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Single Chain White-Light-Emitting Polyfluorene Copolymers Containing Iridium Complex Coordinated on the Main Chain

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ABSTRACT: We report the synthesis of single chain white-light-emitting polyfluorene copolymers containing a novel iridium complex with a β-diketonate unit, bis(2-benzothiazol-2-yl-*N*-ethylcarbazole)iridium-1,3-bis(*p*-bromophenyl)1,3-propanedione ($(bec)_2$IrdbmBr), as the red emission unit. The synthesized polyfluorene copolymers containing the carbazole and iridium complex, poly{9,9-bis(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-(*N*-hexylcarbazole-3,6-diyl)-*co*-[bis(2-benzothiazol-2-yl-*N*-ethylcarbazole)iridium-1,3-bis(*p*-bromophenyl)-propanedione-1,3-diyl]} (PFCzIrbecs), were synthesized via palladium-catalyzed Suzuki coupling reactions. These polymers were found to be thermally stable and readily soluble in common organic solvents. Interestingly, the synthesized polymers, PFCzIrbec 05 and PFCzIrbec 2, exhibited two strong emission bands in both the blue and red spectral regions. Light-emitting devices based on these polymers were fabricated in an ITO/PEDOT:PSS/poly(TPD)/polymers/TPBi/LiF/Al configuration. We obtained white light emission from a single polymer chain by incorporating $(bec)_2$IrdbmBr as the red emission unit into a BOPF and carbazole main chain as the host and blue emission. This device exhibited good performance. In particular, EL device fabricated with PFCzIrbec 2 was found to emit white light consisting of simultaneous blue and red emission with CIE coordinates of (0.31, 0.32), which are close to the standard for white light emission. Moreover, the EL spectrum of PFCzIrbec 2 was stable with respect applied voltage, and CIE coordinates were almost not changed at various driving voltages.

Introduction

In the past few years, conjugated polymers have attracted scientific and technological interest due to their potential applications in organic thin-film transistors,[1] nonlinear optical devices,[2] photovoltaic cells,[3] and polymer light-emitting diodes (PLEDs).[4] In particular, concern about PLED devices for flat panel display has increased due to its suitable properties.[5] PLEDs have been found to be of considerable importance as active materials in new technology fields because their optical and electrical properties can be adjusted by manipulating their chemical structures.[6−9]

Recently, polymer blend systems, produced via the combination of a polymer "host" and a heavy metal complex "guest", showed improved device properties compared with conventional fluorescent OLEDs.[10] The phosphorescent blending system, however, intrinsically suffers from efficiency and stability limitations due to energy loss by energy transfer from the host to low-lying triplet states, aggregation of dopants, even at low doping concentrations, and potential phase separation, which results in the fast decay of efficiency with increasing current density.[11] To address these issues, a recent study introduced heavy-metal complexes by directly incorporation into polymer main chains.[12,13] Phosphorescent polymer light-emitting diodes (PhPLEDs) containing complexes between metal centers and the polymer main chain, directly[12] or via pendant group,[13] have many advantages compared to blend systems that consist of dopants in a host matrix. Cao et al. reported that phosphorescent chelating copolymers based on the linkage isomer of 2-(1-naphthalene)pyridine and 2-(2-naphthalene)pyridine−bicycloiridium complexes exhibited high external efficiencies with no remarkable efficiency decay.[12a] To graft metal complexes onto polymer main chains, Yang et al. reported the introduction of *N*-alkylcarbazole units with a terminal diketone group to provide a ligand for the formation of iridium complexes in the side chains.[13]

Single chain white-light-emitting polymers, for use as PLEDs, offer several advantages, such as simple fabrication processes, ease of scaling up production, and the absence of material complications arising from phase separation or the dependence of electroluminescence the driving voltage. Recently, several advances in the synthesis of single chain white-light-emitting polymers containing a phosphorescent unit have been reported. Yang et al. reported that fluorene-based copolymers containing fluorenone and an iridium complex on the main chain exhibited white light emission produced by a fluorenone defect characteristic in the polymer main chain.[14] Peng et al. reported that a binary copolymer containing red iridium complexes attached to the side chain of polyfluorene exhibited white light emission.[15] This research introduced green emission segments into the main chain, which assisted an energy transfer process from the fluorene units to the iridium complex, and strengthened the otherwise weak green intensity of the emission band. The control of the monomer feed ratios in this system was difficult because of used four kinds of monomers and controlled two kinds of monomers carefully. The single chain polymer without green segments,

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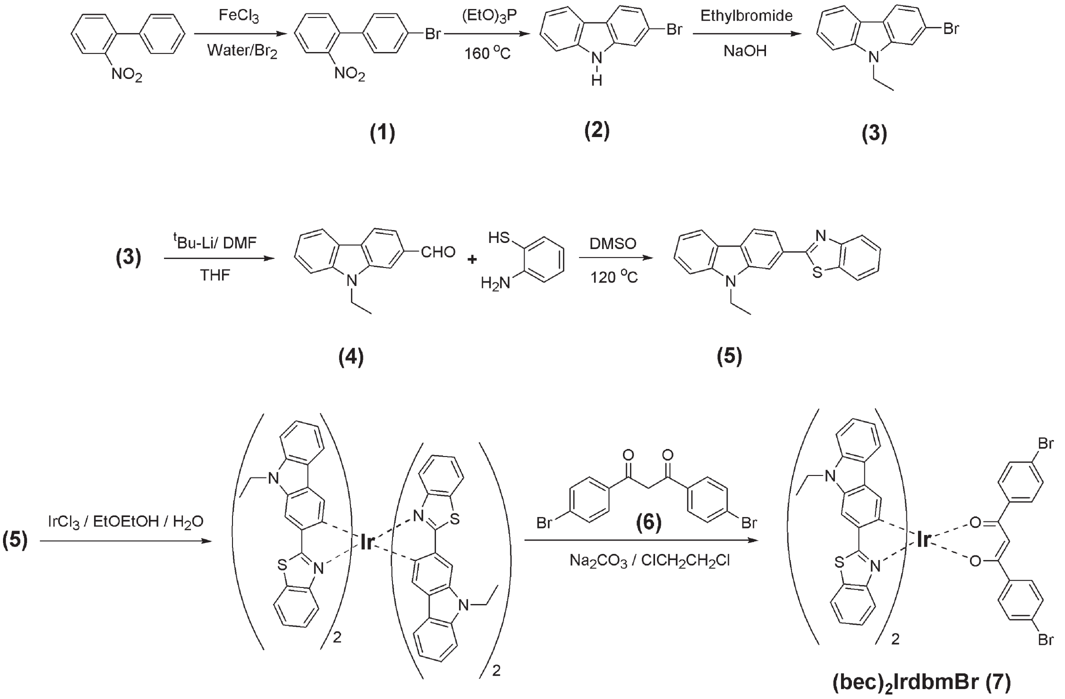
Scheme 1. Synthetic Routes of the (bec)$_2$IrdbmBr



however, is easier to control feed ratio of monomers due to adjusting only iridium complex.

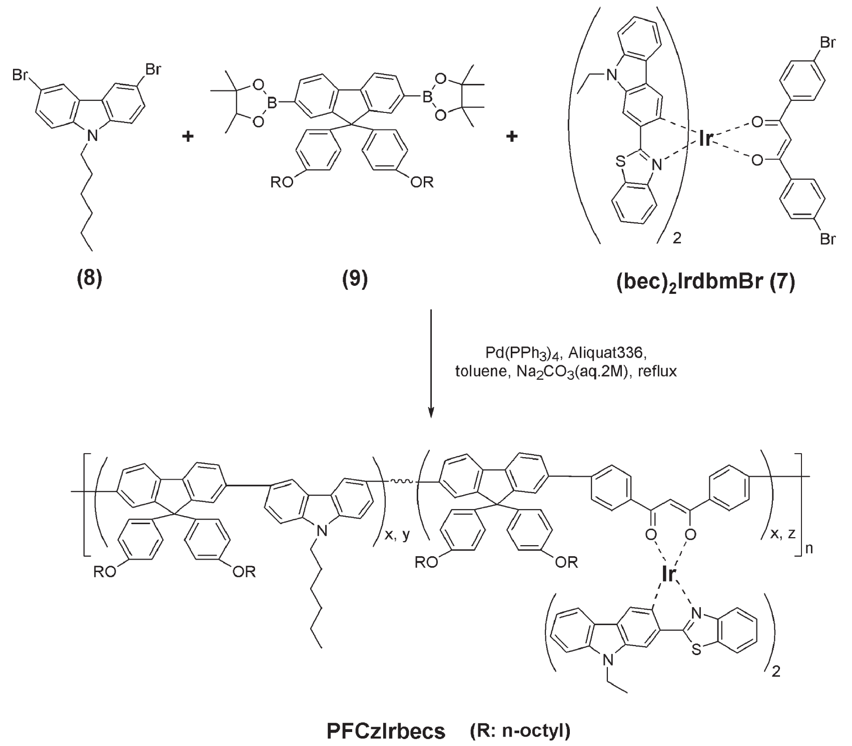
Carbazole-containing polymers are important in organic materials chemistry due to their high stability, processability, and hole-transporting properties. In particular, carbazole is used as a host material to take advantage of its high triplet energy level.[16] The ligand of the novel iridium complex described here, bis(2-benzothiazol-2-yl-*N*-ethylcarbazole)iridium-1,3-bis(*p*-bromophenyl)1,3-propanedione ((bec)$_2$IrdbmBr), consists of a carbazole scaffold with a substituted benzothiadiazole moiety. In particular, substitution at the 2-position in the carbazole was used to tune the HOMO energy level of the iridium complex. The iridium metal center is located in the *para* position with respect to the nitrogen atom on the 2-position-substituted carbazole. From this architecture, carbazole may donate electrons from its nitrogen lone pair to the metal center, raising the HOMO energy level, thus inducing to a red shift.[16]

In this article, we report the synthesis of polyfluorene copolymers containing carbazole and novel iridium complexes in the main chain without the use of green emission segments, such as fluorenone or benzothiadiazole. We believed that this attempt was more suitable synthetic procedure for realizing white-light-emitting polymers due to easier controlled monomer ratios. Novel iridium complexes with an ancillary dibromo-β-diketonate unit can be incorporated into the polymer main chain. We systematically investigated the synthesis, thermal stability, optical properties, and electrical properties of the resulting polymers. The synthetic routes to the iridium complex monomers, (bec)$_2$IrdbmBr, and copolymers, PFCzIrbecs, are shown in the Schemes 1 and 2.

Experimental Details

Measurements. NMR spectra were recorded using a Bruker AM 400 MHz spectrometer with tetramethylsilane as an internal reference. Elemental analysis was performed using an EA 1110 Fisons analyzer. UV−vis and PL spectra were recorded using Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. Thermogravimetric analysis (TGA) was carried out using a TA Q500 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetric (DSC) measurements were made using TA Q100 instrument and operated under a nitrogen atmosphere at a heating rate of 10 °C/min. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard. Cyclic voltammetry (CV) was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu$_4$NBF$_4$ (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of each polymer was coated onto a Pt wire electrode by dippng the electrode into a solution of the polymer. The measurements were calibrated using ferrocene as standard. EL devices were fabricated on glass substrates coated with indium−tin oxide (ITO). The device configuration was ITO/PEDOT:PSS/poly(TPD)/polymer/TPBi/LiF/Al structures. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from Bayer. The spin-casting yielded uniform PEDOT:PSS films with thicknesses of ~40 nm. To help hole transporting ability from anode and PEDOT:PSS, poly(*N*,*N*′-bis(4-butylphenyl)-*N*,*N*′-bis(phenyl)benzidine), poly(TPD), stacked on PEDOT:PSS layer which was purchased from American Dye Source, Inc. Poly(TPD) solution in chlorobenzene was then spin-coated onto the PEDOT:PSS layer and yielded uniform films with thickness of ~50 nm. Each polymer solution in *p*-xylene was then spin-coated onto the poly(TPD) layer. The spin-casting yielded uniform polymer films with thicknesses of ~40 nm. A 40 nm thick 2,2′,2′′-(1,3,5-benzinetriyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBi) electron transporting layer was deposited, and a 0.5 nm thick lithium fluoride (LiF) layer and a 100 nm thick aluminum (Al) layer were subsequently deposited at pressures below 10^{-6} Torr. EL spectra of the devices were obtained using a Konica-Minolta CS-1000A. The current−voltage−luminance characteristics were measured using a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a calibrated Si photodiode placed at an angle normal to the device's surface. Transient electrophosphorescences were measured by a digital oscilloscope (Tektronix TDS5054B) and a photomultiplier tubes (PMT) through a

Scheme 2. Synthetic Routes of the Copolymers PFCzIrbecs



monochromator (ARC 275), biasing with an Agilent 8114A pulse generator. All measurements were carried out at room temperature under an ambient atmosphere.

Materials. 2-Nitrobiphenyl, 2-aminobenzenethiol, 1-bromooctane, 1-bromohexane, 1-bromoethane, 3,6-dibromocarbazole, 2,7-dibromofluorenone, *N*,*N*-dimethylformamide (99.8%, anhydrous), dimethyl sulfoxide, bromine, iron(III) chloride, triethyl phosphite, 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, phenol, tetrahydrofuran, *N*-bromosuccinimide, toluene (99.8%, anhydrous), Aliquat 336, and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich. All chemicals were used without further purification. 4-Bromo-2-nitrobiphenyl (**1**), 2-bromo-9*H*-carbazole (**2**), 1,3-bis(4-bromophenyl)propane-1,3-dione (**6**), 3,6-dibromo-*N*-hexylcarbazole (**8**), and 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**9**) were synthesized according to procedures outlined in the literature.[17−19] Solvents with analytical grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of 2-Bromo-*N*-ethylcarbazole (3). 2-Bromo-9*H*-carbazole (**2**) (6 g, 24.4 mmol), sodium hydroxide (5.85 g, 146 mmol), and 1-bromoethane (4 g, 36.7 mmol) were dissolved in 100 mL of dimethyl sulfoxide (DMSO). The reaction mixture was then stirred at room temperature. After 24 h, the reaction mixture was extracted using dichloromethane/brine, and then the organic layer was separated and concentrated. The crude product was purified by column chromatography using hexane/ethyl acetate (8:2, v/v) as the eluent. The resulting solid was recrystallized in dichloromethane and methanol, and then the white solid was dried in vacuo. The resulting product yield was 73% (4.9 g). ^{1}H NMR (CDCl$_3$, ppm): 8.01 (d, 1H), 7.96 (d, 1H), 7.59 (s, 1H), 7.51 (t, 1H), 7.40−7.37 (m, 2H), 7.30 (t, 1H), 4.30 (q, 2H), 1.45 (t, 3H). ^{13}C NMR (CDCl$_3$, ppm): 140.63, 139.93, 125.98, 122.31, 121.81, 121.77, 121.44, 120.32, 119.25, 119.15, 111.44, 108.56, 37.49, 13.65. Anal. Calcd for $C_{14}H_{12}BrN$; C, 61.33; H, 4.41; N, 5.11. Found: C, 61.29; H, 4.40; N, 5.05.

Synthesis of *N*-Ethylcarbazole-2-carbaldehyde (4). Compound **3** (4.5 g, 16.4 mmol) was dissolved in THF (150 mL) at −78 °C. To a solution was added, by syringe, 20 mL (32.8 mmol) of *tert*-butyllithium (1.7 M in hexane). The mixture was stirred at −78 °C for 2 h. *N*,*N*-Dimethylformamide (2 mL, 24.6 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 1 h, warmed to room temperature, and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over MgSO$_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography using hexane/ethyl acetate (8:2, v/v) as the eluent. The resulting solid was recrystallized in dichloromethane and hexane, and then the yellow solid was dried in vacuo. The resulting product yield was 76% (2.8 g). ^{1}H NMR (CDCl$_3$, ppm): 10.13 (s, 1H), 8.12 (m, 2H), 7.92 (s, 1H), 7.70 (d, 1H), 7.52 (t, 1H), 7.40 (d, 1H), 7.25 (t, 1H) 4.35 (q, 2H), 1.42 (t, 3H). ^{13}C NMR (CDCl$_3$, ppm): 192.51, 141.57, 139.43, 133.70, 128.04, 127.49, 121.87, 121.39, 121.09, 120.44, 119.48, 109.27, 108.85, 37.59, 13.76. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.59; H, 5.89; N, 6.30.

Synthesis of 2-Benzothiazol-2-yl-*N*-ethylcarbazole (5). Compound **4** (2.32 g, 10.4 mmol) and 2-aminobenzenethiol (1.33 mL, 12.5 mmol) were dissolved in DMSO (150 mL). The mixture was stirred at 120 °C for 24 h. The mixture was poured into water, extracted with dichloromethane, and dried over MgSO$_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography using hexane/ethyl acetate (8:2, v/v) as the eluent. The resulting solid was recrystallized in dichloromethane and methanol, and then the green solid was dried in vacuo. The resulting product yield was 42% (1.43 g). ^{1}H NMR (CDCl$_3$, ppm): 8.26 (s, 1H), 8.16−8.12 (m, 3H), 7.93−7.91 (m, 2H), 7.52 (m, 2H), 7.44−7.42 (m, 2H), 7.27 (t, 1H), 4.45 (q, 2H), 1.50 (t, 3H). ^{13}C NMR(CDCl$_3$, ppm): 169.17, 154.46, 141.24, 140.16, 135.30, 131.05, 126.64, 126.20, 125.48, 124.89, 123.07, 122.62, 121.50, 120.89, 120.70, 119.37, 118.99, 108.79, 107.37, 37.69, 13.84. Anal. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53; S, 9.76. Found: C, 76.82; H, 4.91; N, 8.56; S, 9.49.

Synthesis of Bis(2-benzothiazol-2-yl-*N*-ethylcarbazole)iridium-1,3-bis(*p*-bromophenyl)1,3-propanedione (7) ((bec)$_2$IrdbmBr). A mixture of compound **5** (0.7 g, 2.13 mmol), IrCl$_3$·3H$_2$O (0.30 g, 0.85 mmol), 2-ethoxyethanol (20 mL), and distilled water (5 mL) was stirred under argon at 120 °C for 24 h. After cooling, the mixture was poured in the water and washed several times using petroleum ether. The above μ-chloro-bridged dimer (0.5 g, 0.33 mmol), compound **6** (0.45 g, 1.17 mmol), and anhydrous sodium carbonate (0.11 g, 1.03 mmol) in 1,2-dichloroethane (20 mL) were refluxed in an argon atmosphere for 24 h. After cooling to room temperature, the crude product was flash chromatographed on a silia gel with a dichloromethane as a eluent and further purified by recrystallization from dichloromethane and methanol. The resulting product yield was 14.3% (0.15 g). ^{1}H NMR (TC-d_4, ppm): 8.13 (s, 1H), 8.10 (m, 3H), 7.82 (m, 2H), 7.79 (m, 4H), 7.60 (m, 4H), 7.43−7.24 (m, 8H), 7.23 (m, 3H), 7.11 (m, 3H), 6.72 (s, 1H), 4.11 (q, 4H), 1.49 (t, 6H). m/z = 1228.23 (M$^+$).

General Polymerization Procedure. Into 100 mL two-neck flask were added dibromo compounds and diborolan compound in 25 mL of anhydrous toluene. Water-soluble Pd(0) complex, tetrakis(triphenylphosphine)palladium (1 mol %), was transferred into the mixture in a drybox. Subsequently, 2 M aqueous sodium carbonate deaerated for 30 min, and the phase transfer catalyst, Aliquat 336 (several drops), in toluene purged under nitrogen for 1 h was transferred via cannula. The reaction mixture was stirred at 80 °C for 3 days, and then the excess amount of bromobenzene, the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture is cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymer fibers are collected by filtration and reprecipitation from methanol and acetone. The polymers are purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues and column chromatographyed with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated a several times. The resulting polymers were soluble in common organic solvents. Yield: 56−60%.

PFCzIrbec 05. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**9**) (1 equiv), 3,6-dibromo-*N*-hexylcarbazole (**8**) (0.995 equiv), and (bec)$_2$IrdbmBr (**7**) (0.005 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): aromatic and vinylene; 7.75−6.73 (~49H), aliphatic; 4.11−3.75 (~10H), 1.74−0.84 (~47H).

PFCzIrbec 2. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxy-phenyl)-fluorene (**9**) (1 equiv), 3,6-dibromo-*N*-hexylcarbazole (**8**) (0.98 equiv), and (bec)$_2$IrdbmBr (**7**) (0.02 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): aromatic and vinylene; 7.75−6.73 (~49H), aliphatic; 4.11−3.75 (~10H), 1.74−0.84 (~47H).

PFCzIrbec 4. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**9**) (1 equiv), 3,6-dibromo-*N*-hexylcarbazole (**8**) (0.96 equiv), and (bec)$_2$IrdbmBr (**7**) (0.04 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): aromatic and vinylene; 7.75−6.73 (~49H), aliphatic; 4.11−3.75 (~10H), 1.74−0.84 (~47H).

PFCzIrbec 5. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**9**) (1 equiv), 3,6-dibromo-*N*-hexylcarbazole (**8**) (0.95 equiv), and (bec)$_2$IrdbmBr (**7**) (0.05 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): aromatic and vinylene; 7.75−6.73 (~49H), aliphatic; 4.11−3.75 (~10H), 1.74−0.84 (~47H).

Results and Discussion

Synthesis and Characterization of the Polymers. The cyclometalated iridium complex ((bec)$_2$IrdbmBr) was synthesized successfully. First, iridium trichloride hydrate was reacted with compound **5** to give the μ-chloro-bridged dimeric complex. The iridium complex was subsequently synthesized by treatment of the dimer with compound **6** (dbmBr) in 1,2-dichloroethane, as shown Scheme 1. The copolymers, PFCzIrbecs, were prepared via a palladium-catalyzed Suzuki coupling reaction[20] of compounds **7**, **8**, and **9**. The synthetic routes and structures of the polymers are shown in Scheme 2.

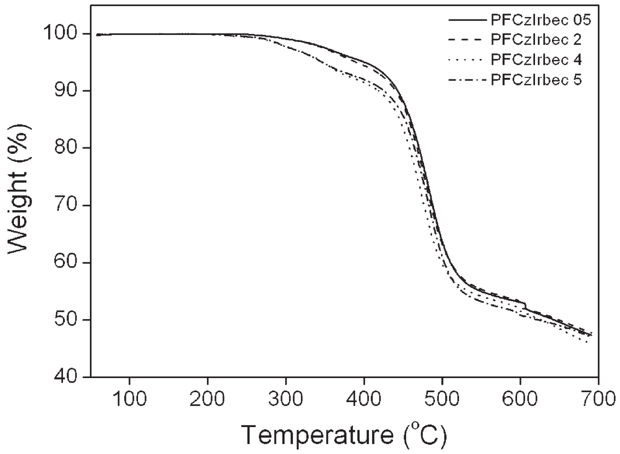


Figure 1. TGA traces of the synthesized PFCzIrbec polymers.

To organize the single chain phosphorescent polymers, we introduced an ancillary dibromo-β-diketonate unit.[11] All PFCzIrbecs copolymers were end-capped with bromobenzene. The feed ratios of the iridium complexes were 0.5, 2, 4, and 5 mol % quantity of compound **9**. All copolymers were found to be soluble in common organic solvents, such as tetrahydrofuran (THF), chloroform, and toluene, with no evidence of gel formation. Each copolymer was spin-coated onto an indium−tin oxide (ITO) substrate and found to produce transparent and homogeneous thin films. The weight-average molecular weights (M_w) of the copolymers, as determined by gel permeation chromatography using a polystyrene standard, were found to range from 9100 to 15 400 with polydispersity indices (PDIs) ranging from 1.6 to 2.1. The yields of the copolymers were 56−60%. The thermal transitions of the polymers were studied by differential scanning calorimetry (DSC) under a nitrogen atmosphere. The thermograms for PFCzIrbecs showed a glass transition in the range from 121 to 127 °C, without any features characteristic of the melting of liquid-crystalline phases. The thermal properties of the polymers were determined using thermal gravimetric analysis (TGA) under a nitrogen atmosphere. All polymers were found to exhibit good thermal stability, losing less than 5% of their weight upon heating from 345 to 400 °C. Interestingly, the amount of weight loss at the start of thermal decomposition increased with increasing content of iridium complexes in the polymer main chain. The TGA traces of the PFCzIrbecs are shown in Figure 1. The results of the polymerizations of the synthesized copolymers are summarized in Table 1.

Optical and Electrochemical Properties. The UV−vis absorption spectra of the PFCzIrbecs exhibited absorption maxima at 357 nm. In previous reports, the UV−vis absorption maxima of the PBOPF homopolymer was 391 nm in the film state.[18] The UV−vis absorption maxima of the PFCzIrbecs measured here were blue-shifted, by ~34 nm, with respect to the PBOPF homopolymer.[18] We assume that this effect arose from the ancillary β-diketonate unit and from the kinked carbazole unit in the polymer main chain.[11,22] An ancillary diketonated and kinked carbazole unit in the polymer main chain disturbs the conjugation of the polymer main chain, leading to a shorting of the conjugation length of the molecules and hence to a blue shift in the absorption.[23] The intensity of the two other absorption peaks at 320 and 426 nm increased as the fraction of iridium complex units increased in the polymer main chain. The increased absorption intensity at 320 nm was caused by the ancillary units, and the absorption intensity at 426 nm was due to the iridium complexes.

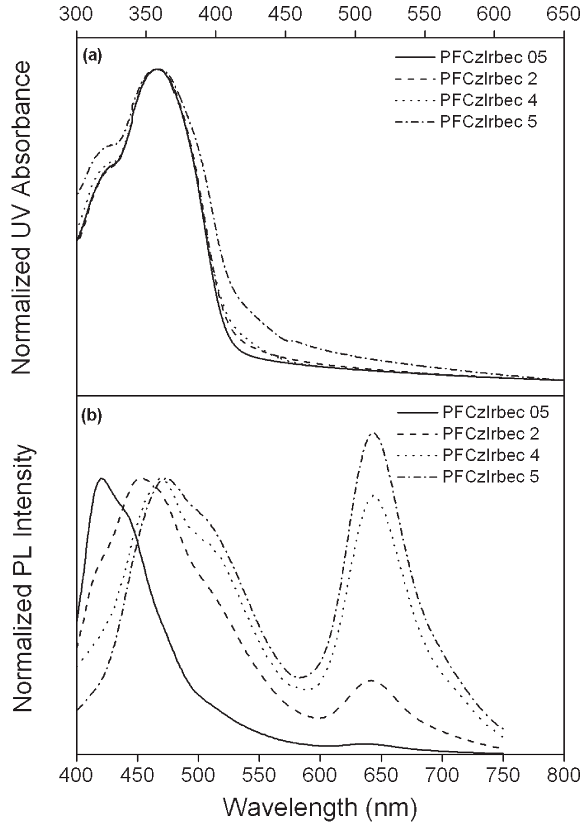


Figure 2. UV–vis absorption (a) and PL emission (b) spectra of the synthesized PFCzIrbec polymers.

Table 1. Physical Properties of the Synthesized PFCzIrbec Polymers

polymer	M_w[a]	PDI[a]	T_d (°C)[b]	yield (%)	in the feed composition
PFCzIrbec 05	13 200	1.7	400	58	1:0.995:0.005
PFCzIrbec 2	10 800	1.7	389	58	1:0.98:0.02
PFCzIrbec 4	15 400	2.1	347	60	1:0.96:0.04
PFCzIrbec 5	9 100	1.6	345	56	1:0.95:0.05

[a] M_w and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. [b] Temperature resulting in 5% weight loss based on initial weight.

The photoluminescence (PL) spectra for the thin films of the polymers were quite different from the spectrum of PBOPF homopolymer. The PL spectrum of PBOPF exhibited an emission maximum at 420 nm.[18] The blue emission peak for the PFCzIrbec polymers shifted slightly to longer wavelengths from 421 to 473 nm. Moreover, the emission at 640 nm increased as the fraction of iridium complex units increased in the polymer main chain. In previous report, the host segment emission spectra due to fluorene and carbazole units disappeared in spite of the low iridium complex content of the polymer main chain.[21] Because intramolecular energy transfer is much more efficient than intermolecular energy transfer,[21a] the polymers containing an iridium complex in the polymer main chain showed full quenching behaviors about host emission. The our synthesized polymers, PFCzIrbec 05 and PFCzIrbec 2, however, exhibited two strong emission spectra in the blue and red spectral regions, suggesting the presence of partial intra- and intermolecular energy transfer in the polymer main chain between host and blue emission segments (fluorene and carbazole units) and iridium complex with diketonated ancillary. Therefore, balanced white emission was obtained. The optical properties of the synthesized polymers are summarized in Table 2.

Table 2. Summary of the Optical Properties and Energy Levels of the Synthesized PFCzIrbec Polymers

polymer	film, λ_{max} (nm)[a] absorption	film, λ_{max} (nm)[a] emission	$E_{onset,ox}$ (V)	E_{HOMO} (eV)[b]
PFCzIrbec 05	357	421	0.83	5.52
PFCzIrbec 2	357	453, 642	0.82	5.51
PFCzIrbec 4	357	468, 644	0.83	5.52
PFCzIrbec 5	359	473, 644	0.86	5.55

[a] Measured as thin films on fused quartz plate. [b] Determined from the onset voltage of the first oxidation potential with reference to ferrocene at 4.8 eV.

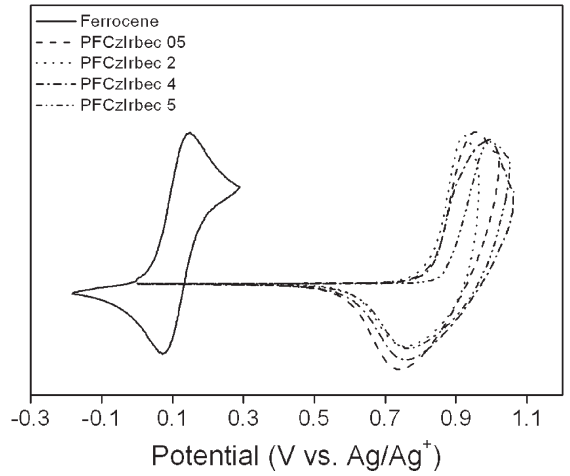


Figure 3. Cyclic voltammograms of the synthesized PFCzIrbec polymers.

The energy levels of their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were characterized by measuring the electrochemical properties of PFCzIrbecs using cyclic voltammetry (CV). A platinum electrode was coated with the polymers and used as the working electrode. The counter electrode was a platinum wire, and the reference electrode was an Ag/$AgNO_3$ (0.01 M) electrode. The electrochemical properties of the copolymers were investigated in an electrolyte consisting of a solution of 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile at room temperature under nitrogen at a scan rate of 50 mV/s. The measurements were calibrated using ferrocene as the standard.[24] Figure 3 shows the oxidation waves and energy levels of the copolymers as a result of the p-type doping. As shown in Figure 3, the onsets of the PFCzIrbec polymer oxidations in the anodic scans were found to occur in the range of 0.82–0.86 V, corresponding to ionization potentials of 5.51–5.55 eV, respectively. Interestingly, the HOMO energy level decreased as the fraction of iridium complex units increased in the polymer main chain. The conjugation length appeared to be disturbed by an ancillary and kinked carbazole unit in the polymer main chain, which led to a shorting of the conjugation length of the molecules and hence to decreased a HOMO energy level for the PFCzIrbecs. Unfortunately, a reduction wave was scarcely obtained. The onsets of oxidation and the energies of the HOMO energy levels of the PFCzIrbecs are listed in Table 2.

Electroluminescence Properties and Current–Voltage–Luminance Characteristics. To investigate the electrical properties and performances of the copolymers in real devices, polymer EL devices with the configuration ITO/PEDOT:PSS (40 nm)/poly(TPD) (50 nm)/polymer (40 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm) were fabricated. The EL

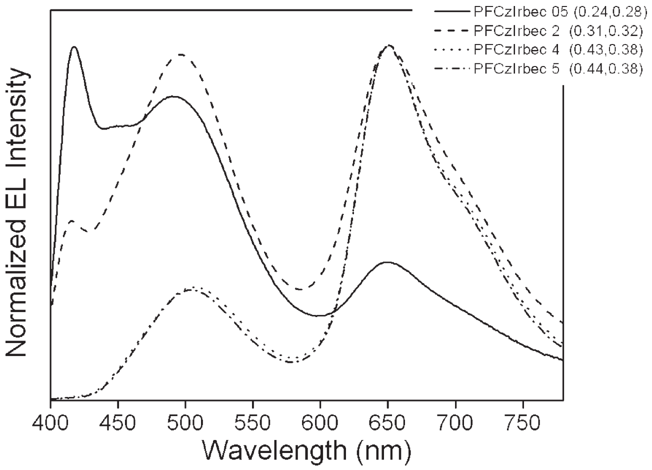


Figure 4. Electroluminescence spectra of synthesized PFCzIrbec devices.

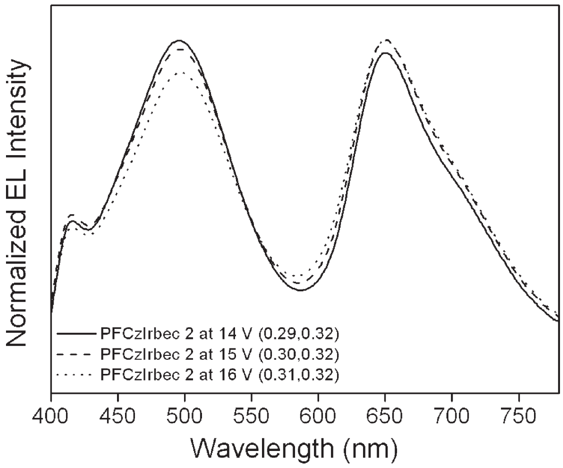


Figure 5. Electroluminescence spectra of the PFCzIrbec 2 device for various driving voltages.

emission spectra of the synthesized polymers were slightly different than the corresponding PL emission spectra, as shown in Figure 4. In particular, the blue emission of EL devices was broader than the bluish green emission measured in the PL experiments. This discrepancy was assumed to result from the charge trapping effects of the iridium complexes. Such results are common for organic host−guest systems, in which the low-energy state units act as charge-trapping sites.[20] Additionally, as mentioned the energy transfer of phosphorescent complexes occurs via competitive intra- and intermolecular pathways. The polymers that contained a low fraction of iridium complexes, PFCzIrbec 05 and PFCzIrbec 2, exhibited two strong emission bands in the range 490 and 650 nm, indicating that PFCzIrbec 05 and PFCzIrbec 2 contained well-balanced partial intra- and intermolecular energy transfer pathways in the polymer main chain. Moreover, the EL emission bands of PFCzIrbec 05 and PFCzIrbec 2 were broad, covering the visible range from 400 to 750 nm. The peaks in the blue region arose from the BOPF and carbazole segments, and the peaks in the red region at 650 nm originated from the iridium complexes.

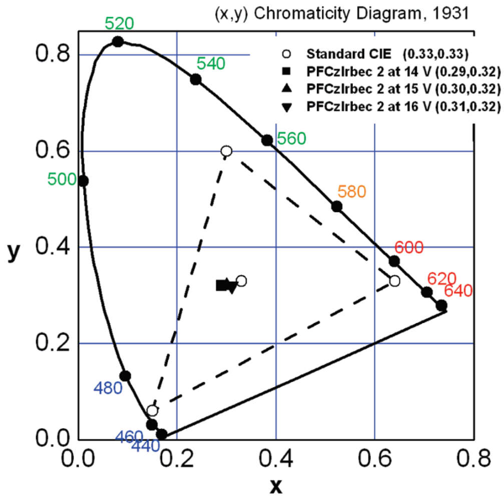


Figure 6. CIE coordinates of PFCzIrbec 2 device for various driving voltages.

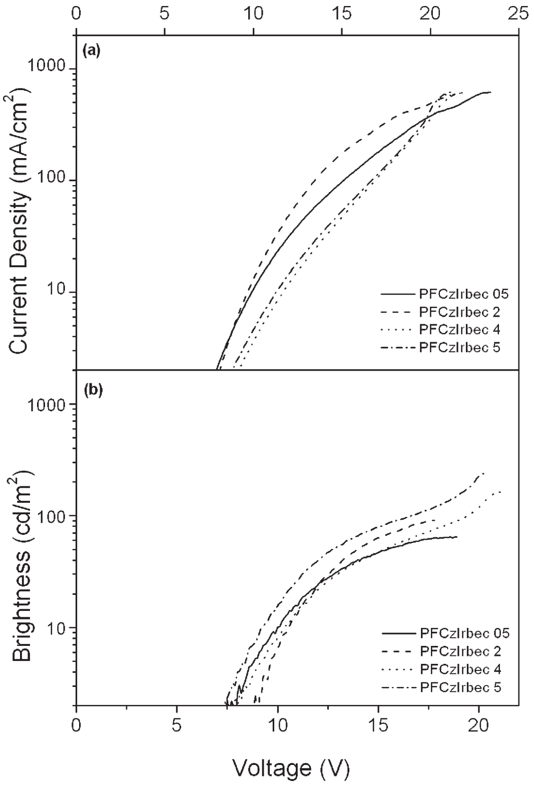


Figure 7. Voltage−current (*V*−*I*) (a) and voltage−luminance (*V*−*L*) (b) characteristics of the synthesized PFCzIrbec polymers.

Of these EL spectra, those of PFCzIrbec 05 and PFCzIrbec 2 consist of well-balanced bluish green and red regions, with CIE coordinates at 16 V of (0.24, 0.28) and at 15 V of (0.31, 0.32), respectively, which were close to those of pure white light (0.33, 0.33). Most importantly, the white light emission is stable, and the EL spectra are insensitive to the driving voltage. The EL spectrum of PFCzIrbec 2 was stable with respect to the voltage; the CIE coordinates were found to be (0.29, 0.32), (0.30, 0.32), and (0.31, 0.32) at various driving voltages. The dependence of the EL emission spectrum of PFCzIrbec 2 on voltage is shown in Figure 5. These results indicated that the use of this polymer ensures color purity in the EL device, which makes these polymers of great interest for display applications. As mentioned above, we have obtained stable white-light-emitting polymers, without the use of green segments. This approach to white emission is the first report of the use of iridium complexes in polymer main chains.

The voltage−current (*V*−*I*) and voltage−luminance (*V*−*L*) characteristics of the devices are shown in Figure 7,

Table 3. Summary of the EL Device Performances of the Synthesized PFCzIrbec Polymers

polymer	$\lambda_{\max}$ (nm)	$V_{\text{turn-on}}$ (V)	current efficiency (cd/A)	EQE (%)	CIE coordinates (x, y)[a]
PFCzIrbec 05	417, 490, 651	7.5	0.18	0.14	(0.24, 0.28)
PFCzIrbec 2	415, 495, 651	8.8	0.05	0.04	(0.31, 0.32)
PFCzIrbec 4	507, 650	7.5	0.26	0.33	(0.43, 0.38)
PFCzIrbec 5	505, 651	7.2	0.40	0.47	(0.44, 0.38)

[a] Determined from EL spectra (Figure 4).

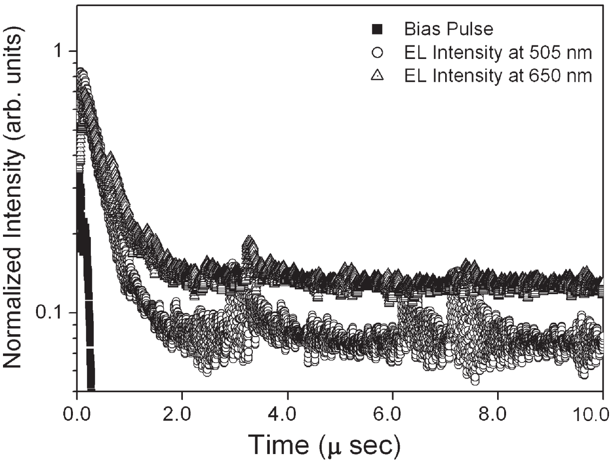


Figure 8. Transient electrophosphorescent spectra of the synthesized PFCzIrbec 4 device.

and their performances are summarized in Table 3. The turn-on voltages of the PFCzIrbec devices ranged from 7.2 to 8.8 V, and their maximum brightness values fell in the range 65−242 cd/m^2. The $V-I$ and $V-L$ curves shifted to slightly higher voltages with increased presence of iridium complexes in the copolymers. This phenomenon arose from charge-trapping and resulted in discrepancies between the EL and PL spectra.[25] To investigate the characteristics of the EL spectra of PFCzIrbecs, the triplet excited-state lifetimes of PFCzIrbec 4 were measured by transient electrophosphorescence measurements. The initial EL decay at 650 nm was slower than the EL decay at 505 nm. As a consequence, the spectrum of PFCzIrbec 4, at 650 nm, appeared to be phosphorescence emission from the synthesized iridium complex.[26] Transient electrophosphorescent spectra of PFCzIrbec 4 are shown in Figure 8.

Unfortunately, our research did not show high EL device efficiencies compared other work that contained iridium complex in the polymer main chain.[27] We assumed that our synthesized copolymers have similar iridium molecular structure in our previous work that contained iridium complex with diketonated ancillary, and it triplet energy back-transfer between fluorene or carbazole segments and iridium unit could occur.[11,21b] We believe that these electroluminescence characteristics could be further improved in future work by optimizing the film morphology, layer thickness, and postproduction treatment conditions.

Conclusions

We have successfully prepared BOPF-based copolymers containing a novel iridium complex as a comonomer. To organize the single chain phosphorescent polymers, we introduced an ancillary dibromo-β-diketonate. White light emission was obtained from a single polymer chain by incorporating bis(2-benzothiazol-2-yl-*N*-ethylcarbazole)iridium-1,3-bis(*p*-bromophenyl)-1,3-propanedione ((bec)$_2$IrdbmBr) as the red emission unit into a BOPF and carbazole main chain as the host and blue emission. Devices based on this polymer exhibited good device performances. EL devices fabricated with PFCzIrbec 2 were found to emit white light composed of blue and red emission with CIE coordinates of (0.31, 0.32), which are close to the standard for white light emission. Partial intra- and intermolecular energy transfer was believed to occur within the polymer main chain. Moreover, the EL spectrum of PFCzIrbec 2 was stable with respect to voltage. Thus, in our present work we successfully realized white-light-emitting polymers containing iridium complexes in the polymer main chain, and we obtained stable white-light-emitting polymers without the use of green segments. These results suggest that white PLEDs that utilize a single polymer chain have potential for application in full-color displays.

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