

Synthesis and electroluminescence properties of carbazole-containing 2,6-naphthalene-based conjugated polymers

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ABSTRACT: Three types of carbazole containing 1,5-disubstituted poly(2,6-naphthalene) derivatives, i. e., 2,6-naphthalene homopolymer that has a carbazolyl side chain at 1,5-positions, random copolymers and alternating copolymers consisting of 1,5-dialkoxynaphthalene-2,6-diyl and *N*-phenylcarbazole-2,7-diyl were newly synthesized by Ni-mediated Yamamoto polycondensation and Pd-catalyzed Suzuki coupling reaction. The number-average molecular weights (M_n) of the polymers and their polydispersity indices (M_w/M_n) were $5.4\text{--}8.2 \times 10^3$ and 1.4–1.7, respectively. These polymers exhibited blue photoluminescence in the film states and high fluorescence quantum efficiencies in CHCl_3 ($\phi_f = 0.70\text{--}1.00$). The electroluminescence properties of these polymers were investigated by fabricating a PLED device that has a configuration of ITO/PEDOT(PSS)/polymer/CsF/Al. The device fabricated with the random copolymer exhibited highest performances showing a maximum brightness of 8370 cd/m^2 at 13 V and a maximum efficiency of 2.16 cd/A at 7 V.

Introduction

Low molecular naphthalenes have remarkable inherent properties such as intense fluorescence, strong π -stacking, and good chemical stabilities. With these properties, considerable naphthalene derivatives have been investigated and used as fluorophores of luminescent materials,[1-5] organic semiconductors,[6-11] and a variety of mesogenic cores of liquid crystals.[12-14] In addition to the studies based on small molecular naphthalenes, a variety of polynaphthalenes has been developed and investigated for each purpose. M. Sato et al. have synthesized for the first time polynaphthalenes that have different linkages of 1,4-, 1,5-, 2,6-, and 2,7-positions as conducting polymers.[15] Poly(binaphthyl) derivatives have been synthesized as chiral materials by Habaue et al.[16, 17] Naphthalene containing polymers have also been attracted attention as luminescent materials, and in 1997, M. Hohloch et al. first reported the synthesis and electroluminescence (EL) properties of poly(2,6-naphthylenevinylene) derivatives, which showed a yellow-green emission with a maximum brightness of 70 cd/m². [18] Since then, several poly(2,6-naphthylenevinylene) derivatives have been synthesized to be applied in the PLED and photovoltaic devices.[19-21] Recently, J. Pina et al. have reported the spectral and photophysical studies of poly[(2,6-(1,5-dioctynaphthalene))thiophenes] to improve luminescent properties of polythiophene backbone by incorporating the 2,6-naphthalene moiety.[22] Curiously, in spite of extensive studies in regard to naphthalene containing polymers, there were few reports on conjugated polynaphthalenes. Therefore, we have recently investigated the synthesis and optical properties of a variety of polynaphthalene homopolymers and copolymers.[23] They exhibited notable optical properties that are dependent on the linkage positions of the naphthalene moiety. Among these polymers, the 2,6-linked poly(1,5-dialkoxynaphthalene)s showed the higher fluorescence quantum yields ($\phi_f > 0.7$) and better polymerization yields compared to polynaphthalenes with other linkages. These advantages are attributed to effective extension of π -conjugation along the 2,6-linked polynaphthalene main chain and less steric hindrance around the 2,6-linkage positions.

Poly(1,5-dialkoxy-2,6-naphthalene)s that exhibit intense bluish luminescence are expected to be good emitters for blue PLEDs. Therefore, we preliminarily fabricated PLED devices that have a configuration

of ITO/PEDOT(PSS)/polymer/LiF/Ca/Al using poly(1,5-dialkoxy-2,6-naphthalene) homopolymers and alternating copolymers with phenylene as the emitting layer material. However, their EL performances were very poor, i. e., the maximum luminances were around 100 cd/m² even at high operating voltages and the EL efficiencies were very low (0.03-0.05 cd/A). This poor result might be due to a large barrier of carrier injection from ITO/PEDOT(PSS) (-5.20 eV) to polynaphthalenes (-5.6 eV).[23, 24] In addition to the problem of the carrier injection, appropriate carrier mobility in the emitting layer is required for efficient EL. To achieve a good hole injection and mobility, we designed new poly(2,6-naphthalene) derivatives that contain carbazole moieties. Carbazole-based polymers such as poly(*N*-phenylcarbazole-2,7-ylene)s have somewhat higher HOMO levels (ca. -5.5 eV)[25] than those of polynaphthalenes, while poly(vinylcarbazole) (PVK) has been known as a hole transporting material[26] regardless of the low HOMO level (-5.8 eV). Therefore, we adopt two strategies to improve performance of poly(2,6-naphthalene) derivatives for PLEDs. One is introduction of carbazole side chains into 1,5-positions of the naphthalene moiety of the poly(2,6-naphthalene) homopolymer, the other is random or alternating copolymerization of 1,5-dihexyloxynaphthalene-2,6-diyl and *N*-phenylcarbazole-2,7-diyl. In this paper, we report the synthesis of above-mentioned polymers, their optical properties, and EL performance of PLEDs.

Experimental

Materials

Bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from Kanto Chemical Co Inc., and were used under an argon atmosphere. 2,6-Dibromo-1,5-dihydroxynaphthalene (**1**) was synthesized from 1,5-dihydroxynaphthalene by the procedure in the literature.[27] *N*-(6-Bromohexyl)carbazole (**2**) was prepared according to a synthetic procedure of *N*-alkylcarbazoles with 1,6-dibromohexane.[28] 2,6-Dibromo-1,5-dihexyloxynaphthalene (**4**), *N*-phenyl-2,7-dibromocarbazole (**5a**) and *N*-(4-(2-ethylhexyloxy)phenyl)-2,7-dibromocarbazole (**5b**) were prepared according to literature procedures.[19, 29] Other reagents and solvents were purchased from

Kanto Chemical, Tokyo Chemical Industry, Aldrich and Nacalai Tesque Inc. *N,N*-Dimethylformamide (DMF), acetonitrile and tetrahydrofuran (THF) were used after purification by distillation using an appropriate drying reagent such as molecular sieves and Na, respectively, under argon. Other chemicals were used as received without further purification.

1,5-Bis[6-(carbazol-9-yl)hexyloxy]-2,6-dibromonaphthalene (3)

1,5-Bis[6-(carbazol-9-yl)hexyloxy]-2,6-dibromonaphthalene (**3**) was synthesized by the modified procedure reported in our previous work.[23] Under an argon atmosphere, a solution of 2,6-dibromo-1,5-dihydroxynaphthalene **1** (0.760 g, 2.39 mmol), KOH (0.530 g, 9.45 mmol) in EtOH (25 ml) was refluxed for 30 minutes. Afterwards, *N*-(6-bromohexyl)carbazole **2** (3.20 g, 9.69 mmol) was added to the solution, which was successively refluxed for 24 hours, cooled to room temperature, and dissolved in CH₂Cl₂. The organic layer was washed with NaOH aq, water and brine, and was dried over anhyd. Na₂SO₄. After removing the solvent, the resultant black residue was chromatographed on silica gel (CH₂Cl₂/hexane= 1:1) to afford a yellow solid, which was recrystallized from hexane/CH₂Cl₂ to obtain pure **3** (0.80 g, yield: 41 %). ¹H NMR (270 MHz, CDCl₃) δ= 1.55, 1.65 (m, 8H), 1.91 (m, 8H), 4.01 (t, *J* = 6.43, 4H), 4.35 (t, *J* = 7.25, 4H), 7.23 (m, 4H), 7.48 (m, 8H), 7.57 (d, *J* = 9.06, 2H), 7.65 (d, *J* = 9.06, 2H), 8.10 (d, *J* = 7.75, 4H). ¹³C NMR (270 MHz, CDCl₃) δ= 25.9, 27.2, 29.0, 30.1, 43.0, 74.2, 108.5, 113.7, 118.7, 119.2, 120.3, 122.7, 125.5, 129.9, 130.9, 140.3, 152.5. C₄₆H₄₄Br₂N₂O₂ (816.66): Calcd. C 67.65, H 5.43, Br 19.57, N 3.43, O 3.92; Found. C 68.64, H 5.69, Br 18.26, N 3.23.

***N*-phenyl-2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)carbazole (6a)**

Under an argon atmosphere, to a solution of *N*-phenyl-2,7-dibromocarbazole (**5a**) (0.150 g, 0.399 mmol), PdCl₂[1,1'-Bis(diphenylphosphino)ferrocene](II) (0.0195 g, 0.0239 mmol), KOAc (0.234 g, 2.39 mmol) in DMF (5 ml) was added bis(pinacolato)diborane (0.223 g, 0.878 mmol), which was refluxed for 24 hours. After cooling to room temperature, CH₂Cl₂ was added to the solution. The organic layer was washed with water and brine, and was dried over anhyd. Na₂SO₄. After evaporation, a black residue was obtained, which was purified by a silica gel chromatography (CH₂Cl₂/hexane= 2:1) to afford a white solid. The recrystallization of the solid from EtOH gave pure **6a**

(0.070 g, yield: 29 %). ^1H NMR (270 MHz, CDCl_3) δ = 1.33 (s, 24H), 7.60, 7.62, 7.65 (m, 5H), 7.74 (d, J = 7.74, 2H), 7.80 (s, 2H), 8.14 (d, J = 7.74, 2H). ^{13}C NMR (270 MHz, CDCl_3) δ = 24.9, 83.8, 116.1, 119.8, 125.4, 125.9, 127.4, 127.6, 129.9, 137.5, 140.9. $\text{C}_{30}\text{H}_{35}\text{BNO}_4$ (495.23): Calcd. C 72.76, H 7.21, N 2.83; Found. C 72.03, H 6.99, N 2.97.

***N*-[4-(2-Ehtyl-hexyloxy)phenyl]-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolate)carbazole (6b)**

A similar procedure to the synthesis of **6a** except for using *N*-[4-(2-ethylhexyloxy)phenyl]-2,7-diiodocarbazole as the starting material was carried out. After recrystallization from EtOH, a white solid of **6b** was obtained (0.090 g, Yield: 60 %). ^1H NMR (270 MHz, CDCl_3) δ = 0.98, 0.99 (m, 6H), 1.33 (s, 24H), 1.51, 1.55 (m, 8H), 1.78, 1.81 (m, 1H), 3.95 (d, 2H), 7.12 (d, J = 9.06, 2H), 7.39 (d, J = 9.06, 2H), 7.72 (d, J = 7.75, 2H), 7.74 (s, 2H), 8.13 (d, J = 7.75, 2H). ^{13}C NMR (270 MHz, CDCl_3) δ = 11.3, 14.2, 23.2, 24.0, 24.9, 29.2, 30.7, 39.6, 70.8, 83.7, 115.6, 116.1, 119.8, 125.2, 125.6, 128.9, 129.8, 141.4, 158.6. $\text{C}_{38}\text{H}_{51}\text{BNO}_5$ (623.44): Calcd. C 73.21, H 8.25, N 2.25; Found. C 72.44, H 7.82, N 2.30.

Poly[1,5-bis[6-(carbazol-9-yl)hexyloxy]-2,6-naphthalene] (P1)

Under an argon atmosphere, a solution of $\text{Ni}(\text{cod})_2$ (0.110g, 0.400 mmol), 2,2'-bipyridine (0.0700 g, 0.448 mmol) and 1,5-cyclooctadiene (0.100 g, 0.924 mmol) in DMF (1 ml) was heated to 80 °C for 30 minutes. The monomer **3** (0.150 g, 0.184 mmol) dissolved in THF (1 ml) under argon was added to the DMF solution. The reaction solution was heated at 80 °C for 2 days. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/ NH_3 aq and from methanol, respectively, to afford **P1** (0.10 g) as a light yellow solid (yield: 85 %). ^1H NMR (270 MHz, CDCl_3) δ = 0.98, 1.09 (br, 8H), 1.34, 1.52, 1.68, 1.79 (m, 8H), 3.56 (br, 4H), 3.99 (t, 4H), 7.02, 7.04, 7.07, 7.14, 7.29, 7.90, 7.97(m, aromatic-CH). ^{13}C NMR (270 MHz, CDCl_3) δ = 25.8, 26.8, 29.0, 30.1, 43.0, 73.5, 108.5, 114.6, 118.7, 120.2, 122.6, 125.5, 129.8, 140.2, 152.7. $(\text{C}_{46}\text{H}_{44}\text{N}_2\text{O}_2)_n$ (656.87) $_n$: Calcd. C 84.11, H 6.75, N 4.26, O 4.87; Found. C 83.04, H 6.75, N 4.08.

Poly[1,5-dihexyloxy-2,6-naphthalene-co-*N*-(4-hexyloxyphenyl)-2,7-carbazole] (P2)

Under an argon atmosphere, a solution of Ni(cod)₂ (0.133g, 0.485 mmol), 2,2'-bipyridine (0.0757 g, 0.485 mmol) and 1,5-cyclooctadiene (0.0524 g, 0.485 mmol) in DMF (1.4 ml) was heated to 80 °C for 30 minutes. The monomer **4** (0.100 g, 0.206 mmol) and **5a** (0.0182 g, 0.0364 mmol) dissolved in toluene (1.4 ml) under argon were added to the DMF solution. The reaction solution was kept heating at 80 °C for 3 days. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/NH₃ aq and from methanol, respectively, to afford **P2** as a light yellow solid (0.060 g, yield: 88 %). ¹H NMR (270 MHz, CDCl₃) δ = 0.78–1.60 (br, –CH₂–CH₃, 30H) 3.76, 4.16 (br, O–CH₂, 5H), 6.84–7.11, 7.51–8.26 (br, Ar–H, 7H). ¹³C NMR (270 MHz, CDCl₃) δ = 14.1, 22.7, 25.7, 25.8, 26.1, 29.4, 30.3, 31.7, 68.3, 73.9, 104.9, 110.6, 114.7, 115.6, 117.2, 117.8, 118.5, 119.9, 121.9, 126.6, 127.4, 127.7, 128.5, 128.9, 129.4, 129.6, 129.9, 130.7, 136.7, 142.0, 152.4, 152.8, 155.0, 158.4. (C_{25.6}H_{33.45}N_{0.15}O_{2.15})_n (377.69)_n: Calcd. C 81.43, H 8.93, N 0.56, O 9.11; Found. C 81.29, H 8.38 N 0.71.

Poly[1,5-dihexyloxy-2,6-naphthalene-co-N-[4-(2-ethylhexyloxy)phenyl]-2,7-carbazole] (P3)

P3 was similarly synthesized according to the synthetic procedure of **P2** except for using **5b** in the feed ratio of **4** : **5b** = 50 : 50, to afford a pale yellow solid (0.033 g) in 33 % yield. ¹H NMR (270 MHz, CDCl₃) δ = 0.70–1.88 (br, m, –CH₂–CH₃, 27H), 3.53, 3.88 (br, O–CH₂, 3H), 6.75, 7.07 (br, m, Ar–CH₂, 2H), 7.29–8.14 (m, Ar–CH₂, 10H). ¹³C NMR (270 MHz, CDCl₃) δ = 11.3, 14.2, 22.6, 22.7, 23.2, 24.0, 25.7, 26.1, 29.2, 29.4, 30.3, 30.7, 31.7, 39.6, 68.2, 70.8, 76.5, 108.6, 110.6, 114.5, 115.6, 117.8, 119.9, 120.3, 121.6, 122.0, 126.0, 126.3, 128.0, 128.6, 128.8, 129.7, 130.0, 131.0, 136.7, 140.2, 142.0, 142.3, 152.0, 152.4, 154.9, 158.6. (C₄₈H₅₇NO₃)_n (695.97)_n: Calcd. C 82.84, H 8.26, N 2.01, O 6.90; Found. C 82.60, H 7.94, N 2.67.

Poly(1,5-dihexyloxy-2,6-naphthalene-alt-N-phenyl-2,7-carbazole) (P4)

Under an argon atmosphere, a solution of **4** (0.0982 g, 0.202 mmol), **6a** (0.100 g, 0.202 mmol), and Pd(PPh₃)₄ (0.00233 g, 0.00202 mmol) in toluene (2 ml) was heated to 85 °C for 10 minutes, and then 2M K₂CO₃ aq (2 ml) was added to the reaction solution, which was reacted at 85 °C for 3 days. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from

methanol/HCl aq, reprecipitated from methanol/NH₃ aq and methanol, respectively, to afford a pale green solid of **P4** (0.110 g, yield: 95 %). ¹H NMR (270 MHz, CDCl₃) δ = 0.69–1.52 (br, m, –CH₂–CH₃, 22H) 3.54, 4.04 (br, m, O–CH₂, 4H), 7.18–8.20 (br, m, Ar–H, 15H). ¹³C NMR (270 MHz, CDCl₃) δ = 14.1, 22.6, 25.8, 30.4, 31.7, 73.9, 110.6, 117.8, 118.3, 120.0, 122.0, 122.2, 127.2, 127.5, 129.1, 129.7, 129.9, 130.5, 136.8, 137.5, 141.5, 152.4, 152.6. (C₄₀H₄₁NO₂)_n (567.77)_n: Calcd. C 84.62, H 7.28, N 2.47; Found. C 76.80, H 6.92, N 2.25.

Poly[1,5-dihexyloxy-2,6-naphthalene-*alt*-N-[4-(2-ethylhexyloxy)phenyl]-2,7-carbazole] (P5)

P5 was similarly synthesized according to the synthetic procedure of **P4** except for using **6b** as the monomer to obtain a pale yellow solid (0.065 g) in 73 % yield. ¹H NMR (270 MHz, CDCl₃) δ = 0.69–1.52 (br, m, –CH₂–CH₃, 22H) 3.54, 4.04 (br, m, O–CH₂, 4H), 7.18–8.20 (br, m, Ar–H, 15H). ¹³C NMR (270 MHz, CDCl₃) δ = 14.1, 14.2, 22.6, 22.8, 25.7, 25.8, 30.4, 31.7, 31.8, 73.9, 74.5, 110.6, 113.3, 117.8, 118.4, 120.0, 122.0, 122.1, 122.2, 122.3, 127.2, 127.5, 129.1, 129.7, 129.9, 130.9, 136.3, 136.8, 137.5, 141.5, 152.4, 152.6. (C₄₈H₅₇NO₃)_n (695.99)_n: Calcd. C 82.84, H 8.26, N 2.01; Found. C 79.77, H 7.95, N 1.84.

Characterization of materials

¹H NMR and ¹³C NMR spectra were measured with a JEOL EX-270 at 270 MHz in CDCl₃. Photoluminescence and UV-vis absorption spectra of materials in CHCl₃ and coating polymer films on a quartz glass plate were recorded on a U-3500 spectrophotometer (Hitachi) and a FP-750 spectrofluorometer (Jasco). The fluorescence quantum yields in CHCl₃ were estimated using 9,10-diphenylanthracene (ϕ_{fl} = 0.90) in cyclohexane as a standard. Average molecular weights (M_n and M_w) of the polymers were estimated by gel permeation chromatography (GPC) using polystyrene standards in THF. Thermal gravimetric analysis (TGA) was carried out by EXTAR 6000 TG/DTA (SII) at a heating rate of 10 °C/min under an argon atmosphere. Electrochemical measurements of the polymers were carried out by cyclic voltammetry with a polymer film coated on a Pt disc electrode (diameter: 5 mm) as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode

(SCE) as the reference electrode in acetonitrile (0.1 M Et₄NBF₄) at a scan rate of 50 mV/s under an argon atmosphere. Ionization potentials (vs vacuum) of the polymers were estimated from the onset of their oxidation in cyclic voltammograms on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level,[30] and the HOMO levels were basically followed by the equation: HOMO level= $E_{\text{onset}} + 4.4$.[31]

Fabrication of PLED

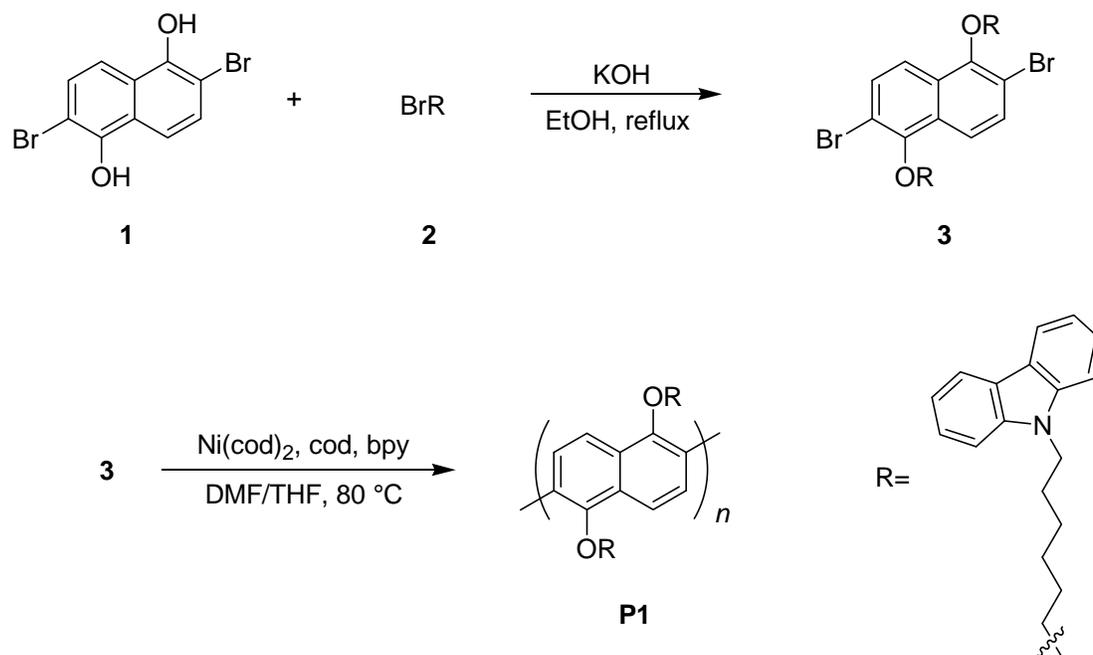
The EL devices were fabricated on a patterned indium tin oxide (ITO) coated (150 nm) glass substrate with a sheet resistance of 10.2–11.8 Ω/sq. The substrate was cleaned with a 10 % base solution (Clea 635N, Kanto Chemical Co Inc.) in an ultrasonic bath for 5 minutes, washed under running water for 5 minutes, dried using a spincoater, and irradiated with a UV light (NL-UV253, Filgen). On top of the substrate, an aqueous solution of poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (Baytron P VP AI 4083, H. C. Starck) was spin-coated in 90 nm thickness, then dried on a hot plate at 200 °C for 15 minutes. After cooling to room temperature, polymers in toluene (0.80–1.30 wt %) were spin-coated on the substrate. For the polymers which were difficulty in dissolving in toluene at the concentration, a small amount of 1,2-dichloroethane was added. After the spin-coating, the devices were dried under a pressure of 0.3 Torr at room temperature for 90 minutes. The emitting layers were obtained in 40–90 nm thickness. After that, CsF was vacuum-deposited in 2 nm thickness and finally Al was deposited in 150 nm thickness under $1.5\text{--}2.3 \times 10^{-6}$ Torr.

Results and discussion

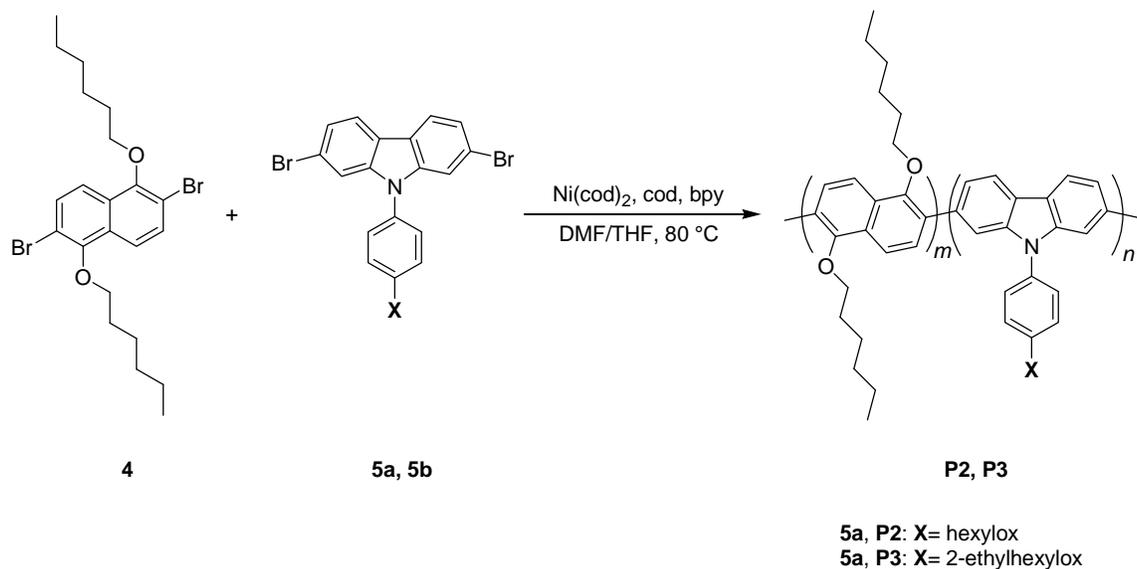
Synthesis and characterization of polymers

The synthetic routes of the polymers are shown in Schemes 1, 2 and 3. The polymerization results are summarized in Table 1. As shown in Scheme 1, the homopolymer (**P1**) was prepared from **3** by the Ni-mediated dehalogenative polycondensation.[32, 33] The number-average molecular weight (M_n) of **P1** was 5.4×10^3 , and the degree of polymerization (DP) was 8. The carbazole moiety in the side chain

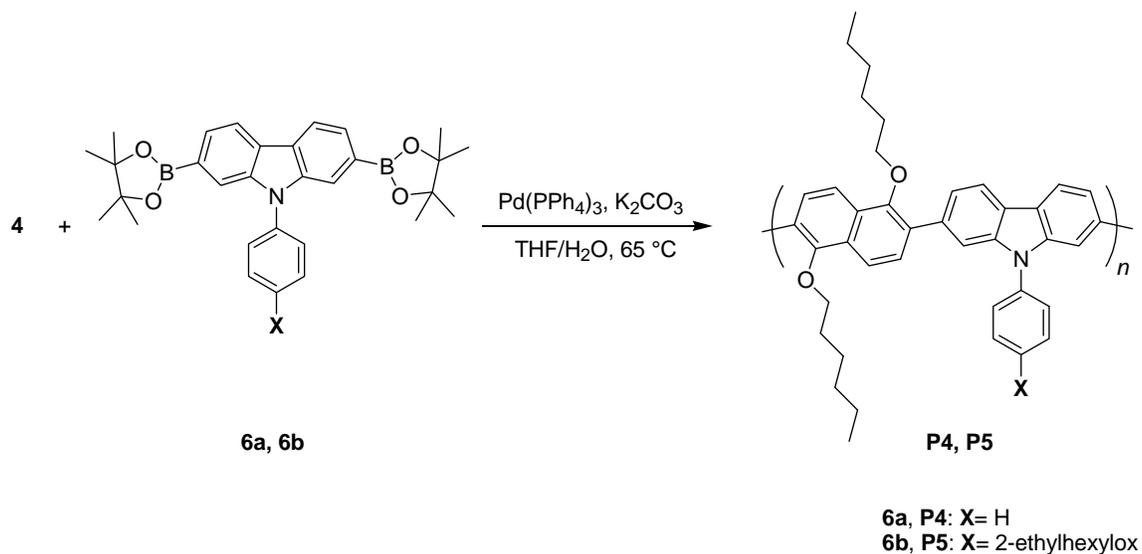
might decrease the solubility of the polymer, which resulted in the low M_n . Scheme 2 shows the synthetic route of the random copolymers **P2** and **P3**, which were prepared by the Ni-mediated polymerization using a mixture of monomers (2,6-dibromo-1,5-dihexyloxynaphthalene and 2,7-dihalogeno(*N*-phenyl)carbazole derivatives) in the molar ratio of 85:15 for **P2** and 50:50 for **P3**, respectively. Both polymers were soluble in common organic solvents such as THF, CHCl_3 , and DMF. The polymerization results indicated that **P2** had the higher molecular weight than **P3**. The composition ratios of the naphthalene and carbozaole units in **P2** and **P3** were estimated by elemental analysis and ^1H NMR. The composition ratios found for **P2** and **P3** were almost same to the feed ratios. Scheme 3 shows the synthetic route of the alternating copolymers (**P4** and **P5**) that are synthesized by the Pd-catalyzed Suzuki coupling reaction[34] using 2,6-dibromo-1,5-dihexyloxynaphthalene **4** and corresponding carbazole-2,7-diboronic acid ester. **P4** was poor soluble in organic solvents, which is due to having no alkyl side chains at the carbazole unit. On the other hand, **P5** having the 2-ethylhexyloxy side chain at the carbazole unit showed a good solubility. Figure 1 shows TGA curves of the polymers under an argon atmosphere. Temperatures at 5 wt % loss in TGA of **P1-P5** were 369, 365, 381, 365, and 366 °C, respectively, which suggest that these polymers have high thermal stability.



Scheme 1. Synthetic route of **P1**.



Scheme 2. Synthetic route of **P2** and **P3**.



Scheme 3. Synthetic route of **P4** and **P5**.

Table 1. Polymerization results.

Polymer	Yield (%)	$M_n (\times 10^3)^a$	$M_w (\times 10^3)^a$	T_d^b ($^\circ\text{C}$)	Ratio of naphthalene:carbazole	
P1	85	5.4	8.1	369	—	
P2	88	8.2	13.4	365	83 : 17 ^c	89 : 11 ^d
P3	33	5.9	8.3	381	32 : 68 ^c	48 : 52 ^d
P4	95	6.9	11.9	365	—	

^a Average molecular weights were determined by using polystyrene standards in THF.

^b Decomposition temperature (5% weight loss).

^c Estimated by elemental analysis.

^d Estimated by ¹H NMR.

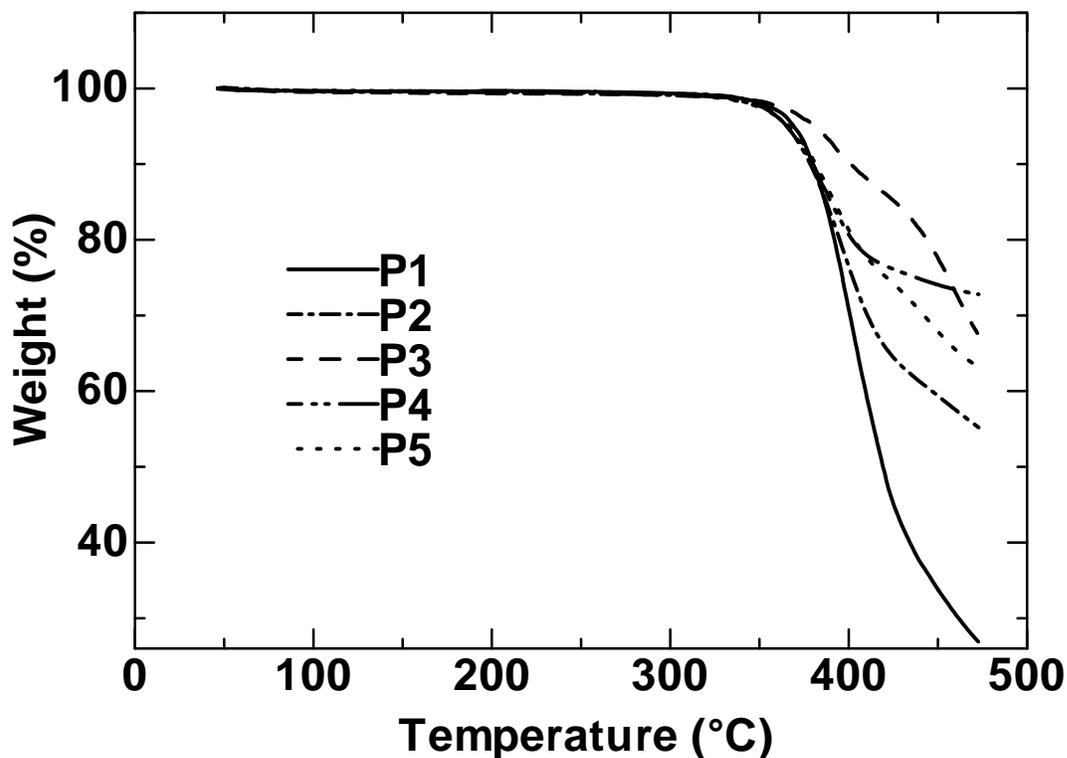


Figure 1. TGA curves of the polymers at a heating rate of $10^{\circ}\text{C min}^{-1}$ under Ar.

Absorption and photoluminescence properties

Figure 2 shows the absorption and photoluminescence (PL) spectra of **P1-P5** in CHCl_3 , and the spectral results are summarized in Table 2. All the polymers showed an absorption band around 300-380 nm, which is due to π - π^* transition of the conjugated main chain. In the previous papers, the absorption maxima (λ_{max}) of poly(2,6-naphthalene) and poly(*N*-phenylcarbazole-2,7-ylene) were found at around 330 nm and 380 nm, respectively,[23, 29] which means that the former has shorter π -

conjugation length than the latter. **P1** that is the homopolymer of the naphthalene unit showed the absorption λ_{\max} at about 330 nm with sharp and distinct absorption peaks at 333 and 341 nm. The two additional absorption bands are attributed to the carbazole portion in the side chains.[35] **P2** and **P3** that are the random copolymers of the naphthalene and carbazole units showed λ_{\max} at 349 and 373 nm, respectively. The presence of the carbazole unit in the polymer main chain contributes to increase the π -conjugation of the polymer. Similarly, **P4** and **P5** that are alternating copolymers of the naphthalene and carbazole units showed almost the same absorption λ_{\max} at about 365 nm. Consequently, **P3** showed the longest absorption λ_{\max} . The highest content of the carbazole portions might contribute the longest conjugation, otherwise the random copolymerization might have an advantage to take more coplanar conjugated sequences in the polymer.

Table 2. Absorption and photoluminescence spectral data of the polymers.

polymer	Abs. λ_{\max} (nm)		PL λ_{\max} (nm)		CIE (x, y) film	$\phi_{\text{fl}}^{\text{a}}$
	in CHCl ₃	film ^b	in CHCl ₃	film ^b		
P1	333, 341	334, 348	385	386, 461	0.15, 0.15	0.70
P2	349	350	390	407, 478	0.14, 0.20	0.90
P3	373	369	412	431, ^c 453, 483 ^c	0.15, 0.13	1.00
P4	364	365	404	417, 452, 480	0.16, 0.15	0.78
P5	365	380	402	415, 455, 484	0.15, 0.17	0.97

^a Fluorescence quantum efficiencies in CHCl₃ were determined by using 9,10-diphenylanthracene in cyclohexane ($\phi_{\text{fl}}=0.90$) as a standard.

^b Polymer films cast on a glass substrate from a CHCl₃ solution.

^c Shoulder peaks.

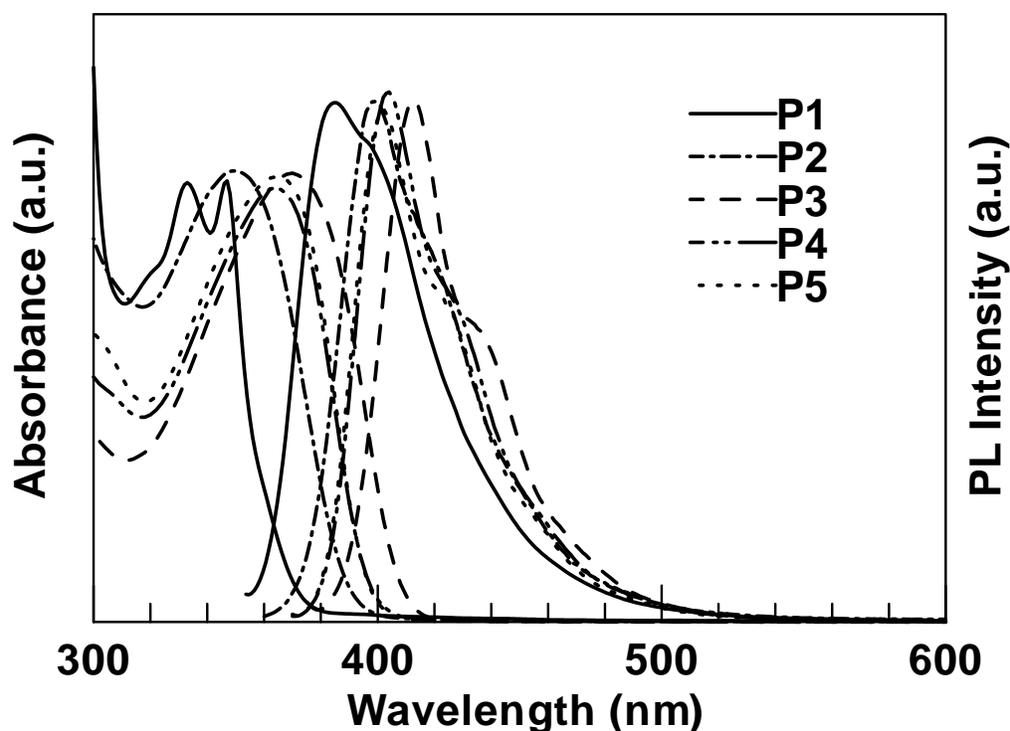


Figure 2. UV-vis and PL spectra of the polymers in CHCl_3 .

The PL spectra of the polymers in CHCl_3 are also dominated by the electronic properties of each polymer backbone. The PL spectrum of **P1** was typical of poly(2,6-naphthalene)s, which had an emission peak at around 390 nm in the region of blue-violet color. The PL peaks of **P2-P5** were found in the longer region in wavelength than **P1**. Of all the polymers, **P3** had the emission peak at 412 nm that was the longest in wavelength, and the PL spectrum was close to that of poly(*N*-phenylcarbazole-2,7-ylene).[29] These red shifts are dependent on the conjugation length of each polymer main chain. The fluorescence quantum yields of these polymers in CHCl_3 were high ($\phi_{\text{fl}} = 0.70\text{--}1.00$), being comparable to polycarbazoles and polyfluorenes.

The absorption and PL spectra of the polymers in the thin solid film state are shown in Figure 3, and the optical data are summarized in Table 2. In all cases, the absorption maxima were slightly red-shifted compared with those in solution, which is due to increase of coplanarity of the polymer backbones in the thin film state. In contrast, the PL spectra were quite different from those in solution, i. e., more or

less three peaks (or shoulders) in the region of 380-500 nm and a tailing band in the longer region were observed. In the case of **P1**, the spectrum with apparent two emission bands at 386 and 461 nm is typical of poly(1,5-dialkoxy-2,6-naphthalene)s that usually have two emission bands at about 400 and 480 nm.[23, 36] The random copolymer **P2** in which the rate of content of the naphthalene units is higher than the carbazole unit shows a poly(naphthalene)-based PL spectrum having λ_{\max} at 407 and 478 nm. While, the random copolymer **P3** in which the rate of content of the carbazole unit is highest shows a poly(carbazole)-based PL spectrum having the intense band at 453 nm with shoulder bands at about 431 and 481 nm, which is similar to those of poly(2,7-carbazole)s in the film state.[29] The PL spectra of the alternating copolymers, **P4** and **P5**, are similar each other and basically consist of three PL bands (at around 415, 450, and 480 nm) and the tailing one in the longer region (>500 nm). In all cases, the PL peak that is observed shortest in wavelength originates from excited states of conjugated sequences having considerable dihedral angles in isolated polymer chains, which could be almost identical to the emission in dilute solution. The other peaks in the longer wavelength and the tailing band have possibilities of emissions from ground state aggregates and excimeric emissions. To present clear explanations, we need more detail experiments in PL spectroscopy.

In spite of broadening of the PL spectra by overlapping of each PL band in the film state, their PL colors are within the range of pure blue as the CIE coordinates shown in Table 2 suggest.

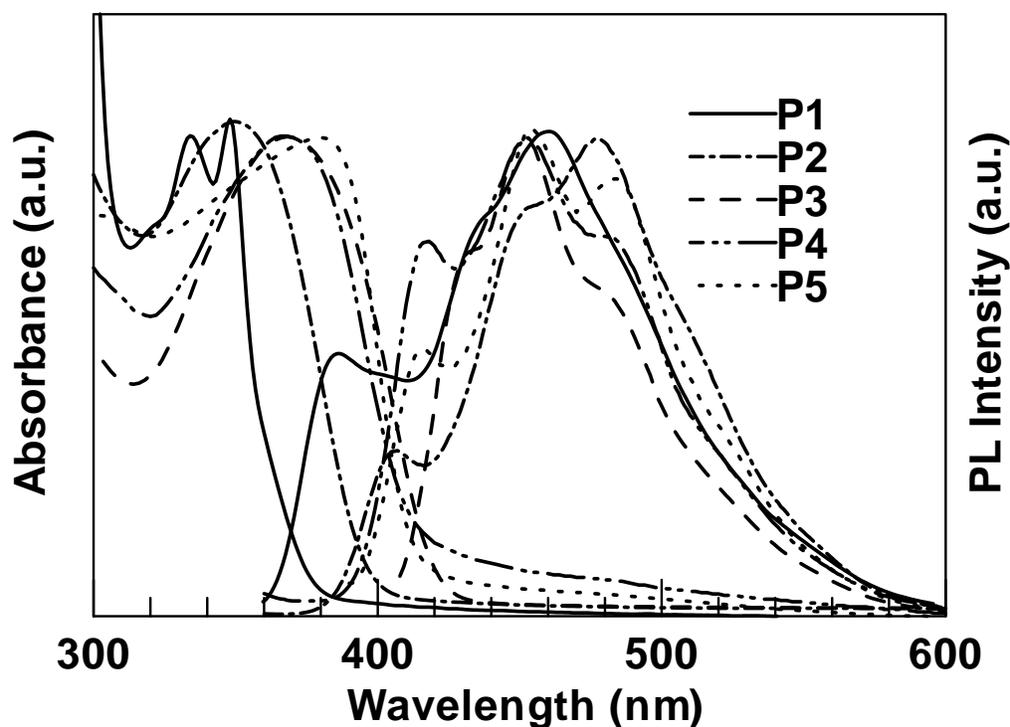


Figure 3. UV-vis and PL spectra of the polymers in the film states.

Electrochemical properties

The HOMO energy levels of the polymers are estimated by the conventional electrochemical method,[30, 31] and the results are summarized in Table 3. The onsets of the oxidation peak of the polymers were in the range of 1.26–1.30 V (vs. SCE), which means that the HOMO levels are almost equal around 5.64–5.68 eV and also almost identical to the HOMO level of poly(1,5-bis(dihexyloxy)-2,6-naphthalene) (5.65 eV) whether or not the polynaphthalene has the carbazole unit in the main chain. The structural differences between the random and alternating copolymers also little affect the HOMO level of the materials.

Table 3. Electrochemical characteristics of the polymers.

	E_{onset} (V vs SCE)	HOMO (eV)	LUMO (eV)	E_g (eV) ^a
P1	1.26	-5.64	-2.64	3.00
P2	1.30	-5.68	-2.88	2.80
P3	1.30	-5.68	-2.88	2.80
P4	1.30	-5.68	-2.98	2.70
P5	1.30	-5.68	-2.78	2.90

^a Energy gaps were estimated from the onset of absorption spectra in the film state.

Electroluminescence properties

The EL properties of the polymers are investigated by constructing PLED devices that have a configuration of ITO/PEDOT(PSS)/polymer/CsF/Al, and the results are summarized in Table 4. Figure 4 displays luminous intensity-current density-voltage (L - J - V) characteristics of the devices. Their turn-on voltages were observed at 6–7 V with a little difference, which suggests that interfacial barriers of carrier injection are similar each other. On the other hand, the maximum brightness (L_{max}) was different depending on the polymer backbones. Figure 5 shows typical of the EL spectra of **P1–P5** observed at 9 V, which are almost invariant in the range of operating voltages from 7 to 12 V. All the EL spectra that have an emission peak at around 490 nm are simpler and narrower than corresponding PL spectra in the film state. Their emission colors were in the range of blue green to green by reference to the CIE coordinates of **P1–P5**. These spectra are very similar to those of poly(2,6-naphthalene)s having strong red-shifted emissions at around 480 nm discussed in the PL spectra in the film state.

The device using **P1** exhibited L_{max} of 500 cd/m² at 12 V, which is more than ten times higher in comparison with the results of devices using other poly(2,6-naphthalene)s in our preliminary investigation. This improvement is attributed to the carbazole side chain assisting hole injection and transport. The devices using **P2** and **P3** that are random copolymers exhibited significantly high L_{max} of 6040 cd/m² at 10 V for **P2** and 8370 cd/m² at 13 V for **P3**, respectively. Of all the polymers, **P2** showed the highest maximum current efficiency (η_{max}) of 2.16 cd/A that is superior to poly(*N*-aryl-2,7-

carbazole)s reported recently.[34] Furthermore, Figure 6 shows EL spectra of **P2** under operating voltages in the range from 7 to 15 V. Little spectral change of EL during the operating voltages suggests high color stability of the device. On the other hand, L_{\max} of the devices fabricating with **P4** and **P5** were rather low, being 50 cd/m^2 and 90 cd/m^2 , respectively. Consequently, the random copolymers exhibited significantly higher performances than the other polymers in this work. The results of electrochemical properties showed no evidences of raising HOMO levels, which suggests that carrier injection is little reflected on these performances. A conformational disorder in random copolymers might prevent undesirable packing that decreases the EL performances, and make effective conjugation sequences for carrier transport.

Table 4. Electroluminescence characteristics of the polymers.

polymer	Turn-on voltage ^a (V)	EL λ_{\max} ^b (nm)	L_{\max} (cd/m^2 [V])	η_{\max} (cd/A [V])	CIE (x , y) ^b
P1	7	488	500 [12]	0.16 [10]	0.20, 0.30
P2	6	488	6040 [10]	2.16 [7]	0.17, 0.29
P3	6	491	8370 [13]	0.90[9]	0.20, 0.32
P4	7	500	50 [12]	0.10 [8]	0.22, 0.41
P5	7	503	90 [15]	0.15 [8]	0.21, 0.43

^a Light output of 1 cd/m^2 .

^b At 9 V.

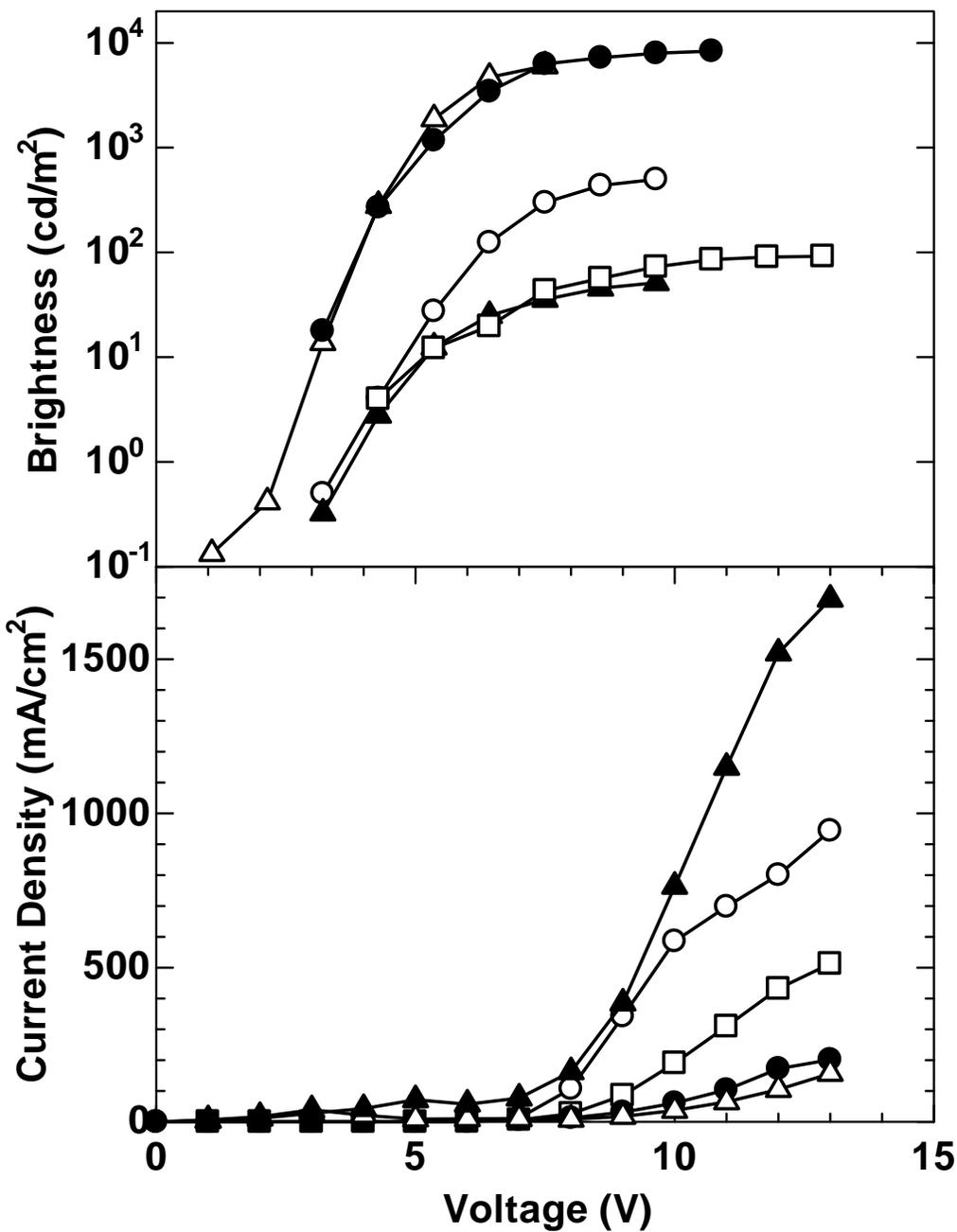


Figure 4. Luminance–current–voltage characteristics of the devices; open circle: **P1**, open triangle: **P2**, filled circle: **P3**, filled triangle: **P4**, open square: **P5**.

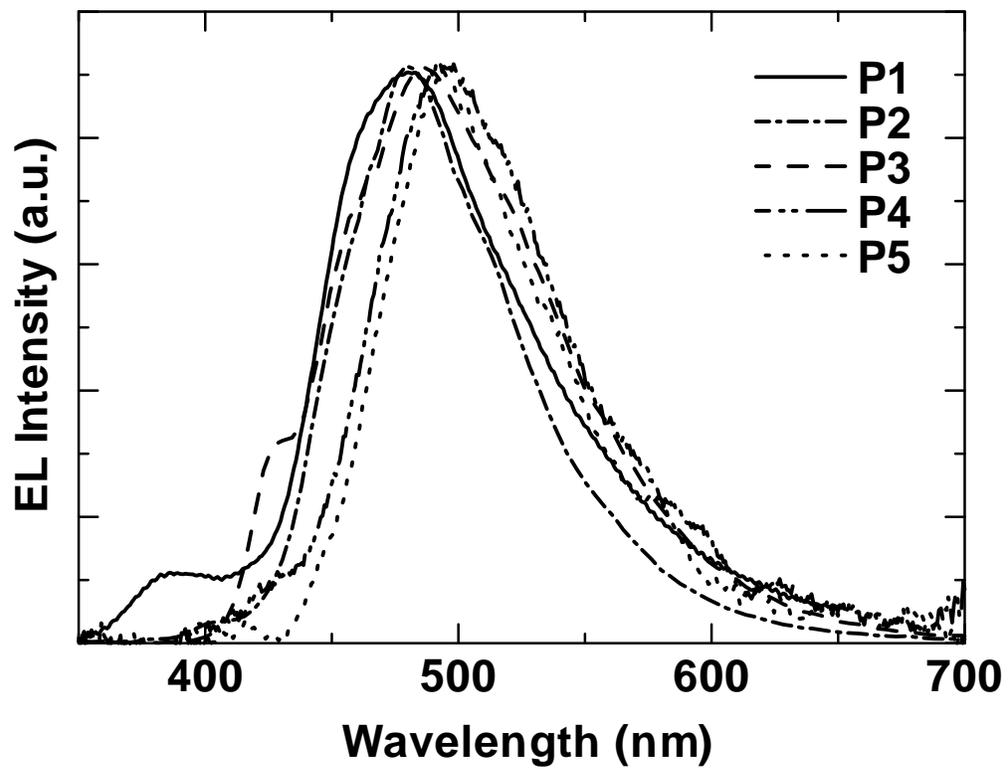


Figure 5. EL spectra of the devices fabricated with **P1–P5** at 9 V operating voltage.

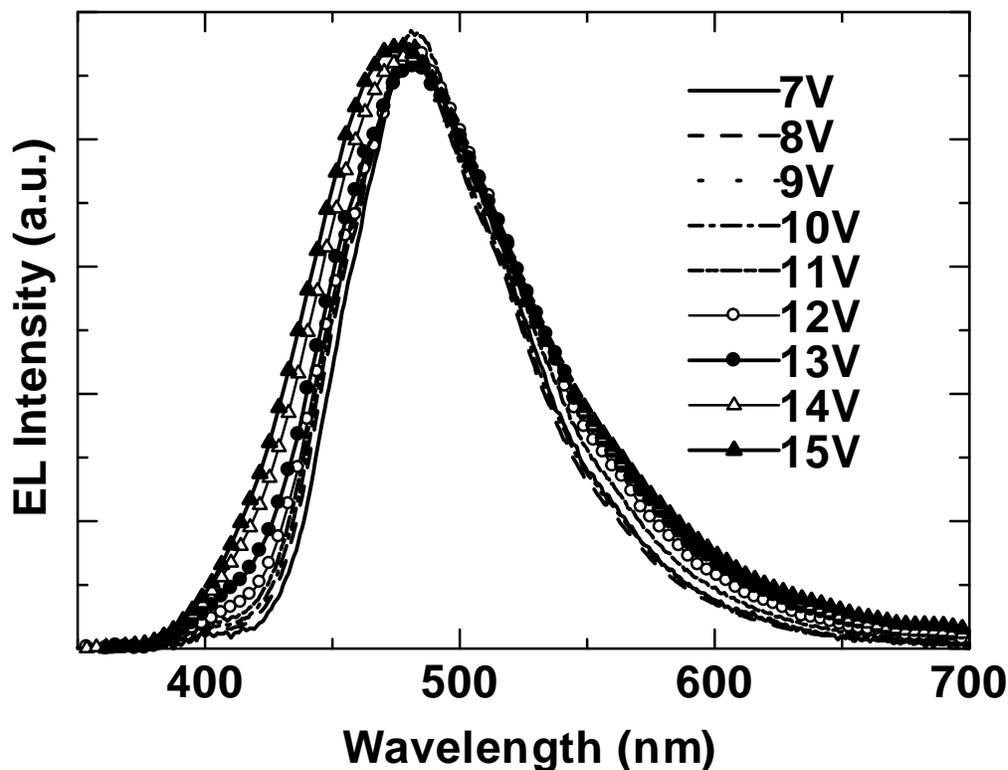


Figure 6. EL spectra of P2-device under operating voltages in the range of 7–15 V.

Conclusions

Novel poly(2,6-naphthalene) derivatives having the carbazole portions in the side chain and main chain were synthesized. They exhibited blue-violet PL with high PL quantum efficiencies of $\phi_{\text{pl}} = 0.70$ –1.00 in CHCl_3 , while they showed pure blue PL in the film state. The considerable red-shifts of PL observed in the film state are mostly attributed to interactions between the planar naphthalene portions and fluorophores. We fabricated the PLED devices that have a configuration of ITO/PEDOT(PSS)/polymer/CsF/Al using these polymers as the emitting layer materials, and investigated their EL performances for the first time. Characteristics of these PLED devices are summarized as below, i. e., they emitted blue-green to green with an EL λ_{max} at around 490 nm, and their EL spectra were invariant and stable during the operating voltages (6–12 V). This suggests that EL of these devices are all dominated by the emissions from the conjugated sequences that include π -stacks

with the planar polynaphthalene backbones. **P1** that is the polynaphthalene homopolymer having the carbazole side chain surely showed an improved EL performance than poly(naphthalene)s that we have previously synthesized. The carbazole side chains might assist carrier injection and transport in the emitting material. The devices embedded with the random copolymers (**P2** and **P3**) as the emitting layer materials exhibited high performances of their brightness and efficiencies, respectively. In addition, the η_{\max} of **P2** (2.16 cd/A) exceeds those of polycarbazole-based PLED devices that have the same configuration.[25] The random copolymerization might bring about preferable conjugated sequences of fluorophores for the stable EL with a balanced carrier transport in these cases. On the other hand, the alternating copolymers of naphthalene and carbazole units (**P4** and **P5**) showed disappointing EL performances. Absence of the strongly emissive polycarbazole sequences in the alternating copolymers might result in the low performance. In conclusion, we have demonstrated that polynaphthalenes have a possibility to be applied in optoelectronic materials in this paper, although the polymers must be modified by taking into account the specific π -electronic interaction of naphthalene portions for further practical applications.

Acknowledgement

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Captions

Scheme 1. Synthetic route of **P1**.

Scheme 2. Synthetic route of **P2** and **P3**.

Scheme 3. Synthetic route of **P4** and **P5**.

Figure 1. TGA curves of the polymers at a heating rate of $10^{\circ}\text{C min}^{-1}$ under Ar.

Figure 2. UV-vis and PL spectra of the polymers in CHCl_3 .

Figure 3. UV-vis and PL spectra of the polymers in the film states.

Figure 4. Luminance–current–voltage characteristics of the devices; open circle: **P1**, open triangle: **P2**, filled circle: **P3**, filled triangle: **P4**, open square: **P5**.

Figure 5. EL spectra of the devices fabricated with **P1–P5** at 9 V operating voltage.

Figure 6. EL spectra of **P2**-device under operating voltages in the range of 7–15 V.

Table 1. Polymerization results.

Table 2. Absorption and photoluminescence spectral data of the polymers.

Table 3. Electrochemical characteristics of the polymers.

Table 4. Electroluminescence characteristics of the polymers.