

Design and Synthesis of New Fluorene-Based Blue Light Emitting Polymer Containing Electron Donating Alkoxy Groups and Electron Withdrawing Oxadiazole

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Abstract: A new polyfluorene-based copolymer having 2-ethylhexyloxy-5-methoxy-1,4-phenylene as an electron donating group and 2,5-diphenyl-oxadiazole as an electron withdrawing group was synthesized by the Suzuki coupling reaction. The obtained copolymer was characterized by ¹H-NMR, ¹³C-NMR, and IR-spectroscopy. The weight average molecular weight (M_w) of the obtained polymer was 18,600 with a polydispersity index of 1.5. The maximum photoluminescence of the solution and film of the polymer was observed at 453 nm and 456 nm, respectively. A double-layer device with the configuration, ITO/PEDOT/copolymer/Al, emitted blue light at 460 nm.

Keywords: blue light emitting, poly(fluorene), electron donating, electron withdrawing.

Introduction

The blue light emission is of particular importance in the development of polymer light emitting diodes (LEDs). Although a number of fully conjugated and partially conjugated polymers have been designed and synthesized in an attempt to realize efficient blue photoluminescence (PL) and electroluminescence (EL),¹⁻¹⁰ but a limited number of these polymers appear promising for use as blue polymer LEDs. In the categories of conjugated polymers for blue light emitting, polyfluorene and its derivatives occupy a significant position. Poly(fluorene)s are attractive as active components of organic light emitting diodes because of their thermal and chemical stability and their exceptionally high solution and solid state fluorescence quantum yields (0.6-0.8).¹¹⁻¹⁴ Moreover, the facile substitution at the 9-position of the fluorene monomer allows control of polymer properties such as solubility, processability, and morphology.

In addition to excellent luminescent properties, OLEDs also need adequate and balanced transport of both injected electrons and holes to allow an efficient recombination of these electrical charges in the luminescent chromophores.^{15,16} Due to their wide energy gaps, blue luminescent polymers usually have high oxidation potentials and low electron affinities. Because of these features, polymeric blue light emitting devices usually face charge injection difficulties

for both types of charge carriers with the currently available anode and cathode materials.

Many ways have been used to modulate the ionization potential (IP), electron affinity (EA), and band gap of polyfluorene derivatives.^{11-14,17,18}

We report here a new synthetic strategy to modulate the ionization potential (IP) and electron affinity (EA) of polyfluorene derivative by using two co-monomers, 2-ethylhexyloxy-5-methoxy-1,4-phenylene as electron donating group and 2,5-diphenyl-oxadiazole as electron withdrawing group. The synthesis and characterization, the optical properties, thermal properties and the electrochemical properties of new copolymer are also discussed.

Experimental

Materials. Tetrahydrofuran (THF) and diethylether were distilled from sodium benzophenone ketyl. Toluene was purified by distillation from CaH₂ and used immediately. Triphenylphosphine was purchased from Aldrich, recrystallized from degassed ethanol, and sublimed under vacuum prior to use. 9,9-Dihexylfluorene, benzoyl chloride, hydrazine, 4-bromobenzoyl chloride, thionyl chloride trimethylborate, n-BuLi (2.5 M in heptane), 2-ethylhexylbromide, 4-methoxyphenol, and tetrakis(triphenylphosphine) palladium (0) were purchased from Aldrich. Other chemicals were used without further purification.

Synthesis of 2,7-Dibenzoyl-9,9-dihexylfluorene. To the mixture of 20 g (60 mmol) of 9,9-dihexylfluorene prepared

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by literature method,³ 32 g (240 mmol) of AlCl₃ and 100 mL of CS₂, 33.7 g (240 mmol) of benzoyl chloride was added and stirred for 48 h. The reaction was terminated with ice and 100 mL of HCl, and extracted with CH₂Cl₂. The crude product was recrystallized in hexane. MP: 54 °C, Yield: 40%. ¹H-NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.8-7.7 (10H, m), 7.6 (2H, m), 7.5 (4H, m) aliphatic (C-H), 2.0 (4H, m), 1.0 (12H, m), 0.8 (6H, m), 0.6 (4H, m). FT-IR (NaCl, cm⁻¹): 3047 (aromatic C-H), 2846 (aliphatic CH₂), 1750 (C=O).

Synthesis of 2,7-Bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene (Monomer 3). After stirring of 14.1 g (27.6 mmol) of 4-bromobenzyl phosphonium salt, 1.56 g (64.4 mmol) of NaH and 80 mL of toluene, 5 g (9.2 mmol) of 2,7-dibenzoyl-9,9-dihexylfluorene was added in the mixture. After stirring for 35 h, the reaction was terminated with 80 mL of 2 N-HCl. The crude product was recrystallized in hexane. Mp: 158 °C, Yield: 38%. ¹H-NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.7-6.8 (26H, m), 7.6 (2H, m), 7.5 (4H, m) aliphatic (C-H), 1.8 (4H, m), 1.0 (12H, m), 0.8 (6H, m), 0.6 (4H, m). FT-IR (NaCl, cm⁻¹): 3040 (aromatic C-H), 2950 (aliphatic CH₂), 1065 (C-Br). Anal. Calcd for C₃₃H₅₂Br₂: C, 75.93; H, 6.18. Found: C, 75.92; H, 6.16. (M⁺ = 848).

Preparation of 1-Methoxy-[4-(2'-ethylhexyl)oxy]benzene diboronic acid (Monomer 2). 2,5-Dibromo-1-methoxy-[4-(2'-ethylhexyl)oxy]benzene (40.0 g, 0.10 mol) obtained by literature method³ was added drop-wise to magnesium powders (7.4 g, 0.30 mol) in boiling THF (250 mL). After the reaction mixture was refluxed for 2 h, the reaction mixture was cooled to -70 °C using liquid nitrogen. Then, the undiluted trimethylborate (42.0 g, 0.40 mol) was added and stirred for 12 h at room temperature. After 2 M H₂SO₄ aqueous solution was added, the organic layer was extracted with ether, washed with water, dried over MgSO₄ and filtered. The solvent was evaporated and crude product was recrystallized in hexane to give product of white crystal. (Yield = 20%). ¹H-NMR (CDCl₃, 500 MHz (ppm): aromatic (C-H), 7.1 (2H, s), -OCH₂- and -OCH₃ 3.8 (5H, m), aliphatic (C-H) 1.8-0.9 (15H, m). FT-IR (KBr, cm⁻¹): 3500-3150 (O-H), 2846 (aliphatic CH₂), 1200 (C-O-C).

Preparation of Bis-(4'-bromobenzoyl) hydrazide. To the mixture of hydrazine monohydrate (2.28 g, 45.5 mmol) and 20 mL of triethylamine, 4-bromobenzoyl chloride (20 g, 91 mmol) was slowly dropped. After refluxing for 6 h, the solvent was evaporated. And then, the product was washed with methanol and water. (Yield = 71%). FT-IR (KBr, cm⁻¹): 3250 (N-H), 3020 (aromatic C-H), 1600 (amide C=O).

Preparation of 2,5-Bis(4',4''-dibromophenyl)-1,3,4-oxadiazole (Monomer 1). Thionyl chloride (45 g, 0.38 mol) and 130 mL of toluene were added in the bis-(4'-bromobenzoyl) hydrazide (30 g, 94.3 mmol). After the mixture was refluxed for 24 h, the solvent was evaporated. The product was washed with methanol. (Yield = 95%). ¹H-NMR (CDCl₃,

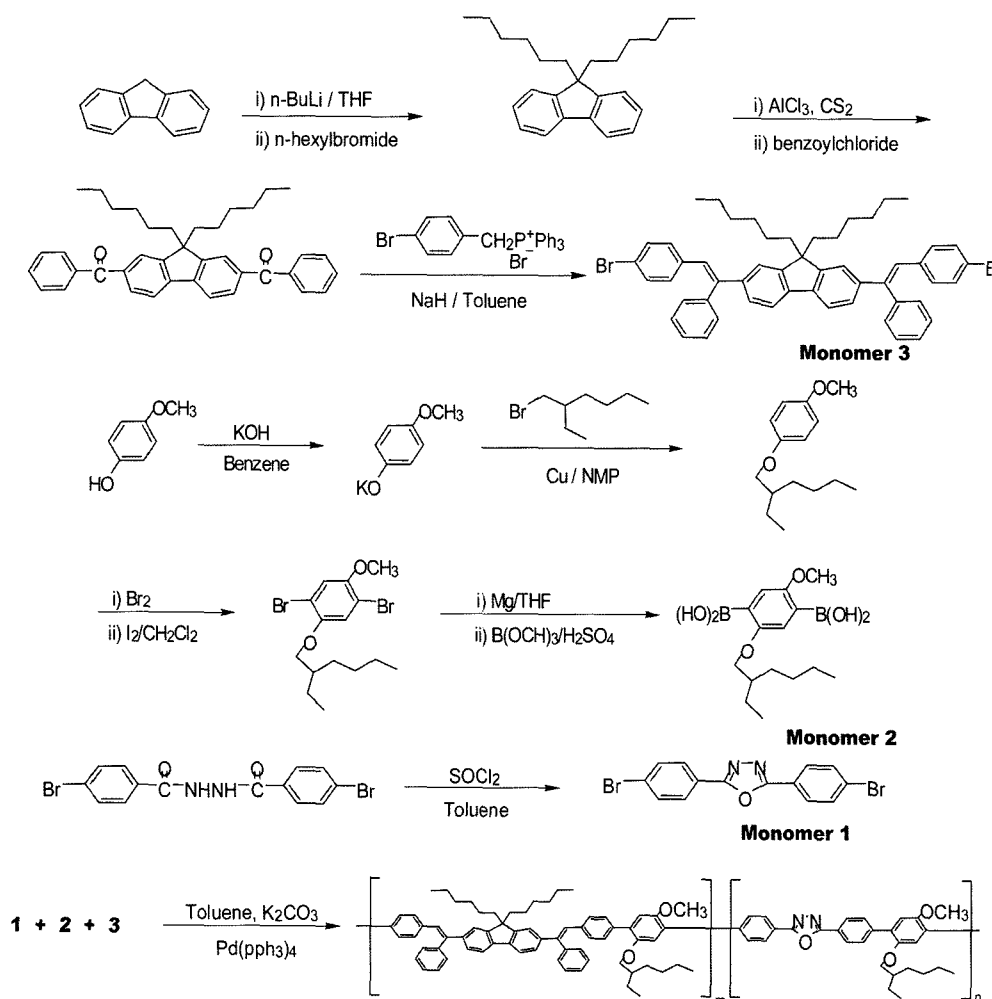
500 MHz (ppm): aromatic (C-H) 8.0 (4H, d), 7.7(4H, d), FT-IR (KBr, cm⁻¹): 3050 (C-H), 1530 (C=N-), 1025 (=C-O-C=), Anal. Calcd for C₁₄H₈Br₂N₂O: C, 44.25; H, 2.12. Found: C, 44.23; H, 2.11. (M⁺: 379)

Polymerization. All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1-methoxy[4-(2'-ethylhexyl)oxy]benzene diboronic acid (0.2 g, 0.59 mmol), 2,7-bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene (0.3 g, 0.4 mmol) and 2,5-bis(4',4''-dibromophenyl)-1,3,4-oxadiazole (0.3 g, 0.8 mmol) in 10 mL of THF and 1.1 mL of 2 M K₂CO₃ solution in water was added catalysts, Pd(PPh₃)₄ (17 mg, 1.5 mol%). The reaction mixture was refluxed under nitrogen atmosphere for 24 h. Bromobenzene (0.05 g, 0.318 mmol) was added with small amounts of catalysts for end-capping. After refluxing for 3 h, the reaction mixture was poured into methanol (50 mL) and filtered with glass filter. The residue was dissolved in CHCl₃ and washed with waters. After being dried over MgSO₄, precipitation was twice repeated with chloroform/methanol. (Yield = 60%).

Instrument. Melting points were determined using an Electrothermal Mode 1307 digital analyzer. ¹H-NMR and ¹³C-NMR spectral data were expressed in ppm relative to the internal standard and were measured on a DRX 500 MHz NMR spectrometer. FT-IR spectra were recorded with a Bomem Michelson series FT-IR spectrometer and the UV-visible absorption spectra were recorded in chloroform on a Shimadzu UV-3100 spectrophotometer. Molecular weight and polydispersity index of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly Model M590 pump, μ -styrngel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analyses were performed by Leco Co. CHNS-932. TGA measurements were performed on a Perkin-Elmer Series 7 analysis system under N₂ at a heating rate of 10 °C/min. Cyclic voltammetry measurements of the polymer films were performed on a BAS 100 B/W electrochemical analyzer in acetonitrile with 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) as the supporting electrolyte at a scan rate of 100 mV/s. The potentials were measured against an Ag/AgCl reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

Results and Discussion

The synthetic route of monomer and polymer is sketched in Scheme I. Monomer 1, 2,5-bis(4',4''-dibromophenyl)-1,3,4-oxadiazole is synthesized from thionyl chloride and



Scheme I. Synthesis of monomers and polymer.

bis-(4'-bromobenzoyl) hydrazide obtained by 4-bromobenzoyl chloride and hydrazine. Monomers 2 and 3, 1-methoxy-[4-(2'-ethylhexyl)oxy]benzene diboronic acid and 2,7-bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene are prepared according to the literature method.³ The Suzuki coupling reaction was employed for the polymerization between monomers 1, 2, and 3. The polymerization was proceeded for 24 h in toluene, followed by end capping with bromobenzene for 2 h. The polymer was isolated by pouring the reaction mixture into methanol. The crude polymer was washed with methanol, water, and methanol again, successively. The polymer was obtained as pale yellow powders after being dried under vacuum at room temperature.

The polymer was completely soluble in common organic solvent such as chlorobenzene and chloroform. Uniform and pinhole-free film can be prepared by spin casting from the chlorobenzene solution.

The molecular structure of polymer was confirmed by ^1H - and ^{13}C -NMR and IR (Figure 1). In the ^1H -NMR, the protons of oxadiazole unit are assigned at 8.2 and 7.8 ppm, the

alkoxy protons are assigned at 3.8 ppm, and the methylene protons of dihexyl attached fluorene are assigned at 1.85 ppm, respectively. From these results, it is estimated that the composition of monomer 1 : monomer 2 : monomer 3 is 1 : 1.8 : 0.4, respectively.

The molecular weight of polymer was measured by gel permeation chromatography (GPC) with THF as eluent. M_n and M_w were reported to be 11,800 and 18,600, respectively, against polystyrene standards.

Thermogravimetric analysis (TGA) shows the excellent thermal stability of the polymer. The initial weight loss (5%) was observed at 400 °C, with the main decomposition occurring at 425 °C. Differential scanning calorimetry (DSC) exhibits glass transition at 120 °C in a nitrogen atmosphere at a heating rate of 10 °C/min (Figure 2).

The UV-vis spectrum of the polymer in chloroform solution exhibits an absorption maximum at 385 nm. The optical energy band gap (E_g) of the polymer estimated from the absorption onset was 2.87 eV. The maximum emission in the photoluminescence spectrum of the solution and a film

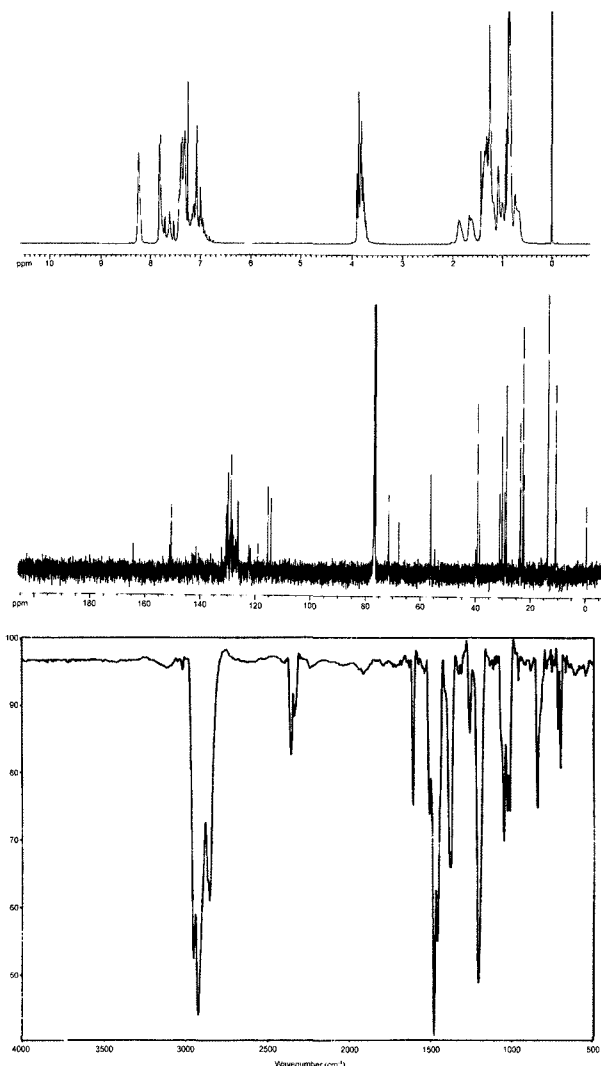


Figure 1. ¹H-NMR, ¹³C-NMR, and IR spectra of polymer.

of polymer was observed at 453 nm and 456 nm, respectively. The red shift relative to solution which is attributed to packing effects in the local geometry is very small. Moreover, the photoluminescence of film reduced long wavelength emission when it is compared with that of poly(9,9-di-*n*-hexyl-fluorene)¹⁷ (Figure 3). It may be due to decreased aggregation because of disorder into backbone and inhibited intermolecular interaction by introduced phenyl pendant and alkoxy substituents.

The oxidation onset potential was determined by cyclic voltammetry (CV) of the polymer film deposited on a platinum electrode at a scan rate 100 mVs⁻¹ in a 0.1 M solution of Bu₄NClO₄ in anhydrous acetonitrile. The onset potential for oxidation was observed at about 1.32 V. According to the equation, the HOMO of the polymer was estimated to be -5.72 eV. From the HOMO and optical band gap of the polymer, the LUMO of the polymer was calculated to be -2.85 eV. It has been reported that the values of the ioniza-

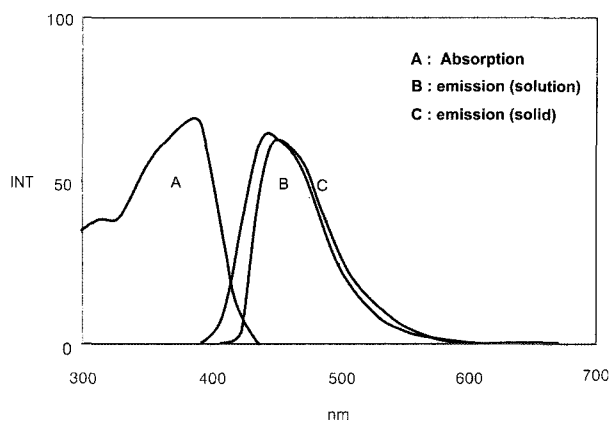


Figure 2. TGA and DSC thermograms of polymer.

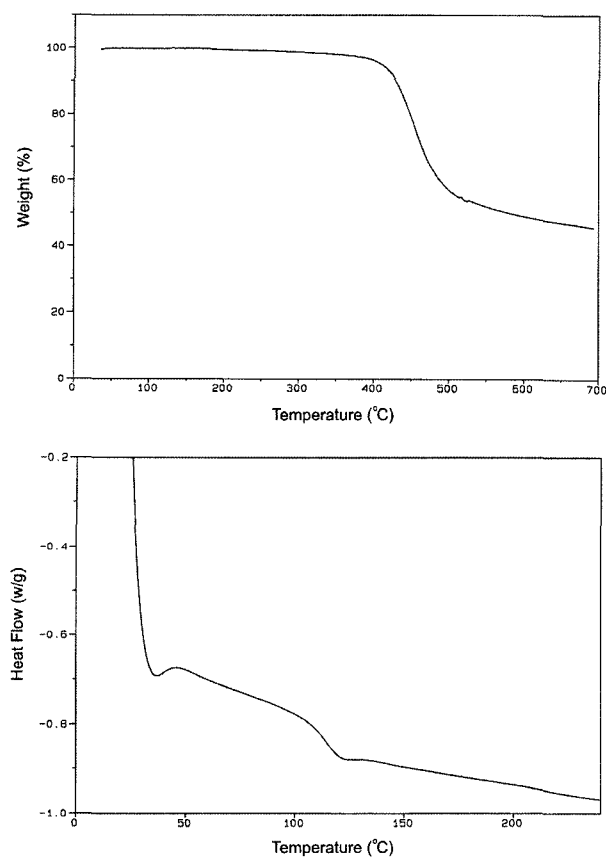


Figure 3. UV-vis and PL spectra of polymer in solution and solid.

tion potential (IP) and the electron affinity (EA) were IP = 5.80 eV and EA = 2.12 eV for poly[2,7-(9,9-dioctylfluorene)], and IP = 5.6 eV and EA = 2.8 eV for poly(fluorenylenevinylene terphenylenevinylene). From the results, it is supposed that the introduction of oxadiazole and alkoxy units allows the modulation of the ionization potential and electron affinity. This should be useful to enhance injection

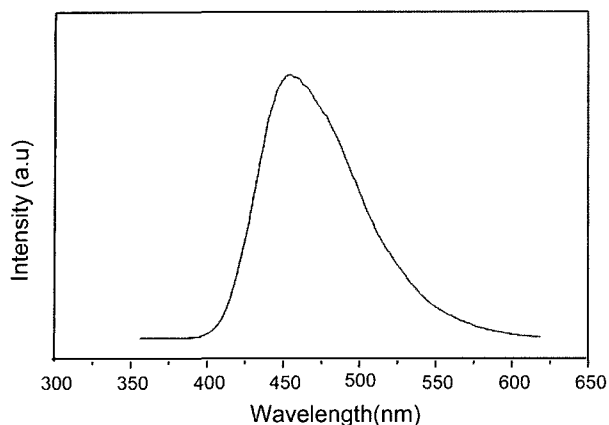


Figure 4. Current-voltage characteristic of ITO/PEDOT/polymer/Al device.

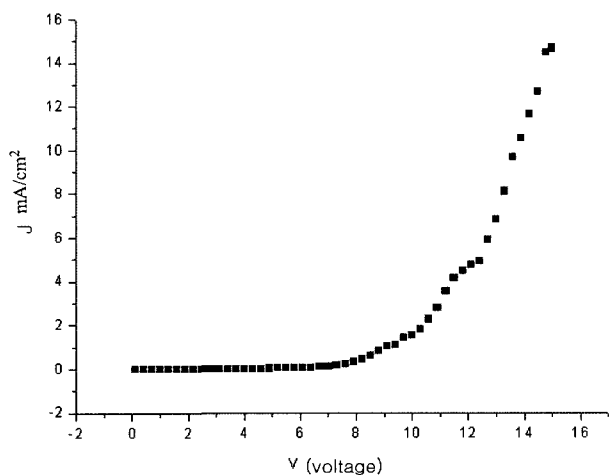


Figure 5. The electroluminescence spectrum of ITO/PEDOT/polymer/Al device.

of holes and electron from anode and cathode, respectively, in light emitting diodes.

Double-layer devices with the configuration as ITO/poly(3,4-ethylenedioxy thiophene) (PEDOT) : poly(styrene sulfonic acid) (PSS)/the obtained polymer/Al were fabricated. Figure 4 represents typical current-voltage measurements in a device. Current arises at 8 V. The device emitted blue light at 460 nm (Figure 5). The electroluminescent spectrum was similar to the PL spectrum of polymer without long wavelength emission due to reduced intermolecular interaction. Further research into optimization of device for enhanced blue light emission is currently underway.

Conclusions

To modulate the ionization potential (IP) and electron affinity (EA) of polyfluorene derivative, the copolymer containing 2-ethylhexyloxy-5-methoxy-1,4-phenylene as elec-

tron donating group and 2,5-diphenyl-oxadiazole as electron withdrawing group was designed and synthesized. The composition of copolymer was characterized by $^1\text{H-NMR}$ spectrum. The obtained copolymer showed good thermal stability with high T_g of 120 °C. The blue emission was obtained in PL and EL spectrum without long wavelength emission due to excimer formation. The increase of ionization potential and decrease reduction potential by introducing of alkoxy and oxadiazole units will lead to a better injections of holes from anode and electrons from cathode, enhancing the performance of device.

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