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Synthesis and Luminescent Properties of Poly(9-(3-vinyl-phenyl)-phenanthrene)

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Recently, interest of polymer light-emitting diode (PLED) fabricated from conjugated polymer has augmented because PLED has advantage property that is well-suited to flexible lighting and solution processed device. In this presentation, we suggest a new polymer host based on phenanthrene, poly(9-(3-Vinyl-phenyl)-phenanthrene) (PVPP). It can be easily synthesized through simple synthetic methods which are Suzuki and Wittig reactions. PVPP film can be obtained from spin coating with solution used by common solvent. It exhibited PL maximum value of 381 nm and broad PL spectrum. Energy transfer smoothly occurred when the three dopants for green, red and yellow were used in PVPP.

Keywords: Polymer Light-Emitting Diodes (PLEDs), Luminescent, Phenanthrene.

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1. INTRODUCTION

Polymer light emitting diodes (PLEDs) have been studied for application of organic light emitting diodes(OLEDs) in large size display.¹ Also, PLEDs have attracted much attention from academic and industrial fields as they are applied to diverse areas such as flat-panel displays and lightings.^{3–5} In particular, PLEDs manufactured using conjugated polymers^{6,7} have received great attention because they have properties well-suited for flexible lightings: low operating voltages, good processability,² and facile color turnability over the full visible range.

Many light-emitting polymers were synthesized and studied, and performance of PLEDs has been improving significantly in recent years. Especially, blue OLED was firstly fabricated with poly(*para*-phenylene) (PPP).⁸ And several conjugated polymers including polyfluorenes (PFs),⁹ poly(p-phenylenevinylene) (PPVs),¹⁰ and poly(phenan-threne)¹¹ have been used for blue emitters.

However, many cases had maximum shift problem of green emission, which is due to excimer formation, molecular aggregation, and inter-chain attractions in the π -conjugated system. In this paper, we synthesized new deep blue light-emitting polymer, poly(9-(3-Vinyl-phenyl)phenanthrene) (PVPP), as a blue host. PVPP has phenanthrene and phenyl groups at side part to prevent effectively molecular aggregation.¹² Moreover, phenyl and phenanthrene groups were linked by meta position to suppress conjugation extension for maintaining deep blue emission.¹³ The advantage of PVPP preparation includes facile synthesis methods such as Suzuki coupling and Witting reaction.

2. EXPERIMENTAL DETAILS

2.1. General Experiment

Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical TLC was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230–400 mesh).

2.2. Synthesis of Compound 1

In a 500 ml round-bottom flask, 10 g of 9-bromophenanthrene (38.89 mmol) was added and dissolved in 150 ml of anhydrous tetrahydrofuran (THF) before stirring. The reaction temperature was maintained at -76 °C, and 25.28 ml of 2.0 M *n*-butyllithium (50.59 mmol) was slowly added to the reaction vessel. After about 10 minutes, 6.07 ml of trimethyl borate (54.45 mmol) was added to the reaction vessel. Once the reaction temperature increased to room temperature after about 1 hour, 7.12 ml

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of 12 M HCl (85.56 mmol) was added. After the reaction, the mixture was extracted using ethyl acetate (EA) and distilled water. Water remaining in the organic layer was dried with $MgSO_4$. The mixture was concentrated by reduced pressure and re-precipitated with THF and hexane to obtain white solid. The yield was 42%.

¹H-NMR (300 MHz, Chloroform) δ (ppm): 8.75–8.71 (*t*, 2H), 8.56–8.53 (*d*, 1H), 8.04 (*s*, 1H), 7.88–7.85 (*d*, 1H), 7.61–7.52 (*m*, 6H), 5.79 (*s*, 3H).

2.3. Synthesis of Compound 2

In a 500 ml round-bottom flask, 3.3 g of Compound 1 (14.86 mmol), 0.69 g of Pd(PPh₃)₄ (0.59 mmol) and 2.08 mL of 3-bromobenzaldehyde (17.83 mmol) were added and dissolved in 100 ml of anhydrous THF. When the temperature increased to 80 °C, 37.15 ml of 2 M K_2CO_3 (74.31 mmol) was added to the reaction vessel. After the reaction, the mixture was extracted using toluene and distilled water. Water remaining in the organic layer was dried with MgSO₄. The mixture concentrated by reduced pressure was purified by primary column using toluene solvent. The purified mixture was concentrated again by reduced pressure and purified by secondary column using methylene chloride (MC):hexane = 1:2. The purified product was concentrated by reduced pressure to remove the solvent at room temperature and obtain solid material in light yellow color. The yield was 38%, a Tecl

¹H-NMR (300 MHz, Chloroform) δ(ppm): 10.12 (*s*, 1H), 8.81–8.75 (*m*, 2H), 8.73–8.07 (*m*, 1H), 8.06–7.98 (*m*, 1H), 7.97–7.90 (*m*, 1H), 7.89–7.80 (*m*, 2H), 7.73–7.66 (*m*, 5H), 7.64–7.58 (*m*, 1H).

2.4. Synthesis of Monomer

In a 500 ml round-bottom flask, 6.65 g of methyltriphenylphosphonium bromide (18.61 mmol) and 2.24 g of KOC(CH₃)₃ (19.85 mmol) were added and dissolved in 150 ml of anhydrous THF. The solution was stirred for 1 hour at 0 °C. Continuously maintaining the temperature at 0 °C, 3.5 g of Compound 2 (12.41 mmol) was dissolved in 50 ml of anhydrous THF and slowly added to the reaction vessel while stirring for 1 hour. If the reaction was not complete, 6.65 g of methyltriphenylphosphonium bromide (18.61 mmol) and 4.48 g of $KOC(CH_3)_3$ (39.7 mmol) were additionally added and stirred at 0 °C. After the reaction, the mixture was extracted using methylene chloride (MC) and distilled water. Water remaining in the organic layer was dried with MgSO₄. The mixture concentrated by reduced pressure was purified by column using developing solvent of chloroform: hexane = 1:10. The purified product was concentrated by reduced pressure and re-precipitated using THF and hexane to obtain white solid material. The yield was 10%.

¹H-NMR (300 MHz, Chloroform) δ(ppm): 8.76–8.68 (*m*, 2H), 7.91–7.85 (*m*, 2H), 7.67–7.40 (*m*, 9H), 6.83–6.74 (*m*, 1H), 5.83–5.77 (*dd*, 1H), 5.30–5.24 (*m*, 1H).

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Scheme 1. Synthetic routes of PVPP.

2.5. Synthesis of Poly(9-(3-vinyl-phenyl)phenanthrene) (PVPP)

In a 100 ml round-bottom flask, 0.2 g of monomer (0.71 mmol) and 0.02 g of azobisisobutynitrile (0.12 mmol) were added for nitrogen substitution and dissolved in 4 ml of anhydrous benzene solvent. Polymerization was maintained at 50 °C while stirring for 12 hours. After the reaction, the mixture was dissolved in small amount of chloroform and recrystallized in excess acetone to obtain white solid polymer. The yield was 55%.

¹H-NMR (300 MHz, Chloroform) δ (ppm) : 8.64–6.04 (broad peaks, aromatic rings), 3.23–1.01 (alkyl groups).

2.6. Characterization

¹H-NMR spectra were recorded using Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm unit. UV-Visible spectra were recorded with HP 8453 UV-VIS-NIR spectrometer. Photoluminescence (PL) spectra were measured using Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis using chloroform solvent. Degradation temperatures (T_d) were determined with thermogravimetric analysis (TGA) by using a TGA4000 (PerkinElmer). Samples were heated to 800 °C at a rate of 10 °C/min.

Table I. Synthesis of various PVPP.

M^a (g)	S^b (ml)	I^c (g)	M_n	M_w	DP
0.2	4	0.01	_	_	_
0.2	4	0.02	29739	48243	1.62
0.2	4	0.04	2048	3877	1.89
0.2	4	0.06	708	943	1.33

Notes: a: Monomer (g), b: solvent (mL), c: initiator (g), temperature: 50 °C, time: 12 h.



Figure 1. UV-Visible absorption and PL spectra of monomer (square) and PVPP (triangle) in chloroform solution $(1.0 \times 10^{-5} \text{ M})$.

2.7. Luminescent Properties

The polymer film was prepared by spin coating of the polymer solution containing 1% by weight in toluene solvent. Spinning was conducted with the condition of 1000 rpm for 15 sec and 2000 rpm for 15 sec. As a result of atomic force microscopy (AFM) for polymer film morphology, roughness of root mean square (RMS) was 0.359 nm. It means that film surface is smooth.

3. RESULTS AND DISCUSSION/ Publishing Tech

Scheme 1 shows synthetic routes of PVPP. They consist of simple three steps for monomer.

The main motivation for this new polymer is based on suggestion of polymer host which has wide band gap and is simply synthesized. Monomer can be obtained through these three steps, and the polymer obtained by polymerization can be used as host material. Especially, in order to obtain wide band gap, PVPP has meta linkage between phenyl group and phenanthrene group. Meta position has advantage of squeezed conjugation length and relatively wide band gap compared to ortho and para position.¹³ Also



Figure 2. UV-Visible absorption and PL spectra of monomer (square) and PVPP (triangle) in spin coated film.

Table II. Optical properties	of monomer	and PVPP.
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	Solution ^a		Film ^b	
Compound	UV _{max} (nm)	PL _{max} (nm)	UV _{max} (nm)	PL _{max} (nm)
Monomer Polymer (PVPP)	296 301	374 379	307 305	379 381

Note: a. Chloroform solution $(1 \times 10^{-5} \text{ M})$, *b.* Spin coating film (1 wt%).

from NMR data, vinyl group protons were disappeared and aromatic protons showed broad proton peak because of polymer characteristics.

Polymer was obtained with high molecule weight and small polydispersity value by changing initiator, solvent (benzene) and reaction temperature. In particular as shown in Table I, equivalent weight change of initiator compared to solvent amount and reaction temperature could optimize molecular weight of polymer. Polymer having Mn of 30,000 was used in this study.

Figures 1 and 2 show UV-Visible (UV) absorption and photoluminescence (PL) spectra of PVPP and its monomer in solution and film state, respectively. These data are summarized in Table II. As shown in UV data of Table II, monomer and polymer had similar maximum values of 296 nm and 301 nm in solution state, which indicate characteristic peak of phenanthrene. In film state, maximum absorption values of monomer and polymer showed 307 nm and 305 nm respectively. The maximum values are mostly higher for the film state than in solution due to the effects of molecule packing in the films.

PL maximum value of monomer and polymer had 374 nm and 379 nm in solution state, respectively. In film state, PL maximum values of monomer and polymer showed 379 nm and 381 nm. In film state is slightly red shifted compared to solution state. This is the same reason as mentioned above.

PVPP showed high T_d value of 380 °C by thermogravimetric analysis (TGA). In order to check thermal stability of PVPP, PL spectrum of PVPP film was examined after heating for 30 min under Ar gas with 100 °C, 200 °C,



Figure 3. UV spectra of (•) C545T, (\blacktriangle) rubrene, (\bigstar) DCM in toluene solution and the PL emission of (\blacksquare) PVPP film as host.

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Figure 4. PL spectra of PVPP film and PVPP films doped with various dopants. ((\blacksquare) PVPP, (\bullet) PVPP+C545T 8%, (\blacktriangle) PVPP+rubrene 8%, (\bigstar) PVPP+DCM 8%).

and 380 °C. As a result, PL maximum values were in the range of 381 to 384 nm indicating similar value of room temperature condition. It means that PVPP has high thermal stability which is applicable to display process.

Highest occupied molecular orbital (HOMO) level and lowest occupied molecular orbital (LUMO) of PVPP was 5.97 eV and 2.15 eV respectively. Also band gap was 3.82 eV. The HOMO energy level was determined with ultraviolet photoelectron yield spectroscopy (AC-2). LUMO level was calculated from the HOMO level and the optical band gap. The optical band gap was derived by determining the absorption edges.

Figure 3 shows the solution UV spectra of C545T, DCM, rubrene which are dopants for green, red and yellow, respectively and PL emission of PVPP as a host. All UV spectra of three dopants overlapped with PVPP emission. From this data, it is expected that when three dopants were used with PVPP as a polymer host, energy transfer can be available from host to dopant.

As a results, Figure 4 shows the PL spectra of PVPP spin-coated film, which was doped using 3 dopants for green, red and yellow: C545T, DCM and rubrene. When three dopants were used in PVPP host polymer, energy transfer happened well from blue color to each color.

4. CONCLUSION

As a new polymer host, PVPP was prepared by simple four steps of synthetic scheme. Spin coating film of PVPP exhibited PL maximum value of 381 nm with broad PL specctrum. Energy transfer happened well when three dopants for green, red and yellow were used in PVPP. PVPP can be a good candidate as a host emitter for solution processible white OLED.

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