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Synthesis and Luminescent Properties of New Blue Polymer Light-Emitting Diodes Material, Poly(9-(3-Vinyl-phenyl)-pyrene)

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Polymer light-emitting diodes (PLEDs) have attracted much attention from academia and industry field because PLED has advantage property that is well-suited to flexible lighting and solution processed device. In this paper, we suggest new blue emitting polymer based on pyrene, poly(9-(3-Vinyl-phenyl)-pyrene) (PVPPy). From NMR data, vinyl group protons were disappeared and aromatic protons showed broad proton peaks because of polymer characteristics. PVPPy film can be obtained from spin coating with solution used by common solvents. It exhibited photoluminescence (PL) maximum value of 468 nm and full width at half maximum (FWHM) value of 73 nm. Three dopants for green, red, yellow were used to PVPPy, all energy transfer was happened well.

Keywords: Polymer Light-Emitting Diodes (PLEDs), Blue Emitting Polymer, Pyrene.

1. INTRODUCTION

Polymer light-emitting diodes (PLEDs) can be applied to various areas such as flat-panel displays and lighting, and thus is drawing much attention from academia and industry areas.[1–4] Especially, the interest in PLED using conjugated polymers[5,6] has augmented because PLED have properties that are well-suited to flexible lightings: good processibility,[7] low operating voltages, and facile color tunability over the full visible range.

Within recent several years, many light-emitting polymers have been developed, and the efficiency is increasing.

As blue OLED, poly(para-phenylene)(PPP)[8] was first used, and various conjugated polymers including polyfluorenes(PFs)[9], poly(*p*-phenylenevinylene)(PPVs),[10] poly(phenanthrene)[11] and such are being used as the blue emitter.

Nevertheless, although the performance of PLED is being improved, the parts that still need to be resolved, such as electroluminescent (EL) efficiencies or luminescent stability, are currently hindering commercialization. Therefore, one of the things that need to be resolved first in this field is to develop new conjugated polymers with high luminescent performance.

Pyrene and its derivatives as blue fluorescent emitter have been recently received the spotlight because they have high quantum efficiency as well as the thermal and chemical stabilies.[12] We synthesized and intend to introduce poly(9-(3-vinyl-phenyl)-pyrene) (PVPPy), which is a new blue emitting polymer based on pyrene as the blue host material.

2. EXPERIMENTAL DETAILS

2.1. General Experiment

The reagents and solvents used in the synthesis were purchased as reagent grade and used without further refinement. All the reactions were executed with the use of dry glassware in nitrogen condition. As for the TLC used in the analysis, Merck 60 F254 silica gel plate was used, and in column chromatography, Merck 60 silica gel (230–400 mesh) was used.

2.2. Synthesis of Compound 1

1-Bromo-pyrene 10 g was added to 500 mL round floor flask, melted in anhydrous tetrahydrofuran (THF) 120 mL,

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and agitated. After reaction temperature was set to −78 °C, 2.0 M *n*-Butyllithium 23.4 mL (50.59 mmol) was added into reaction mixture slowly. In 10 minutes, triisopropyl borate 10 mL was added to reaction mixture. When reaction temperature increased to room temperature in an hour, 12 M HCl 7.2 mL was added. The reaction was completed, compound was extracted with ethyl acetate (EA) and water, and the organic layer was dried with anhydrous $MgSO_4$ and filtered. After the compound was concentrated under reduced pressure, white solid was obtained in 51%.

^{1}H-NMR (300 MHz, THF-d_8) δ (ppm): 8.89–8.85 (*m*, 1H), 8.32–8.28 (*m*, 1H), 8.21–8.15 (*m*, 3H), 8.14–8.03 (*m*, 3H), 8.01–7.94 (*m*, 1H), 7.10 (*s*, 2H).

2.3. Synthesis of Compound 2

Compound (1) 6 g, $Pd(PPh_3)_4$ 0.564 g, 3-bromobenzaldehyde 0.118 ml was added to 500 ml round bottom flask, and melted with toluene 100 ml/ethanol 33 ml. The mixture was stirred under nitrogen at 70 °C, 2 M K_2CO_3 1.52 ml was added to reaction mixture. After the reaction was completed, the compound was extracted with toluene and water, and then the organic layer was dried with anhydrous $MgSO_4$ and filtered. The reaction mixture was purified to 1st column with toluene solvent. The reaction mixture was purified again to 2nd column at THF:hexane = 1:12 ratio. After the solvents were removed in room temperature, white solid substance was obtained in 35%.

^{1}H-NMR (300 MHz, THF-d_8) δ (ppm): 10.88–10.13 (*m*, 1H), 8.32–8.20 (*m*, 3H), 8.18–8.18 (*m*, 3H), 8.11–8.00 (*m*, 2H), 7.96–7.91 (*m*, 3H), 7.80–7.74 (*m*, 2H).

2.4. Synthesis of Monomer

Methyltriphenylphosphonium bromide 6.65 g (18.61 mmol) and $KOC(CH_3)_3$ 2.24 g (19.85 mmol) were added to 500 ml round bottom flask, melted with 150 ml anhydrous THF, and agitated for an hour while remaining at 0 °C. The reaction mixture was extracted with methylene chloride (MC) and water, and then the organic layer was dried with anhydrous $MgSO_4$ and filtered. The reaction mixture was purified to column with mixed solvent of Chloroform:hexane (1:10). After the product was concentrated under reduced pressure, white solid substance was obtained in 45%.

^{1}H-NMR (300 MHz, THF-d_8) δ (ppm): 8.23–8.18 (*m*, 1H), 8.17–8.12 (*m*, 5H), 8.10–7.97 (*m*, 3H), 7.71–7.69 (*m*, 1H), 7.59–7.49 (*m*, 3H), 6.91–6.81 (*m*, 1H), 5.92–5.85 (*dd*, 1H), 5.31–5.26 (*dd*, 1H).

2.5. Synthesis of Poly(9-(3-Vinyl-phenyl)-pyrene) (PVPPy)

Monomer 0.2 g (0.66 mmol) and azobisisobutynitrile 0.02 g (0.12 mmol) were added to 100 ml round bottom flask in nitrogen, and melted with 4 ml anhydrous benzene solvent. The polymer was agitated for 12 hours while remaining at 50 °C. The reaction was completed, the reaction mixture was melted in small amount of chloroform. The reaction mixture was recrystallized to excess amount of methanol, and white solid polymer was obtained in 55%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.01–6.24 (broad peaks, aromatic rings), 1.65–1.21 (alkyl groups).

2.6. Characterization

As for 1H-NMR spectrum Bruker, AM-300 spectrometer was used, and as for chemical shift values, ppm unit was recorded. UV-Visible (UV-Vis) spectra were measured with HP 8453 UV-VIS-NIR spectrometer, and PL spectra were measured with the use of Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). Polymer molecular weight and polydispersity were measured through gel permeation chromatography (GPC) analysis with the use of chloroform solvent.

2.7. Luminescent Properties

Polymer film was produced through spin coating with the use of polymer solution that includes 1 wt% of toluene solvent.

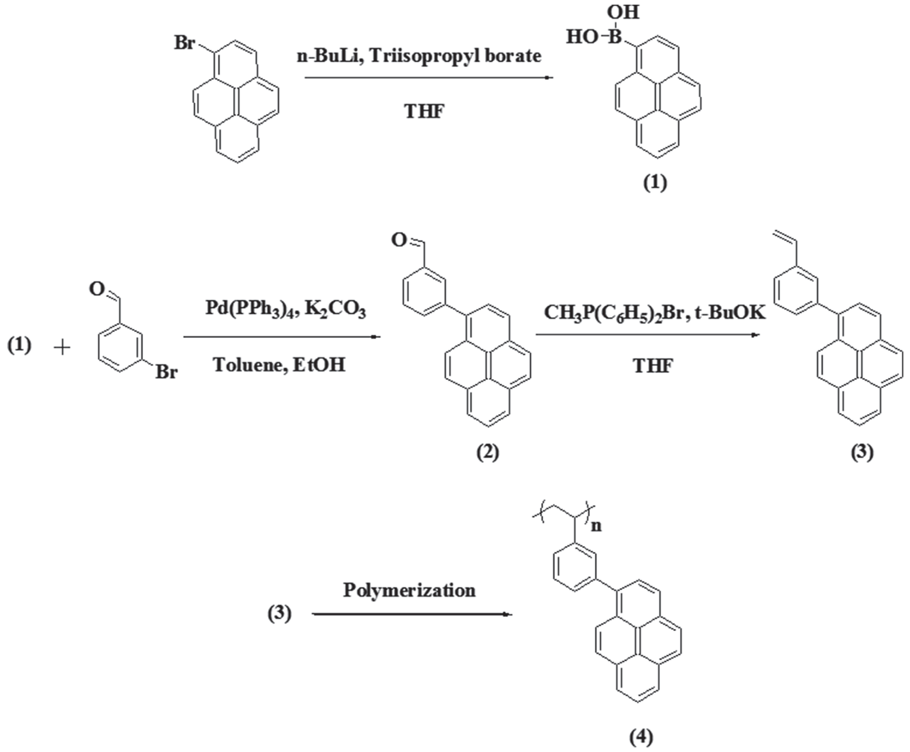
3. RESULTS AND DISCUSSION

Main motivation of this PVPPy is based on suggestion of general blue emitting material. Other typical blue polymers such as PPV or fluorene have synthetic scheme of more than 7 steps. On the other hand, monomer could be obtained through simple 3 steps as in Scheme 1, and through high-polymerization, the high polymer which can be used as host material was obtained. For usages of facile blue polymer preparation, such synthetic scheme is a great advantage.

Especially, for a large band gap, PVPPy was molecule-designed to have meta-linkage between phenyl group and pyrene group. Meta position has the advantage that it has shorter conjugation length and relatively wider band gap compared to ortho and para position.[13] Examining NMR data, due to the characteristics of high polymer, protons of vinyl group disappear and aromatic proton exhibit broader proton peaks.

Figures 1 and 2 respectively show UV-Visible (UV) absorption and photoluminescence (PL) spectra for PVPPy and monomer in solution state and film state. This data was briefly organized in Table I. In solution, monomer exhibits maximum absorption wavelength of 281, 346 nm and polymer exhibits similar values at 282, 347 nm, and also in film state, monomer exhibits maximum absorption wavelength of 286 nm, 355 nm, and polymer exhibits similar values at 288 nm, 363 nm.

In case of PL, monomer and polymer have PL maximum values of 396 nm, 476 nm respectively in solution state, and of 475 nm, 468 nm respectively in film state. In case of monomer PL_{max} in film state, it could be understood by relatively the packed state of monomer film. However,



Scheme 1. Synthetic routes of PVPPy.

polymer in film state showed relatively unpacked state, which cause 468 nm. In case of polymer solution state (PL_{max}: 476 nm), it can be explained by the interaction between polymer and solvent.

In Figure 3, PL emission of PVPPy and solution UV spectra respectively of C545T, DCM, and rubrene, which are green, red, and yellow dopants, were shown. UV spectra of the three dopants overlaps with PVPPy emission. Through this data, it can be predicted that when each of the three dopants are used with PVPPy host, the energy transfer from host to dopant occurs smoothly.

In Figure 4, PL spectra of PVPPy spin-coated film doped with C545T, DCM, and rubrene, which are green, red and yellow dopants, were shown. As the result, dopant emission was observed in each doped film, according to which it could be verified that when the three dopants are used with PVPPy host polymer, the energy transfer from

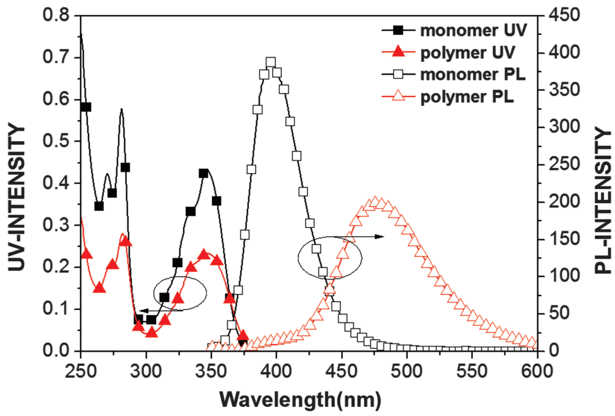


Figure 1. UV-visible absorption and PL spectra of monomer (square) and PVPPy (triangle) in Chloroform solution (1.0×10^{-5} M).

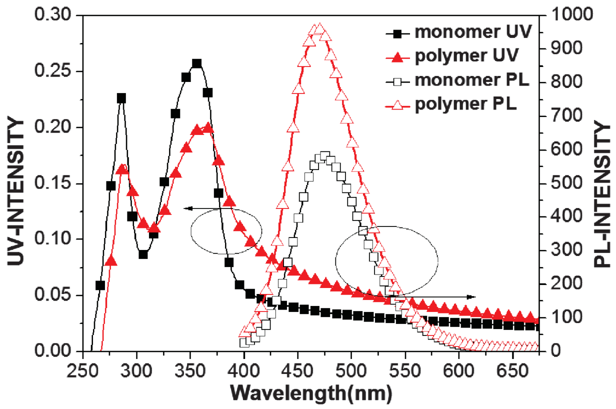


Figure 2. UV-visible absorption and PL spectra of monomer (square) and PVPPy (triangle) in spin coated film.

Table I. Optical properties of monomer and PVPPy.

Compounds	Solution[a]		Film[b]	
	UV_{max} (nm)	PL_{max} (nm)	UV_{max} (nm)	PL_{max} (nm)
Monomer	281, 346	396	286, 355	475
Polymer (PVPPy)	282, 347	476	288, 363	468

Note: [a]Chloroform solution (1×10^{-5} M), [b]Spin coating film(1 wt%).

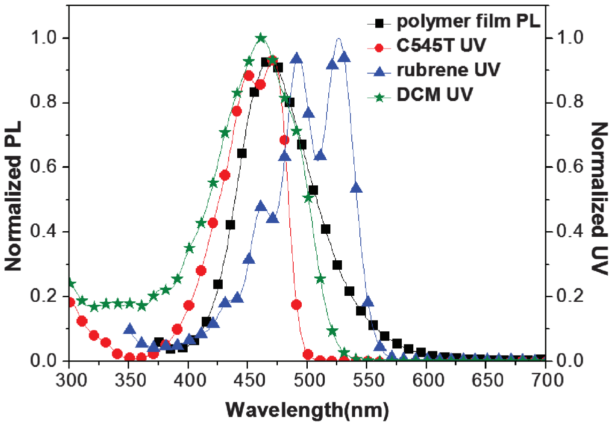


Figure 3. UV spectra of (●) C545T, (▲) rubrene, (★) DCM in toluene solution and the PL emission of (■) PVPPy film as host.

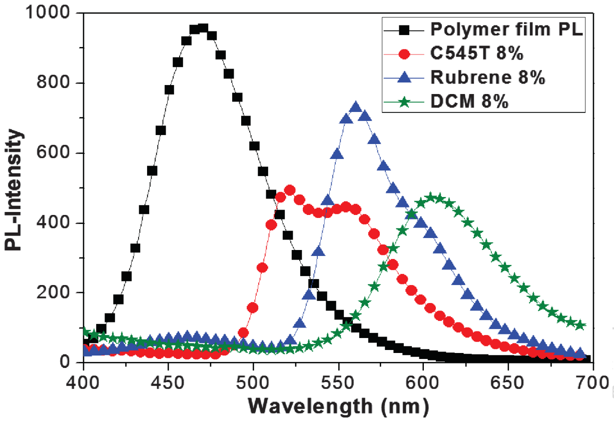


Figure 4. PL spectra of PVPPy film and PVPPy films doped with various dopants. ((■) PVPPy, (●) PVPP + C545T 8%, (▲) PVPP + rubrene 8%, (★) PVPP + DCM 8%).

blue color to each color occurs smoothly. We believe that PVPPy can be applied to the host material having high performance electroluminescent property. Further studies on electroluminescent property are underway.

PVPPy has a broad FWHM of 73 nm. Therefore, if it is used with an appropriate yellow dopant, it is expected that white OLED device of solution process could be produced. Also, since it has a broad PL spectrum, PVPPy is suitable for production of OLED lighting device with high CRI value of 80 or higher.[14]

4. CONCLUSION

Through simple 4 steps, the new blue emitter of PVPPy was synthesized. In spin-coated film, it yields the emission of 468 nm. When PVPPy is applied as the host material to the three dopants of C545T, DCM, and rubrene, energy transfer occurs smoothly, and thus it is suitable as the host material. Also, it has a large FWHM of 73 nm, and thus is expected to be applied to white OLED, and is also a good candidate for OLED lighting device with high CRI value.

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