



Synthesis of fluorene- and anthracene-based π -conjugated polymers and dependence of emission range and luminous efficiency on molecular weight

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ARTICLE INFO

Article history:

Received 25 June 2009

Accepted 27 August 2009

Keywords:

Organic light emitting diode

Molecular weight

Heck coupling reaction

Copolymer

ABSTRACT

In the present work poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene], a fluorene- and anthracene-based copolymer, is synthesized through a Heck coupling reaction. In order to synthesize polymers with high-molecular weight, DMF (P1), DMF/p-Xylene = 1/1 (P2), p-Xylene (P3), and 1,4-Dioxane (P4) are used as solvents, which are an important factor in the synthesis process. The number of average molecular weights (M_n) of the synthesized polymers P1–P4 do not differ significantly, standing at 22,309, 12,369, 29,192, and 39,464, respectively, while their weight average molecular weights (M_w) show considerable differences (i.e. 50,055; 24,042; 125,406; and 231,053). Polymers P1–P4 demonstrate little difference in the results of a thermal analysis, electrochemical analysis, UV–vis analysis, and photoluminescence (PL) spectrum measurement. With regard to electroluminescence (EL) spectrum measurement, however, P1 and P2 show main luminous peaks at 508 nm, while P3 and P4's luminous peaks are seen at 516 nm. Moreover, luminous shoulder peaks were red-shifted with increase of molecular weight of polymers from 460 to 544 nm. In this process, the luminous area is red-shifted from greenish-blue to yellowish-green. The I – V – L measurement results show that the maximum brightness of P1, P2, and P3 ranges from 164 to 303 cd/m^2 and their luminous efficiency is low at 0.031–0.054 cd/A . Meanwhile, the turn-on voltage of P4, having greater molecular weight, is 9.5 V, and its maximum brightness and corresponding luminous efficiency are 736 cd/m^2 and 0.08 cd/A , respectively, implying that the luminous efficiency of devices improves as the molecular weight becomes greater.

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1. Introduction

Since electroluminescence (EL) phenomena in low molecular organic materials (Tang et al.) were announced in 1986, studies on organic semiconductors such as organic light emitting diodes (OLED) [1–4], organic thin film transistors (OTFT) [5,6] and organic photovoltaics (OPVs) [7–11] have been actively conducted. Since EL phenomena in polymers were discovered in 1990 by Friend Group, polymer-based organic semiconductors, in particular, have drawn great attention [12]. Unlike main stream display devices such as LCD or PDP, OLED has its own luminescent compounds and can be applicable to a flexible display. Therefore, it has been seen as the next-generation display.

Compared to OLED, the low molecular polymer light emitting diode (PLED) on which many studies have recently been performed has a simple compound structure and superior mechanical characteristics. Unlike the vacuum evaporation-based low molec-

ular OLED, wet processing is possible. Because spin coating, ink-jet printing and roll to roll methods are applicable, in other words, this device has a low manufacturing cost and is scalable to wider areas [13,14]. Since it is still inferior to low molecular weight organic materials in terms of efficiency and oxidation stability, however, further studies need to be conducted.

To enhance the efficiency of polymer luminescent materials, high-molecular weight polymers, a recombination-enabled molecular structure and good solubility in an organic solvent are required. In addition, electron trap should be removed through purification [15–17]. In particular, the molecular weight of polymers greatly impacts the oxidative stability as well as efficiency. Many studies have revealed that large fluctuations in efficiency were observed even in materials with the same structure depending on the change in the molecular weight of the polymers. The high-molecular polymers can create entangled polymer networks and effectively promote electron–hole recombination. In addition, they can have longer charge transport lengths in molecules by extended n -conjugation length. With the increase in electronic stability, they can also increase the life span and efficiency of compounds [18,19].

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To control the molecular structure at the synthesis of π -conjugated polymers, a variety of coupling reactions such as Yamamoto coupling and Suzuki coupling have been used [20,21]. Among the coupling reactions, Heck coupling reaction is very sensitive to reaction temperatures, time, solvents and the type and concentration of ligand. Once reaction conditions are optimized, therefore, polymers with very high-molecular weight can be synthesized [22].

In this paper, fluorene–anthracene-based poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene], which is superior in oxidative stability and easily color-tuned, has been synthesized through the Heck coupling reaction. With the different application of solvents – DMF (P1), DMF: p-Xylene = 1:1 (P2), p-Xylene (P3) and 1,4-Dioxane (P4) – which can have great impact on the degree of polymerization, the change in molecular weight caused by the solvents and the properties were analyzed.

Furthermore, UV absorbance and PL in the solution and film were measured. Based on the results of UV–vis spectroscopy and cyclic voltammetry (CV) in film, specifically, band-gap and HOMO and LUMO levels were analyzed. For comparative analysis of the EL characteristics of the synthesized polymers (P1–P4), devices have been designed into the structure of ITO/PEDOT:PSS (25 nm)/polymer (80 nm)/BaF₂ (2 nm)/Ba (2 nm)/Al (200 nm).

2. Experimental

2.1. Materials

All reagents and chemicals were purchased from Aldrich. Chloroform was dried over CaCl₂ and THF, toluene were dried over sodium. Other reagents and chemicals were used as received.

2.2. Instruments

¹H NMR spectra were recorded at 400 MHz on a Brüker AMX400 spectrometer, using the resonances of the solvent as an internal reference. Chemical shift (δ) are reported in ppm downfield from TMS. UV–vis spectrometer was recorded on a Agilent 8453 UV-visible spectroscopy system. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a TA Instrument 2050. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt plate as working electrode, counter electrode, and Ag/AgCl electrode as reference electrode, in a 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) acetonitrile solution. Electric data were recorded using a Keithley 236 source-measure unit and all characterizations were carried out in an ambient environment. The luminance of device was measured with Spectra Scan PR-670.

2.3. Synthesis

2.3.1. Synthesis of 2-pentyl-9,10-bis(4-vinylphenyl)-9,10-dihydroxyanthracene 2

To a 3-neck flask were added magnesium turning (0.3 g, 12.4 mmol) and dry THF (20 ml) under nitrogen atmosphere. To the reaction mixture was slowly added 4-bromostyrene (2.27 g, 12.4 mmol), which was dissolved in dry THF (10 ml). The reaction mixture was refluxed for 5 h, following to be cooled at room temperature. To the solution was added 2-pentylanthraquinone (1.63 g, 5.87 mmol) for 1 h and the reaction mixture was stirred for 2 h. The reaction mixture was washed with 0.1N HCl, following to extract with CH₂Cl₂. The organic layer was dried with sodium sulfate and the solvent was removed with rotary evaporator. The

crude product was purified by silica-gel column chromatography to give white solid (2.22 g, 4.56 mmol), yield = 77.7%. ¹H NMR (CDCl₃, ppm): δ 0.55(m, 3H), 0.73(m, 1H), 1.00(d, 1H), 1.08(s, 4H), 1.42(m, 2H), 2.65(s, 1H), 5.22(d, 2H), 5.72(d, 2H), 6.99(dd, 1H), 7.06–7.45(m, 15H).

2.3.2. Synthesis of 2-pentyl-9,10-bis(4-vinylphenyl)anthracene 3

To a solution of potassium iodide (16.6 g, 0.1 mol) and NaH₂PO₄·H₂O (16.6 g, 0.12 mol) in acetic acid (200 ml) was slowly added compound 2 (2.22 g, 4.56 mmol), which was dissolved in dioxane (20 ml). The mixture was refluxed for 10 h at 80 °C. After the reaction mixture was cooled at room temperature, deionized water (1 L) was added. A precipitate was collected by filtration, and washed with water. After drying in vacuo, the residue was purified column chromatography on silica gel to give pale yellow compound 3 (1.43 g, 3.16 mmol), yield = 69.3%. ¹H NMR (CDCl₃, ppm): δ 0.62(m, 3H), 0.89(m, 1H), 1.06(d, 1H), 1.21(s, 4H), 1.55(m, 2H), 5.35(dd, 2H), 5.89–5.93(m, 2H), 6.82–6.96(m, 2H), 7.20–7.84(m, 15H).

2.4. General procedure of polymerization through the Heck reaction

To a solvent (5.6 ml) were added 3 (0.225 g, 0.35 mmol) and 2,7-dibromo-9,9-dioctylfluorene (0.195 g, 0.35 mmol). To the solution were added Pd(OAc)₂ (0.003 g, 0.014 mmol), tri(o-tolyl) phosphine (0.026 g, 0.0805 mmol) and triethylamine (1.659 ml). The mixture was refluxed for 2 days at 110 °C, followed by be cooled to room temperature. After the mixture was quenched by 1N HCl (30 ml), the organic layer, which was extracted by chloroform, was washed by brine several times. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed by rotary evaporation. A powder was obtained by filtration was reprecipitated with methanol several times. The polymer was further purified by washing methanol, acetone and hexane, respectively, in a Soxhlet apparatus for 24 h and dried under reduced pressure at 50 °C.

2.4.1. Poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene]. P1

Yellow solid 0.1831 g (yield = 20%). ¹H NMR (CDCl₃, ppm): δ 0.64–0.96(m, 16H), 1.14–1.30(d, 23H), 1.58(s, H), 1.64(s, H), 2.1(d, 3H), 7.26–7.82(m, 25H).

2.4.2. Poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene]. P2

Yellow solid 0.2740 g (yield = 75%). ¹H NMR (CDCl₃, ppm): δ 0.64–0.96(m, 16H), 1.14–1.30(d, 23H), 1.58(s, H), 1.64(s, H), 2.1(d, 3H), 7.26–7.82(m, 25H).

2.4.3. Poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene]. P3

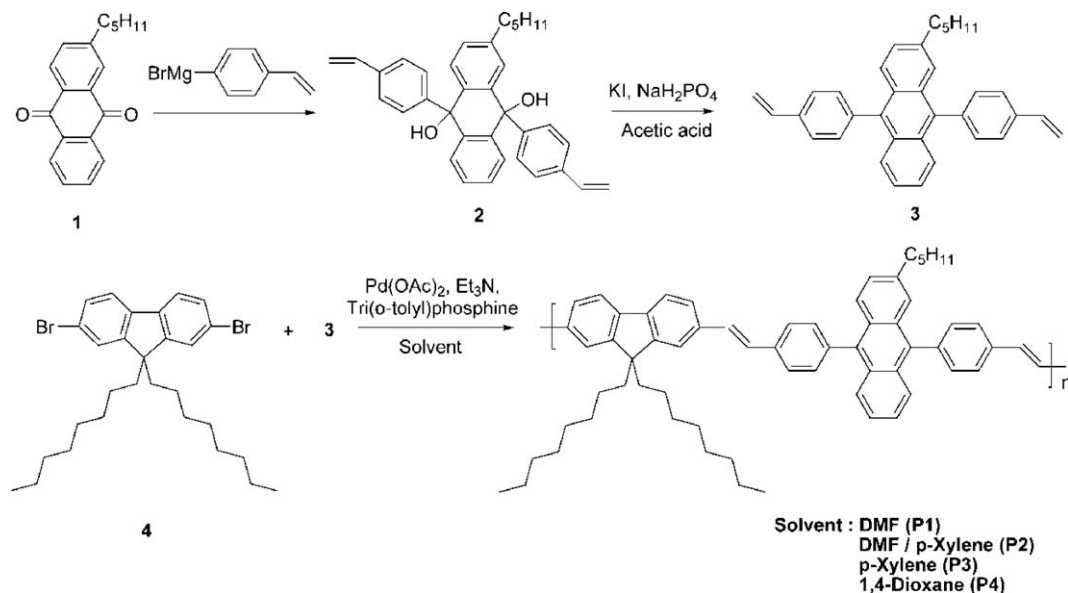
Yellow solid 0.2477 g (yield = 65%). ¹H NMR (CDCl₃, ppm): δ 0.64–0.96(m, 16H), 1.14–1.30(d, 23H), 1.58(s, H), 1.64(s, H), 2.1(d, 3H), 7.26–7.82(m, 25H).

2.4.4. Poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene]. P4

Yellow solid 0.2503 g (yield = 69%). ¹H NMR (CDCl₃, ppm): δ 0.64–0.96(m, 16H), 1.14–1.30(d, 23H), 1.58(s, H), 1.64(s, H), 2.1(d, 3H), 7.26–7.82(m, 25H).

2.5. Device fabrication and characterization

OLED device was fabricated on prepatterned indium tin oxide (ITO) with a sheet resistance of 10–20 Ω /sq. The substrate was ultrasonically cleaned with acetone, detergent, deionized water,



and isopropyl alcohol. An oxygen plasma treatment was performed for 10 min as the final step of the substrate cleaning, to improve the contact angle just before film coating. Onto ITO glass, a layer of polyethylenedioxythiophene–polystyrene sulfonic acid (PEDOT–PSS) film was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG.) for 40 s at the speed of 3000 rpm, aiming to improve the hole injection and to prevent the possibility of leakage. The PEDOT–PSS film was dried at 110 °C for 20 min in a vacuum oven. The solution of copolymers in chlorobenzene was prepared in a nitrogen-filled dry box and spin-coated on top of the ITO/PEDOT–PSS surface for 40 s at the speed of 3000 rpm. A thin layer of BaF₂ (2 nm), Ba (2 nm) as an electron injection cathode and the subsequent 200-nm thick aluminum protection layers were then thermally deposited by vacuum evaporation. The cathode area defines the active area of the device. The EL layer spin-coating process and the device performance tests were carried out in air conditions. Luminance was calibrated with a PR-670 SpectraScan Spectrophotometer (Photo Research) after the encapsulation of devices with UV-curing epoxy and thin cover metal can.

3. Results and discussion

As described in Scheme 1, 2-pentyl-9,10-bis(4-vinylphenyl)anthracene is obtained in the form of a pale yellow powder through the Grignard reaction (yield: 78%) and dehydrolysis reaction (yield: 70%). The ¹H NMR measurement results show that the outcomes of the reaction have aromatic areas from 6.87 to 7.83 ppm, multi and double vinyl groups at 5.9 and 5.3 ppm, and an aliphatic carbons peak from 0.6 to 1.5 ppm. Scheme 2 represents a high-molecular structure where 2-pentyl-9,10-bis(4-vinylphenyl)anthracene (0.225 g, 0.35 mmol) and 2,7-dibromo-9,9-dioctyl-9H-fluorene (0.195 g, 0.35 mmol) are compounded through the Heck coupling reaction. The polymerization process is carried out for 48 h, using DMF(N,N'-dimethyl formamide) as a solvent and Pd(OAc)₂ as a catalyst, by raising the temperature up to 110 °C on the bases of tri(o-tolyl) phosphine (0.026 g, 0.0805 mmol) and triethylamine (1.659 ml). The compounding solvent is synthesized using DMF (P1), DMF/p-Xylene = 1/1 (P2), p-Xylene (P3) and 1,4-Dioxane (P4), respectively. The obtained polymers (i.e. P1, P2, P3 and P4) easily dissolve in chloroform, THF, toluene, xylene, and dioxane but not in NMP, DMF and DMSO.

The structure of the obtained copolymers is verified through ¹H NMR measurement. The ¹H NMR spectra of P1–P4 are almost identical as their repetitive units of copolymer are the same. Fig. 1 illustrates the ¹H NMR spectra of P1–P4. The NMR graph shows a broad peak, with a multiplet, doublet, singlet, singlet, doublet, and multiplet observed at 0.64, 1.14, 1.58, 1.64, 2.1, and 7.26 ppm, respectively. Situated at the double-bond carbon between fluorene and benzene, a proton is found at 5.3 and 5.9 ppm on the anthracene monomer, but after compounding is completed, it shifts to 7.3 ppm and becomes part of the aromatic area.

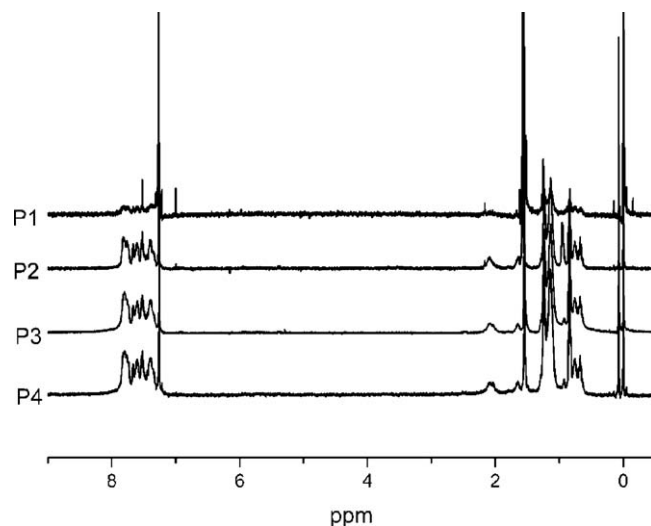


Fig. 1. ¹H NMR spectra of P1–P4.

Table 1
Molecular weight data of polymers.

Polymer	Yield (%)	<i>M_n</i>	<i>M_w</i>	<i>M_p</i>	<i>M_w/M_n</i>
P1	20	22,309	50,055	27,721	2.24
P2	75	12,369	24,021	15,930	1.94
P3	65	28,192	125,406	42,325	4.45
P4	69	39,463	231,053	54,203	5.86

Molecular weights and polydispersity indexes determined by GPC in THF on the basis of polystyrene calibration.

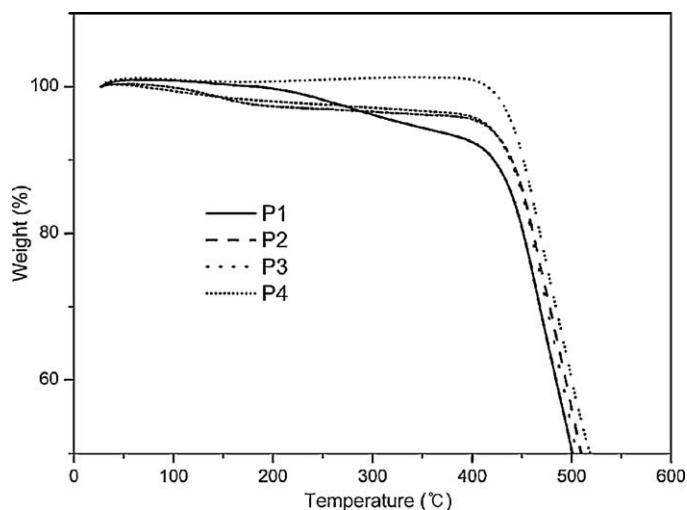


Fig. 2. TGA curves of polymers.

The molecular weights of the polymers are measured with gel permeation chromatography (GPC), and the results are shown in Table 1. The results show significantly greater molecular weight for P3 and P4 than that of P1 and P2. The number average molecular weights of P1 and P2 (M_n) are 22,309 and 12,369, while those of P3 and P4 (M_n) stand at 28,192 and 39,464. The weight average

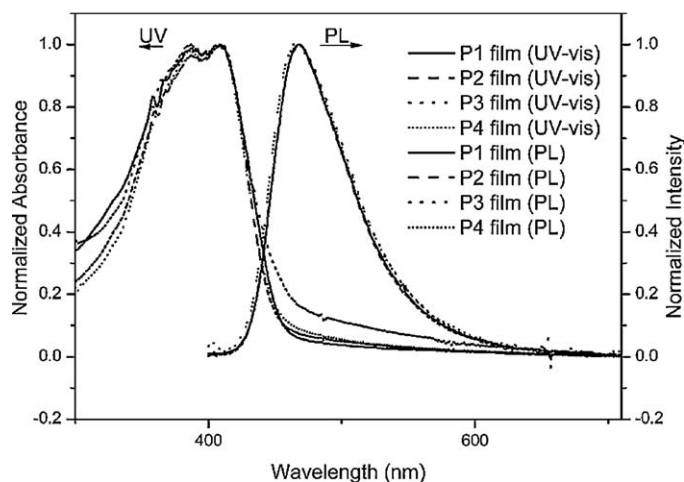
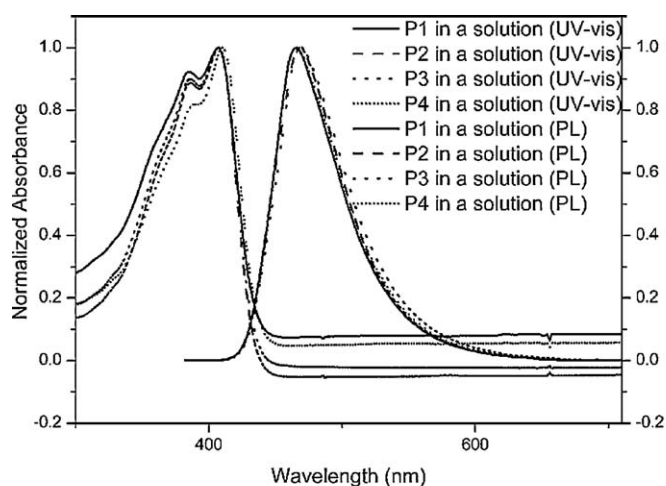


Fig. 3. UV-vis absorption spectra and PL data of polymers (a) in a solution and (b) in a film.

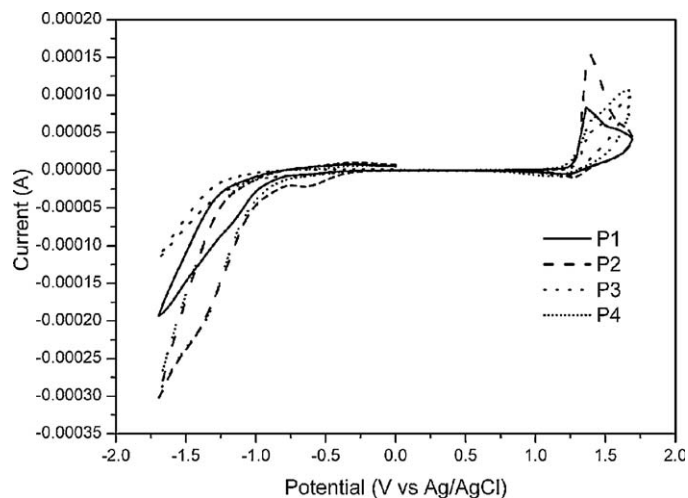


Fig. 4. Cyclic voltammograms of synthesized polymers.

molecular weights (M_w) of P1 and P2 are 50,055 and 24,021, but those of P3 and P4 far exceed those values, standing at 125,406 and 231,053. Such differences in molecular weight found upon the polymerization of these polymers are believed to be attributable to their differing solubility levels owing to the polarity of solvents. As compounding proceeds, electrons are increasingly delocalized as net π -conjugation length increases, reducing the polarity of the polymers. In the case of p-Xylene and 1,4-Dioxane, their polar and benzene ring-based structures stabilize the high-molecular backbone, which includes generally rigid aromatic rings, easily dissolving polymers with high-molecular weight. Meanwhile, the high polarity of DMF is seen to rather reduce solubility as the degree of polymerization increases and thereby limit molecular weight.

Presented in Fig. 2 are the results of a thermo-gravimetric analysis (TGA) on the synthesized polymers. Similar to conventional fluorine-based polymers, P1, P2, P3, and P4 show highly stable thermal properties up to 400 °C.

Fig. 3 illustrates UV-vis absorption and photoluminescence (PL) spectra measured in the chloroform solution of P1–P4 and on the film.

P1, P2, P3, and P4 record similar maximum UV absorption peaks of 384–388 and 407–410 nm in the solution and on the film. This demonstrates the typical non-crystalline characteristics of the synthesized polymers, which is similar maximum UV absorption peaks between in the solution and on the film because of poor π – π stacking properties in polymer chains. This paper calculates E_{onset} and band-gap ($E_g = 1240/\lambda_{\text{onset}}$ in eV) on the basis of the UV measurement results, and E_g is shown to be 2.7 eV. By emitting a 365 nm ultraviolet ray, photoluminescence (PL) is observed in all four polymers, with their luminous wavelengths at 464 nm in the solution and at 468 nm on the film.

Table 2
Electrochemical properties of polymers.

Polymer	Oxidation potential (V)		Energy level (eV)	
	E_{ox}	$E_{\text{onset,ox}}$	HOMO	LUMO
P1	1.4	1.22	–5.62	–2.76
P2	1.4	1.22	–5.62	–2.76
P3	1.36	1.18	–5.58	–2.72
P4	1.4	1.22	–5.62	–2.76

All potentials are given vs Ag/AgCl electrode. Final oxidation potential and onset oxidation potential were calculated from the oxidation potentials under the assumption that the absolute energy level of Fc/Fc⁺ was 4.8 eV below a vacuum.

Table 3
Electroluminescence performances of polymers.

Polymer	Turn-on voltage (V) ^a	Luminous efficiency (cd/A)	Maximum brightness (cd/m ²)	λ _{max} (nm)
P1	5	5.4 × 10 ⁻²	272.7	464, 508, 542
P2	5	3.1 × 10 ⁻²	164.6	460, 508, 544
P3	7	5.2 × 10 ⁻²	303.9	512, 542
P4	9.5	8 × 10 ⁻²	752.3	516, 544

^a Turn on voltage under forward bias.

Cyclic voltammetry (CV) of the synthesized polymers is presented in Fig. 4 [23–26]. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) is applied to the acetonitrile solution; a platinum (Pt) electrode is used as the counter electrode (CE) and an Ag/AgCl electrode as the reference electrode (RE), and the measured values are corrected using ferrocene. The obtained polymers show constant oxidation potential values at 1.36–1.4 V (Table 2). Having great molecular weight, P3 and P4 see a continued increase in current even after oxidation, indicating they have better electrochemical properties than P1 and P2. Values obtained from CV measurement are substituted into Eq. (1) to derive the HOMO levels of the polymers; using optical band-gaps calculated with the aforementioned UV–vis measurement results, their LUMO levels are determined from the differences between HOMO energy levels and optical band-gaps. These results are fully described in Table 3. All the polymers

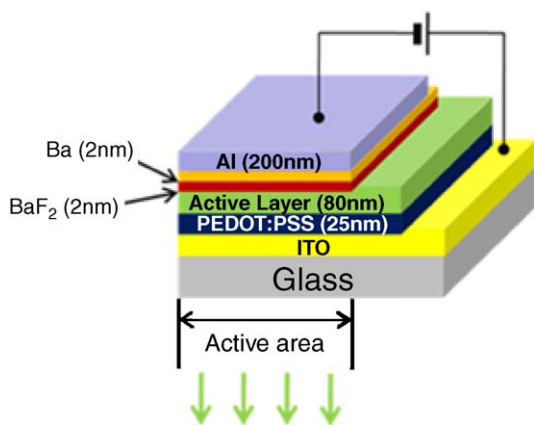


Fig. 5. A structure of fabricated device in this study. ITO/PEDOT:PSS (25 nm)/polymer (80 nm)/BaF₂ (2 nm)/Ba (2 nm)/Al (200 nm).

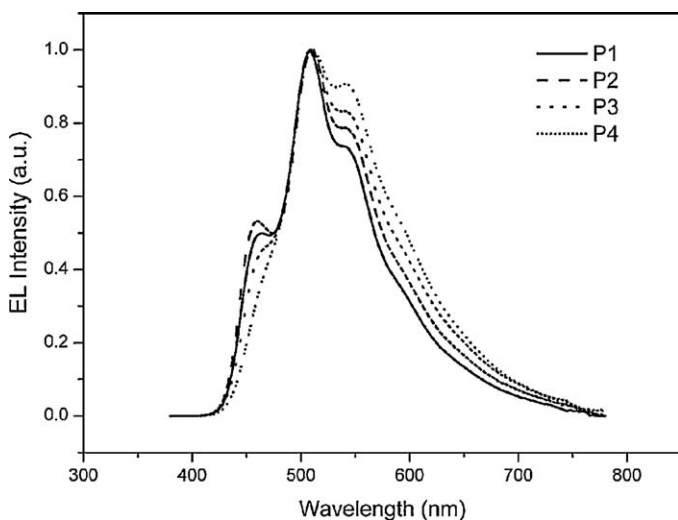


Fig. 6. EL spectra of the devices of the polymers.

demonstrate a HOMO energy level of -5.6 eV and a LUMO energy level of -2.7 eV.

$$E_{\text{HOMO}} = -[E_{\text{onset(vs Ag/AgCl)}} - E_{\text{onset(Fc/Fc+vs Ag/AgCl)}}] - 4.8 \text{ eV} \quad (1)$$

Fig. 5 represents a PLED device structure that is produced with polymers P1–P4 as active layers.

A 25 nm layer of PEDOT/PSS is applied as a vacuum transfer layer onto ITP glass whose surface is enhanced using ultrasound and UV–Ozone, and the luminous material of the polymer is spin-coated at a velocity of 3000 rpm. BaF₂ and Ba are deposited as a buffer layer and electron transfer layer, respectively, to a thickness of 2 nm at 0.1 and 0.2 □/s each. As a cathode, an Al layer of 200 nm is deposited at 5 □/s using a thermal evaporator. To prevent oxidation induced by moisture and oxygen, encapsulation is performed within a glove box using a getter and a glass cover.

Fig. 6 shows the EL spectrum of the PLED devices. P1, P2, P3, and P4 all record a π – π^* transition peak at 508–516 nm and a shoulder peak at 460 and 544 nm. The intensity of the shoulder peak at short wavelength declines as the molecular weight increases, with no peak demonstrated in the case of P4, while the shoulder peak tends to increase at long wavelength. Therefore, as illustrated in Fig. 7, the luminous area shifts from greenish-blue to yellowish-green with an increase in molecular weight. This is because the greater molecular weight of polymers leads to an increase in π -conjugation length and orbital overlap and eventually causes a red-shift in the luminous area [27,28].

Fig. 8 presents the results of I – V – L measurement on the devices. Having smaller molecular weight, P1, P2, and P3 have a turn-on voltage of 5–7 V and a maximum brightness of 164–303 cd/m²; their luminous efficiency is also at a low level of 0.031–0.054 cd/A. Meanwhile, the turn-on voltage of P4, which has greater molecular weight, is 9.5 V; its current density also increases as the voltage level rises more carriers are injected. Its maximum brightness is 736 cd/m² and the luminous efficiency 0.08 cd/A, demonstrating better EL properties than the other polymers with smaller

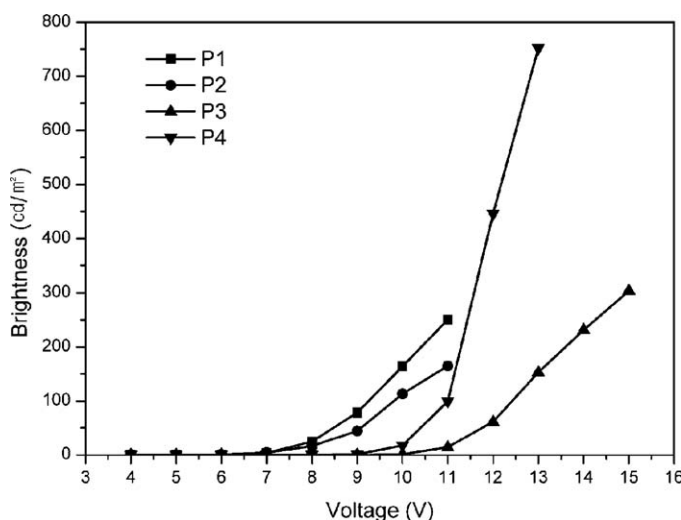


Fig. 7. Voltage–brightness curves of the devices based on P1–P4.

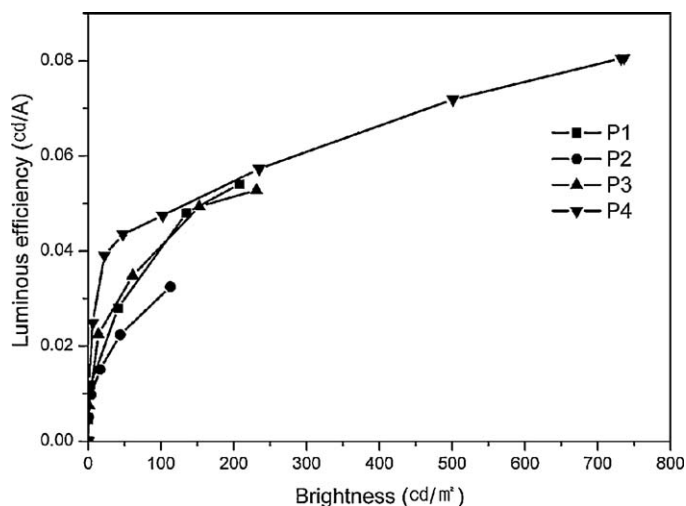


Fig. 8. Dependence of the luminous efficiency on the brightness of the devices based on P1–P4.

molecular weight. This is attributable to the creation of entangled polymer networks following an increase in molecular weight and subsequent improvement in the efficiency of recombination between holes and electrons.

4. Conclusion

Poly[9,9-dioctylfluorene-co-2-pentyl-9,10-bis(4-vinylphenyl)anthracene], which is based on fluorine and anthracene derivatives that can be easily color-tuned using Heck coupling reaction, has been successfully produced in this work. The greatest molecular weight has been found when 1,4-Dioxane is used as a compounding solvent. CV, UV–vis absorption spectrum, and PL spectrum showed little variation by molecular weight, but EL measurement results demonstrated that the luminous area was red-shifted from greenish-blue to yellowish-green as the molecular weight increases. With respect to polymers with small molecular weights (i.e. P1, P2 and P3), their maximum brightness is 164–303 cd/m² and their luminous efficiency is as low as 0.031–0.054 cd/A. On the other hand, the turn-on voltage of P4, having greater molecular weight, is 9.5 V, and its maximum brightness

and corresponding luminous efficiency are 736 cd/m² and 0.08 cd/A, respectively, implying that the luminous efficiency of devices improves as the molecular weight becomes greater.

Acknowledgement

This paper was supported by Konkuk University in 2008.

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