}$), 94%), 247 (M$^+$ + 1 − (OC$_{12}$H$_{25}$ and C$_{10}$H$_{21}$), 72%), 231 (M$^+$ + 1 − (OC$_{12}$H$_{25}$ and OC$_{10}$H$_{21}$), 70%). Elem. Anal. Calcd. for C$_{40}$H$_{60}$O$_2$: C, 83.86%; H, 10.56%. Found: C, 83.73%; H, 10.40%.

## Synthesis of 1,4-bis(bromomethyl)-2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)benzene (6)

Benzoyl peroxide (0.03 g, 0.12 mmol) and N-bromo-succinimide (1.068 g, 6 mmol) were added to a solution of Compound (5) (1.716 g, 3 mmol) in 50 mL of carbon tetrachloride. After reflux heating at 80°C for 16 h, the mixture was cooled down 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 crude product was immersed in methyl alcohol, filtered, washed with methyl alcohol and dried under dynamic vacuum to give 1,4-bis(bromomethyl)-2-decyloxy-5-(2′-(6′-dodecyloxy)naphthyl)benzene (6) as a gray white solid (0.81 g) in 36% yield. Melting point: 54.3–55.0°C, ^{1}H NMR (CDCl$_3$): δ 8.29 (d, J = 8.76 Hz, 1H, aromatic C—H), 7.84 (s, 1H, aromatic C—H), 7.80 (s, 1H, aromatic C—H), 7.62 (d, J = 8.76 Hz, 1H, aromatic C—H), 7.30 (d, J = 7.23 Hz, 2H, aromatic C—H), 7.17 (s, 1H, aromatic C—H), 7.02 (s, 1H, aromatic C—H), 4.57 (s, 2H, —CH$_2$Br), 4.43 (s, 2H, —CH$_2$Br), 4.20 (t, J = 6.42 Hz, 2H, —OCH$_2$), 4.11 (t, J = 6.27 Hz, 2H, —OCH$_2$), 1.94–1.27 (m, 36H, aliphatic C—H), 0.88 (m, 6H, aliphatic 2× CH$_3$). FTIR (KBr pellet, cm^{-1}): 3012 (C—H stretching of aromatic ring), 2924, 2854 (C—H stretching of alkyl side chains), 1599, 1507 (C=C stretching of aromatic ring), 1467, 1345 (—CH$_2$— segmental bending of alkyl side chains), 1272 (C—O—C asymmetric stretching), 1237, 1212, 1131 (C—H in plane bending of aromatic ring), 1057 (C—O—C symmetric stretching), 826 (C—H out-of-plane bending of aromatic ring). FABMS$^+$ m/z: 731 (M$^+$ + 1, 70%), 651 (M$^+$ + 1 − Br, 66%), 574 (M$^+$ + 1 − OC$_{10}$H$_{21}$, 16%), 571 (M$^+$ + 1 − 2Br, 45%). Elem. Anal. Calcd. for C$_{40}$H$_{58}$Br$_2$O$_2$: C, 65.75%; H, 8.00%. Found: C, 65.69%, H, 7.89%.

Polymerization of Compound (6)

The 1,4-bis(bromomethyl)-2-decyloxy-5-(2′-(6′-dode-cyloxy)naphthyl)benzene [Compound (6)] (0.73 g, 1 mmol) was dissolved in 60-mL dry 1,4-dioxane. The solution was heated at 96°C under nitrogen atmosphere for 15 min, and then a fresh solution of t-BuOK (0.291 g, 2.6 equiv.) in 1,4-dioxane (2.6 mL) was added into the solution drop by drop. The solution was further stirred for about 5 min at 96°C and then excess t-BuOK (0.224 g, 2.0 equiv.) in 1,4-diox-ane (2 mL) was syringed into the reaction solution. The solution was cooled to 50°C after stirring for additional 8 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 of acetic acid was 1.5 times that of the base. After stirring for 20 min, the mixture was poured into 70-mL water under stirring and was further stirred for 10 min. Finally, crude DDN-PPV was precipitated from the mixture by adding 200-mL methyl alcohol. The crude DDN-PPV was filtered, washed with some methyl alcohol, and dried under dynamic vacuum to give orange solids (0.51 g) in 89% yield. The crude DDN-PPV was further purified through dissolving in 40-mL THF (50°C) and being precipitated by adding 50-mL methyl alcohol. The precipitated DDN-PPV was filtered, washed with 50-mL methyl alcohol, and dried at room temperature under reduced pressure. Finally, pure DDN-PPV was obtained as dark orange solids (0.40 g) in 71% yield.
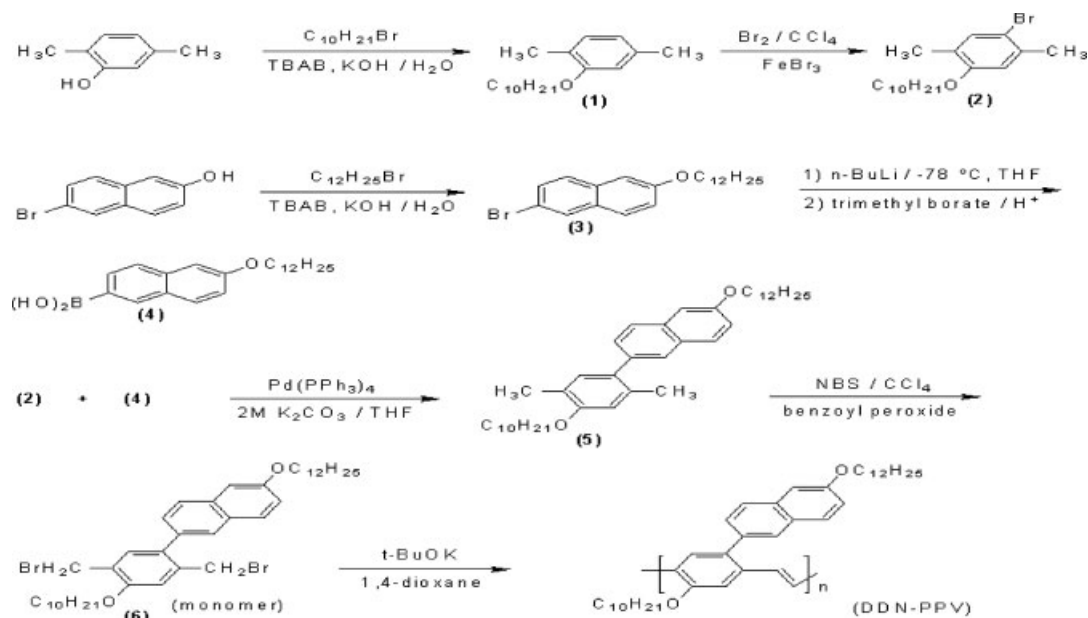
Scheme 1 Synthesis route for the monomer and polymer.

The ^{1}H NMR and FTIR spectra of the DDN-PPV are illustrated in the Results and Discussion section.

Instrument

Melting points of compounds at different synthesis stages were determined on a Buchi B-540 apparatus. The ^{1}H and ^{13}C NMR spectra of the specimen solutions in CDCl$_3$ were measured by a Bruker Avance 300 spectrometer (300 MHz). FTIR spectra were recorded by a Perkin-Elmer Spectrum One spectrometer. The UV/vis spectra of the samples in CHCl$_3$ were measured by a Shimadzu UV-160 spectrophotometer. The mass spectra were measured by a Bruker APEX II spectrometer. Elemental analyses were taken with a Heraeus CHN-O-Rapid Analyzer. The fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. The thickness of DDN-PPV ultrathin film was measured by a Kosaka Laboratory ET-4000M photometer. The weight– and number–average molecular weights of DDN-PPV were measured by a gel permeation chromatographer (GPC) of the Analytical Scientific Instrument 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 TGA-7 thermogravimetric analyzer under a nitrogen stream and with a heating rate of 10°C/min.

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 DDN-PPV film with a thickness of 90 nm was then spin-coated on the PEDOT layer with a spin rate of 500 rpm and duration of 15 s. Prior to the above-mentioned spin-coating, the 1.14 wt % DDN-PPV solution in *p*-xylene was filtered through a 0.45-μm pore size filter. For the fabrication of a cathode, a 10-nm layer of calcium (Ca) was deposited on the DDN-PPV layer under a high vacuum of 5×10^{-6} Torr. Finally, a protecting layer of 100-nm thick 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.

RESULTS AND DISCUSSION

The synthesis route for the monomer and polymer is illustrated in Scheme 1 and related descriptions in the Experimental section. The monomer was prepared via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions from the starting materials of 2,5-dimethylphenol and 6-bromo-2-naphthol. The DDN-PPV was obtained by a method similar to the Gilch procedure. The weight–average molecular weight (M_w), number–average molecular weight (M_n), polydispersity (M_w/M_n), and degree of polymerization (X_n) of the DDN-PPV obtained by GPC measurement are 217,574 g/mol,
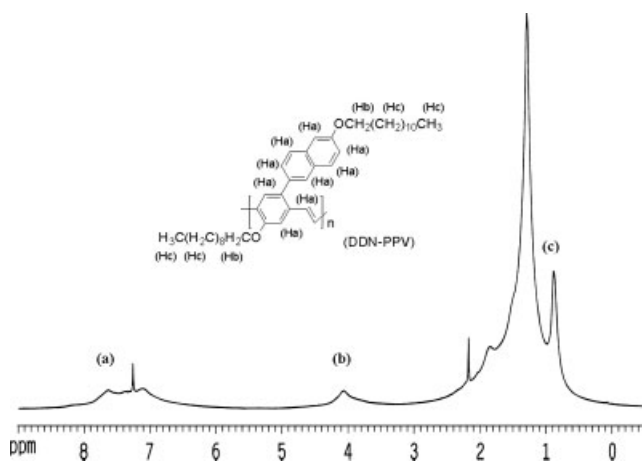
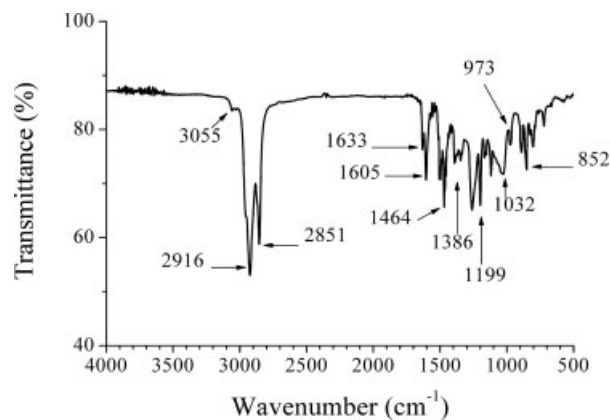**Figure 1** ^{1}H NMR spectrum of the DDN-PPV in CDCl$_3$.

20,817 g/mol, 10.45, and 36, respectively. The X_n is calculated by using the equation $X_n = M_n/M_o$, where M_o is the molecular weight of the repeat unit. The X_n implies an average number of the repeat units present in a polymer chain.

Structure analysis of the DDN-PPV

The ^{1}H NMR spectrum of the DDN-PPV solution in CDCl$_3$ is shown in Figure 1. The peak of CDCl$_3$ is at 7.25 ppm. Figure 1 shows that the two proton peaks of 1,4-bisbromomethyl groups of the monomer [compound (**6**)] at 4.57 and 4.43 ppm have disappeared and a new broad peak has appeared in the range of 6.8–7.9 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 range of 3.8–4.2 and 0.5–2.0 ppm, respectively.

The formation of TBB defects in the PPV derivatives prepared by the 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 head-to-head (or tail-to-tail) coupling reaction results in a presence of CH$_2$—CH$_2$ groups in the polymer main chains. The ^{1}H NMR signals of these CH$_2$—CH$_2$ groups should locate at around 2.7–2.9 ppm.[16] However, there are no such signals around 2.7–2.9 ppm in Figure 1. This indicates that the polymerization process for the DDN-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 5-(2′-(6′-dodecyloxy)naphthyl) substituent on the phenylene ring of Compound (**6**). The other reason is that the bromomethyl group in the ortho position relative to 2-decyloxy substituent on the phenylene ring of Compound (**6**). 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 (**6**).

Figure 2 shows FTIR spectrum of the DDN-PPV. The absorption peak at 3055 cm^{-1} is due to the C—H stretching of aromatic ring. The peaks at 2916 and 2851 cm^{-1} are due to C—H stretching of the alkyl side chains and those at 1633 and 1605 cm^{-1} are due to the aromatic ring stretching. The absorption peaks at 1464 and 1386 cm^{-1} are due to —CH$_2$— segmental bending of the alkyl side chains and the one at 1199 cm^{-1} is due to the C—H in plane bending of aromatic ring. The peak at 1032 cm^{-1} is due to the symmetric C—O—C bond stretching and the one at 973 cm^{-1} is due to the C—H out-of-plane bending of *trans*-vinylene unit. The peak at 852 cm^{-1} is due to the C—H out-of-plane bending of aromatic ring. The results of FTIR spectrum also confirm the formation of DDN-PPV.

Figure 2 FTIR spectrum of the DDN-PPV film on KBr.

Optical properties of the DDN-PPV

Figure 3 shows UV/vis spectra of the DDN-PPV film (a) and solution in CHCl$_3$ (b). The DDN-PPV
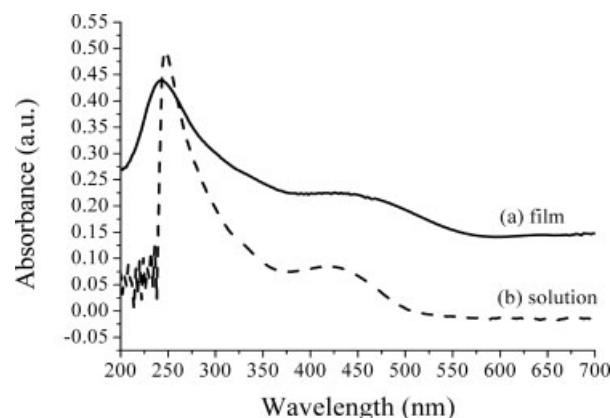
Figure 3 UV/vis spectra of the DDN-PPV film (a) and solution in CHCl$_3$ (b).

film and its solution exhibit two absorption peaks at 250 and 438 nm. For the identification of these two peaks, UV/vis spectrum of the DDN-PPV is compared with that of the poly(2,5-didecyloxy-*p*–phenylenevinylene) (decyloxy-PPV) film reported in literature.[19] The decyloxy-PPV and DDN-PPV have a similar structure except that the former is without the 6′-dodecyloxynaphthyl substituent. UV/vis spectrum of the decyloxy-PPV film exhibits only one absorption peak at 470 nm. This peak is due to the π→π* transition of PPV conjugated segments. The absorption peak of decyloxy-PPV at 470 nm is in close vicinity to that of the DDN-PPV at 438 nm. This leads to the conclusion that the π→π* transition of PPV conjugated segments causes the absorption peak of DDN-PPV at 438 nm. Consequently, the other absorption peak of DDN-PPV at 250 nm is due to the π→π* transition of the 6′-dodecyloxynaphthyl substituent.
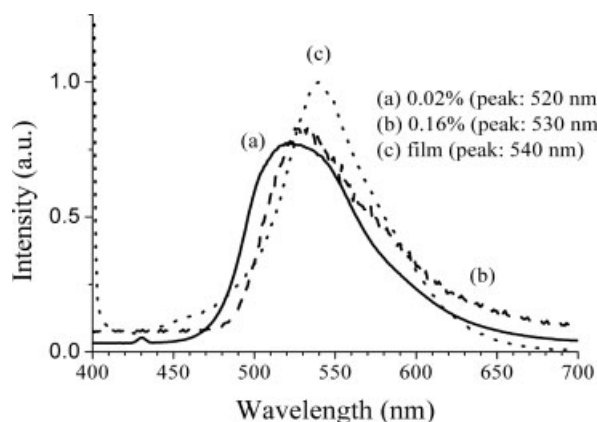
The optical energy (*E*, in eV) is described by the following eqs. (1) and (2):
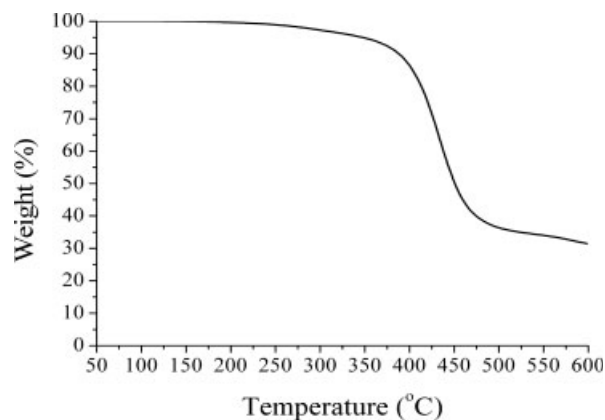
$$E = h \times c/\lambda \tag{1}$$

$$1 eV = 1.602 \times 10^{-19} \tag{2}$$

where *h* is the Planck constant (6.63 × 10⁻³⁴ J s), *c* is the light velocity (3 × 10⁸ m/s), and λ is the wavelength of absorption threshold. Using the value of absorption threshold λ (580 nm) [Fig. 3(a)], we deduce that the energy band gap of DDN-PPV film is 2.13 eV.

The DDN-PPV is easily soluble in common organic solvents, such as chloroform, THF, and *p*-xylene. This is due to the presence of asymmetric substituents on the phenylene rings. Because of the good solubility, the DDN-PPV is easily spin-coated as a smooth thin film on various substrates. Figure 4 shows the photoluminescence (PL) spectra (the ex-


**Figure 5** TGA thermogram of the DDN-PPV under a nitrogen stream.

cited wavelength, 390 nm) of the DDN-PPV film and solutions. PL emission peaks of the DDN-PPV in THF at the concentrations of 0.02 and 0.16 wt % are 520 and 530 nm, respectively. On the other hand, the emission peak of DDN-PPV film is at 540 nm. The wavelength of the emission peak increases as the concentration of the DDN-PPV goes up. The PL emission has a red shift of about 20 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 π→π* transition of the conjugated segments smaller. Thus the energy transfer process takes place more easily in a film state than in a solution state.[19]

Thermal stability of the DDN-PPV

Figure 5 shows the results of TGA measurement of DDN-PPV. There is no appreciable weight loss before 250°C. The weight loss begins to increase pronouncedly at 275°C, at which the decomposition of

Figure 4 PL spectra of the DDN-PPV solution in THF [(a) 0.02%, (b) 0.16%] and the DDN-PPV film (c).
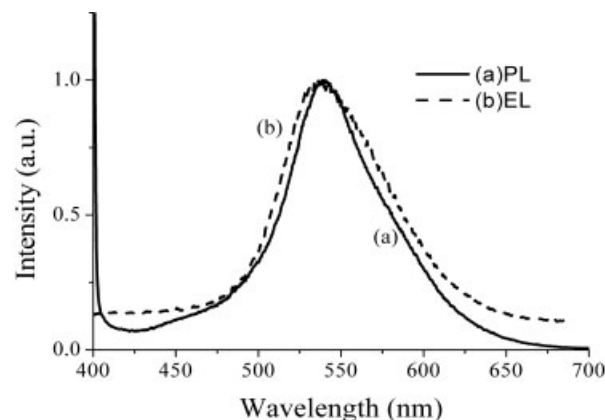
Figure 6 PL (a) and EL (b) spectra of the DDN-PPV film.
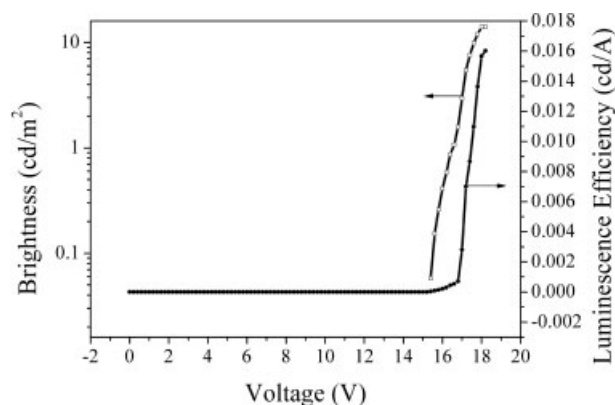
Figure 7 Luminescence efficiency–voltage–brightness curve of the ITO/PEDOT/DDN-PPV/Ca/Ag device.

alkoxy substituent starts to take place. The weight loss reaches 5% as the temperature increases to 325°C. The weight loss above 450°C is due to the decomposition of the rigid conjugated main chains as is observed with polyaniline.[20] The high thermal resistance property of the DDN-PPV is significant to its application in LED devices.

Performance of LED application

Figure 6 shows the photoluminescence (PL) and electroluminescence (EL) spectra of the DDN-PPV film. The EL spectrum of the ITO/PEDOT/DDN-PPV/Ca/Ag device shows a maximum emission band at around 538 nm, which corresponds to the yellowish-green light. On the other hand, the PL spectrum of the DDN-PPV film shows an emission maximum at 540 nm. Both spectra are in good agreement with each other in this study. This result means that EL of the device occurs at the same emission center of PL in the DDN-PPV film as in the case of poly(2,5-didecyloxy-*p*-phenylenevinylene).[19]

Figure 7 shows the luminescence efficiency–voltage–brightness characteristics of the device. The turn-on voltage of the device is about 16.6 V. The maximum brightness and luminance efficiency of the device are 14 cd/m^2 and 0.016 cd/A, respectively, both at a voltage of 18.2 V. We hope that a higher EL performance of the device could be obtained by optimizing the device structure in our future work.

CONCLUSIONS

A new soluble luminescent DDN-PPV without TBB defects was prepared in this study by a method similar to the Gilch procedure. The monomer [com-

pound (**6**)] was successfully synthesized via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions from the starting materials of 2,5-dimethylphenol and 6-bromo-2-naphthol. The incorporation of a decyloxy substituent and a 6′-dodecyloxynaphthyl substituent in the respective 2-position and 5-position of the phenylene ring makes the DDN-PPV soluble in organic solvents and suppresses the occurrence of TBB defects. The energy band gap of DDN-PPV film is 2.13 eV. The PL emission of DDN-PPV has a red shift of about 20 nm from a dilute solution state (0.02 wt %) to a film state. The shift is probably due to a more aggregated conformation of the polymer main chains in a film state than in a solution state. With the DDN-PPV acting as a light emitting material, the EL spectrum of the device shows an emission peak at 538 nm. The maximum brightness of the device is 14 cd/m^2 at a voltage of 18.2 V.

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