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Synthesis and Electroluminescence of New Polyfluorene Copolymers Containing Iridium Complex Coordinated on the Main Chain

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ABSTRACT: We have synthesized new light-emitting polyfluorene copolymers containing a novel iridium complex with a β-diketonate unit as an ancillary and characterized them by gel permeation chromatography (GPC), UV−vis absorption spectrophotometer, PL emission spectrofluorometer, and cyclic voltammetry. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DCS) measurements indicated that the copolymers have good thermal and morphological stability. The synthesized polyfluorene copolymers with the iridium complex, PFIrptbs, were synthesized through palladium-catalyzed Suzuki coupling reactions. These polymers were found to be thermally stable and readily soluble in common organic solvents. The UV−vis absorption and PL emission spectra of the synthesized polymers did not show significant energy transfer from PBOPF segments to the iridium complex units. Light-emitting devices based on these polymers were fabricated with an indium−tin oxide/poly(3,4-ethylene dioxythiphene):poly(styrenesulfonate) (PEDOT:PSS)/polymers/Balq/LiF/Al configuration. Examination of the electroluminescence (EL) emissions of the synthesized showed that the EL intensity of the orange color slightly increased with increasing content of the iridium complex. In particular, the device using PFIrptb 025 exhibits a maximum brightness of 2260 cd/m^2 and a maximum current efficiency of 1.10 cd/A.

Introduction

In the past few years, electroluminescent polymers have attracted much scientific and technological research interest because of their potential applications in organic thin-film transistors,[1] nonlinear optical devices,[2] photovoltaic cells,[3] and polymeric light-emitting diodes (PLEDs).[4] In particular, since a group from Cambridge reported initially on the fabrication of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV),[5] luminescent conjugated polymers 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, heavy-metal complexes have been doped into charge-transporting hosts as efficient phosphorescent emitters because of their high emission efficiency compared with conventional fluorescent organic light-emitting diodes (OLEDs).[10] In particular, polymer light-emitting diodes (PLEDs) based on phosphorescent heavy-metal complexes as dopants in a polymer matrix have attracted considerable attention because to the ease of fabrication of PLEDs by processing the materials from solution, such as by spin-coating or printing techniques.[11a] Although high-efficiency OLED/PLED devices with phosphorescent dye doping systems have been obtained,[11] the blending system may intrinsically suffer from efficiency and stability limitations because of possible 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 fast decay of efficiency with increasing current density. To address these issues, a study has recently appeared in which the heavy-metal complexes were directly incorporated into the polymer main chain.[12] In these polymeric phosphors, phosphorescent metal complexes can be attached as pendant groups to the nonconjugated inert main chain or conjugated main chain.

Cyclometalated iridium complexes provide distinct features applicable to phosphorescent dopants used in OLEDs: the general features include (1) complexes with suitably designed ligands give high phosphorescence quantum yields in solution, (2) the high ligand field strength of a carbon atom bonding to the iridium atom provides high emission energy, which potentially covers the whole range of visible light from blue to red, (3) the cyclometalating ligands are formally monoanionic and can thus be used to prepare neutral tris-coordinated complexes, (4) the ligands afford high design freedom, and (5) the complexes are thermally and chemically stable under ambient conditions.[13] An alternative approach to tuning the emission color of the emitting complex involves modifying the CN ligand. This approach has been explored in some depth since the first report of efficient electrophosphorescence from Ir(ppy)$_3$-based OLEDs.[14] For the majority of efficient phosphorescent materials, the lowest excited state is ^{3}LC-dominant; thus, the excited state energy can be varied over a wide spectral range by employing different cyclometalating ligands in the complexes.

In this article, we report the synthesis of polyfluorene copolymers containing novel iridium complexes on the main chain. The synthesized novel iridium complex, (ptb)$_2$IrdbmBr, has extended

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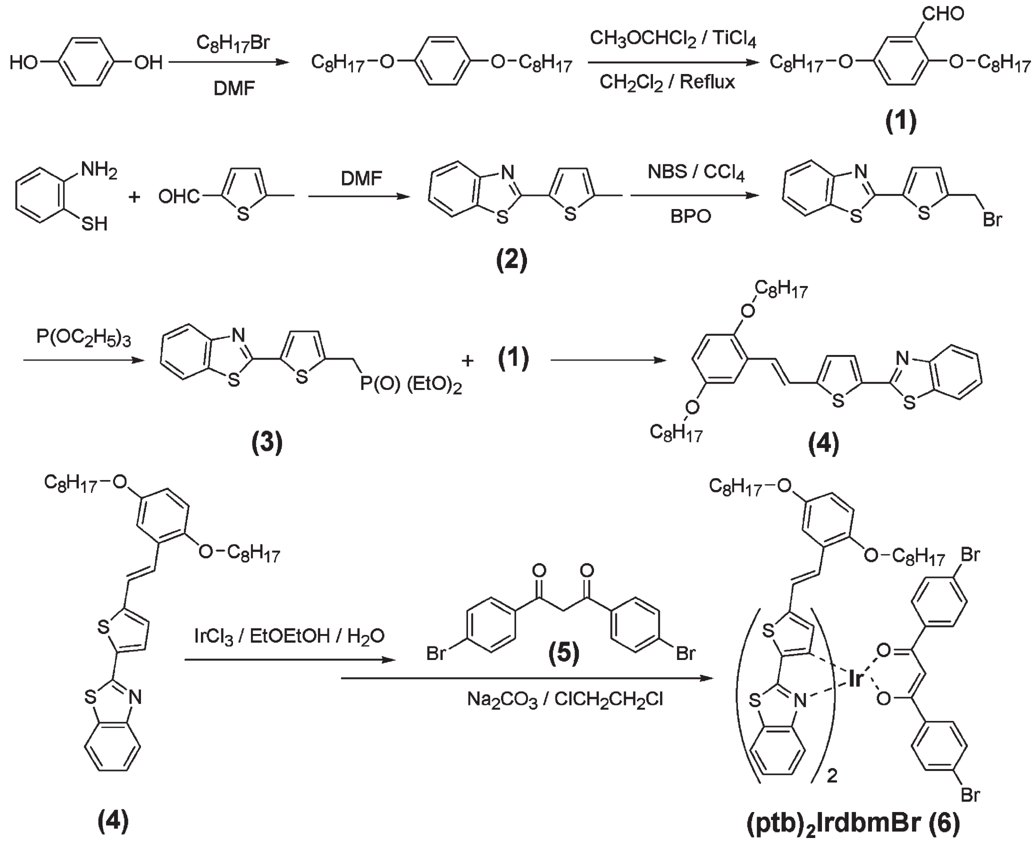
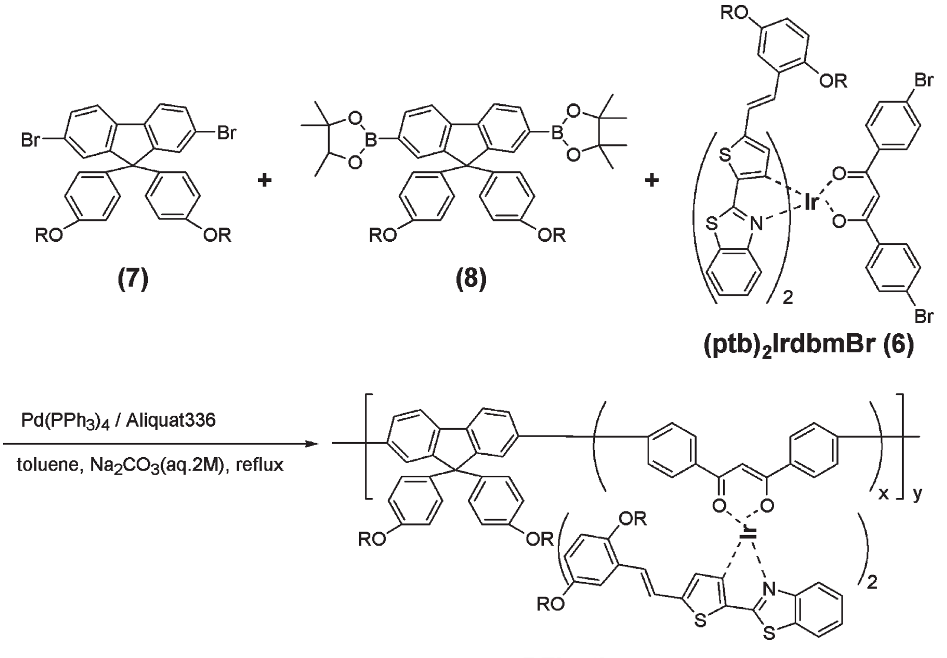
Scheme 1. Synthetic Routes of (ptb)$_2$IrdmbBr



Scheme 2. Synthetic Routes of Copolymers PFIrptbs



PFIrptbs (R: n-octyl)

π-conjugated ligands and long alkyl chains. We expect that the extended π-conjugated chain is able to control the HOMO energy level and the long alkyl chain contributes to the solubility of the iridium complex and compatibility.[15] Also, a novel iridium complex with a dibromo-β-diketonate unit as an ancillary 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 for the new PBOPF-based copolymers, PFIrptbs, are given in the Schemes 1 and 2.

Experimental Details

Measurements. NMR spectra were recorded using a Bruker AM 300 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 measurements were made using a 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 was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu_4NBF_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 dipping the electrode into a solution of the polymer. The measurements were calibrated using ferrocene as standard. LED devices were fabricated on glass substrates coated with indium−tin oxide (ITO). The device configuration was ITO/PEDOT:PSS/polymer/Balq/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 TIO anode from a solution purchased from Bayer. Each polymer solution in chlorobenzene was then spin-coated onto the PEDOT:PSS layer. The spin-casting yielded uniform polymer films with thicknesses of ~40 nm. A 40 nm thick bis(2-methyl-8-quinolinolate)-4-(phenylphenolata)aluminum (Balq) electron-transporting layer was deposited, and a 1 nm thick lithium fluoride layer and a 70 nm thick aluminum layer were subsequently deposited at pressures below 10^{-6} Torr. EL spectra of the devices were obtained using a Minolta CS-1000. Current−voltage−luminance ($I-V-L$) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 as the luminance detector. Transient electrophosphorescences were measured by Agilent 8114A pulse generator. All measurements were carried out at room temperature under an ambient atmosphere.

Materials. Hydroquinone, 2-benzenethiol, 5-methylthiophene-2-carbaldehyde, 1-bromooctane, 2,7-dibromofluorenone, toluene (99.8%, anhydrous), *N,N*-dimethylformamide (99.8%, anhydrous), 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, *N*-bromosuccinimide, and Aliquat336 were purchased from Aldrich. All chemicals were used without further purification. 2,5-Bis(octyloxy)benzaldehyde (**1**), 2-(5-methylthiophene-2-yl)benzothiazole (**2**), 1,3-bis(4-bromophenyl)propane-1,3-dione (**5**), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) were synthesized according to procedures outlined in the literature.[12b,16] Tetrakis(triphenylphosphine)palladium(0) was purchased from DNF solution Co. Solvents with analytical grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of 2-{5-[2-(2,5-Bis(octyloxy)phenyl)vinyl]thiophene-2-yl}benzothiazole (4). Phosphate compound **3** (2.6 g, 7.1 mmol) and compound **1** (1.74 g, 7.1 mmol) were dissolved in 50 mL of tetrahydrofuran (THF). An excess amount of potassium *tert*-butoxide in methanol was added into this mixture. 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 resulting solid was recrystallized in dichloromethane and methanol, and then the yellow solid was dried in vacuo. The resulting product yield was 50% (2.0 g). ^{1}H NMR ($CDCl_3$, ppm): 8.01 (d, 1H), 7.80 (d, 1H), 7.50 (d, 1H), 7.44 (m, 2H), 7.32 (m, 1H), 7.23 (m, 1H), 7.00 (d, 1H), 6.98 (d, 1H), 6.77 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm): 161.17, 153.71, 153.13, 151.13, 147.64, 135.00, 134.60, 129.15, 126.35, 125.76, 125.05, 122.78, 121.59, 121.33, 115.31, 115.18, 113.61, 112.45, 69.37, 68.59, 31.82, 31.80, 29.30, 26.20, 26.05, 22.64, 14.08. Anal. Calcd for $C_{23}H_{38}O_3$; C, 76.20; H, 10.56; O, 13.24. Found: C, 75.97; H, 10.05.

Synthesis of Iridium Complexes (6) ((ptb)$_2$IrdbmBr). A mixture of compound **4** (1.46 g, 2.5 mmol), $IrCl_3 \cdot 3H_2O$ (0.36 g, 1.0 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 (1.0 g, 0.52 mmol), compound **5** (0.7 g, 1.8 mmol), and anhydrous sodium carbonate (0.17 g, 1.6 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 silica gel with a dichloromethane as a eluent and further purified by recrystallization from dichloromethane and hexane. The resulting product yield was 52% (0.45 g). ^{1}H NMR ($CDCl_3$, ppm): 8.01 (d, 1H), 7.80 (d, 1H), 7.51(d, 1H), 7.44 (m, 2H), 7.32 (m, 1H), 7.23 (d, 1H), 7.01 (d, 1H), 7.00 (d, 1H), 6.77 (m, 2H), 3.90 (m, 4H), 1.83−1.74 (m, 4H), 1.50−1.29 (m, 2H), 0.86 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): 178.78, 172.56, 156.82, 153.17, 151.25, 1551.02, 150.93, 139.08, 133.38, 131.53, 131.47, 131.36, 128.50, 127.39, 126.82, 125.45, 124.93, 123.76, 122.17, 118.30, 115.35, 113.94, 111.69, 69.54, 68.53, 31.82, 31.79, 29.34, 29.26, 29.21, 26.129, 26.02, 22.71, 22.36, 14.17, 14.09. $m/z = 1722.27$ (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)palladiuim (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, Aliquat336 (several drops), in toluene purged under nitrogen for 1 h were 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 chromatographed with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated several times. The resulting polymers were soluble in common organic solvents. Yield: 45−65%.

PFIrptb 005. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) (1 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**) (0.999 95 equiv), and (ptb)$_2$IrdbmBr (**6**) (0.000 05 equiv) were used in this polymerization. ^{1}H NMR ($CDCl_3$, ppm): aromatic and vinylene; 7.75−6.73 (~42H), aliphatic; 3.90−3.75 (~8H), 1.74−0.84 (~90H). Element Anal. Found: C, 84.61; H, 8.44.

PFIrptb 01. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) (1 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**) (0.999 equiv), and (ptb)$_2$IrdbmBr (**6**) (0.001 equiv) were used in this polymerization. ^{1}H NMR ($CDCl_3$, ppm): aromatic and vinylene; 7.75−6.73 (~42H), aliphatic; 3.90−3.75 (~8H), 1.74−0.84 (~90H). Element Anal. Found: C, 84.93; H, 8.68.

PFIrptb 025. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) (1 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**) (0.9975 equiv), and (ptb)$_2$IrdbmBr (**6**) (0.0025 equiv) were used in this polymerization. ^{1}H NMR ($CDCl_3$, ppm): aromatic and vinylene; 7.75−6.73 (~42H), aliphatic; 3.90−3.75 (~8H), 1.74−0.84 (~90H). Element Anal. Found: C, 83.56; H, 8.42.

PFIrptb 05. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) (1 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**) (0.995 equiv), and (ptb)$_2$IrdbmBr (**6**) (0.005 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic and vinylene; 7.75−6.73 (∼42H), aliphatic; 3.90−3.75 (∼8H), 1.74−0.84 (∼90H). Element Anal. Found: C, 85.18; H, 8.67.

PFIrptb 3. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**8**) (1 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**7**) (0.97 equiv), and $(ptb)_2$-IrdbmBr (**6**) (0.03 equiv) were used in this polymerization. ^{1}H NMR ($CDCl_3$, ppm): aromatic and vinylene; 7.75−6.73 (∼42H), aliphatic; 3.90−3.75 (∼8H), 1.74−0.84 (∼90H). Element Anal. Found: C, 82.55; H, 8.41.

Results and Discussion

Synthesis and Characterization of the Polymers. The synthetic routes and structures of the polymers are shown in Scheme 2. To organize the single chain phosphorescent polymers, we introduced a dibromo-β-diketonate unit as an ancillary. In addition, the synthesized novel ligands of the iridium complex have an increased π-conjugation length as a result of adjusting HOMO level. A series of conjugated copolymers were synthesized through palladium-catalyzed Suzuki coupling reactions.[17] The comonomer, $(ptb)_2$IrdbmBr, was added as a dilute solution in toluene because only a very small amount of it was used in the reaction. The concentration of the solution was 1 M solution (1 mg/1 mL). All of the PFIrptbs were end-capped with bromobenzene. The feed ratios of $(ptb)_2$IrdbmBr were 0.005, 0.1, 0.25, 0.5, and 3 mol % of the total amount of monomer. We wanted to make sure about the amount of the iridium complex in the polymer, using elemental analysis. Unfortunately, we could not confirm real ratio of iridium complex in the polymers except PFIrptb 3. We assumed that the iridium complexes were difficult to introduce in the polymer main chain due to bulkiness or activaty,[18] which were hardly detected through elemental analysis. All of the 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 number-average molecular weights (M_n) of the copolymers, as determined by gel permeation chromatography using a polystyrene standard, were found to range from 25 300 to 37 700 with polydispersity indices (PDIs) ranging from 2.2 to 2.5. The yields of the copolymers were from 45% to 65%. The synthesized phosphorescent polymers containing a β-diketonate unit as an ancillary showed higher molecular weights compared with the previous literatures reporting compounds that have a β-diketonate unit as an ancillary.[19] We assume that our synthesized polymers do not have a kinked unit such as a carbazole unit.[12a] The thermal transitions of the polymers were studied using differential scanning calorimetry (DSC) under a nitrogen atmosphere. The thermograms for PFIrptbs each contained only a glass transition range from 97 to 100 °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). All of the polymers were found to exhibit good thermal stability, losing less than 5% of their weight on heating to ∼430 °C in TGA runs under a nitrogen atmosphere. The differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) traces of the PFIrptbs are shown in Figure 1. The results of the polymerizations of the synthesized copolymers are summarized in Table 1.

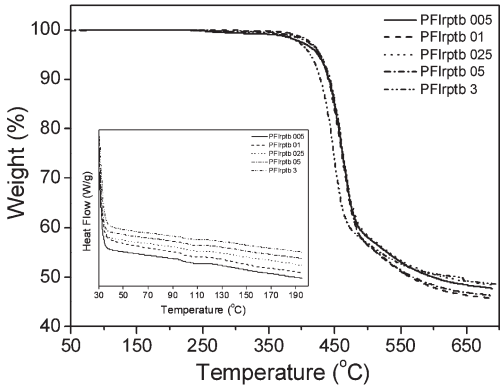


Figure 1. TGA traces of the synthesized PFIrptb polymers (inset: DSC thermograms).

Table 1. Physical Properties of the Synthesized PFIrptb Polymers

polymer	M_n[a]	PDI[a]	T_d (°C)[b]	T_g (°C)	in the feed composition
PFIrptb 005	32 300	2.5	420	97	99.995:0.005
PFIrptb 01	25 300	2.2	430	99	99.9:0.1
PFIrptb 025	37 700	2.4	430	98	99.75:0.25
PFIrptb 05	29 900	2.3	430	100	99.5:0.5
PFIrptb 3	29 200	2.4	410	99	97:3

[a] M_n 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.

Optical, Photoluminescence, and Electrochemical Properties. The UV−vis absorption spectra of the PFIrptbs exhibit absorption maxima at about 386−388 nm. In the previous literature, the UV−vis absorption maximum of the PBOPF homopoymer is 391 nm in the film state.[16a] Compared with these results, the UV−vis absorption maxima of the PFIrptbs are at lower wavelengths than that of the PBOPF homopolymer[16a] by approximately 3−5 nm. We assume that this effect is due to the β-diketonate unit as an ancillary in the polymer main chain. An ancillary in the main chain disturbs the conjugation of the polymer main chain because of the nonconjugated structure of the β-diketonate unit, leading to a shorting of the conjugation length of the molecules and hence to a blue shift in the absorption.[20] The PL spectra of all of the polymers contain emission maxima at about 420 nm. The PL emissions of the PFIrptbs are similar to those of PBOPF homopolymers.[16a] These PL emission spectra indicate that the energy transfer from the BOPF segments to the $(ptb)_2$IrdbmBr units in the polymer chain is not strong, which suggests that $(ptb)_2$IrdbmBr units are not involved with the polymer main chain processes and possess their own independent π-systems.[18] The normalized UV−vis absorption spectra and PL emission spectra of the PFIrptbs are shown in Figure 2.

The normalized UV−vis absorption and PL emission spectra of $(ptb)_2$IrdbmBr in chloroform solution are shown in Figure 3. The maximum in the UV−vis absorption of the $(ptb)_2$IrdbmBr monomer appears at about 400−450 nm. As mentioned above, the maximum in the PL emission spectrum of the PBOPF is near 420 nm, which will overlap significantly with the absorption spectrum of $(ptb)_2$IrdbmBr; this indicates that efficient energy transfer from the BOPF segments to the $(ptb)_2$IrdbmBr units is possible. We assumed that the energy transfer occurred effectively when the device was operated, although it did not show energy transfer in the PL study. The optical properties of the synthesized polymers are summarized in Table 2.

To investigate the energy levels of their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs), the electrochemical properties of PFIrptbs were investigated by cyclic voltammetry (CV). A platinum electrode was coated with the polymers and used as

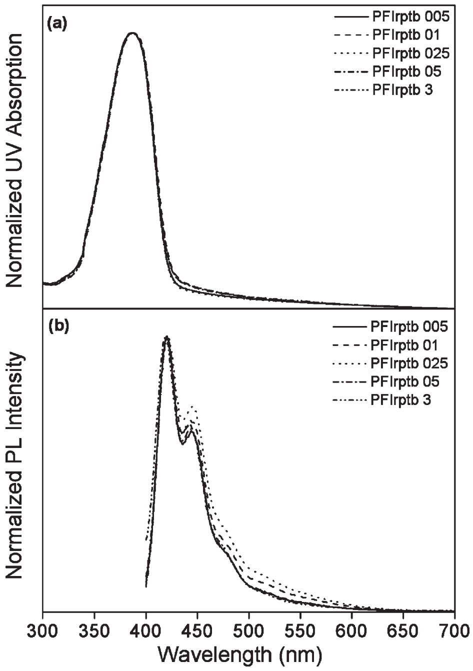


Figure 2. UV–vis absorption (a) and PL emission (b) spectra of the synthesized polymers.

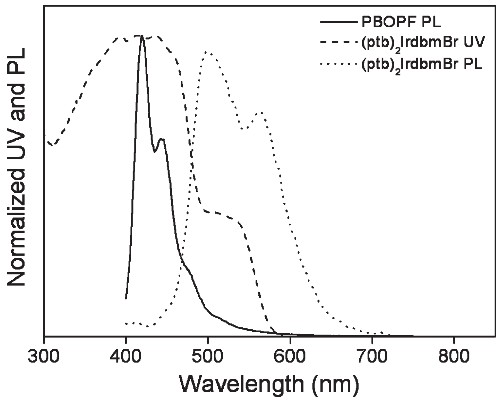


Figure 3. UV–vis absorption and PL emission spectra of (ptb)$_2$IrdbmBr and PBOPF.

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

	film, λ_{max} (nm)[a]			
polymer	absorption	emission	$E_{onset,ox}$ (V)	E_{HOMO} (eV)[c]
PFIrptb 005	387	420	1.01	5.81
PFIrptb 01	388	420	1.02	5.82
PFIrptb 025	386	419	1.02	5.82
PFIrptb 05	388	421	1.01	5.81
PFIrptb 3	386	421	1.02	5.82
(ptb)$_2$IrdbmBr	414[b]	500, 560[b]	0.62	5.33

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

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.[21] Figure 4 shows the oxidation waves and energy levels of the copolymers as a result of the p-type doping. As shown in Figure 4, in the anodic scan and energy diagram, the onsets of oxidation of (ptb)$_2$IrdbmBr and PFIrptbs, especially PFIrptb 01 and PFIrptb 3, were found to occur at 0.62–1.10 V, corresponding to ionization potentials of 5.33–5.82 eV, respectively. Unfortunately, a reduction wave was scarcely obtained. The onsets of oxidation and the energies of the HOMO levels of the PFPTRs are listed in Table 2.

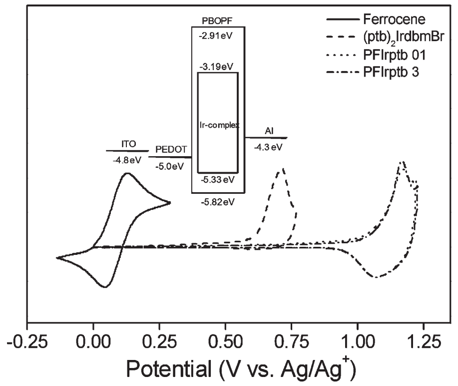


Figure 4. Cyclic voltammograms of the synthesized polymers and iridium complex (inset: the proposed energy levels of PBOPF, (ptb)$_2$IrdbmBr, and PFIrptbs).

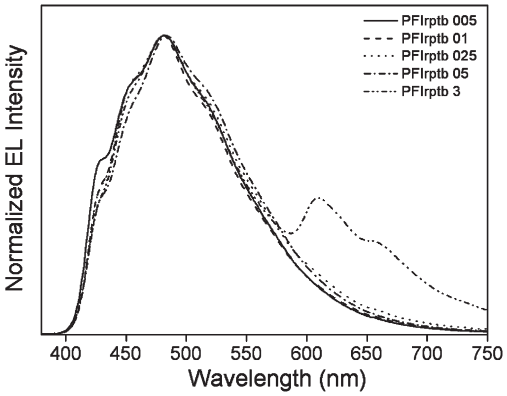


Figure 5. Electroluminescence spectra of the PFIrptb devices with ITO/PEDOT:PSS/polymer/Balq/LiF/Al configurations.

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/poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/polymer (40 nm)/Balq (40 nm)/LiF (1 nm)/Al (70 nm) were fabricated. The EL emission spectra of the synthesized polymers are different from the corresponding PL emission spectra, as shown in Figure 5. The blue emission of the BOPF segments is broader than the bluish-green emission. The EL spectra of the synthesized polymers differ from the PL emission spectra because of energy transfer from the higher energy state of the BOPF segments to the lower energy state of the (ptb)$_2$IrdbmBr units. Such results are common for organic host–guest systems, in which the low-energy state units act as charge-trapping sites.[22] The voltage–luminance (*V*–*L*) and voltage–current efficiency characteristics of the devices are shown in Figure 6, and their performances are summarized in Table 3. The turn-on voltages of the PFIrptb devices range from 6.3 to 7.6 V, and their maximum brightness are in the range 430–2260 cd/m^2. The *V*–*L* and

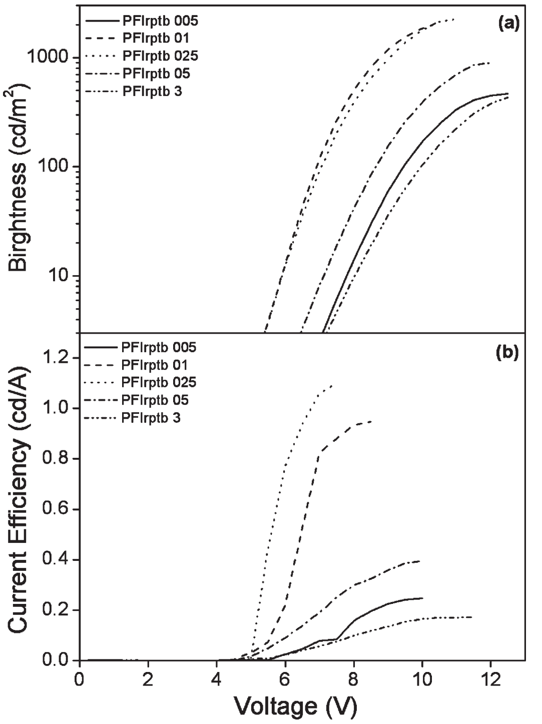


Figure 6. Voltage−luminance (*V*−*L*) (a) and voltage−current efficiency (b) characteristics of the synthesized PFIrptb polymers.

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

polymer	$\lambda_{\max}$ (nm)	luminance$_{\max}$ (cd/m^2)	current efficiency (cd/A)	EQE (%)
PFIrptb 005	482	470	0.25	0.12
PFIrptb 01	481	2130	0.95	0.48
PFIrptb 025	481	2260	1.10	0.57
PFIrptb 05	483	900	0.40	0.20
PFIrptb 3	482	430	0.17	0.10

voltage−current efficiency curves shift to slightly lower voltages as the number of (ptb)$_2$IrdbmBr units in the copolymers is decreased. The PFIrptb 025 device has the best performance, with a maximum brightness of 2260 cd/m^2 at 11 V and a maximum current efficiency of 1.1 cd/A at 7.5 V. We suggest that PFIrptb 025 produces balanced electron and hole injection in the device and that the energy transfer is efficient between the blue-light-emitting BOPF segments and the orange-light-emitting (ptb)$_2$IrdbmBr units. This suggestion is confirmed by the energy levels of the host polymer and monomer, which were determined from the CV measurements.

In general, the inclusion of iridium complex such as red units in the main chain of a phosphorescent polymer has a substantial effect on the PL and EL emission spectra with the extent of the red shift in the emission spectra depending on the iridium complex content of the polymer.[19] As mentioned above, we expect that energy transfer from PBOPF segments to the iridium complex would occur effectively. Unfortunately, we did not observe this phenomenon in PFIrptb 005 to PFIrptb 05. PFIrptb 3, however, was the only system in which phosphorescent emission appeared at 610 nm due to partial energy transfer. To investigate the characteristics of the EL spectra of PFIrptb 3 at 480 and 610 nm, the triplet excited-state lifetimes of PFIrptb3 were measured by transient electrophosphorescence measurements. The initial EL decay at 610 nm was slower than the EL decay at 480 nm. As a consequence of this result, we believe that the spectrum at 610 nm in PFIrptb3 was phosphorescent emission from the synthesized iridium complex.[24] The transient electrophosphorescent spectra of PFIrptb3 are shown in Figure 7.

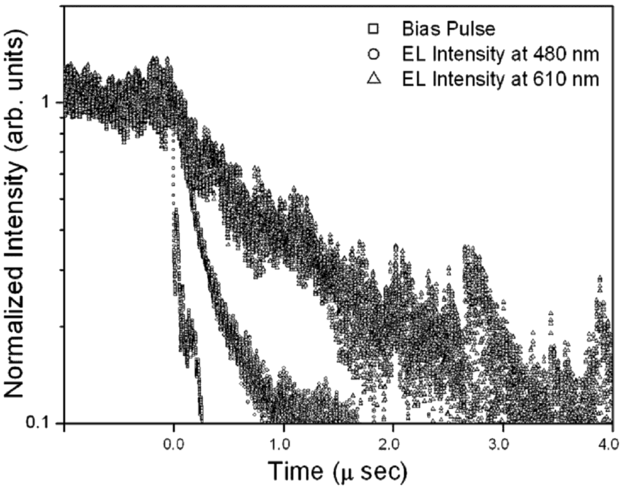


Figure 7. Transient electrophosphorescent spectra of the PFIrptb3.

In addition, we simulated the triplet energy level used previous investigate[23] the cause of the low efficiency. According to this previous work, the PBOPF homopolymer and (ptb)$_2$IrdbmBr have triplet energy levels at 2.1 and 2.42 eV, respectively; that is, the triplet energy state of (ptb)$_2$-IrdbmBr is higher than that of PBOPF. Accordingly, we assumed that energy back-transfer from the triplet level of the iridium complex to that of PBOPF occurred.[15] Although we could not obtain a high efficiency phosphorescent polymer because of energy back-transfer, the polymers showed good efficiency with the newly designed ligands. To solve the remaining problems, we will make an attempt to introduce units that have a high triplet energy level into the polymer main chain. Through this approach, we may expect better results by introducing more appropriate units in the main chain that should help energy transfer to the iridium complex.

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 a dibromo-β-diketonate unit as an ancillary. Also, the synthesized novel ligands of the iridium complex have an increased π-conjugation length as a result of adjusting HOMO level. The PFIrptbs were synthesized through palladium-catalyzed Suzuki coupling reactions and were found to be thermally stable and readily soluble in common organic solvents. The PFIrptb 025 device showed the best performance, with a maximum brightness of 2260 cd/m^2 at 11 V and a maximum current efficiency of 1.1 cd/A at 7.5 V. We suggest that PFIrptb 025 produces balanced electron and hole injection in the device and that the energy transfer is efficient between the blue-light-emitting BOPF segments and the orange-light-emitting (ptb)$_2$IrdbmBr units. Although we could not obtain a high efficiency phosphorescent polymer because of energy back-transfer, the polymers have shown good efficiency with the newly designed ligands. To solve the remaining problems, we will attempt to introduce units that have a high triplet energy level into the polymer main chain. Through this approach, we may expect better results by introducing more appropriate units in the main chain that should help energy transfer to the iridium complex.

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