

Synthesis and Characterization of Alternating Copolymers Derived from Indeno[1,2-*b*]fluorene for Blue Light-Emitting Diodes

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ABSTRACT: Three blue light-emitting alternating copolymers derived from 6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene (IF) and 4,4'-diphenyl ether (DPE), *N,N'*-di(4-phenyl)aniline (TPA), or 3,6-*N*-octylcarbazole (CZO), named as PIF-DPE, PIF-TPA, and PIF-CZO, respectively, were synthesized by Suzuki coupling reaction. The chemical structure, optoelectronic and thermal properties of the copolymers were characterized by ¹H-NMR, elemental analysis, gel permeation chromatography, cyclic voltammetry, thermogravimetric analysis, and differential scanning calorimetry. Photoluminescence peaks of the copolymers of PIF-DPE, PIF-TPA, and PIF-CZO in THF solution and solid state were around 432, 419, and 411 nm, and the preliminary light-emitting devices based on

the copolymers of PIF-DPE, PIF-TPA, and PIF-CZO emit blue light with the maximal emission peaks at around 437, 449, and 438 nm, respectively. The control of conjugated length of the copolymers and the achievement of blue light-emitting conjugated polymers based on indeno[1,2-*b*]fluorene, which satisfy both color purity and relatively high eye sensitivity, were achieved by the introduction of kink linkages into the polyindeno[1,2-*b*]fluorenes backbone. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1409–1417, 2012

Key words: conjugated polymers; indeno[1,2-*b*]fluorene; light-emitting diodes; synthesis

INTRODUCTION

Polymeric light-emitting diodes (PLEDs) have attracted intense academic and industrial interests because of the potential use in flat displays and general lighting sources in last decades.^{1,2} Although many approaches have been made to design and synthesize blue-emitting polymers such as poly-*p*-phenylenes (PPPs),^{3,4} polyfluorenes (PFs),^{5–8} and poly(*N*-alkylcarbazole)^{9,10} for high performance

PLEDs for achieving full color displays, efficient and stable blue electroluminescent conjugated polymers are still lacking compared to green and red emitters reported by now. Among the blue-emitting polymers, PFs and PFs derivatives are regarded as the most promising candidates for blue light-emitting diodes because of their exceptional optoelectronic properties such as good thermal and chemical stability, high fluorescence quantum yield, good film-forming, and hole-transporting properties.^{6,7} To achieve desired blue emission color, it is critical to avoid the formation of the excimers and nematic type packing arrangement which leads to a red-shifted emission and a reduced emission efficiency, via introduction of some large bulk side chains to the 9-position of the fluorene or by the introduction of kink linkages to the PFs backbone.^{11–15} However, the emission peaks of these PFs and PFs derivatives at around 425 nm are not optimal for blue light emission,^{16–18} as they are far away from the preferred blue emission peak (~440–450 nm) for both high color purity and good match for human eye sensitivity.^{19,20}

As a good optical and chemical analogs to PFs, polyindeno[1,2-*b*]fluorenes (PIFs) not only have all

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the good optoelectronic properties of PFs as described above^{21,22} but also show the advantage of the bathochromically shifted emission wavelength leading to a blue emission color matched for the human eye.^{19,20} Therefore, PIFs were regarded as one of the ideal blue light-emitting materials and have been studied intensively in recent years.^{20–22} Many blue light-emitting polymers based on indeno[1,2-*b*]fluorene with the enhanced color purity and good sensitivity to the human eyes have been synthesized by the introduction of some bulk side chains to the 6,12-positions of the indeno[1,2-*b*]fluorene or by the introduction of kink linkages to the PIFs backbone. For example, in 2001, Marsitzky et al. reported a random copolymer based on indeno[1,2-*b*]fluorene named as PIF-*co*-anthracene²⁰; the PLEDs based on PIF-*co*-anthracene showed an electroluminescence peak around 447 nm with two shoulder peaks around 475 and 506 nm. Following, in 2004, Towns et al. reported the synthesis and characterization of poly(tetraaryllindeno[1,2-*b*]fluorenes) (PTA-IFs), the emission from devices based on the PTA-IFs had maxima in the blue at 435 and 455 nm with a long tail into the red.²³ In 2005, Kim et al. reported the blue light-emitting named as PIFs,^{21,22} the PLEDs based on the polymers showed an electroluminescence peak around 445 nm with two shoulder peaks around 465 and 500 nm. Although, the electroluminescent (EL) emission maximal of all these polymers based on indeno[1,2-*b*]fluorene show relative eye sensitivity, the EL emission shoulder peaks around 500 nm should be decreased or eliminated, and the color purity of these copolymers needs to be further increased.

In this article, we report the synthesis and characterization of three novel alternating copolymers derived from 6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene (IF) and the kink linkages such as 4,4'-diphenyl ether (DPE), *N,N'*-di(4-phenyl)aniline (TPA), or 3,6-*N*-octylcarbazole (CZO) by Suzuki coupling reaction named as poly{(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-2,8-diyl-*alt*-diphenylether-4,4'-diyl} (PIF-DPE), poly{(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-2,8-diyl-*alt*-diphenylaniline-4,4'-diyl} (PIF-TPA), and poly{2,8-(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-*alt*-*N*-9-octylcarbazole-3,6-diyl} (PIF-CZO), respectively. The obtained polymers are readily soluble in common organic solvents such as toluene, chloroform, and tetrahydrofuran (THF). The band gaps of the copolymers are between 2.90 and 3.06 eV, entitled as wide band gap semiconducting polymers. PL peaks of the copolymer of PIF-DPE, PIF-TPA, and PIF-CZO in THF solution and solid states were around 432, 419, and 411 nm, and the PLEDs with the configuration as ITO/PEDOT:PSS/PVK/copolymer/Ba/Al based on the copolymers of PIF-DPE, PIF-TPA, and PIF-CZO emit blue light with

the peaks at around 437, 449, and 438 nm, respectively, and the CIE (Commission Internationale de L'Éclairage) 1931 color coordinate of (0.18, 0.14, PIF-DPE), (0.20, 0.16, PIF-TPA), and (0.18, 0.13, PIF-CZO), respectively. It indicated that the controlling of conjugated length of the copolymers and the achievement blue light-emitting conjugated polymers, which satisfy both color purity and relatively high eye sensitivity, were achieved by the introduction of kink linkages into the PIFs backbone.

EXPERIMENTAL SECTION

Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. Di(4-bromophenyl) ether was purchased from TCI Chemical Co. and recrystallized in ethanol before use. All the solvents were further purified under a nitrogen flow. 3,6-Dibromocarbazole,²⁴ 2,8-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene²⁵ and *N,N'*-di(4-bromophenyl)aniline^{26,27} were prepared following the already published procedures and characterized by the GC-MS or FAB-MS and ¹H-NMR spectra before use.

General methods

¹H-NMR spectra were recorded on a Bruker DRX 300 spectrometer operating at 300 MHz and was referred to tetramethylsilane. GC-MS and FAB-MS were obtained on GC-MS (TRANCE2000, Fiunigan. Co.) and FAB-MS (VG ZAB-HS). Analytical GPC was obtained using a Waters GPC 2410 in THF via a calibration curve of polystyrene standards. Elemental analysis was performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). UV-visible absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra were taken by Fluorolog-3 spectrofluorometer under 370 nm light excitation. Cyclic voltammetry was measured on a Potentiostat/Galvanostat model 283 electrochemical workstation (Princeton Applied Research) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN), with platinum and saturated calomel electrodes as the working and reference electrodes, respectively.

Device fabrication and measurement

PLEDs were fabricated on prepatterned indium-tin oxide (ITO) substrate with a sheet resistance of 15–20 Ω/square. The substrate was cleaned by a surfactant scrub, underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water,

followed by acetone and isopropanol. Oxygen plasma treatment was made for 4 min as the final step of substrate cleaning to improve the contact angle just before film coating. A layer of PEDOT : PSS (From Clevios) with 40 nm thickness was spin coated onto ITO and then baked on a hot plate at 150 °C in air to improve hole injection and smooth surface roughness. Poly(*N*-vinylcarbazole) (PVK) film with a thickness of 40 nm was subsequently deposited from chlorobenzene solution onto PEDOT : PSS layer to serve as the hole transport layer. The solution of the copolymers in toluene was prepared in a nitrogen-filled glove box and then spin coated on the top of the PVK layer. The typical thickness of the emitting layer was 70–80 nm as determined by a profiler (Tencor Alfa-Step 500). Finally, 4 nm of barium and 100 nm of aluminum layer were thermally deposited onto the films with a shadow mask at a base pressure of 3×10^{-4} Pa. The deposition speed and thickness of the barium and aluminum layers were monitored by a thickness/rate meter (model STM-100, Sycon). The cathode area defines the active area of the device. The typical active area of the devices in this study is 0.17 cm². The spin coating of the EL layer and device performance tests were carried out within a glove box (Vacuum Atmosphere Co.) with nitrogen circulation. The current–voltage (I–V) characteristics were measured with a Keithley 236 source-measurement unit, and the luminance was measured by a calibrated silicon photodiode. The luminance was further calibrated by a spectrophotometer (SpectraScan PR-705, Photo Research) after encapsulation of devices with UV-curing epoxy and thin cover glass. The EL spectra were collected by a PR-705 photometer.

Synthesis

3,6-Dibromo-*N*-octylcarbazole²⁴

To NaH (1.6 g, 60%) suspended in anhydrous THF (50 mL) under nitrogen flow, the 3,6-dibromocarbazole (6.5 g, 20 mmol) solution in THF (25 mL) was added dropwise under vigorously stirring. The small gas bubble was given off, and the color of reaction solution was turned from white to pea green. After stirred about 0.5 h under ambient temperature, the reaction was refluxing and 1-bromooctane (4.64 g, 24 mmol) was added dropwise. After that, the reaction mixture was kept refluxing overnight under nitrogen atmosphere. In final, the reaction was quenched with water and extracted with CH₂Cl₂. The organic phase was dried with anhydrous MgSO₄, and the solvent was removed under reduced pressure. Then, the crude product was purified by chromatography (silica gel, eluent: hexane/ethyl acetate = 10 : 1) to give white solid in 85%

yield. ¹H-NMR (300 MHz, CDCl₃, δ = ppm): 8.10 (s, 2H), 7.53 (d, 2H), 7.22 (d, 2H), 4.18 (t, 2H), 1.79 (m, 2H), 1.31–1.21 (m, 10H), 0.86 (t, 3H); Formula: C₂₀H₂₃Br₂N, Calcd: C, 54.94; H, 5.30; N, 3.20; Br, 36.55. Found: C, 54.93; H, 5.29; N, 3.20; Br, 36.5.

General procedure of polymerization

Carefully purified 2,8-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene (0.5 mmol), dibromo compound (0.5 mmol), Pd (PPh₃)₄ (0.5–2.0 mol %), and several drops of Aliquat 336 were dissolved in a mixture of toluene and aqueous 2M Na₂CO₃. The solution was refluxed with vigorous stirring for 36 h under an argon atmosphere. At the end of polymerization, the polymers were end-capped with phenylboronic acid and bromobenzene to remove bromine and boronic ester end groups to avoid a possible quenching effect or excimer formation by boronic and bromine end groups in LEDs.^{28,29} The mixture was then poured into methanol, and the precipitated material was recovered by filtration and purified by flash column chromatography. The resulted polymers were air-dried overnight, followed by drying under vacuum.

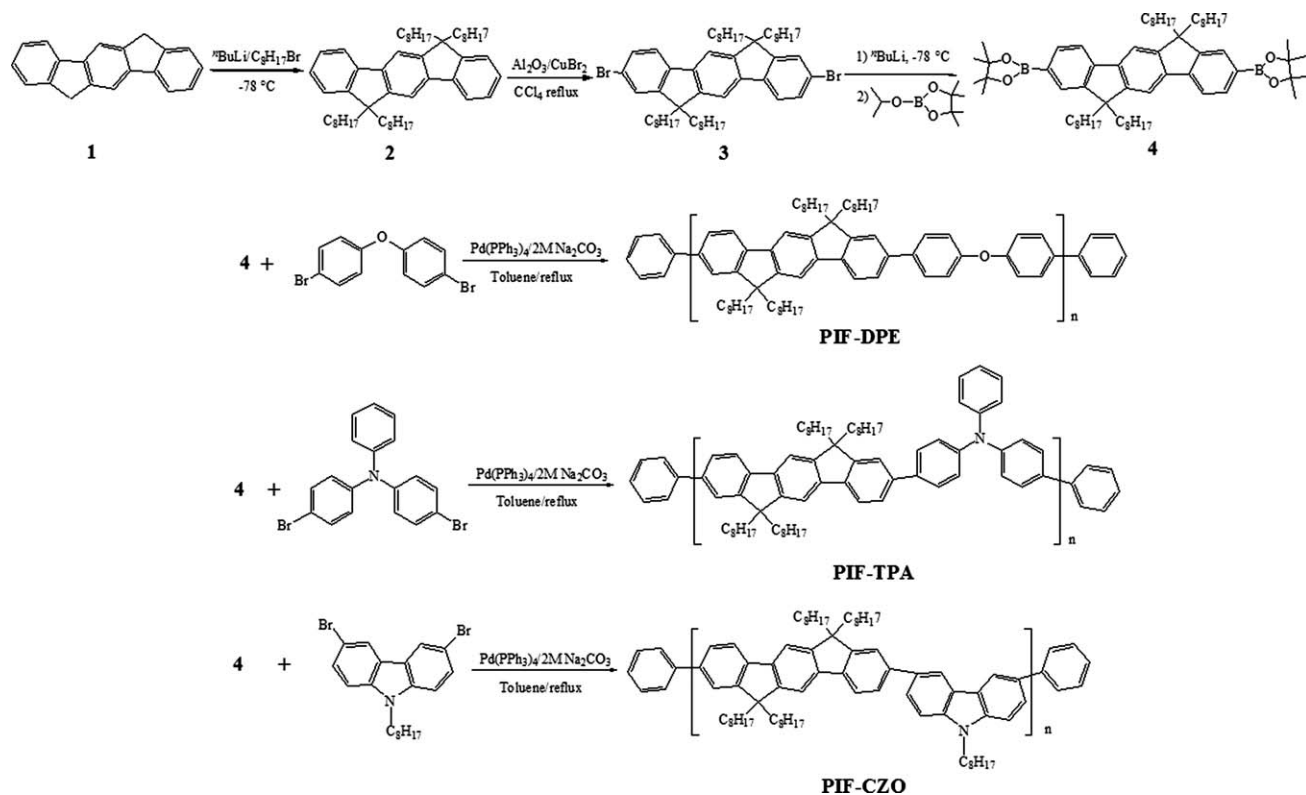
*Poly[(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-2,8-diyl-*alt*-diphenylether-4,4'-diyl]*. Yield of 85%. ¹H-NMR (CDCl₃, 400 MHz, δ = ppm), 7.79–7.04 (m, 16H), 2.06 (br, 8H), 1.26–1.07 (m, 42H), 0.80 (t, 18H). Elemental analysis found for PIF-DPE: C, 88.45; H, 9.67; O, 1.81; *M_n* = 14,400 g/mol (*M_w*/*M_n* = 2.10).

*Poly[(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-2,8-diyl-*alt*-diphenylaniline-4,4'-diyl]*. Light yellow powder in a yield of 73%. ¹H-NMR (CDCl₃, 300 MHz, δ = ppm), 7.84–7.32 (m, 17H), 2.12 (br, 8H), 1.25–1.07 (m, 42H), 0.8 (t, 18H); Elemental analysis found for PIF-TPA: C, 89.14; H, 9.18; N, 1.45; *M_n* = 14,200 g/mol (*M_w*/*M_n* = 2.84).

*Poly[2,8-(6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene)-*alt*-*N*-9-octylcarbazole-3,6-diyl]*. Light yellow powder in a yield of 76%. ¹H-NMR (CDCl₃, 300 MHz, δ = ppm), 7.84–7.32 (m, 14H), 4.21 (t, 2H); 2.02 (br, 8H), 1.45–1.03 (m, 52H); 0.89 (t, 3H); 0.80 (t, 18); Elemental analysis found for PIF-CZO: C, 88.48; H, 10.07; N, 1.40; *M_n* = 23,300 g/mol (*M_w*/*M_n* = 2.84).

RESULTS AND DISCUSSION

The general synthetic route toward the monomers and copolymers is outlined in Scheme 1. 3,6-Dibromo-*N*-octylcarbazole²⁴ and *N,N'*-di(4-bromophenyl)aniline^{26,27} were synthesized by the published procedures. 2,8-Bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene²⁵ was synthesized by the modified procedures. Following the polymer synthetic route in Scheme 1, the



Scheme 1 Synthetic route of the monomers and the copolymers.

alternating copolymers from 2,8-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene and bis(4-bromophenyl) ether, bis(4-bromophenyl)aniline, or 3,6-dibromo-*N*-octylcarbazole were synthesized by the palladium-catalyzed Suzuki coupling reaction named as PIF-DPE, PIF-TPA, and PIF-CZO, respectively. The resulted polymers are good soluble in common organic solvents and solution processibility. The number-average molecular weights (M_n) of these polymers were determined by GPC using a polystyrene standard, ranging from 14,200 to 23,300 g/mol with a polydispersity index (PDI; M_w/M_n) between 2.10 and 2.84 (Table I). We note that the actual ratios of tetraoctylindeno[1,2-*b*]fluorene (IF) to the linkage unit such as 4,4'-diphenyl ether, *N,N'*-di(4-phenyl)aniline, and 3,6-*N*-octylcarbazole in the copolymers estimated by elemental analysis (listed in Table I) are in

good agreement with the feeding ratios of the two monomers within experimental error. It indicated that the alternating copolymers were synthesized successfully.

Figure 1 shows the UV absorption spectra of the new polymers in THF solution and film coated onto silex glass. The data of optical properties of the polymers are summarized in Table II. As shown in the absorption spectra, the polymer PIF-DPE in the THF solution depicted absorption maxima (λ_{max}) at 398 nm. The absorption spectrum of PIF-TPA monitored in THF solution displays one absorption peak at around 362 nm with shoulder absorption at around 375 nm. The absorption spectrum of PIF-CZO monitored in THF solution displays one absorption peak at around 369 nm with shoulder absorption at around 386 nm. The absorption of the copolymers in solid thin film is similar to the absorption spectra of

TABLE I
Molecular Weights of the Copolymers and Their Composition Determined by Elemental Analysis

Copolymers	M_n ($\times 10^3$)	M_w/M_n	C content in the copolymers (%)	N content in the copolymers (%)	O content in the copolymers (%)	The feed ratios of IF/L-unit	IF/L-unit in the copolymers
PIF-CZO	23.3	2.84	89.13	1.18	—	50 : 50	50 : 50.07 ^a
PIF-TPA	14.2	2.84	89.53	1.24	—	50 : 50	50 : 49.91 ^a
PIF-DPE	14.4	2.1	89.08	—	1.63	50 : 50	50 : 49.85 ^b

^a Molar ratio of IF/L-unit (CZO or TPA respectively) in the copolymers calculated from C and N element contents in the copolymers.

^b Molar ratio of IF/L-unit (DPE) in the copolymers calculated from C and O element contents in the copolymers.

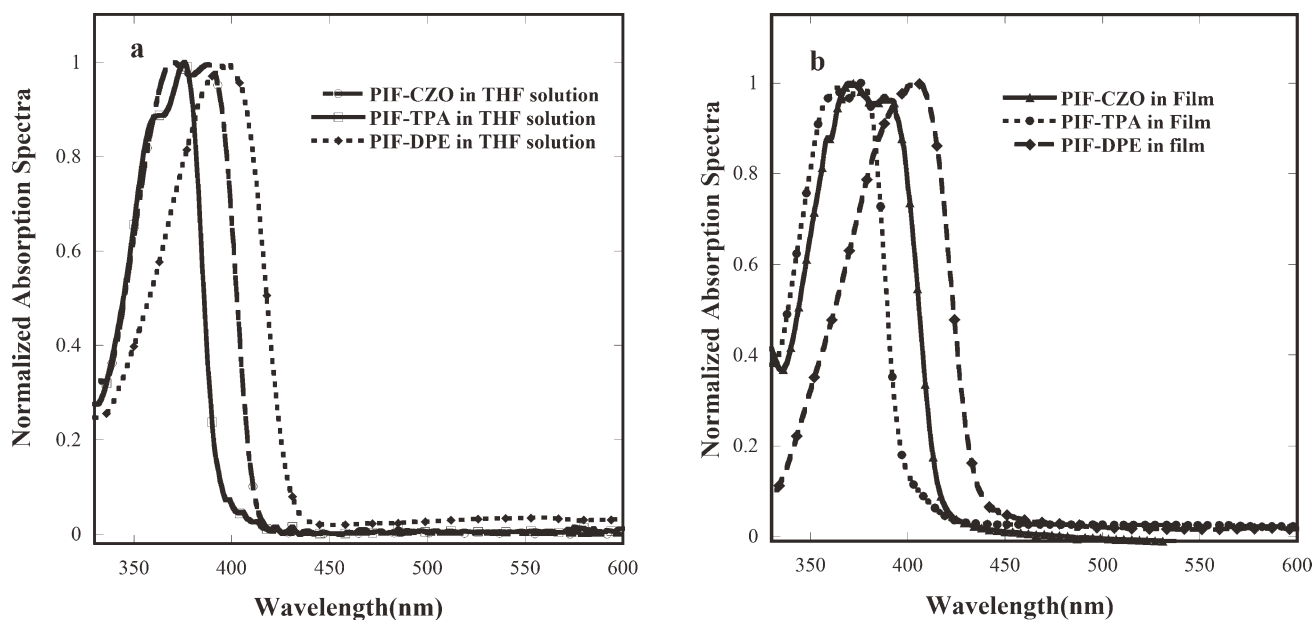


Figure 1 Normalized absorption spectra of the copolymers in THF solution (a) and solid thin film (b).

TABLE II
Optoelectronic and Electrochemical Properties of the Copolymers

Copolymer	Abs		PL		PL QE%	HOMO (eV)	LUMO (eV)	E_g^a	E_g^b
	Solution	FILM	Solution	Film					
PIF-DPE	398	404	431, 456	435, 455	48.9	-5.19	-2.36	2.86	2.83
PIF-TPA	362, 375	365, 377	414, 440	420, 445	43.1	-5.14	-2.13	3.02	3.01
PIF-CZO	369, 386	370, 388	410, 431	411, 436	52.8	-5.10	-2.18	2.96	2.92

^a Calculated from the onset of the absorption spectra of the copolymers in solid states.

^b Calculated from the onset potential of reduction and oxidation waves of the copolymers in solid states.

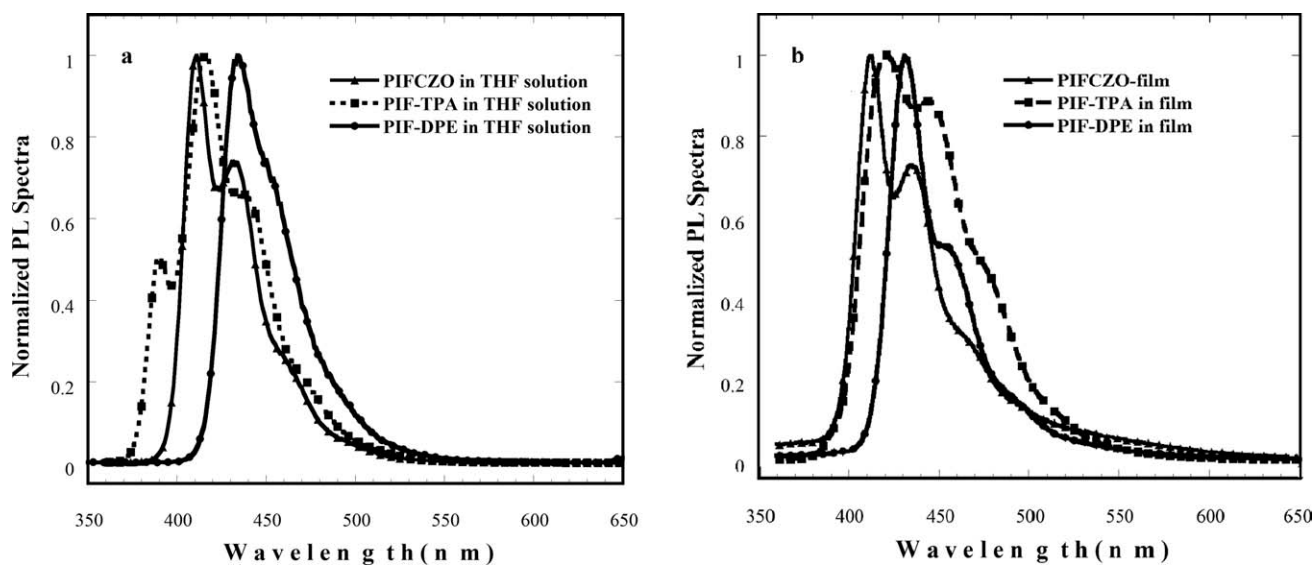


Figure 2 Normalized photoluminescence spectra of the copolymers in THF solution (a) and solid thin film (b).

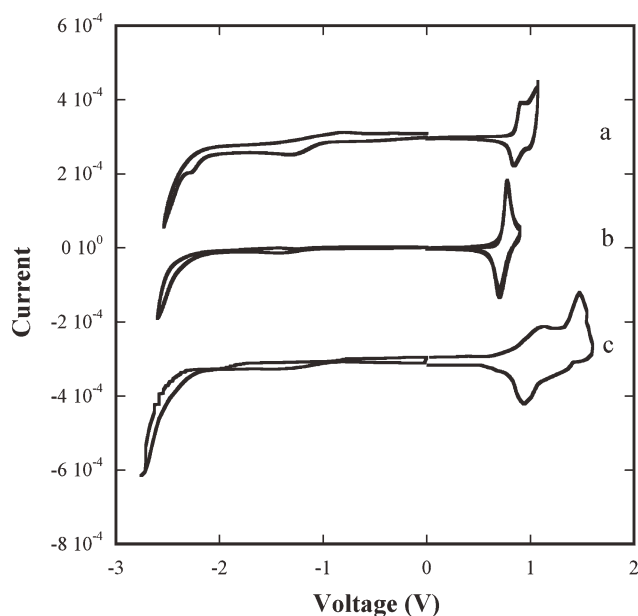


Figure 3 Electrochemical curves of the copolymers (a, PIF-DPE; b, PIF-CZO; PIF-TPA).

the copolymers in THF solution except the absorption spectra of the copolymers in solid thin film are red-shifted several nanometers (1–6 nm) [Fig. 1(b)]. On the other hand, compared to the maximal absorption peaks of the poly(tetraalkyl)indeno[1,2-*b*]fluorenes around 420 nm,²² which are attributed to the of π - π^* electron delocalization of the indeno[1,2-*b*]fluorene in the polymer backbone, the maximal absorption peaks of PIF-DPE, PIF-TPA, and PIF-CZO are blue-shifted about 50–60 nm. It can be attributed to reduction of the π -conjugation lengths

of main chain by introducing of linkages into the polymer backbone. The optical band gap of the copolymers estimated from extrapolation of the onset band gap wavelength of the polymers in solid thin film are 2.86 eV for PIF-DPE, 3.02 eV for PIF-TPA, and 2.96 eV for PIF-CZO, respectively.

The PL spectra of the polymers in THF solution (5×10^{-5} mol/L) and in thin films obtained by using Fluorolog-3 spectrofluorometer (Jobin Yvon) under an excitation at 370 nm are presented in Figure 2(a) and 2(b), respectively. The PL emission peaks of the polymers and the absolute quantum efficiencies (QE) are summarized in Table II. The PL spectrum of PIF-DPE monitored in THF solution displays one absorption peak at around 431 nm with a shoulder emission peak at around 455 nm. The PL spectrum of PIF-TPA monitored in THF solution displays one absorption peak at around 414 nm with a shoulder emission peak at around 440 nm. The PL spectrum of PIF-CZO monitored in THF solution displays one absorption peak at around 410 nm with two shoulder emission peak at around 380 nm and 431 nm. The PL spectra of PIF-DPE and PIF-TPA in film show similar emission properties except the maximal emission peaks are red-shifted about 2–5 nm, and the shoulder emission peaks at around 440–450 nm are slightly increased when compared with those for the copolymer in solution. The PL spectrum of PIF-CZO in film displays one emission peak at around 411 nm and only one shoulder emission peak at around 436 nm. All the copolymers show high PL quantum yields (Table II). On the other hand, as comparison of the PL properties of PIFs, the emission peaks of the copolymers are blue shifted about

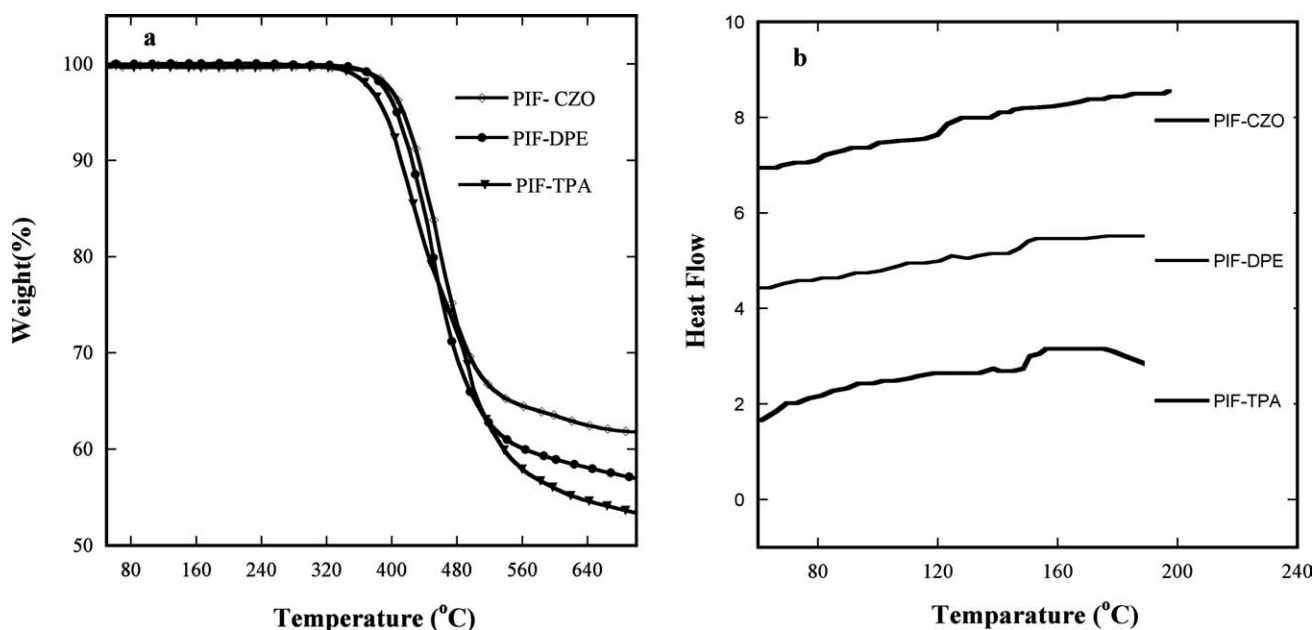


Figure 4 TGA (a) and DSC (b) curves of the polymers.

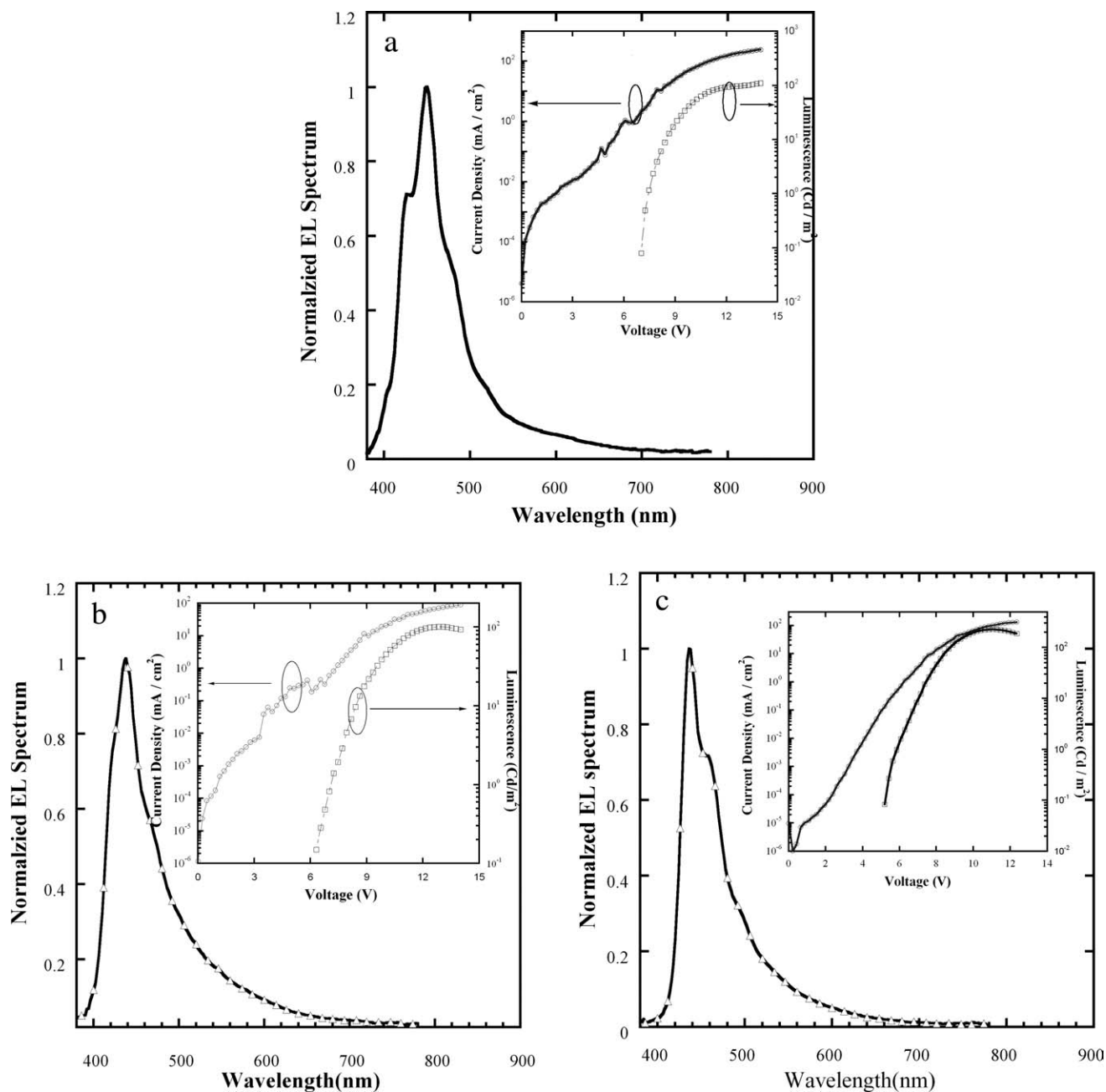


Figure 5 Normalized EL spectra of the copolymers (a, PIF-TPA; b, PIF-CZO; and c, PIF-DPE) and properties of the LEDs based on the copolymers with the devices configuration as ITO/PVK/copolymer/Ba/Al (inner).

20 nm. It verified again that the conjugated length of the copolymers were decreased by the introducing of kink linkages in the PIF backbone.

The electrochemical behaviors of PIF-DPE, PIF-TPA, and PIF-CZO were characterized by cyclic voltammetry. Figure 3 shows the CV curves of the copolymers. The onset potentials for oxidation waves of PIF-DPE, PIF-TPA, and PIF-CZO were at around 0.79, 0.74, and 0.70 V, respectively. The onset potentials for reduction waves of PIF-DPE, PIF-CZO, and PIF-TPA were at around -2.36 , -2.13 , and -2.18 V, respectively. HOMO and LUMO levels of

the copolymers calculated by empirical formulas $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4)$ eV and $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4)$ eV³⁰ are listed in Table II. The electrochemical band gap of the copolymer deduced from the HOMO and LUMO energy levels of the copolymer are about 2.83 eV for PIF-DPE, 3.01 eV for PIF-TPA, and 2.92 eV for PIF-CZO. The electrochemical band gaps of the copolymers are agreement with the optical band gap of the copolymers in film within experimental error (Table II).

Thermal stabilities and thermally induced phase transition behaviors of the copolymers were

TABLE III
Device Characterization Results of the Copolymers

Devices	Data at LE_{max}			V_{on} (V)	L_{max} (Cd/m ²)	CIE
	LE (Cd/A)	V (V)	J (mA/cm ²)			
PVK/PIF-TPA	0.08	10	66	7	108	0.20, 0.16
PVK/PIF-CZO	0.22	9.1	10	6.3	100	0.18, 0.13
PVK/PIF-DPE	0.36	8.5	21	5.2	229	0.18, 0.14

determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. TGA curves of the copolymers were presented in Figure 4(a) in which all of the copolymers exhibit an onset degradation temperature (T_d) higher than 400 °C under nitrogen with similar degradation patterns. These data demonstrate that the copolymers show excellent thermal stability. DSC curves of the copolymers were presented in Figure 4(b). No crystallization and melting peaks were observed for any copolymers that we investigated. On the other hand, the polymers did not display the liquid crystalline phase transition behaviors shown in poly[6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene-2,8-diyl]²² indicating that the order of the polymers were decreased upon incorporation of the linkage units such as 4,4'-diphenyl ether, *N,N'*-di(4-phenyl)aniline, and 3,6-*N*-octylcarbazole to the PIFs backbone.

To investigate the EL properties of the polymers, PLEDs based on solution-processed technology were fabricated with a configuration of ITO/PEDOT:PSS/PVK/polymer/Ba/Al. As shown in Figure 5, the EL emission peaks of the devices based on PIF-

DPE, PIF-TPA, and PIF-CZO are located at 437, 449, and 438 nm, with blue-shifted shoulders located at around 445, 420, and 475 nm, respectively. More significantly, when compared with the EL spectra of reported conjugated polymers based on indeno[1,2-*b*]fluorene such as double spiro-polyindeno[1,2-*b*]fluorene,¹⁹ PIF-*co*-anthracene[1,2-*b*]fluorenes,²⁰ and poly(tetraarylindeno[1,2-*b*]fluorene,^{21,22} the distinct shoulder emission peaks around 500 nm of the devices based on copolymers-based indeno[1,2-*b*]fluorene were almost completely removed in the PLEDs based on PIF-DPE, PIF-TPA, and PIF-CZO, and the peak width at half height (PWHH) about 10–20 nm of the EL emission peaks of our copolymers is reduced about 10–20 nm when compared with the PWHH of reported conjugated polymers based on indeno[1,2-*b*]fluorene.^{20–23} The CIE 1931 color coordinate of polymers are around (0.18, 0.14) for PIF-DPE, (0.20, 0.16) for PIF-TPA, and (0.18, 0.13) for PIF-CZO (Table III, Fig. 6), respectively. Furthermore, the EL emission maximum of our copolymers appeared around 440 nm are two–three times to eye sensitive wavelength region compared to PFs. These results indicate that blue light-emitting materials, which satisfy both color purity and relatively high eye sensitivity, were achieved by the introduction of kink linkages into the PIFs backbone.

CONCLUSIONS

In summary, three blue light-emitting conjugated copolymers derived from 6,6',12,12'-tetraoctylindeno[1,2-*b*]fluorene (IF) and 4,4'-diphenyl ether (DPE), *N,N'*-di(4-phenyl)aniline (TPA), or 3,6-*N*-octylcarbazole (CZO) named as PIF-DPE, PIF-TPA, and PIF-CZO, respectively, which were synthesized by Suzuki coupling reaction. The resulted copolymers are soluble in common organic solvent and show good solution processibility. The chemical structures, molecular weights, electrochemical and thermal properties of the copolymers were characterized by ¹H-NMR, GPC, CV, TGA, and DSC. PL peaks of the copolymer of PIF-CZO, PIF-DPE, and PIF-TPA in THF solution and solid states were around 411, 435, and 420 nm, and prototype light-emitting diodes with the configuration as ITO/PVK/copolymer/Ba/Al based on the copolymer of PIF-CZO, PIF-DPE,

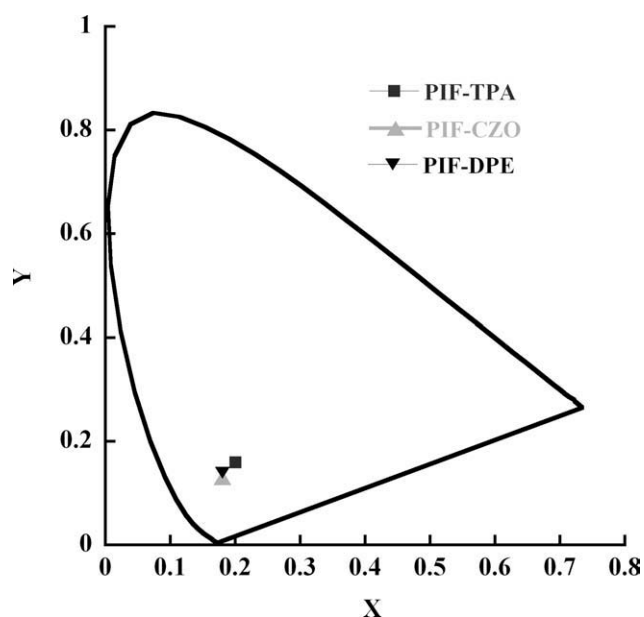


Figure 6 CIE of the emission for the devices based on copolymers.

and PIF-TPA emit blue light with the peaks at around 438, 437, and 449 nm, respectively. The EL emission of the copolymers was in the deep blue region with the CIE 1931 color coordinate of (0.18, 0.14, PIF-DPE), (0.20, 0.16, PIF-TPA), and (0.18, 0.13, PIF-CZO), respectively. The peak width at half height of our copolymers is reduced about 10–20 nm when compared with the EL spectra of reported indeno[1,2-*b*]fluorene-based polymers, and the EL emission peaks of the copolymers are around 437–449 nm, suggesting 2–3 times eye sensitive. It indicated that the blue light-emitting materials that satisfy both color purity and relatively high eye sensitivity were achieved by the introduction of kink linkages like 4,4'-diphenyl ether, *N,N'*-di(4-phenyl) aniline, and 3,6-*N*-octylcarbazole units into the PIF main chain.

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