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Synthesis and Characterization of New Poly(silole-fluorene) Copolymers

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New poly(silole-fluorene) copolymers were designed and synthesized. Copolymers were obtained by Suzuki coupling reaction with different ratio of fluorene and silole. The obtained copolymers were characterized by the spectroscopic methods such as FT-IR and ^{1}H-NMR spectroscopies. The resulting copolymers were soluble in common organic solvents such as toluene, tetrahydrofurane, chloroform, chlorobenzene, etc. The obtained copolymers showed thermal stabilities, which were characterized by TGA and DSC. PLEDs with device configurations of ITO/PEDOT:PSS/Copolymer I∼VI/LiF/Al. The best device performances, with maximum brightness of 231.5 cd/m^2 at a current density (J) of 408.3 mA/cm^2, and a maximum luminance efficiency of 0.115 cd/A, were achieved in the composition of fluorene and silole moiety (0.9:0.1).

Keywords: Polyfluorene, Silole Moiety, OLED, PLED.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs)[1] have attracted attention due to their possible applications in flat panel displays.[2] Polymer light-emitting diodes (PLEDs)[3] also have attracted considerable interest due to their applications in large-area flat panel displays[4] with high-efficiency. For the highly efficient PLED devices, charge injection and transport from both the anode and cathode should be balanced at the emitting layer to yield high maximum exciton formation.[5] Polyfluorene[6,7] derivatives are well known for blue light emission.[8]

It is reported that the silole moiteies are able to transport electrons efficiently. Silole-containg molecules have low LUMO energy level by a $\sigma^* \rightarrow \pi^*$ conjugation and increase their electron affinities[9] and have been used as electron-transporting[10] with the high electron mobility.

In this study, we designed the copolymer with fluorene as blue emitting moiety and silole as possessing high electron transport ability. We studied the physical, optical, electrochemical properties and performance of PLED according to the composition of fluorene and silole moiety.

2. EXPERIMENTAL DETAILS

2.1. Material Preparation

All reagents and catalysts were purchased from Aldrich and UMICORE. Other solvents were purchased from duksan and were further purified prior to use. All reagents purchased comercially were used without further purification.

2.2. Synthesis

2.2.1. Synthesis of Bis(phenylacetyl)diphenylsilane (1)

n-Butyllithium (2.5 M in hexane, 70.8 mL, 0.761 mol) was slowly added to phenyl acetylene (13.9 g, 0.136 mol) in anhydrous tetrahydrofuran (THF) (200 mL) at − 78 °C. After 1 h stirring at room temperature, diphenyl dichlorosilane (15 g, 0.059 mol) was slowly dropped into the mixture at − 78 °C and stirred at room temperature. After 12 h, the reaction was terminated by the addition of ice water and extracted with ethyl acetate (EA). The crude product was purified by column chromatography and re-crystallization with hexane/EA: 20/1 as eluent. Yield: 13 g (57%). $m \cdot p$: 174 °C. FT-IR (KBr) (cm^{-1}): 3069–3000 (aromatic C–H), 1487, 1441, 1426 (aromatic $\mathrm{C{=}C}$), 2148 ($\mathrm{C{\equiv}C}$), 1112 (Si–C); ^{1}H NMR (300 MHz , $\mathrm{CDCl_3}$, ppm) $\delta = 7.89$∼7.92 (dd, 4 H), 7.60∼7.74 (dd, 4 H), 7.35∼7.51 (m, 6 H), 7.09∼7.28 (m, 6 H). Anal. Calcd. for $\mathrm{C_{28}H_{20}Si}$: C, 87.45; H, 5.24. Found: C, 86.85; H, 5.30.

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2.2.2. Synthesis of 2,5-di(bromopyridyl)-1,1-diph-enyl-3,4-diphenylsilole (2)

Lithium (0.032 g, 0.004 mol) and naphthalene (4.2 g, 0.032 mol) in THF (50 mL) were stirred for 6 h. Bis(phenylacetyl)diphenylsilane (3 g, 0.007 mol) in THF was dropped to the mixture at −78 °C. After 1 h stirring at room temperature, 1 M $ZnCl_2$ was slowly added to the mixture at 0 °C and stirred for further an hour. 2,6-dibromopyridine (3.8 g, 0.016 mol) and $PdCl_2(PPh_3)_2$ was added and the result solution was refluxed for 16 h at 85~90 °C. Once the reaction was completed, the crude product was worked up with water. The product was extracted with EA. The crude product was purified by column chromatography with hexane/EA: 20/1 as eluent and re-crystallization with methylene chloride (MC) and hexane. Yield: 2 g (36%). *m* · *p*: 244~255 °C. FT-IR (KBr) (cm^{-1}): 3046 (aromatic C–H), 1465, 1427 (aromatic C=C), 1566 (C=N), 1116 (Si–C), 1023 (C–Br); 1 H NMR (300 MHz, $CDCl_3$, ppm) $\delta = 7.9$ (*d*, 4 H), 7.3~7.45 (*m*, 6 H), 7.12~7.2 (*t*, 6 H), 7.09~6.9 (*m*, 8 H), 6.35~6.45 (*m*, 2 H). Anal. Calcd. for $C_{38}H_{26}Br_2N_2Si$: C, 65.34; H, 3.75; N, 4.01. Found: C, 55.14; H, 3.85, N, 4.26.

2.2.3. Synthesis of 2,7-bis(ethyleneboronate)-9,9′-dihexylfluorene (3)

Synthesis was referenced by literature method.[11] Yield: 14 g (95%). *m* · *p*: 120 °C. FT-IR (KBr) (cm^{-1}): 3053, 3033 (aromatic C–H), 2964–2842 (aliphatic C–H), 1488, 1472, 1453 (aromatic C=C); ^{1}H NMR (300 MHz , $CDCl_3$, ppm) $\delta = 7.68$~7.84 (*m*, 6 H), 4.43 (*s*, 8 H), 1.99~2.06 (*m*, 4 H), 1.01~1.27 (*m*, 12 H), 0.73~0.79 (*t*, 6 H), 0.58 (br *s*, 4 H). Anal. Calcd. for $C_{29}H_{40}B_2O_4$; C, 73.44; H, 8.50; O, 13.44. Found: C, 73.40; H, 8.49; O, 13.55.

2.2.4. Synthesis of Poly(2,7-(9,9′-dihexyl fluorene)$_{99}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenylsilole$_1$) (Copolymer I) (4)

2,5-Di(bromopyridyl)-1,1-diphenyl-3,4 diphenyl silole (0.01 g, 0.014 mmol), 2,7-dibromo-9,9′-dihexyl fluorene (0.345 g, 0.701 mmol) and 2,7-bis(ethyleneboronate)-9,9′-dihexylfluorene (0.33 g, 0.611 mmol) were dissolved in THF (30 mL) and 2 M K_2CO_3 (50 mL). After degassing, $Pd(PPh_3)_4$ was added to the mixture and stirred for 72 h at 80 °C. Subsequently, phenylboronic acid and bromobenzene were injected into the reaction mixture and the reaction was stirred for 6 h. After precipitation

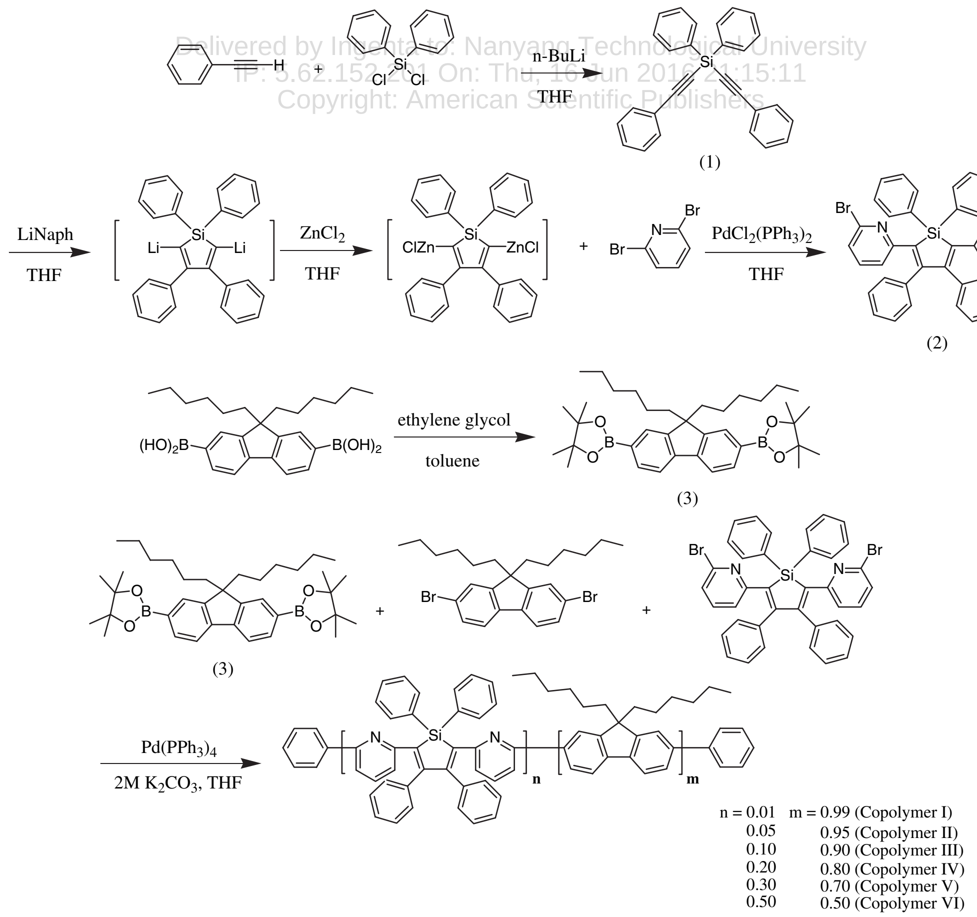

Figure 1. Synthetic routes of copolymer.

from methanol, the desired polymer was obtained. Yield: 0.58 g (50%). FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C); ^{1}H NMR (300 MHz, CDCl$_3$, ppm) $\delta = 7.87 \sim 7.81$ (*m*, 9 H), 7.4∼7.7 (*m*, 18 H), 6.6∼7.2 (*m*, 5 H), 2.1 (br *s*, 4 H), 1.16∼1.58 (*s*, 12 H), 0.79∼0.81 (*d*, 10 H), ^{13}C NMR (300 MHz, CDCl$_3$, ppm) $\delta = 13.9$, 22.5, 23.6, 23.7, 29.1, 29.7, 29.8, 31.4, 31.7, 40.1, 40.4, 55.3, 121.1, 121.4, 126.2, 127.2, 127.5, 128.4, 128.7, 130.1, 134.3, 139.0, 152.5. Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55; H, 6.81, N, 3.12.

2.2.5. Synthesis of Poly(2,7-(9,9′-dihexylfluorene)$_{95}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenylsilole)$_5$) (Copolymer II) (5)

Copolymer II was synthesized with the same method used for Copolymer I. Yield: 0.42 g (35%), FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C). Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55; H, 6.81, N, 3.12.

2.2.6. Synthesis of Poly(2,7-(9,9′-dihexylfluorene)$_{90}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenylsilole)$_{10}$) (Copolymer III) (6)

Copolymer III was synthesized with the same method used for Copolymer I. Yield: 0.32 g (29%), FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C). Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55; H, 6.81, N, 3.12.

2.2.7. Synthesis of Poly(2,7-(9,9′-dihexylfluorene)$_{80}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenylsilole)$_{20}$) (Copolymer IV) (7)

Copolymer IV was synthesized with the same method used for Copolymer I. Yield: 0.25 g (20%), FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C). Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55; H, 6.81, N, 3.12.

2.2.8. Synthesis of Poly(2,7-(9,9′-dihexylfluorene)$_{70}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenylsilole)$_{30}$) (Copolymer V) (8)

Copolymer V was synthesized with the same method used for Copolymer I. Yield: 0.32 g (37%), FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C). Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55; H, 6.81, N, 3.12.

2.2.9. Synthesis of Poly(2,7-(9,9′-dihexylfluorene)$_{50}$-co-2,5-(dipyridyl-1,1-diphenyl-3,4-diphenyl-silole)$_{50}$) (Copolymer VI) (9)

Copolymer VI was synthesized with the same method used for Copolymer I. Yield: 0.2 g (27%), FT-IR (KBr) (cm^{-1}): 3059 (aromatic C–H), 2907–2854 (aliphatic C–H), 1440 (aromatic C=C), 1567 (C=N), 1115 (Si–C). Anal. Calcd. for $(C_{63}H_{60}N_2Si)_n$: C, 86.65; H, 6.93; N, 3.21. Found: C, 85.55: H, 6.81, N, 3.12.

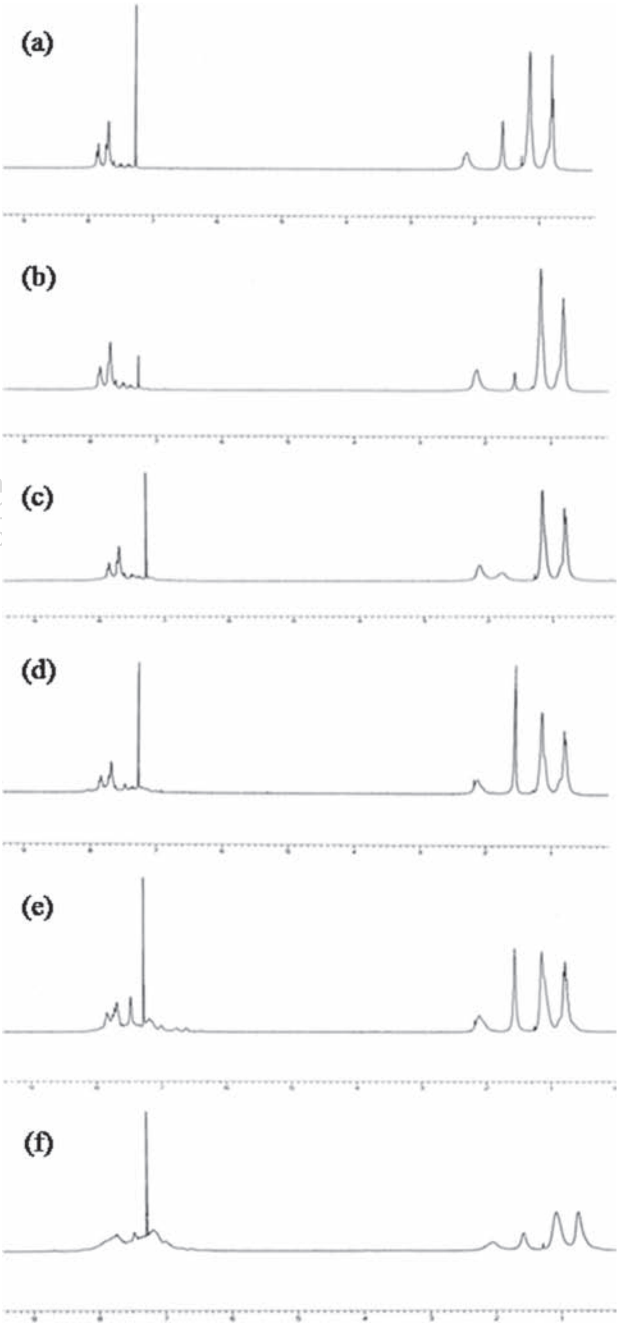

Figure 2. ^{1}H-NMR of copolymer (a) copolymer I, (b) copolymer II, (c) copolymer III, (d) copolymer IV, (e) copolymer V, (f) copolymer VI.

Table I. The thermal, optical and electrochemical properties of the copolymer.

						UV (nm)		PL (nm)				
	M	M_w	PDI	T_g (°C)	$T_{5\%}$ (°C)	Solution	Film	Solution	Film	HOMO (eV)	LUMO (eV)	E_g^{el} (eV)
Copolymer I	10,980	19,900	1.81	88	280	384	380	424, 443	449, 476	−5.61	−3.16	2.45
Copolymer II	8,090	13,120	1.62	87	289	379	378	448	483	−5.63	−3.21	2.42
Copolymer III	8,510	12,650	1.48	104	294	377	373	424, 445	484	−5.61	−3.39	2.22
Copolymer IV	9,560	14,310	1.49	115	312	373	369	421, 442	486	−5.62	−3.44	2.18
Copolymer V	11,180	17,660	1.57	134	314	363	363	419, 444	485	−5.63	−3.46	2.17
Copolymer VI	5,690	8,250	1.45	142	320	353	351	417, 447, 474	488	−5.64	−3.49	2.15

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the Copolymer

The synthesis of Copolymer I~VI were prepared as depicted in Figure 1. Copolymer I~VI were obtained by Suzuki coupling reaction with different ratio of fluorene and silole moiety (0.99: 0.01, 0.95: 0.05, 0.90: 0.10, 0.80: 0.20, 0.70: 0.30, 0.50: 0.50). The obtained copolymers were purified by precipitation using methanol. The structure of copolymer was studied by ^{1}H-NMR. The copolymer composition was comfirmed by ^{1}H-NMR integration. As the decreasing ratio of fluorene, the integration of alkyl protons was decreased (Fig. 2). The copolymers showed good solubility in common organic solvents, such as methylene chloride, tetrahydrofuran, chloro-form, toluene and chlorobenzene. Gel permeation chromatography (GPC) analysis determined the weight average molecular weight (M_W) to be around 8,200~19,900 with a polydisoersity index (PDI) of around 1.45~1.81, against polystyrene standards. The molecular weights and polydis persity indexes of the copolymers were summarized in Table I.

3.2. Thermal Analysis

The thermal properties of the polymers were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The 5% weight loss of the copolymers was observed around from 280 °C to 314 °C. As the increasing ratio of the silole moiety, the thermal stability was increased. From the DSC data of the copolymers the glass transition temperature (T_g) was observed at 88~134 °C. The glass transition temperature was gradually increased as the increasing ratio of silole moiety. The introduction of rigid silole moiety can lead good to increase thermal stability. Therefore the drawback of low T_g of dialkyl fluorene can be overcome (Fig. 3).

3.3. Optical and Electrochemical Properties Analysis

The UV-visible absorption and photoluminescence spectra of the polymer both in chloroform (1×10^{-5} M) and film state are shown in Figure 4. The UV-visible absorption was blue shift as increasing of mole ratio of silole moiety from 384 to 363 nm for solution and 380 to 362 nm for film, respectively. It can be explained by the introduction of kinked structure of meta pyridine-silole as well as inhibited intermolecular interaction. In general, it is reported that poly-fluorene have low color purity due to the excimer formaion in the long wavelength range. In the new developed copolymers, the excimer emission doesn't represent because the ramdomly introduced meta-kinked silole moiety[12] is able to prevent the intermolecular interaction.

The electrochemical behaviors of these polymers were investigated by cyclic voltammetry (CV). Their HOMO, LUMO and band gap were summarized in Table I. HOMO energy level of the copolymers were −5.61~−5.64 eV and LUMO energy level were −3.16~−3.49 eV.

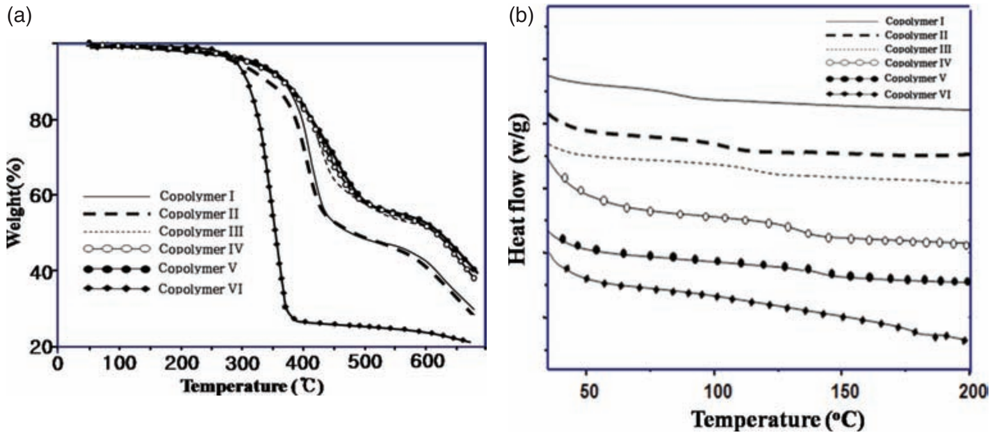

Figure 3. The thermal properties of copolymer (a) TGA and (b) DSC curve.

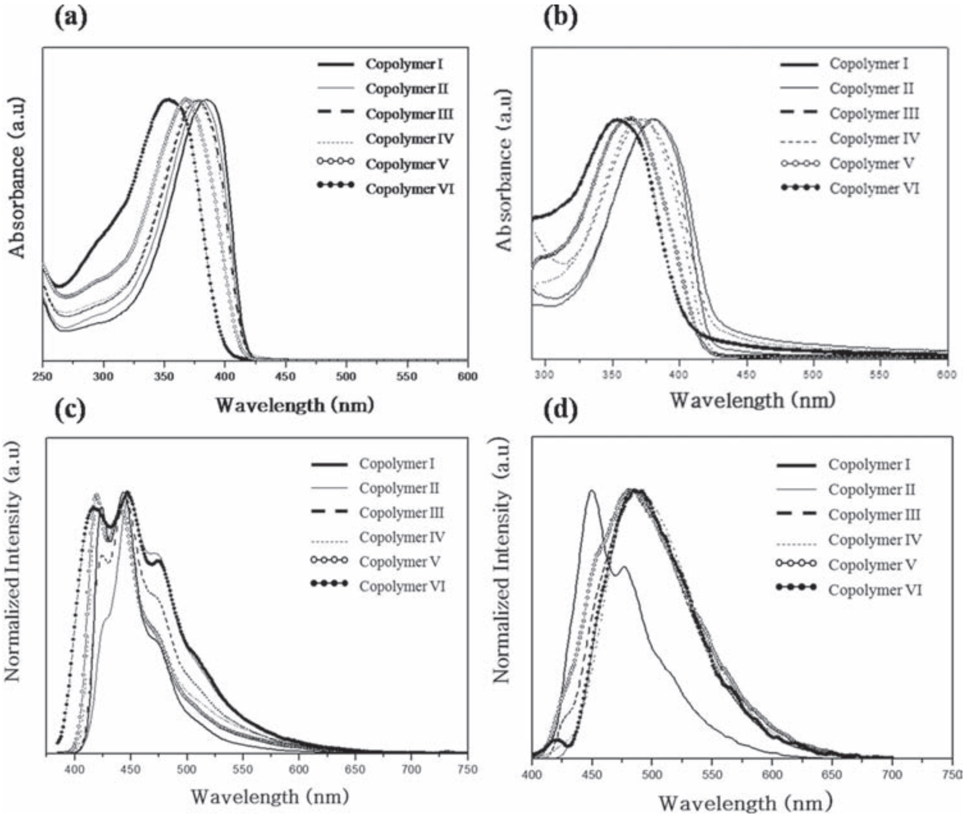

Figure 4. The optical properties of copolymer (a) UV-visible spectra copolymer in solution, (b) UV-visible spectra in film, (c) PL spectra in solution and (d) PL spectra in film.

The copolymer shows the decreased LUMO energy level as increasing silole ratio because of electron-withdrawing property of silole moiety.

3.4. Device Performance

Devices with the configuration of indium tin oxide (ITO)/PEDOT:PSS/Copolymer/LiF/Al were fabricated. The CIE chromaticity coordinates and device performance are summarized in Table II. The maximum luminance efficiency of 0.115 cd/A and maximum brightness of 231.5 cd/m^2 with CIE (0.24, 0.38) was observed for copolymer II. Luminance efficiencies of copolymers are extremely low. That is attributed to imperfect intra- and intermolecular energy transfer from fluorene moiety to silole moiety or partial excimer format of fluorene moiety in the aggregation state.[13]

Table II. Device performance characteristics of the ITO/PEDOT:PSS/Copolymer/LiF/Al device in air at room temperature.

	V_{on}	Luminance efficiency (cd/A)	J (mA/cm^2)	Brightness (cd/m^2)	CIE (x, y)
Copolymer I	6	0.053	280.4	80	(0.16, 0.11)
Copolymer II	8	0.115	408.3	231.5	(0.24, 0.38)
Copolymer IV	11	0.011	523.9	41	(0.26, 0.38)
Copolymer V	11	0.066	206.2	22	(0.38, 0.48)
Copolymer VI	4	0.0005	249.0	0.23	(0.26, 0.51)
Copolymer VII	3	0.0006	355.4	2.21	(0.34, 0.41)

4. CONCLUSION

The new blue copolymers with different composition of silole and dihexyl fluorene were synthesized by Suzuki-coupling reaction. As the increased composition of silole moiety, the T_g of copolymers was increased. Moreover, the λ_{max} of UV-vis was blue-shifted, and LUMO level was decreased due to introduction of non-copolanar silole electron transporting property. The maximum current efficiency of 0.115 cd/A and maximum brightness of 231.5 cd/m^2 with CIE (0.24, 0.38) was observed at copolymer II.

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