



## Pure color and stable blue-light emission-alternating copolymer based on fluorene and dialkoxynaphthalene

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### ABSTRACT

A new blue-light emitting polymer that alternates between fluorene and alkoxy-naphthalene structure has been developed. The fluorene and naphthalene units were highly distorted with an angle of 76.22° according to theoretical calculations. The obtained polymer has a weight average molecular weight of 273,800 with a polydispersity index of 2.35, good solubility and high thermal stability with a  $T_g$  of 176 °C. The film photoluminescence (PL) spectrum (405 nm) is consistent with that of solution and the PL spectra of the polymer did not show any peak in the long wavelength region even after annealing for 24 h at 100 °C. The double-layered device with an ITO/PEDOT/polymer/LiF/Al structure has a turn-on voltage of about 5.4 V, maximum brightness of 110 cd/m<sup>2</sup> and an electroluminescent efficiency of 0.09 cd/A. The OLED generates pure blue EL emission ( $\lambda_{\max}$  = 405 nm) with excellent CIE coordinates ( $x$  = 0.15,  $y$  = 0.10) as well as stable blue EL emission that is not altered by voltage increase.

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### 1. Introduction

Organic semiconductors have a number of attractive features, including solution processability, band gap tuning by chemical structures, and self-organization, in terms of serving as a potential replacement for conventional inorganic semiconductors. The discovery of electroluminescence (EL) in a polymeric semiconductor has led to extensive research in this field, and considerable progress has been documented in several recent papers [1–5].

Electroluminescence from polymeric semiconductors can sweep the full range of the visible spectra. Amongst a variety of EL conjugated polymers, blue-light emission is deemed desirable since it is generally more difficult to fabricate such LEDs from inorganic semiconductors. Also, full-color exhibition and white-light devices require blue light. For blue emission, conjugated polymers should have a large band gap and defined optical properties [6–15].

There have been numerous attempts to synthesize polymers with a large band gap to emit blue color. In particular, poly(alkyl-fluorene)s (PFs) are considered by several researchers and industrial groups to be the most promising blue-light emitting material due to their chemical and thermal stabilities, high photoluminescence quantum efficiency and easy processability through

an introduction of solubilizing groups in the 9-position of the fluorene ring. A major drawback in obtaining blue EL from PFs is the long wavelength tails in the emission spectra. Long wavelength tails become more serious upon exposure to heat. This leads to problems of color purity and color stability of the light emitted from LEDs fabricated with PFs. On going efforts have focused on suppressing excimer formation and improve efficiency in PFs. Other approaches to addressing this problem include: the introduction of copolymerization with anthracene and carbazole; end-capping with sterically hindered groups; hole-trapping moieties; introducing sterically hindered substituent at the 9-position of fluorene; combining with cross-linked hole-transporting layers; and introducing spirobifluorene groups [16–21].

Recently, it was found that the introduction of a bulky naphthyl side chain can cause the polymers to impose even great steric hindrance. This leads to improved thermal stability with higher glass-transition temperatures while resulting in negligible structural defects due to the asymmetric structure [22–25].

In this study, we synthesized a new blue-light emitting polymer that alternates between a fluorene and alkoxy-naphthalene structure. Because of steric interaction between the hydrogen at the 3-position of fluorene and the hexyloxy group at the 3-position of naphthalene, rigid fluorene and naphthalene units are distorted with each other, and the main chain will be distorted such that it yields a stable blue emission. Furthermore, the introduced alkoxy-naphthalene unit inhibits intermolecular interaction, and provides an amorphous property, good solubility and easy hole injection due to the bulky hexyloxy group. Also, the rigid structure

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of naphthalene reduces the vibronic mode resulting in increased efficiency. Thus, it is expected this polymer will have high efficient and high color pure blue emission.

## 2. Experiment

### 2.1. General

$^1\text{H}$  NMR spectra data were expressed in parts per million relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrometer, and the UV–vis absorption spectra obtained in chloroform on a Shimadzu UV 3100 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model M590 pump  $\mu$ -styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analysis was performed by Leco Co. CHNS-932. TGA and DSC measurements were performed on a Perkin–Elmer series 7 analysis system under  $\text{N}_2$  at a heating rate  $10^\circ\text{C}/\text{min}$ . The photoluminescence spectra were recorded on a Perkin–Elmer LS-50 fluorometer utilizing a lock-in power meter (Newport 818-SL).

Cyclic voltammetry was carried out in a two-compartment cell with a model with platinum electrodes at a scan rate of  $10\text{ mV/s}$  against an  $\text{Ag}/\text{Ag}^+$  (0.1 M  $\text{AgNO}_3$  in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in acetonitrile.

Fabrication of the LED: poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indium-tin oxide coated glass substrate that had been washed with water, acetone, and isopropyl alcohol sequentially. A thin polymer film was spin coated (3000 rpm, 50 s) from a filtered (0.2 m filter) 1.0 wt% polymer solution in chlorobenzene on a PEDOT layer. An aluminium electrode was deposited on top of the device at a high vacuum (below  $1 \times 10^{-5}$  Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were carried out room temperature in air.

### 2.2. Materials

1,5-Dihydroxynaphthalene, bromine, triethyl borate, 4,4'-dibromobenzophenone,  $\text{K}_2\text{CO}_3$ , potassium *t*-butoxide, 1-bromohexane, and tetrakis(triphenylphosphine) palladium(0) were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) and diethyl ether were purified by distillation from sodium in the presence of benzophenone. Methylene chloride was purified by distillation after drying over calcium hydride ( $\text{CaH}_2$ ). Other chemicals were used unless otherwise specified.

### 2.3. Synthesis

#### 2.3.1. Synthesis of 2,6-dibromo-1,5-dihydroxynaphthalene

After dihydroxynaphthalene (20 g, 0.125 mol) was dissolved in acetic acid (550 mL), the catalytic amount of  $\text{I}_2$  was added and the flask was heated to  $80^\circ\text{C}$ . In the mixture,  $\text{Br}_2$  (40 g, 0.25 mol) dissolved in acetic acid was slowly dropped. The mixture was cooled to room temperature, and the crude solid product was filtered. The product was purified by petroleum ether (57%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) [ppm]  $\delta$  6 (s, 2H), 7.5 (d, 2H), 7.7 (d, 2H) FT-IR (KBr,  $\text{cm}^{-1}$ ): 3400 (O–H str), 3050 (aromatic C–H str), 2950 (aliphatic C–H str), 1180 (aromatic C–Br str).

#### 2.3.2. Synthesis of 2,6-dibromo-1,5-dihexyloxynaphthalene

1-Bromohexane (10.38 g, 63 mmol), NaI (0.94 g, 63 mmol), KOH (5 g, 15.7 mmol) was dissolved in ethanol. After the mixture was refluxed for 48 h, ethanol was evaporated. The mixture was extracted with ethyl acetate, and washed with 10% aqueous NaOH and water. The crude product was separated by column chromatography with hexane as eluent (25%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) [ppm]  $\delta$  7.75 (m, 2H), 7.64 (m, 2H), 4.09 (s, 4H), 1.8 (m, 4H), 1.6 (m, 4H), 1.4 (m, 8H), 1.2 (m, 6H) FT-IR (KBr,  $\text{cm}^{-1}$ ): 2950 (aliphatic C–H str), 3050 (aromatic C–H str), 1180 (aromatic C–Br str).

#### 2.3.3. Synthesis of 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene

The synthesis was followed by literature method [5].  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) [ppm]  $\delta$  7.8–7.7 (m, 6H), 4.43 (s, 8H), 2.0 (m, 4H), 1.2 (m, 12H), 0.75 (t, 6H), 0.58 (br s, 4H), FT-IR (KBr,  $\text{cm}^{-1}$ ): 3053 (aromatic C–H str), 2964 (aliphatic C–H str), 1453 (B–O str).

### 2.4. Polymer synthesis

The polymer was prepared from palladium catalyzed Suzuki coupling reaction.

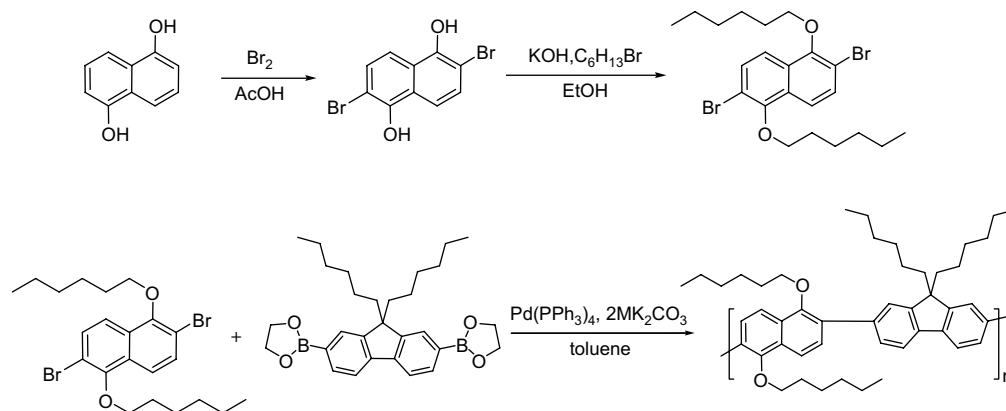
All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene (1.786 mmol), 2,6-dibromo-1,5-dihexyloxynaphthalene (1.786 mmol) in 10 mL THF and 4 mL 2 M  $\text{K}_2\text{CO}_3$  solution in water was added catalysts,  $\text{Pd}(\text{PPh}_3)_4$  (8.4 mg, 0.6 mol%). The reaction mixture was heated at  $80^\circ\text{C}$  under nitrogen atmosphere for 8 h. Bromobenzene (0.05 g, 0.318 mmol) was added and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end capping. After 2 h, the reaction mixture was poured into methanol (50 mL) and filtered with glass filter. The residue was dissolved in  $\text{CHCl}_3$  and washed with water. After being dried over  $\text{MgSO}_4$ , precipitation was twice repeated with chloroform/methanol. Yield = 65%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) [ppm]  $\delta$  8.2 (m, 2H), 7.9 (m, 2H), 7.8–7.5 (m, 6H), 3.8 (s, 4H), 2.1 (s, 4H), 1.8 (m, 8H), 1.6–1.2 (m, 28H), 1.0–0.8 (m, 12H) FT-IR (KBr,  $\text{cm}^{-1}$ ): 3050 (aromatic C–H str), 2950 (aliphatic C–H str) Anal. Calcd for  $\text{C}_{47}\text{H}_{62}\text{O}_2$ : C, 85.71; H, 9.42. Found: C, 85.66; H, 9.31.

## 3. Results and discussion

2,6-Dibromo-1,5-dihexyloxynaphthalene was synthesized with 2,6-dibromo-1,5-dioxynaphthalene prepared by the bromination of 1,5-dihydroxynaphthalene, described in Scheme 1.

The polymerization was carried out by the palladium catalyzed Suzuki coupling reaction with 2,6-dibromo-1,5-dihexyloxynaphthalene and 9,9-dihexyl-2,7-di(1',2'-ethylborate) fluorene. The structure of the polymer was confirmed by  $^1\text{H}$  NMR, IR and elemental analyses. Fig. 1 shows the  $^1\text{H}$  NMR and IR spectra of polymer. The polymer composition can be estimated by the integration area of the peaks from the  $^1\text{H}$  NMR. The peak at 3.8 ppm is attributed to the protons connected to oxygen in the naphthalene unit. The peak at 2.1 ppm is attributed to the protons adjacent to the ninth position of fluorene. The structures of both model compounds of obtained polymer and reported polymer with fluorene unit and phenylene were compared. Theoretical calculations were carried out for the characterization of 3-dimensional structures using PM3 parameterization in the HyperChem 5.0 program (Hypercube), in order to fully optimize the molecular structures [26].

The twisted angle of model compound of obtained polymer is  $76.2^\circ$  while that of the model compound of the poly(fluorene-phenylene) derivative is  $52.52^\circ$ . The distorted structure is attributed to the steric interaction between the hydrogen at the 3-position of fluorene and the hexyloxy group at the 3-position of naphthalene.



**Scheme 1.** Synthetic scheme of monomer and polymer.

The molecular weight of the polymer was determined by gel permeation chromatography (GPC) using polystyrene as a standard and THF as an eluent. The polymer has an average molecular weight ( $M_w$ ) of 273,800 with a polydispersity index of 2.35. The resulting polymer possesses excellent thermal stability. The polymer displays a glass-transition temperature ( $T_g$ ) at 176 °C and an onset thermal decomposition temperature ( $T_d$ ) above 330 °C. (Fig. 2) The polymer was readily soluble in common organic solvents including chloroform, THF, toluene, chlorobenzene, etc. Transparent, uniform, and pin-free thin film on a variety of substrates can be obtained by spin coating polymer solution in chloroform or toluene.

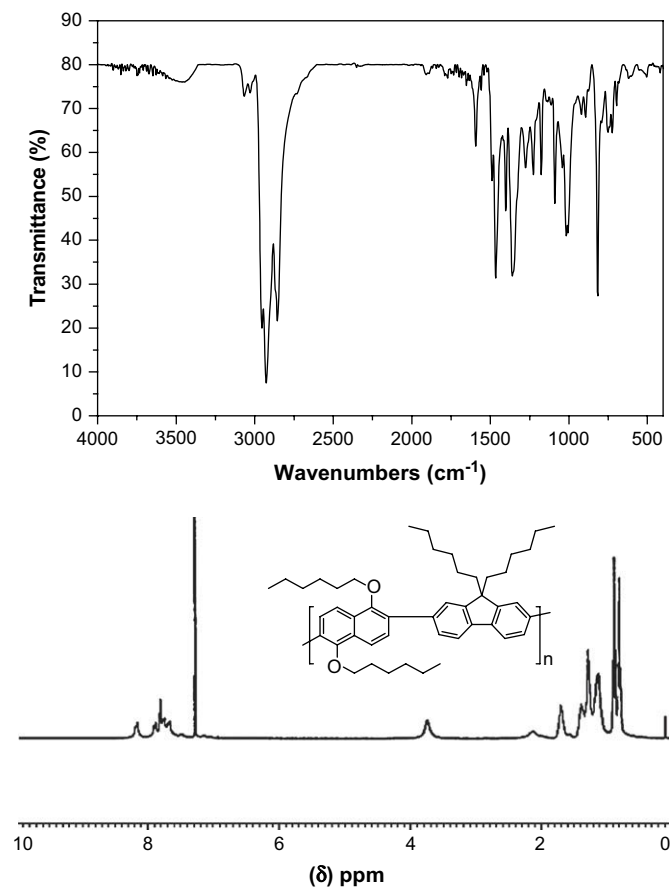
Fig. 3 shows the optical absorption and photoluminescence spectra of the polymer in both solution and solid. The polymer in a chloroform solution exhibited a maximum absorption at 366 nm due to the  $\Pi \rightarrow \Pi^*$  transition of the conjugated polymer backbone with a shoulder at 285 nm, which is a characteristic peak of the naphthalene unit. The absorption of the thin film also shows its maximum rate at 366 nm with the absorption edge at 400 nm. The maximum absorption peak of the polymer is 20 nm blue shifted compared with poly(9,9-dihexylfluorene), indicating that the introduced naphthalene unit has a distorted polymer backbone.

Under excitation of 365 nm, bright blue fluorescence was observed both in solution and film. The PL spectrum of the film was fairly consistent with that of the dilute solution with a maximum emission peak of 405 nm, indicating that the intermolecular interaction is inhibited due to the distorted backbone. The maximum emission peak of the polymer was also consistent with that of poly(fluorene) except for the long wavelength emission due to the intermolecular interaction of poly(fluorene). The maximum emission peak of the polymer is 40 nm blue shifted compared with those of poly(1,4-phenylene)-2,7-(9,9-dioctylfluorene) and poly[(4,4'-biphenylene)-2,7-(9,9-dioctylfluorene)] [23]. This result can also be explained by the distorted structure of obtained polymer as shown in theoretical calculation of model compounds. From the optical absorption threshold, the optical band gap is calculated to 3.15 eV.

The high steric effect can interfere with the self-quenching process, and a polymer with a high PL quantum efficiency ( $60 \pm 10\%$  using a dilute quinine sulfate solution as a standard) can be obtained [7].

Cyclic voltammetry was performed on a film of polymer deposited on a carbon electrode measured in  $\text{AgNO}_3$  (0.01 M)/ $\text{Bu}_4\text{NBF}_4$  (0.1 M)/acetonitrile with a platinum counter electrode and silver reference electrode, calibrated against ferrocene. The oxidation peak potentials of poly(9,9-dihexylfluorene) and the obtained polymer were measured to be similarly  $E_{\text{ox}} = 1.3$  V and 1.36 V, respectively. This result indicates that while the introduction of 1,5-dihexyloxynaphthalene does not affect the oxidation potential and the maximum emission wavelength of poly(fluorene), it affects the intermolecular interaction, reducing the excimer formation derived from intermolecular interaction and heightening color purity. It may also be explained by the distorted structure resulted from the steric interaction between the introduced rigid hexyloxynaphthalene unit and fluorene unit, as expected in the theoretical calculation.

The PL spectra of the polymer before and after thermal annealing are studied at 100 °C in air for several hours. The PL spectra of the polymer did not show any peak in the long wavelength region due to keto defect sites or aggregates/excimers even after annealing for 24 h at 100 °C in air.



**Fig. 1.**  $^1\text{H}$  NMR and IR spectra of polymer.

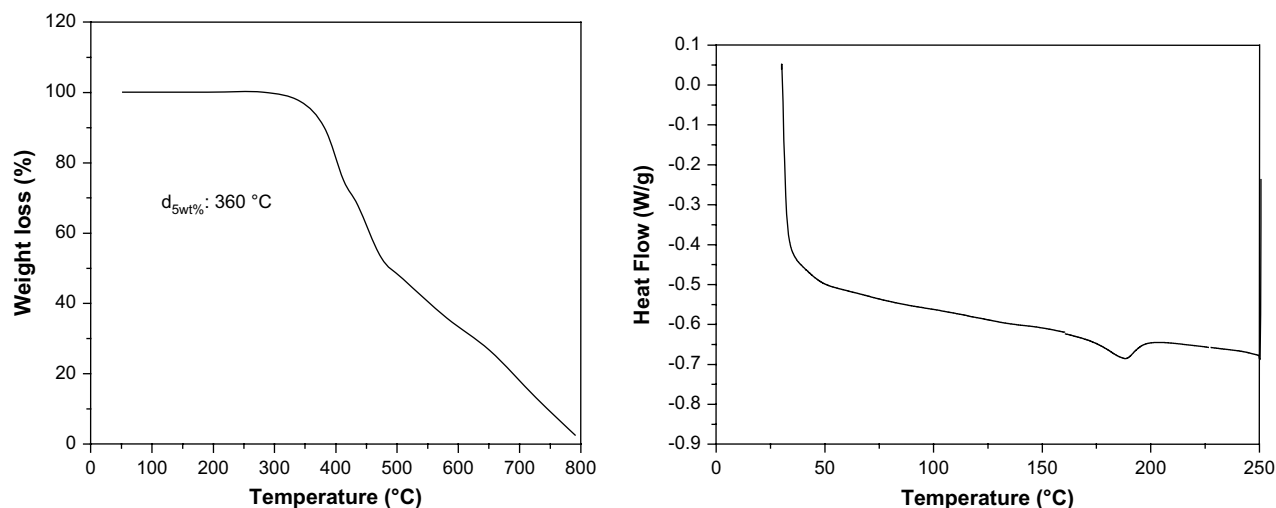


Fig. 2. TGA and DSC of polymer.

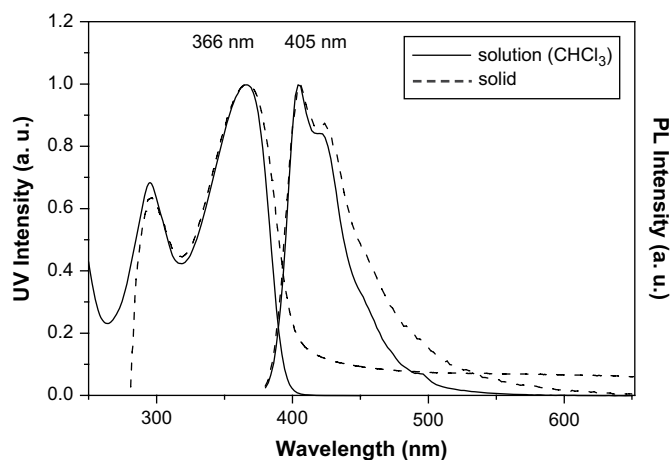


Fig. 3. The optical absorption and photoluminescence spectra of polymer in both solution and solid.

In general, an amorphous polymer has higher external quantum efficiency than a semi-crystalline polymer, because of the low refractive index of the amorphous polymer.

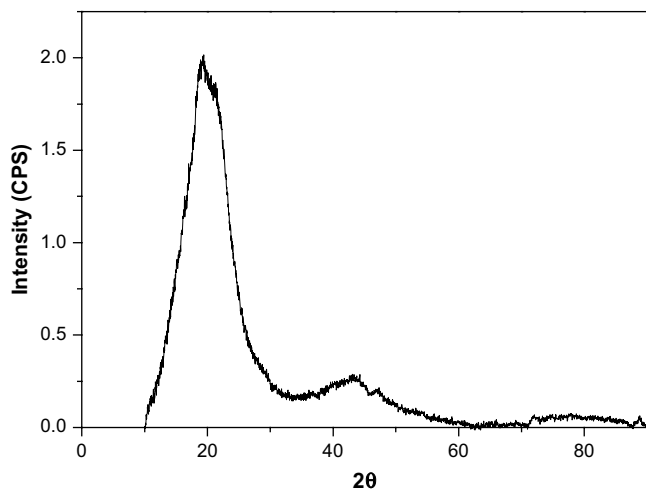


Fig. 4. X-ray diffraction of polymer.

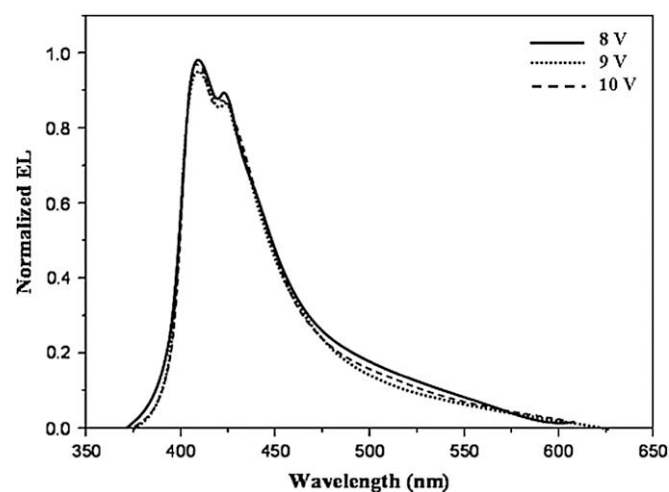


Fig. 5. Electroluminescence spectrum of polymer.

The ratio of the half-height width to diffraction angle ( $\Delta 2\theta/2\theta$ ) of X-ray for the polymer is higher than 0.5. (Fig. 4) The value of a resulting polymer was similar with the value of a typical amorphous polymer [27].

A double-layered PLED with a configuration of ITO/PEDOT/polymer/LiF/Al was fabricated to investigate the EL properties of the polymer. The double-layered device has a turn-on voltage at about 5.4 V. Bright pure blue electroluminescence was observed, and the maximum brightness of 110 cd/m<sup>2</sup> and electroluminescent efficiency of 0.09 cd/A were obtained.

Fig. 5 shows the electroluminescence spectrum, where the maximum emission is located at about 405 nm, indicating a deep pure blue-light emission. Also, the EL spectrum of the polymer is consistent with PL the spectrum regardless of any voltage increase. Based on the EL spectrum, the CIE (Commission Internationale de l'Éclairage) chromaticity coordinates were calculated to be ( $x=0.15$ ,  $y=0.10$ ), which is a high color pure blue emission relative to the reported blue-light emitting polymers. In order to achieve a higher EL performance, optimization of the device structure will be necessary.

#### 4. Conclusion

We have synthesized a novel blue-light emitting polymer, which is composed of fluorene and alkoxy naphthalene, by a Suzuki

coupling reaction. The introduction of 1,5-dialkoxynaphthalene for copolymerization with fluorene does not affect the oxidation potential or maximum emission wavelength of poly(fluorene), but it induces the distorted structure and suppresses intermolecular interaction. As a result, the film PL emission was consistent with that of the solution. Furthermore, the film PL emission did not show any peak in the long wavelength region which is due to the keto defect sites or aggregates/excimers despite annealing for 24 h at 100 °C in air. The OLED with the configuration of ITO/PEDOT:PSS/polymer/Al generates stable blue EL emission with excellent CIE coordinates that are not altered by increased voltage.

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