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Synthesis and characterization of fluorene-carbazole and fluorene-phenothiazine copolymers with carbazole and oxadiazole pendants for organic light emitting diodes

Shuhei Yamada [a,g,1], Seijung Park [a,1], Suhee Song [a,1], Mihee Heo [b], Joo Young Shim [a], Youngeup Jin [c], Il Kim [d], Heesoo Lee [e], Kyungmee Lee [f], Kohji Yoshinaga [g], Jin Young Kim [b,]**, Hongsuk Suh [a,]*

[a] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, South Korea
[b] Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology, Ulsan 689-798, South Korea
[c] Department of Industrial Chemistry, Pukyong National University, Busan 608-739, South Korea
[d] The WCU Center for Synthetic Polymer Bioconjugate Hybrid Materials, Department of polymer Science and Engineering, Pusan National University, Busan 609-735, South Korea
[e] School of Materials Science and Engineering, Pusan National University, Busan 609-735, South Korea
[f] Department of Chemistry, Sungkyunkwan University, Gyeonggi-do, South Korea
[g] Department of Applied Chemistry, Kyushu Institute of Technology Faculty of Engineering, Fukuoka 804-8550, Japan

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ABSTRACT

We report the synthesis and characterization of new series of the fluorene based polymers with carbazole and oxadiazole pendants for the generation of the white emission out of the EL device. In the fluorene backbone, hole transporting units such as carbazole or phenothiazine were incorporated to improve the EL brightness and efficiency. The **PFCzOxd-*co*-PCZs** and **PFCzOxd-*co*-PPTZs** in EL spectra showed maximum peaks at around 430 nm and additional large peaks at around 530 and 500 nm, respectively. In case of **PFCzOxd-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz**, the EL spectra of the polymers showed two distinct peaks comprising the maximum at 427 nm, which corresponds to the EL spectra of the conjugated backbone, and additional broad peaks at around 540 and 530 nm, respectively. The CIE coordinates of the devices from **PFCzOxd-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz** were (0.28, 0.33) and (0.25, 0.32), respectively, approaching the value of the standard white of National Television System Committee (NTSC) (0.33, 0.33).

1. Introduction

Conjugated polymers have been utilized as active materials in several kinds of electronic devices such as thin film transistor [1], photovoltaic cell [2,3], and organic light emitting diodes (OLEDs) [4], including flexible displays [5]. OLEDs have attracted much attention with several advantages over conventional devices including low driving voltage, wide viewing angle, and a simple manufacturing process [6–9]. Much effort has been devoted to the fabrication of white-organic-light-emitting diodes (WOLEDs), because of possible applications for low-cost room illumination. One of the methods of the realization of WOLED is the multilayer device system with red, green and blue light emitting materials [10–12]. Although the multilayer devices show high efficiencies and long lifetimes, the fabrication of the multilayers using spin-coating process is unsuitable with polymeric light emitting materials which are soluble only in organic solvents. Another method is using a single light emitting layer with red, green, and blue light emitting polymer blends [13,14]. Even though using polymer blends is a promising process for the generation of white light emission, phase separation, low efficiency, and voltage dependence of emitting color limit their utilization. Recently, several groups achieved the fabrication of WOLEDs from polyfluorene-based polymers containing red and green light emitting portions on the backbones [15–18]. In these cases, the color of the emission was easily tuned by adjusting the composition of the polymers to control the partial energy transfer to red, or green emissive units.

We previously reported the results of white light emission from poly(9-(6-(9*H*-carbazolyl)hexyl)-9-(6-(4-(5-phenyl-1,3,4-oxadiazolyl)-phenoxy)hexyl)-9*H*-fluorene) (**PFCzOxd**), containing carbazole and oxadiazole units as pendants, due to the peak at 426 nm and broad peak around 540 nm which is attributed to the aggregations caused by the

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* Corresponding author. Tel.: +82 51 510 2203.
** Corresponding author.
E-mail addresses: jykim@unist.ac.kr (J.Y. Kim), hssuh@pusan.ac.kr (H. Suh).
[1] These authors contributed equally to this work.

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carbazole and oxadiazole units [19]. The OLEDs fabricated with **PFCzOxd** [19] generated electroluminescence (EL) with excellent Commission Internationale d'Enclairage (CIE) coordinates ($x = 0.31$, $y = 0.33$) for the white color. In this paper, we report the synthesis and characterization of new series of the fluorene based polymers with carbazole and oxadiazole pendants for the generation of the white emission out of the EL device. In the fluorene backbone, hole transporting units such as carbazole or phenothiazine were incorporated to improve the EL properties since carbazole and phenothiazine units have good hole transporting behavior caused by the electron lone pair on nitrogen or sulfur atoms. The carbazole and phenothiazine were incorporated into the backbone to perform as hole transporter to improve hole injection and hole trapping site for efficient electron-hole recombination to yield emitting excitons [20].

2. Experimental

2.1. Materials and instruments

The materials, 2-(4-(6-bromohexyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole (**1**), 2,7-dibromo-9-(6-(9*H*-carbazolyl)hexyl)-9-(6-(4-(5-phenyl-1,3,4-oxadiazolyl)phenoxy)hexyl)-9*H*-fluorene (**3**), 2,7-dibromo-9,9-bis(6-(9*H*-carbazolyl)hexyl)-9*H*-fluorene (**4**), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (**5**), 2,7-dibromo-9-(heptadecan-9-yl)-9*H*-carbazole (**6**), and 3,7-dibromo-10-octyl-10*H*-phenothiazine (**7**) were synthesized according to the procedure outlined in the literature [19–24]. The hole-injection-transport material, PEDOT:PSS, was purchased from H.C. Starck with Clevios PH grade. All used reagents for organic synthesis were purchased from Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer and chemical shift were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230–400 mesh ASTM). Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV254. Molecular weight and polydispersities of the polymer were determined by gel permeation chromatography (GPC) with a polystyrene standard calibration. The differential scanning calorimetry analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermogravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. Fast atom bombardment (FAB) mass spectra were determined using at Korea Basic Science Institute Seoul Branch and Korea Basic Science Institute Daegu Branch. Cyclic voltammetric waves were produced by using an EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s. UV spectra were recorded with Varian CARY-5E UV/vis spectrophotometer. The PL and EL spectra were measured using Oriel InstaSpec IV CCD detection systems. For PL spectrum measurement, a xenon lamp was used as the excitation source and incident beam took the maximum absorption peak of the polymers. For the determination of device characteristics, current–voltage (*I*–*V*) characteristics were measured using a Keithley 2400 source measure unit.

2.2. EL device fabrication and measurements

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting chlorobenzene solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and calcium (20 nm) and aluminum (100 nm) electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current density–voltage (*J*–*V*) and luminance–voltage (*L*–*V*) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit equipped with a calibrated photo-multiplier tube. EL device was totally fabricated and measured in glove box. The CIE coordinates numbers are calculated automatically by the Keithley 2400 Source Measure Unit, for the EL measurement.

2.3. Synthesis of 2,7-dibromo-9,9-bis(6-(4-(5-phenyl-1,3,4-oxadiazolyl)phenoxy)hexyl)-9H-fluorene (2)

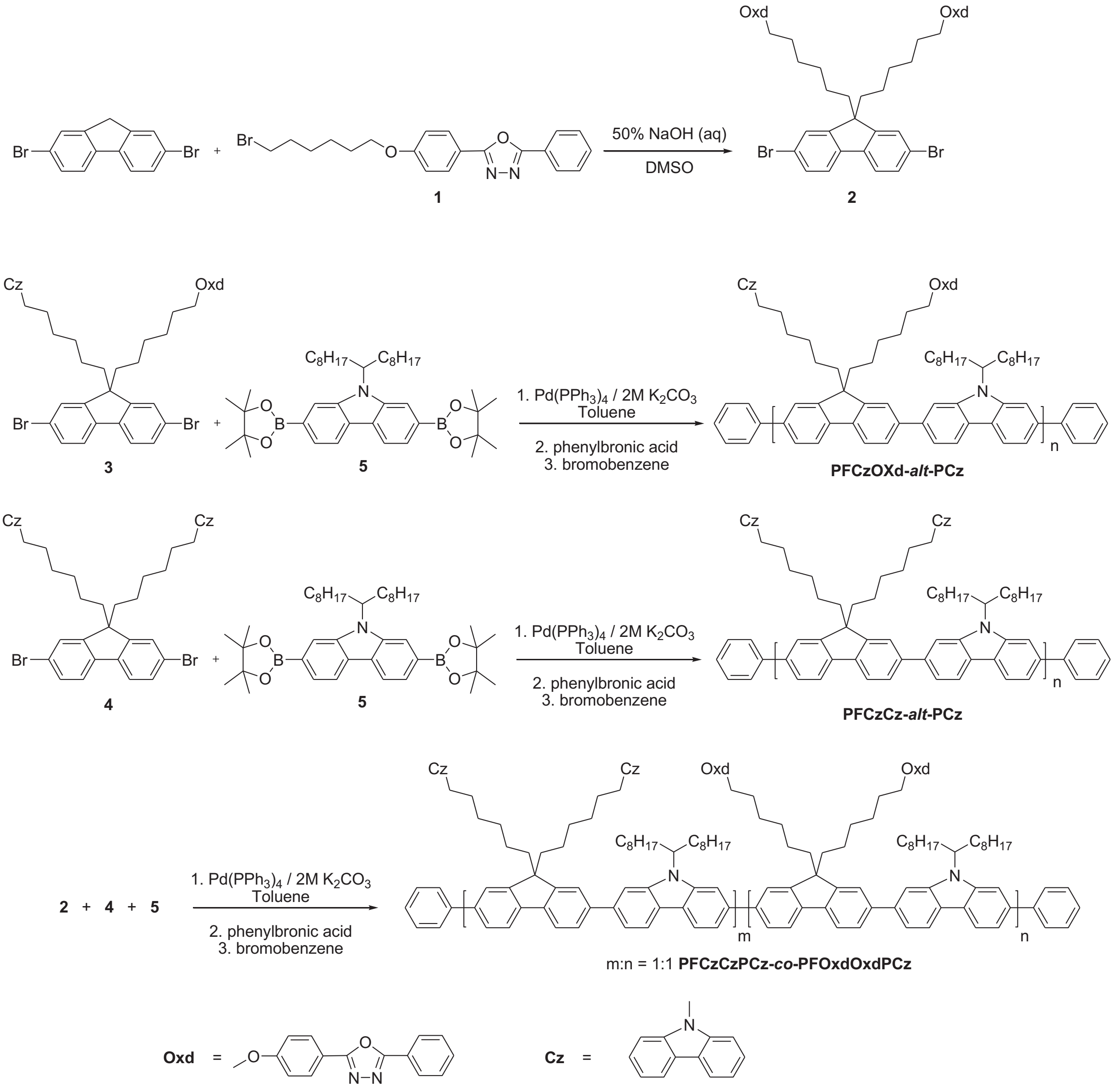
A solution of 2,7-dibromo-9*H*-fluorene (5 g, 15.4 mmol), 2-(4-(6-bromohexyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole (**1**) (12.4 g, 30.8 mmol), and catalytic amounts of triethylbenzyl ammonium chloride in 200 mL of DMSO was stirred at 60 °C for 1 h under argon. The reaction mixture was treated with 4 mL of 50% NaOH aqueous solution at room temperature and then stirred for 5 h. An excess amount of ethyl acetate was added to the resulting mixture to generate a precipitation of NaOH. After collection of NaOH by filtration, the organic phase was washed with water, dried over $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate/hexane = 1/2 as eluent) to get 5.60 g (37%) of the target product as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15–8.10 (m, 4H), 8.05 (d, 4H, $J = 9.0$ Hz), 7.56–7.44 (m, 12H), 6.99 (d, 4H, $J = 9.0$ Hz), 3.93 (t, 4H, $J = 6.3$ Hz), 2.00–1.93 (m, 4H), 1.67–1.62 (m, 4H), 1.29–1.16 (m, 8H), 0.90–0.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 164.82, 164.31, 162.08, 152.48, 139.32, 131.75, 130.55, 129.27, 128.88, 127.04, 126.33, 124.32, 121.80, 121.50, 116.36, 115.15, 68.28, 55.84, 40.37, 29.78, 29.19, 25.88, 23.84. HRMS (m/z FAB$^+$) Calcd for $C_{53}H_{48}Br_2N_2O_2$ 964.2022, found 965.2215.

2.4. Synthesis of alternating copolymers via Suzuki coupling polymerization

Carefully purified monomer **3** (or **4** or (**2** + **4**)), monomer **5**, and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) as the catalyst dissolved in a mixture of toluene (3 mL) and aqueous 2 M K_2CO_3 (2.5 mL). The mixture was refluxed with vigorous stirring for 3 days under argon atmosphere. After 72 h, phenylboronic acid was added to the reaction then 12 h later, bromobenzene was added and the reaction mixture refluxed overnight to complete the end-capping reaction. After the mixture was cooled to room temperature, it was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove catalyst residues and to generate **PFCzOxd-*alt*-PCz** (with monomer **3**), **PFCzCz-*alt*-PCz** (with monomer **4**), and **PFCzCzPCz-*co*-PFOxdOxdPCz** (with monomer **2+4**). The yields of the polymers ranged from 40 to 60%. The resulting polymers were soluble in THF, $CHCl_3$, ODCB and toluene.

PFCzOxd-*alt*-PCz: 8.18 (s), 8.12–7.99 (m), 7.87 (s), 7.73 (s), 7.51–7.50 (m), 7.40–7.14 (m), 6.94 (d), 4.17 (s), 3.90 (s), 2.40 (s), 2.15 (s), 1.99 (s), 1.67 (m), 1.27–1.15 (m), 0.89–0.78 (m).

PFCzCz-*alt*-PCz: 8.02 (s), 8.06 (d), 7.87 (s), 7.71 (m), 7.55–7.41 (m), 7.38–7.15 (m), 4.68 (s), 4.17–4.15 (m), 2.38 (s), 2.19 (s), 2.11 (s), 1.96 (s), 1.82 (s), 1.72 (s), 1.27–1.14 (m), 0.83–0.78 (m).



Scheme 1. Synthetic routes for the monomer and the polymers.

PFCzCzPCz-*co*-PFOxdOxdPCz: 8.16 (s), 8.11–8.03 (m), 7.99 (s), 7.87–7.69 (m), 7.60–7.39 (m), 7.36–7.13 (m), 6.97 (d), 4.69 (s), 4.15 (s), 3.89 (d), 2.38 (s), 1.98–1.59 (m), 1.25 (s), 1.14–0.77 (m).

2.5. Synthesis of random copolymers via Yamamoto polymerization

In a three neck flask was placed bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) (350 mg, 1.27 mmol), 2,2′-dipyridyl (200 mg, 1.27 mmol), 1,5-cyclooctadiene (0.16 mL, 1.27 mmol), and *N*,*N*-Dimethylformamide (DMF) (8 mL). After three freezing-thaw cycles, the catalyst was heated to 80 °C for 30 min to form the purple complex. The reaction mixture was treated with monomer **3** and monomer **6** (or monomer **7**) in 5 mL of toluene and heated at 80 °C for 4 days. After cooling to room temperature, the reaction mixture was poured into the mixture of 1 N HCl solution (100 mL), acetone (100 mL), and methanol (200 mL), and stirred for 6 h. The precipitate was filtered, redissolved in chloroform and precipitated again with large amount methanol. The yields of the polymers ranged from 40 to 50%. The resulting polymers were soluble in THF, CHCl$_3$, ODCB and toluene. The comonomers feed ratios of **3** to **6** are 99:1, 97:3, 95:5 and 90:10, and the corresponding copolymers were named as **PFCzOxd-co-PCz1**, **PFCzOxd-co-PCz3**, **PFCzOxd-co-PCz5**, and **PFCzOxd-co-PCz10**, respectively. The comonomers feed ratios of **3**–**7** are 99:1, 97:3, 95:5 and 90:10, and the corresponding copolymers were named as **PFCzOxd-*co*-PPTZ1**, **PFCzOxd-*co*-PPTZ3**, **PFCzOxd-*co*-PPTZ5**, and **PFCzOxd-*co*-PPTZ10**, respectively. **PFCzOxd-*co*-PCz1**: 8.05–7.93 (m), 7.77–7.47 (m), 7.39–7.10 (m), 6.88 (d), 4.07 (s), 3.78 (s), 2.05 (s), 1.59–1.12 (m), 0.88–0.82 (m).

PFCzOxd-*co*-PCz3: 8.062–7.949(m), 7.671–7.491(m), 7.338–7.138(m), 6.861(d), 4.084(s), 3.793(s), 2.012(s), 1.691–1.135 (m), 0.974–0.888(m).

PFCzOxd-*co*-PCz5: 8.06–7.95 (m), 7.78 (s), 7.67 (s), 7.49 (s), 7.36–7.14 (m), 6.86 (d), 4.09 (s), 3.79 (s), 2.08 (s), 1.29–1.14 (m), 0.89–0.79 (m).

PFCzOxd-*co*-PCz10: 8.05–7.94 (m), 7.66–7.47 (m), 7.39–7.12 (m), 6.85 (d), 4.07 (s), 3.78 (s), 2.02 (s), 1.25–1.13 (m), 0.88–0.78 (m).

PFCzOxd-*co*-PPTZ1: 8.07–7.99 (m), 7.66–7.47 (m), 7.26–7.14 (m), 6.86 (s), 4.07 (s), 3.78 (s), 2.06 (s), 1.57–1.13(m), 0.87–0.81 (m).

PFCzOxd-*co*-PPTZ3: 8.06–7.95 (m), 7.78–7.31 (m), 7.27–7.14 (m), 6.87 (d), 4.08 (s), 3.79 (s), 2.05 (s), 1.59–1.13 (m), 0.88–0.83 (m).

PFCzOxd-*co*-PPTZ5: 8.05–7.94 (m), 7.78–7.40 (m), 7.33–7.11 (m), 6.86 (d), 4.08 (s), 3.79 (s), 2.06 (s), 1.65–1.13 (m), 0.88–0.75 (m).

PFCzOxd-*co*-PPTZ10: 8.06–7.94 (m), 7.80–7.40 (m), 7.38–7.14 (m), 6.87 (d), 4.08 (s),0 3.79 (s), 2.06 (s), 1.71–1.13 (m), 0.89–0.80 (m).

3. Results and discussion

3.1. Synthesis and characterization

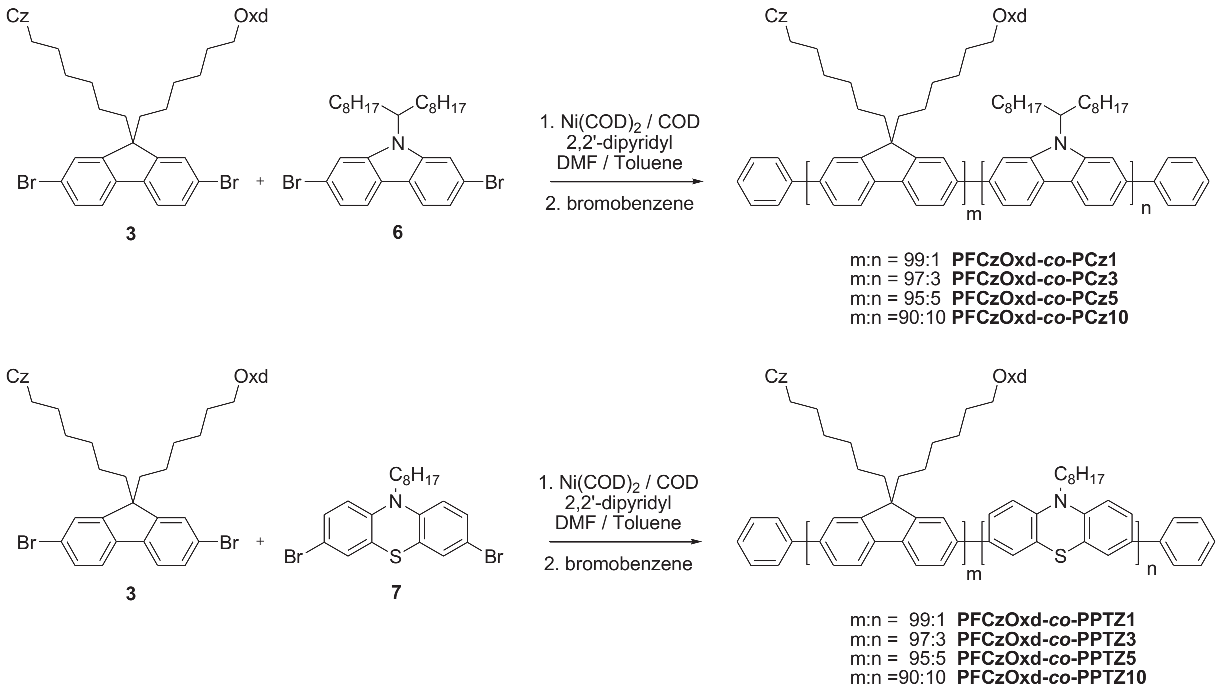
The general synthetic routes toward the monomer and polymers are outlined in Scheme 1 and Scheme 2. The monomers (**3**, **4**, **5**, **6**, and **7**) used for the polymerization were synthesized and purified carefully according to the procedure outlined in the literature [19–23]. The monomer **2** was synthesized by the alkylation of 2,7-dibromo-9*H*-fluorene with 2-(4-(6-bromohexyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole (**1**) in the presence of catalytic amounts of triethylbenzyl ammonium chloride and 50% NaOH aqueous solution. The polymerization was affected by the Pd(0)-catalyzed Suzuki coupling polymerization. In case of poly(9-(6-(9*H*-carbazolyl)hexyl)-9-(6-(4-(5-phenyl-1,3,4-oxadiazolyl)phenoxy)hexyl)-9*H*-fluorene-*alt*-9-(heptadecan-9-yl)-9*H*-carbazole) (**PFCzOxd-*alt*-PCz**) (or poly(9,9-bis(6-(9*H*-carbazolyl)hexyl)-9*H*-fluorene-*alt*-9-(heptadecan-9-yl)-9*H*-carbazole) (**PFCzCz-*alt*-PCz**)), the molar feed ratio of monomer **3** (or **4**) and diboromic ester monomer **5** was 1:1. In case of poly(2-(9-(heptadecan-9-yl)-9*H*-carbazol-2-yl)-9,9-bis(6-(9*H*-carbazolyl)hexyl)-9*H*-fluorene-*co*-2-(9-(heptadecan-9-yl)-9*H*-carbazol-2-yl)-9,9-bis(6-(4-(5-phenyl-1,3,4-oxadiazolyl)phenoxy)-hexyl)-9*H*-fluorene) (**PFCzCzPCz-*co*-PFOxdOxdPCz**), the molar feed ratio of monomer **2**, **4** and **5** was 1:1:2. Monomer **3** was copolymerized with monomer **6** or **7** by using nickel-catalyzed Yamamoto coupling methods, using bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), 2,2′-dipyridyl, and 1,5-cyclooctadiene. To generate the copolymers, poly(9-(6-(9*H*-carbazolyl)hexyl)-9-(6-(4-(5-phenyl-1,3,4-oxadiazolyl)-phenoxy)hexyl)-9*H*-fluorene-*co*-9-(heptadecan-9-yl)-9*H*-carbazole) (**PFCzOxd-*co*-PCz**), different ratios of monomer **3** and **6** were used. The feed ratios of fluorene unit with carbazole and oxadiazole pendants and carbazole unit fragments were 99:1, 97:3, 95:5, and 90:10 for the syntheses of **PFCzOxd-co-PCz1**, **PFCzOxd-co-PCz3**, **PFCzOxd-co-PCz5**, and **PFCzOxd-co-PCz10**, respectively. To generate the copolymers, poly(9-(6-(9*H*-carbazolyl)hexyl)-9-(6-(4-(5-phenyl-1,3,4-oxadiazolyl)phenoxy)hexyl)-9*H*-fluorene-*co*-10-octyl-10*H*-phenothiazine) (**PFCzOxd-*co*-PPTZ**), different ratios of monomer **3** and **7** were also used. The comonomer feed ratios of monomer **3** to phenothiazine unit are 99:1, 97:3, 95:5, and 90:10 and the corresponding polymers were named as **PFCzOxd-*co*-PPTZ1**, **PFCzOxd-*co*-PPTZ3**, **PFCzOxd-*co*-PPTZ5**, and **PFCzOxd-*co*-PPTZ10**, respectively. The carbazole or phenothiazine unit in the polymer backbones was introduced to improve the device performance. All the resulting polymers were soluble in organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and ODCB.

Table 1
Characterization of the synthesized polymers.

Polymers	M_n[a]	M_w[a]	PDI[a]	DSC(T_g)[b]	TGA(T_d)[c]
PFCzOxd-*alt*-PCz	12 000	47 000	3.92	74	375
PFCzCz-*alt*-PCz	16 000	58 000	3.63	84	407
PFCzCzPCz-*co*-POxdOxdPCz	12 000	46 000	3.83	83	394
PFCzOxd-*co*-PCz1	34 000	1 37 000	4.03	108	364
PFCzOxd-*co*-PCz3	36 000	1 31 000	3.64	101	367
PFCzOxd-*co*-PCz5	35 000	1 17 000	3.34	104	341
PFCzOxd-*co*-PCz10	43 000	1 43 000	3.32	100	361
PFCzOxd-*co*-PPTZ1	30 000	1 08 000	3.60	107	362
PFCzOxd-*co*-PPTZ3	38 000	1 16 000	3.05	106	371
PFCzOxd-*co*-PPTZ5	52 000	1 65 000	3.17	109	343
PFCzOxd-*co*-PPTZ10	32 000	1 00 000	3.13	108	371

[a] Molecular weight and Polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards.
[b] Glass temperature was measured by DSC under N$_2$.
[c] Onset decomposition temperature (5% weight loss) was measured by TGA under N$_2$.

The polymerization results including molecular weight, polydispersity (PDI), and thermal stability of the polymers were



Scheme 2. Synthetic routes for the copolymers by Yamamoto polymerization.

Table 2
Characteristics of the UV-vis absorption and photoluminescence.

Polymers	Solution			Film			EL λ_{max} (nm)
	Abs λ_{max} (nm)	PL λ_{max} (nm)	Fwhm[a] of PL	Abs λ_{max} (nm)	PL λ_{max} (nm)	Fwhm[a] of PL	
PFCzOxd-*alt*-PCz	383	418	39	383	427	43	427, 541
PFCzCz-*alt*-PCz	386	418	39	383	428	45	425
PFCzCzPCz-*co*-POxdOxdPCz	383	418	39	383	428	47	425, 529
PFCzOxd-*co*-PCz1	388	419	40	384	430, 537	117	427, 543
PFCzOxd-*co*-PCz3	388	419	40	385	428, 534	100	428, 547
PFCzOxd-*co*-PCz5	387	419	40	383	429, 537	118	426, 541
PFCzOxd-*co*-PCz10	388	419	40	383	429, 539	144	428, 550
PFCzOxd-*co*-PPTZ1	384	418	41	383	430, 480	109	429, 488
PFCzOxd-*co*-PPTZ3	385	418	41	384	484	111	487
PFCzOxd-*co*-PPTZ5	386	418	42	383	487	111	492
PFCzOxd-*co*-PPTZ10	384	418	42	383	490	86	490

[a] Full width at half-maximum of PL spectra.

summarized in Table 1. In the case of the copolymers via Suzuki coupling polymerization, the number-average molecular weights (M_n) and weight-average molecular weights (M_w) were 12 000–16 000 and 46 000–58 000, respectively. In the case of the random copolymer via Yamamoto polymerization, the number-average molecular weights (M_n) and weight-average molecular weights (M_w) were 30 000–52 000 and 1 00 000–1 65 000, respectively. The thermal properties of the polymers were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) as shown in Table 1. DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. TGA was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. TGA showed that copolymers are thermally stable with only about 5% weight loss at temperatures of 341–407 °C, which could afford the advantages for the PLED device fabrication. The polymers showed good thermal stability with

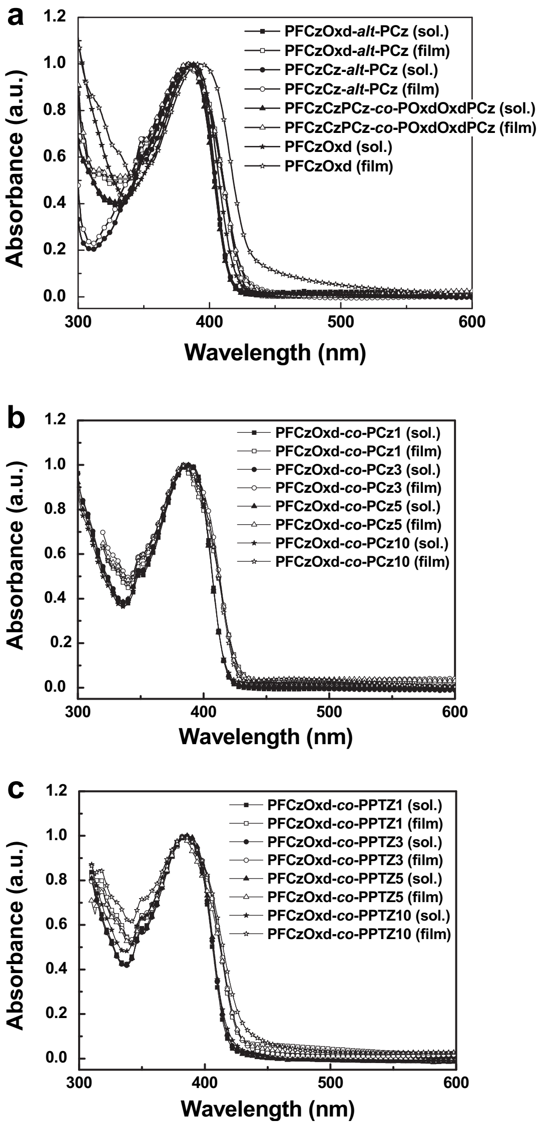


Fig. 1. UV–vis absorption spectra of the polymer: alternating copolymer (a), random copolymer with PCz units (b) and random copolymer with PPTZ units (c).

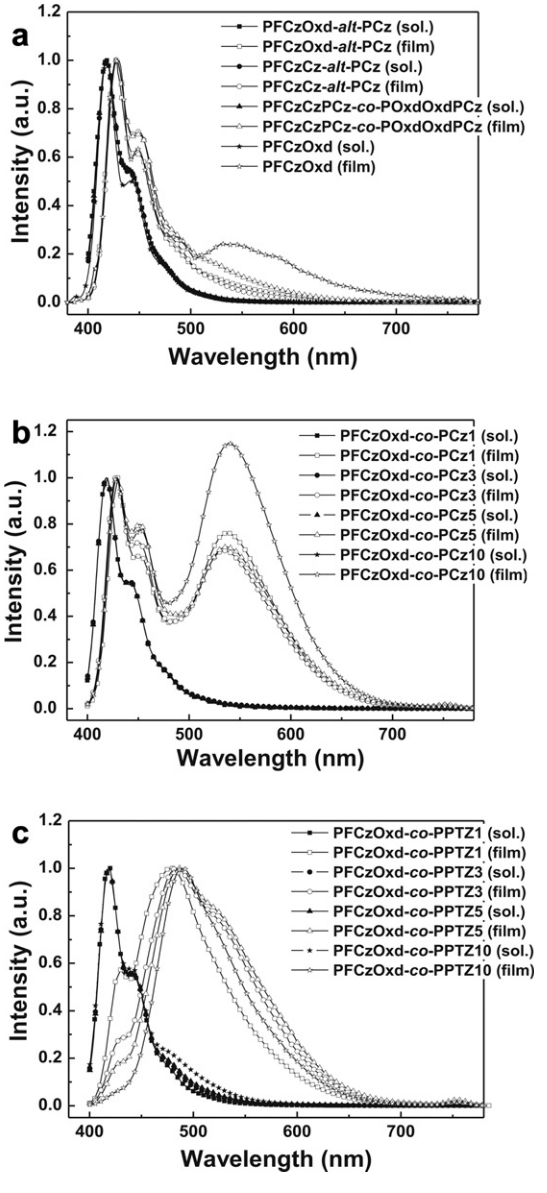


Fig. 2. PL emission spectra of the polymer: alternating copolymer (a), random copolymer with PCz units (b) and random copolymer with PPTZ units (c).

Table 3
Electrochemical potentials and energy levels of the polymers.

Polymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
PFCzOxd-*alt*-PCz	0.87	−5.67	−2.78	2.89
PFCzCz-*alt*-PCz	0.86	−5.66	−2.76	2.90
PFCzCzPCz-*co*-POxdOxdPCz	0.88	−5.68	−2.80	2.88
PFCzOxd-*co*-PCz1	0.88	−5.68	−2.79	2.89
PFCzOxd-*co*-PCz3	0.88	−5.68	−2.78	2.90
PFCzOxd-*co*-PCz5	0.89	−5.69	−2.78	2.91
PFCzOxd-*co*-PCz10	0.89	−5.69	−2.79	2.90
PFCzOxd-*co*-PPTZ1	0.88	−5.68	−2.78	2.90
PFCzOxd-*co*-PPTZ3	0.88	−5.68	−2.78	2.90
PFCzOxd-*co*-PPTZ5	0.87	−5.67	−2.77	2.90
PFCzOxd-*co*-PPTZ10	0.87	−5.67	−2.79	2.88

[a] Onset oxidation and reduction potential measured by cyclic voltammetry.
[b] Calculated from the oxidation potentials.
[c] Calculated from the HOMO energy levels and optical band gap.
[d] Optical energy band gap was estimated from the onset wavelength of the optical absorption.

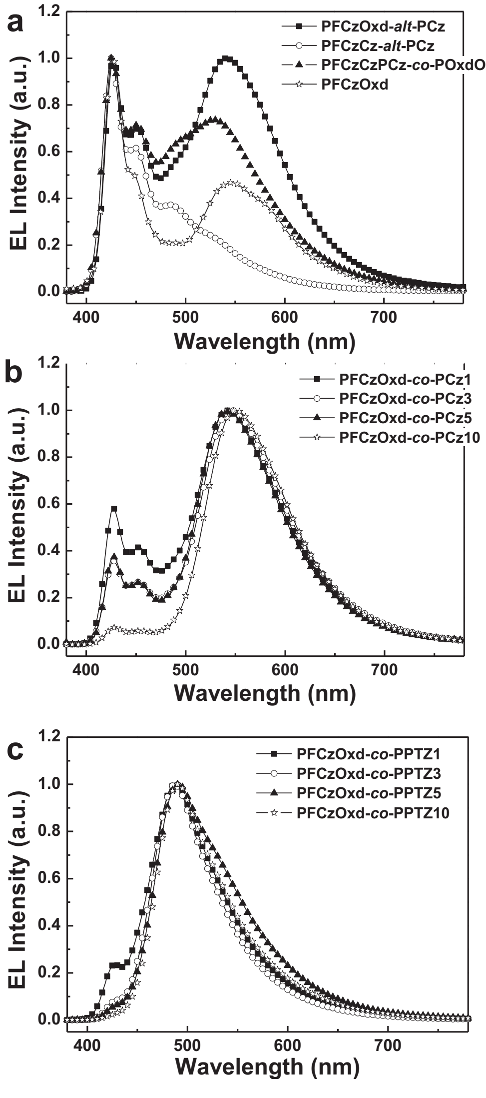


Fig. 3. EL spectra of the polymer: alternating copolymer (a), random copolymer with PCz units (b) and random copolymer with PPTZ units (c).

a glass transition temperature (T_g) of 74–109 °C, using DSC performed at a temperature range of 30–250 °C.

3.2. Optical properties

The absorption and photoluminescence (PL) properties of the synthesized polymers were investigated in chloroform solutions and the thin films by spin-coating on quartz plates from the solutions in ODCB, as summarized in Table 2. As shown in Fig. 1, the adsorption peaks, corresponding to $\pi-\pi^*$ transition of the conjugated backbones, appear at around 380–390 nm. The absorption spectra of the films are very similar to those of the solutions with all of the polymers. The absorption onset wavelengths of the polymers in the film states were around 430 nm, which corresponds to the band gap of 2.88 eV. The edge of the absorption spectra are red-shifted caused by interactions between conjugated polymer chains in film, which results in a higher degree of exciton–exciton annihilation [25].

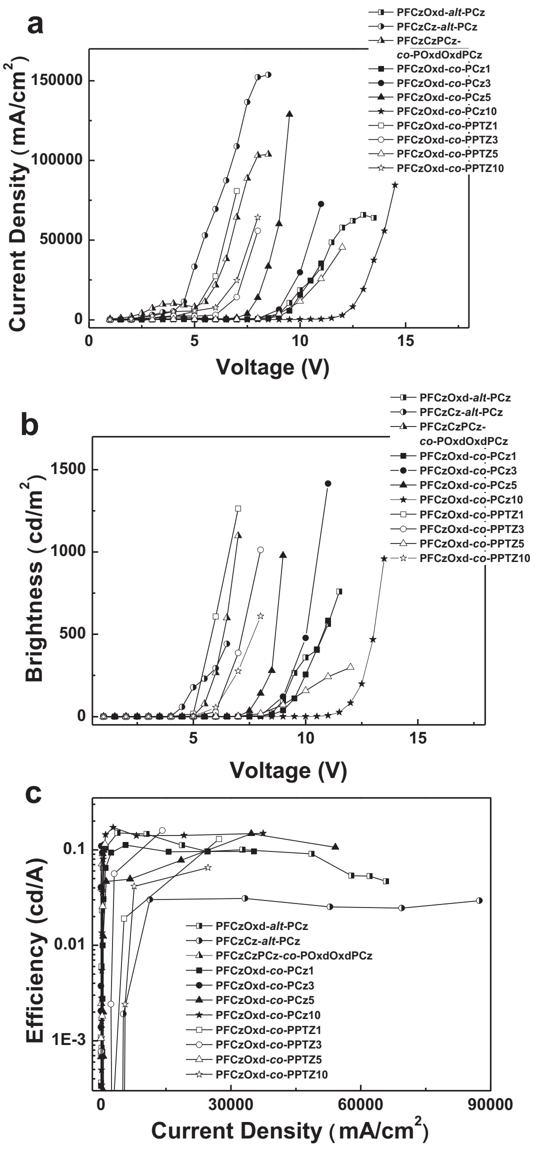


Fig. 4. Current density–voltage–luminescence (*J*–*V*–*L*) characteristics and efficiency of OLED with the configuration of ITO/PEDOT:PSS/Polymer/Ca/Al. Current density–voltage characteristics (a), luminescence–voltage characteristics (b), and efficiency (c).

Table 4
Device performance characteristics of devices with the configuration of ITO/PEDOT/polymer/Ca/Al.

Polymers	Turn-on voltage[a] (V)	Voltage[b]	Current density[b] (mA/cm^2)	Luminance[b] (cd/m^2)	LE$_{max}$[c] (cd/A)	CIE (x, y)[d]
PFCzOxd-*alt*-PCz	7.5	11.5	48600	760	0.15	(0.28, 0.33)
PFCzCz-*alt*-PCz	3.5	6.5	87400	440	0.03	(0.18, 0.17)
PFCzCzPCz-*co*-POxdOxdPCz	4.5	7.0	64400	1100	0.10	(0.25, 0.32)
PFCzOxd-*co*-PCz1	7.5	11.0	35300	580	0.11	(0.33, 0.42)
PFCzOxd-*co*-PCz3	7.0	11.0	72700	1420	0.11	(0.36, 0.46)
PFCzOxd-*co*-PCz5	4.0	7.0	60200	980	0.15	(0.33, 0.44)
PFCzOxd-*co*-PCz10	10	13.5	37400	960	0.17	(0.41, 0.52)
PFCzOxd-*co*-PPTZ1	4.0	7.0	80800	1260	0.13	(0.21, 0.34)
PFCzOxd-*co*-PPTZ3	4.0	8.0	55800	1000	0.16	(0.20, 0.37)
PFCzOxd-*co*-PPTZ5	6.5	12.0	45400	300	0.12	(0.24, 0.42)
PFCzOxd-*co*-PPTZ10	4.5	8.0	64200	610	0.07	(0.22, 0.41)

[a] Voltages required to achieve a brightness of 1 cd/m^2.
[b] Measured under the condition of maximum brightness.
[c] Maximum luminescence efficiency.
[d] Calculated from the EL spectrum.

Fig. 2 shows the PL spectra of the polymers with the excitation of 380 nm in both chloroform solution and thin film. As shown in Fig. 2 (a), the solutions of the polymers (**PFCzOxd-*alt*-PCz**, **PFCzCz-*alt*-PCz**, **PFCzCzPCz-*co*-PFOxdOxdPCz**) showed PL emission peaks with a maximum at 418 nm, and a shoulder at 440 nm. The PL spectra of their thin films consist of typical vibronically structured bands comprising a maximum at 427 nm, a shoulder at 453 nm, and a broad tail at 490 nm. All of PL emission peaks in the film states were red-shifted about 10–20 nm as compared to those of the solutions, which can be attributed to increased interactions between conjugated polymer chains in film, which results in a higher degree of exciton–exciton annihilation [25]. In case of the random copolymers containing carbazole units in the polymer backbone (Fig. 2 (b)), the PL spectra of the solutions were quite similar as compared to the case of polyfluorene. In contrast the PL spectra of the thin films showed peaks at around 540 nm, caused by the aggregation due to the oxadiazole unit with electron withdrawing effect and carbazole unit with electron donating effect. As compared to the homopolymer, **PFCzOxd** reported previously by us [19] , the intensity of the PL emission peak at long wavelength was enhanced by the incorporation of carbazole units in the backbone as low as 1% on the backbones. The PL emission of the random copolymers containing phenothiazine units was investigated as shown in Fig. 2 (c). The PL emission peaks in the solutions were also quite similar to the case of fluorene. In the film state, all of the polymers showed two PL emission peaks at around 430 nm and 480 nm. With increasing amounts of phenothiazine contents, the PL spectra exhibit decreased peaks at 430 nm and increased peaks at 480 nm. Consequently, the PL emission peak at 430 nm was nearly quenched with phenothiazine contents of 10% in the copolymers.

3.3. Electrochemical properties

The electrochemical properties of the polymer were determined from the band gap estimated from the absorption onset wavelength, and the HOMO energy level which was estimated from the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm^2) coated with a thin polymer film was used as the working electrode. Pt wire and $Ag/AgNO_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the $Ag/AgNO_3$ reference electrode (calibrated by the Fc/Fc$^+$ redox system) was 4.8 eV below the vacuum level. The oxidation potentials derived from the onsets of electrochemical p-doping are summarized in Table 3. HOMO levels were calculated according to the empirical formula ($E_{\mathrm{HOMO}} = -([E_{\mathrm{onset}}]^{\mathrm{ox}} + 4.8)$ eV). The polymers exhibited the absorption onset wavelengths of 426–430 nm in solid thin films, which correspond to the band gaps of 2.88–2.91 eV. The polymers exhibit irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.86–0.89 V, which correspond to HOMO energy levels of $-5.66 \sim -5.69$ eV. The LUMO energy levels of the polymers can be calculated with the HOMO energy levels and optical band gaps. The LUMO energy levels of the polymers were thus determined to be $-2.76 \sim -2.80$ eV.

3.4. Electroluminescence properties

The investigations of electroluminescence properties of the copolymers were conducted by fabricating the devices with the configuration of ITO/PEDOT (40 nm)/polymer (80 nm)/Ca (10 nm)/Al (100 nm). The electroluminescence (EL) spectra of the devices are shown in Fig. 3. In case of **PFCzOxd-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz**, the EL spectra of the polymers showed two distinct peaks comprising the maximum at 427 nm, which corresponds to the peak of the polyfluorene, and additional large one at around 540 and 530 nm, respectively. As compared to homopolymer, **PFCzOxd** [19], the intensities of the long wavelength EL peaks at 540 and 530 nm were obviously enhanced by the incorporation of carbazole units at the polymer backbones. The CIE coordinates of the devices with **PFCzOxd-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz** were (0.28, 0.33) and (0.25, 0.32), respectively, which are close to that of the standard white of National Television System Committee (NTSC) (0.33, 0.33). On the other hand, the EL spectrum of **PFCzCz-*alt*-PCz** exhibited maximum peak at 427 nm and CIE coordinates of (0.18, 0.17), corresponding to blue light emission. In case of **PFCzCz-*alt*-PCz**, there is no oxadiazole unit in any part of the structure. It suggests that the oxadiazole units played an important role in the generation of the long-wavelength peak. The long-wavelength peaks can be attributed to the aggregation caused by the oxadiazole unit with electron withdrawing effect and carbazole unit with electron donating effect. As shown in Fig. 3 (b) and (c), the effects of the carbazole and phenothiazine units on the EL spectra were also investigated. Typical EL spectra of **PFCzOxd-*co*-PCzs** and **PFCzOxd-*co*-PPTZs** were nearly same as compared to the PL of the solid films of the polymers, indicating that the EL and PL phenomena originated from the same excited state. The **PFCzOxd-*co*-PCzs** and **PFCzOxd-*co*-PPTZs** showed additional large peak at around 530 and 500 nm, respectively, caused by the aggregation and the excimer formation. The oxadiazole and carbazole pendents in the fluorine unit do not affect the effective conjugation length of the polymers directly, since the oxadiazole and carbazole moieties were introduced as pendants using non-conjugated chain. However, CIE coordinates of synthesized copolymers for white light is not better than that of PFCzOxd caused by more aggregation between pendant unit and carbazole or phenothiazine units in the backbone. The aggregate is formed by aggregation of several neighboring polymer segments at the ground state [26]. The long-wavelength peaks of EL spectra are enhanced by aggregate at ground state, excimer or exciplex at excited state, and electric-field-induced complex (electromer or electroplex) [25].

The current density–voltage (*J*–*V*), luminescence–voltage (*L*–*V*), and efficiency characteristics of ITO/PEDOT/polymer/Ca/Al devices are shown in Fig. 4 and summarized in Table 4. The maximum brightnesses of the devices were in the range of 300–1420 cd/m^2. The luminescence efficiency of the polymers are higher than 0.1 cd/A, except the cases of **PFCzCz-*alt*-PCz** (0.03 cd/A) and **PFCzOxd-*co*-PPTZ10** (0.07 cd/A). Among all the devices, the device fabricated from **PFCzOxd-*co*-PCz10** showed the best performance with the efficiency of 0.17 cd/A, caused by the hole transporting ability of the carbazole unit in the polymer backbone.

4. Conclusions

We report here the synthesis, characterization and EL properties of novel conjugated copolymers based on fluorene with carbazole and oxadiazole pendants for the generation of the white emission. The polymers exhibited the absorption peak at around 380–390 nm with both of solutions and thin films. The solid films of **PFCzOxd-*co*-PCzs** showed PL emission peak at around 430 nm and 530 nm. The peak at 530 was increasing with higher contents of carbazole unit in the backbone. The solid films of **PFCzOxd-*co*-PPTZs** showed major peak at around 500 nm with decreased peak at 430 nm. In the case of **PFCzOxd-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz**, the EL spectra of the polymers showed two distinct peaks comprising the maximum peak at 427 nm and additional one at around 540 and 530 nm, respectively. The CIE coordinates of the devices with **PFCzCz-*alt*-PCz** and **PFCzCzPCz-*co*-PFOxdOxdPCz** were (0.28, 0.33) and (0.25, 0.32), respectively, approaching the value of the standard white of NTSC (0.33, 0.33).

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Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.polymer.2010.10.061.

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