Synthesis, Characterization, and Photophysics of Electroluminescent Copolymers with a Quinoline-Based Iridium Complex in the Main Chain: A Versatile Method for Constructing Metal-Containing Copolymers

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Received January 13, 2007

A series of novel soluble copolymers based on fluorene monomer in conjugation with carbazole and iridium complex monomers have been synthesized by the Suzuki polycondensation reaction. Iridium complexes based on 2-phenylquinoline or 1-phenylisoquinoline were incorporated into copolymers through a β-diketonate ancillary ligand. The copolymers were characterized by using ^{1}H NMR, ^{13}C NMR, IR, and GPC. TGA/DSC measurements indicated that the copolymers have good thermal and morphological stability. An electrochemical investigation revealed that the HOMO and LUMO energy levels of the monomeric iridium complexes fall within those of the host polymer PFCz. The absorption spectra of the copolymers were dominated by absorptions from the fluorene-*alt*-carbazole backbone, while their photoluminescence (PL) spectra were dominated by emissions from the iridium complexes even at a feed ratio of the complex as low as 0.5 mol %. The copolymers PFCzIrphq emit orange-red light with an emission peak at ca. 590 nm, while PFCzIrpiq emits saturated red light with an emission maximum at ca. 620 nm, with a slight red shift compared with the emissions for the corresponding monomeric iridium complexes, respectively. Light-emitting diodes using the copolymers as emission layers under three types of device configurations were fabricated. The devices with 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) doping display external quantum efficiencies significantly higher than those without PBD. A saturated red-emitting PLED with an emission peak at 628 nm, a maximum external quantum efficiency of 0.6% at the current density (J) of 39 mA/cm^2, and a maximum luminance of 541 cd/m^2 at 16 V was achieved from the device ITO/PEDOT/PFCzIrpiq3+PBD(40%)/Ba/Al.

Introduction

Organic light-emitting diodes (OLEDs) based on phosphorescent heavy-metal complexes doped in small-molecule hosts have made great progress since the realization of high-efficiency OLED devices by using (2,3,7,8,12,13,17,18-octaethyl-21*H*,-23*H*-porphine)platinum(II) (PtOEP) and *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)$_3$) as phosphorescent dyes.[1] Recently, polymer light-emitting diodes (PLEDs) based on phosphorescent heavy-metal complexes as dopants in a polymer matrix have attracted considerable attention, due to the ease of fabrication of PLEDs by processing the materials from solution, such as by a spin coating or printing technique.[2]

Although high-efficiency OLED/PLED devices with phosphorescent dye doping systems have been obtained,[2,3] the blending system may intrinsically suffer from the limitation of efficiency and stability because of the 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, most recently, PLEDs directly using electrophosphorescent polymers have been developed. In the polymeric phosphors, phosphorescent metal complexes can be attached as pendant groups to the nonconjugated inert main chain or conjugated main chain. Lee et al.[4] and Tokito et al.[5] initially reported nonconjugated polyethylene main chains with iridium complexes as side chains by cyclometalation of iridium with pendant phenylpyridine and coordination of iridium with

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10.1021/om070037t CCC: $37.00

pendant β-diketonate, respectively. Furuta et al.[6] reported a near-white-light PLED with up to 4.6% external quantum efficiency by using the same polyethylene main chain with pendant platinum diketonate complexes. Conjugated polyfluorene grafted with cyclometalated iridium complexes and hole-transporting moieties were reported by Chen et al.[7] A red emission PLED device, with an external quantum efficiency of 1.59% ph/el and a luminance of 65 cd/m^2, was obtained.

Alternatively, phosphorescent metal complexes can also be incorporated into a conjugated backbone through cyclometalating ligand units. A series of well-defined oligomers and polymers based on 9,9-dialkylfluorene repeat units in conjugation with iridium complexes were reported by Sandee et al.[8] Maximum external quantum efficiencies of 1.5% and 0.12% ph/el were achieved when the complexes [(btp)$_2$Ir(acac)] (btp = 2-(2′-benzo[*b*]thienyl)pyridinato, acac = acetylacetonate) and [(ppy)$_2$Ir(acac)] (ppy = 2-phenylpyridinato) were covalently attached to a poly(9,9′-dioctylfluorene) backbone, respectively. Applying a fluorene-*alt*-carbazole segment as backbone, Zhen et al.[9] prepared a series of chelating copolymers with iridium complexes in the main chain. A PLED device with a maximum external quantum efficiency of 4.1%, luminance of 1730 cd/m^2, and emission peak at 577 nm was obtained. The preparation of the above copolymers involves dibrominated bis-cyclometalated iridium complexes; these complex monomers are usually not easy to synthesize, and furthermore, they may lead to low phosphor loadings during polycondensation due to gelation of the reaction mixture or formation of highly insoluble products.[8,9]

In this article, we report the synthesis and characterization of a series of novel partially conjugated copolymers containing fluorene-*alt*-carbazole segments and iridium complexes with β-diketonate ancillary ligand and 2-phenylquinoline or 1-phenylisoquinoline cyclometalated ligands. The iridium complexes were incorporated into copolymers via a brominated β-diketonate ancillary ligand. The synthetic strategy avoided the preparation of dibrominated bis-cyclometalated iridium complexes. The thermal, electrochemical, photophysical, and electroluminescent properties of the copolymers will be discussed.

Experimental Section

General Information. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Unity 300 MHz spectrometer using CDCl$_3$ as solvent. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlo Erba 1106 microanalyzer. The molecular weights of the polymers were determined with an Agilent 1100 GPC in THF. The number-average and weight-average molecular weights were estimated by using a calibration curve of polystyrene standards. Infrared spectra were recorded on a Perkin-Elmer 2 spectrometer as films on KBr pellets. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min^{-1} from 30 to 300 °C under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min^{-1} from 25 °C to 600 °C. UV−vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer at room temperature in nitrogen-purged anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at scanning rate of 100 mV/s. A platinum disk and an Ag wire were used as the working electrode and quasi-reference electrode, respectively. The ferrocene/ferrocenium redox couple was used for potential calibration. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.[10]

All reagents commercially available were used as received unless otherwise stated. The solvents (THF, toluene) were purified by routine procedures and distilled under dry argon before using. All reactions were carried out using Schlenk techniques under an argon atmosphere. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) and dibenzoylmethane were purchased from Aldrich. 3,6-Dibromo-*N*-(2-ethylhexyl)carbazole was prepared according to the published procedure.[11]

Synthesis of 1,3-Bis(*p*-bromophenyl)-1,3-propanedione (dbmBr). This compound was synthesized according to a procedure modified from that reported in the literature.[12] A mixture of a sodium hydride in oil dispersion (60%, 0.53 g, 22 mmol) and ethyl *p*-bromobenzoate (2.3 g, 10 mmol) in 30 mL of dry THF was heated to 60 °C. *p*-Bromoacetophenone (2.0 g, 10 mmol) in 20 mL of dry THF was added dropwise to the mixture. After the reaction temperature was held at 60 °C for 1 day, the mixture was poured into water and then neutralized with hydrochloric acid. The resulting precipitate was recrystallized from ethanol to give pale yellow needlelike crystals. Yield: 81%. Mp: 196−199 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 16.7 (s, 1H), 7.8 (d, $J = 6.6$, 4H), 7.6 (d, $J = 7.2$, 4H), 6.7 (s, 1H).

Synthesis of Quinoline Derivative Ligands. In a 10 mL glass tube were placed a magnetic stir bar, 1-chloroisoquinoline or 2-chloroquinoline (1.31 g, 8 mmol), benzeneboronic acid (1.02 g, 8 mmol), Pd(OAc)$_2$ (20.8 mg, 0.08 mmol), anhydrous Na$_2$CO$_3$ (3.4 g, 32 mmol), and tetrabutylammonium bromide (TBAB) (0.32 g, 0.96 mmol). Then 4 mL of H$_2$O and 4 mL of CH$_3$CN were added. The vessel was sealed under argon and placed into the microwave cavity. The reaction mixture was held at 150 °C for 30 min. After it was cooled to room temperature, the mixture was poured into water and then extracted with diethyl ether. The combined organic layers were dried with anhydrous MgSO$_4$. After removal of diethyl ether, the crude product was purified by chromatography using dichloromethane as eluent.

2-Phenylquinoline (phq). Pale yellow powder. Yield: 64%. Mp: 82−83 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.30 (d, $J = 7.8$ Hz, 1H), 8.14 (d, $J = 6.9$ Hz, 2H), 7.84 (t, $J = 9.0$ Hz, 2H), 7.74 (t, $J = 8.1$ Hz, 1H), 7.56−7.44 (m, 5H).

1-Phenylisoquinoline (piq). Yellow needlelike crystal. Yield: 71%. Mp: 93−94 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.60 (d, $J = 5.7$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.7−7.6 (m, 4H), 7.56−7.46 (m, 4H).

Synthesis of Iridium Complexes. A mixture of 2-phenylquinoline or 1-phenylisoquinoline (0.52 g, 2.5 mmol), IrCl$_3$·3H$_2$O (0.36 g, 1.2 mmol), 2-ethoxyethanol (12 mL), and distilled water (4 mL) was stirred under argon at 120 °C for 24 h. After the mixture was cooled, the resulting precipitate was collected by filtration and washed with water, ethanol, and hexane successively. The above chloro-bridged dimer, dibenzoylmethane (0.56 g, 2.5 mmol) or 1,3-bis(*p*-bromophenyl)-1,3-propanedione (0.95 g, 2.5 mmol), and anhydrous sodium carbonate (2.65 g, 25 mmol) in 1,2-dichloroet-

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hane were refluxed under an argon atmosphere for 15 h. After the mixture was cooled to room temperature, the crude product was flash-chromatographed on silica gel with a dichloromethane mobile phase and further purified by recrystallization from dichloromethane and hexane.

(phq)$_2$Ir(dbm) (1). Red powder. Yield: 65%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.45 (d, J = 9.0 Hz, 2H), 8.12 (dd, J = 9.0, 6.6 Hz, 4H), 7.82 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.41 (m, 4H), 7.19 (m, 10H), 6.92 (t, J = 7.8 Hz, 2H), 6.62−6.55 (m, 4H), 5.80 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$, δ): 180.48, 170.50, 151.12, 149.48, 147.40, 141.31, 138.31, 136.59, 130.79, 129.90, 128.87, 128.06, 127.86, 127.42, 127.22, 126.81, 125.95, 121.07, 116.68, 94.88. Anal. Calcd for $C_{45}H_{31}IrN_2O_2$: C, 65.60; H, 3.79; N, 3.40. Found: C, 65.04; H, 3.94; N, 3.52.

(phq)$_2$Ir(dbmBr) (2). Red powder. Yield: 69%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.42 (d, J = 9.0 Hz, 2H), 8.12 (dd, J = 7.2, 6.0 Hz, 4H), 7.89 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.32 (m, 10H), 7.12 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 6.68−6.58 (m, 4H), 5.80 (s, 1H). ^{13}C NMR (300 MHz, CDCl$_3$, δ): 178.17, 169.26, 149.21, 148.20, 146.07, 138.66, 137.20, 135.41, 130.10, 129.56, 127.76, 127.20, 126.77, 126.02, 125.39, 124.81, 123.39, 120.04, 115.46, 93.05. Anal. Calcd for $C_{45}H_{29}Br_2IrN_2O_2$: C, 55.05; H, 2.98; N, 2.85. Found: C, 55.04; H, 3.11; N, 2.98.

(piq)$_2$Ir(dbm) (3). Red powder. Yield: 85%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.99 (s, 2H), 8.45 (d, J = 6.6 Hz, 2H), 8.24 (d, J = 7.2 Hz, 2H), 7.86 (s, 2H), 7.69 (m, 4H), 7.60 (d, J = 8.1 Hz, 6H), 7.37 (t, J = 6.6 Hz, 6H), 6.94 (t, J = 6.6 Hz, 2H), 6.70 (t, J = 7.2 Hz, 2H), 6.47 (s, 1H), 6.45 (s, 2H). ^{13}C NMR (300 MHz, CDCl$_3$, δ): 179.38, 169.49, 152.42, 146.87, 141.52, 140.84, 137.46, 134.17, 130.71, 130.25, 129.84, 128.99, 128.35, 127.74, 127.46, 127.12, 126.55, 120.50, 120.04, 95.10. Anal. Calcd for $C_{45}H_{31}IrN_2O_2$: C, 65.60; H, 3.79; N, 3.40. Found: C, 65.65; H, 3.31; N, 3.12.

(piq)$_2$Ir(dbmBr) (4). Red powder. Yield: 83%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.02 (s, 2H), 8.46 (d, J = 5.4 Hz, 2H), 8.24 (d, J = 7.2 Hz, 2H), 7.87 (s, 2H), 7.7 (s, 4H), 7.60 (d, J = 7.2 Hz, 4H), 7.40 (m, 6H), 6.95 (t, J = 7.2 Hz, 2H), 6.71 (t, J = 7.2 Hz, 2H), 6.47 (s, 1H), 6.45 (d, J = 7.2 Hz, 2H). Anal. Calcd for $C_{45}H_{29}Br_2IrN_2O_2$: C, 55.05; H, 2.98; N, 2.85. Found: C, 54.92; H, 3.02; N, 2.90.

Synthesis of Polymers. As an example, we describe the preparation of PFCzIrpiq05 for synthesis of the polymers: a mixture of complex **4** (3 mg, 0.003 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.15 g, 0.3 mmol), 3,6-dibromo-*N*-(2-ethylhexyl)carbazole (0.13 g, 0.297 mmol), Pd(PPh$_3$)$_4$ (10 mg, 3% mmol), and $K_3PO_4 \cdot 4H_2O$ (0.80 g, 3 mmol) in 5 mL of toluene and 2 mL of distilled water in a Schlenk tube was stirred at 100 °C for 72 h. After the reaction, the resulting polymers were purified by precipitation in methanol twice and washed with acetone in a Soxhlet apparatus for 72 h.

PFCzIrphq05. Yield: 67%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.00−8.20, 7.70−7.13, 4.15, 2.04, 1.33−0.68. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 151.52, 140.78, 139.49, 133.00, 126.23, 125.57, 123.64, 121.69, 120.03, 118.99, 109.57, 56.03, 48.45, 41.48, 40.39, 32.41, 31.96, 30.68, 29.84, 25.40, 24.79, 24.08, 23.58, 15.15, 12.02.

PFCzIrphq1. Yield: 72%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.80−8.20, 8.00, 7.75−7.14, 7.00−6.00, 4.17, 2.05, 1.35−0.69. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 152.18, 141.44, 140.15, 133.66, 126.89, 126.22, 124.29, 122.35, 120.70, 119.67, 110.24, 56.68, 49.09, 42.12, 41.04, 33.07, 32.60, 31.34, 30.51, 26.04, 25.45, 24.75, 24.24, 15.81, 12.69.

PFCzIrphq3. Yield: 79%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.00−8.50, 8.43, 8.31, 8.07, 7.86−7.17, 6.61, 6.00, 4.18, 2.07, 1.49−0.69. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 151.68, 140.77, 139.54, 133.00, 126.15, 125.49, 123.56, 121.60, 119.90, 118.86, 109.37, 55.35, 47.66, 40.66, 39.57, 31.54, 31.07, 29.79, 28.95, 24.45, 23.84, 23.13, 22.63, 14.11, 10.96.

PFCzIrpiq05. Yield: 75%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.00−8.38, 7.86−6.50, 4.26, 2.19, 1.44−0.79. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 150.62, 139.78, 139.48, 131.92, 125.09, 124.43, 122.49, 120.53, 118.86, 117.81, 108.31, 54.29, 46.62, 39.63, 38.51, 30.49, 30.00, 28.75, 27.88, 23.38, 22.79, 22.09, 21.59, 13.04, 9.91.

PFCzIrpiq1. Yield: 80%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.00−8.38, 7.86−6.50, 4.26, 2.19, 1.44−0.79. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 151.89, 141.05, 139.76, 133.20, 127.74, 126.36, 123.77, 121.81, 120.12, 119.08, 109.58, 55.56, 47.90, 40.89, 39.78, 31.75, 29.16, 24.06, 14.34.

PFCzIrpiq3. Yield: 83%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 9.00−8.38, 7.86−6.50, 4.26, 2.19, 1.44−0.79. ^{13}C NMR (300 MHz, CDCl$_3$, δ): 151.90, 141.06, 139.76, 133.21, 126.37, 125.71, 123.77, 121.82, 120.12, 119.09, 109.58, 55.57, 47.91, 40.89, 39.79, 31.75, 31.29, 30.01, 29.15, 24.67, 24.06, 23.35, 22.84, 14.33, 11.18.

Fabrication and Measurement of PLED Devices. The fabrication of electrophosphorescent devices and performance measurement followed a previous procedure.[9] Polymers were dissolved in *p*-xylene and filtered with a 0.45 μm filter. Patterned ITO-coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol and then in an ultrasonic bath. After treatment with oxygen plasma, 150 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-p 4083, Bayer AG) was spin-coated onto the ITO substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of polymers was coated onto the anode by spin-casting inside a drybox. The film thickness of the active layers was around 75−80 nm, measured with an Alfa Step 500 surface profiler (Tencor). A thin layer of Ba (4−5 nm) and subsequently a 200 nm layer of Al were vacuum-evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. Device performances were measured inside a drybox. Current−voltage ($I-V$) characteristics were recorded with a Keithley 236 source meter. EL spectra were obtained with an Oriel Instaspec IV CCD spectrograph. Luminance external quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

Results and Discussion

Synthesis and Characterization. The synthesis of biaryls using a ligandless palladium acetate catalyzed Suzuki reaction in the microwave-assisted system was reported by Leadbeater et al.[13a] In our work, a modification of the above method was applied to prepare the two quinoline-based ligands, 2-phenylquinoline and 1-phenylisoquinoline, by the coupling of 2-chloroquinoline or 1-chloroisoquinoline with benzeneboronic acid, respectively. Considering the poor solubility of the organic substrates in water, acetonitrile was used as the cosolvent for its high dielectric constant as water. In comparison with the conventional preparation of these ligands,[13b,c] which usually involves the use of air-sensitive palladium catalysts and needs a long reaction time, the microwave-assisted method uses air-stable palladium acetate as catalyst and proceeds very quickly (30 min) with good isolated yields. The cyclometalated iridium

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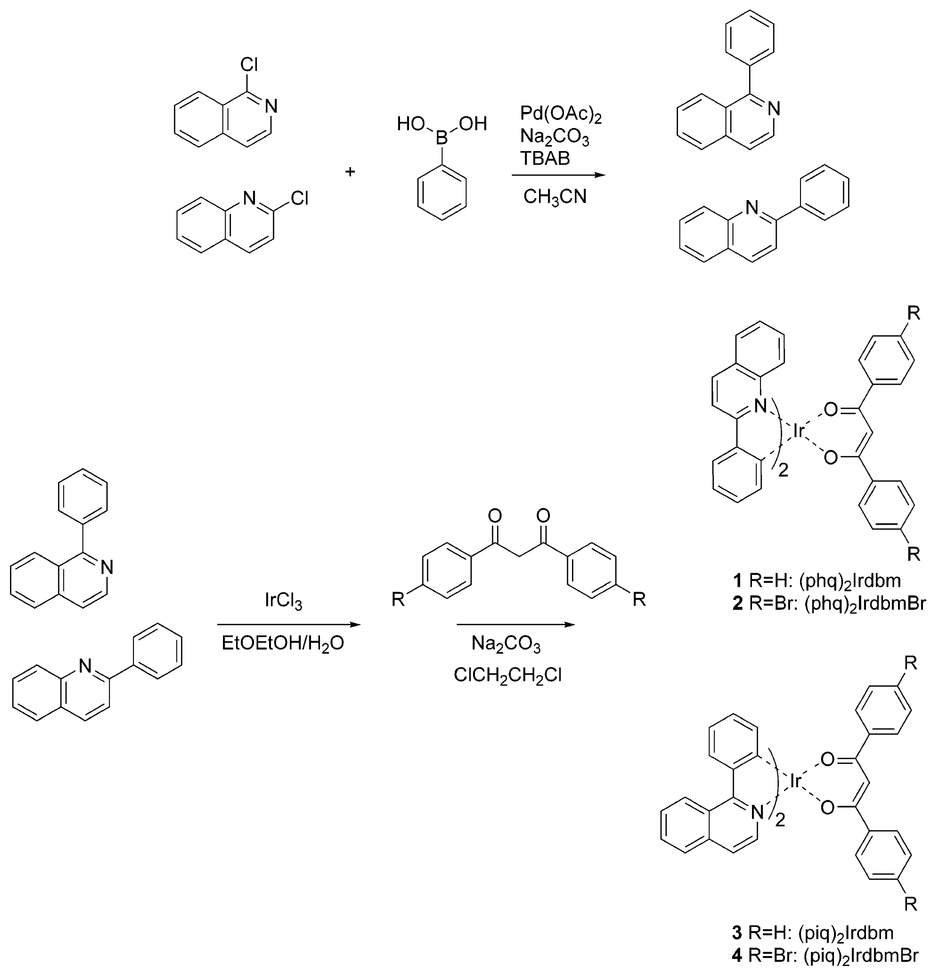
Scheme 1. Synthesis of Iridium Complexes



complexes were synthesized in two steps.[14] The ligands were first reacted with iridium trichloride hydrate to give the corresponding chloro-bridged dimeric complexes. Subsequent treatment of the dimers with dibenzoylmethane (dbm) or 1,3-bis(*p*-bromophenyl)-1,3-propanedione (dbmBr) in 1,2-dichloroethane in the presence of Na$_2$CO$_3$ afforded the monomeric complexes **1**−**4**, as shown in Scheme 1. The iridium complexes **1** and **3**, without bromine substitution at the ancillary ligand, were synthesized for comparison. These complexes were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. Copolymers were prepared via Suzuki polycondensation reactions of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 3,6-dibromo-*N*-(2-ethylhexyl)carbazole, and the iridium complex monomer **2** or **4** (Scheme 2). The starting monomer molar ratios were altered in order to investigate the effect of copolymer compositions on their physical and optical properties. The feed ratios of iridium complexes in the polycondensation are 0.5, 1, and 3 mol %, and corresponding copolymers were named PFCzIrphq05, PFCzIrphq1, and PFCzIrphq3 and PFCzIrpiq05, PFCzIrpiq1, and PFCzIrpiq3, respectively. A copolymer without iridium complexes, denoted PFCz, was also synthesized for comparison. The ^{1}H NMR signal at ca. 5.8 ppm for the series of copolymers PFCzIrphq and ca. 6.5 ppm for the series of copolymers PFCzIrpiq, assigned to the methylene proton between the two carbonyl groups on the β-diketonate ligand, can be observed in the chelating copolymers when feed ratios of iridium complex are 1 and 3 mol %. The actual iridium complex contents were thus estimated to be 0.7 and 2.5 mol % for PFCzIrphq1 and PFCzIrphq3 and 0.8 and 2.3 mol % for PFCzIrpiq1 and PFCzIrpiq3, respectively. The resulting copolymers are readily dissolved in common organic solvents, such as chloroform, toluene, and THF. On the basis of GPC, the number-average molecular weights of the copolymers are between 5800 and 7400 with narrow polydispersities index between 1.3 and 1.5 (Table 1).

The infrared spectra of the copolymers, along with the iridium complex monomers for comparison, were examined and found to be consistent with designed structures (Figure 1). In particular, the band near 1530 cm^{-1}, assigned to the C=C stretching vibration from the dibenzoylmethane,[15] can be seen in the copolymers with the feed ratios of iridium complexes over 1 mol %, suggesting that iridium complexes were successfully incorporated into the copolymers.

Thermal Analysis. The thermal properties of the copolymers were investigated by TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) (Figure 2 and Table 1). The TGA indicates that all copolymers exhibit good thermal stability with 5% weight loss temperatures ranging from 393 to 425 °C. DSC analysis revealed that all copolymers are amorphous solids with glass transition temperatures (T_g) ranging from 148 to 175 °C. The copolymers containing iridium complexes show T_g values higher than those for the fluorene-*alt*-carbazole copolymer PFCz. These high T_g values are in contrast with the low T_g (75 °C) value of poly(9,9-dioctylfluorene) (PFO),[16] indicating that the introduction of a carbazole unit into the backbone greatly improved the morphological

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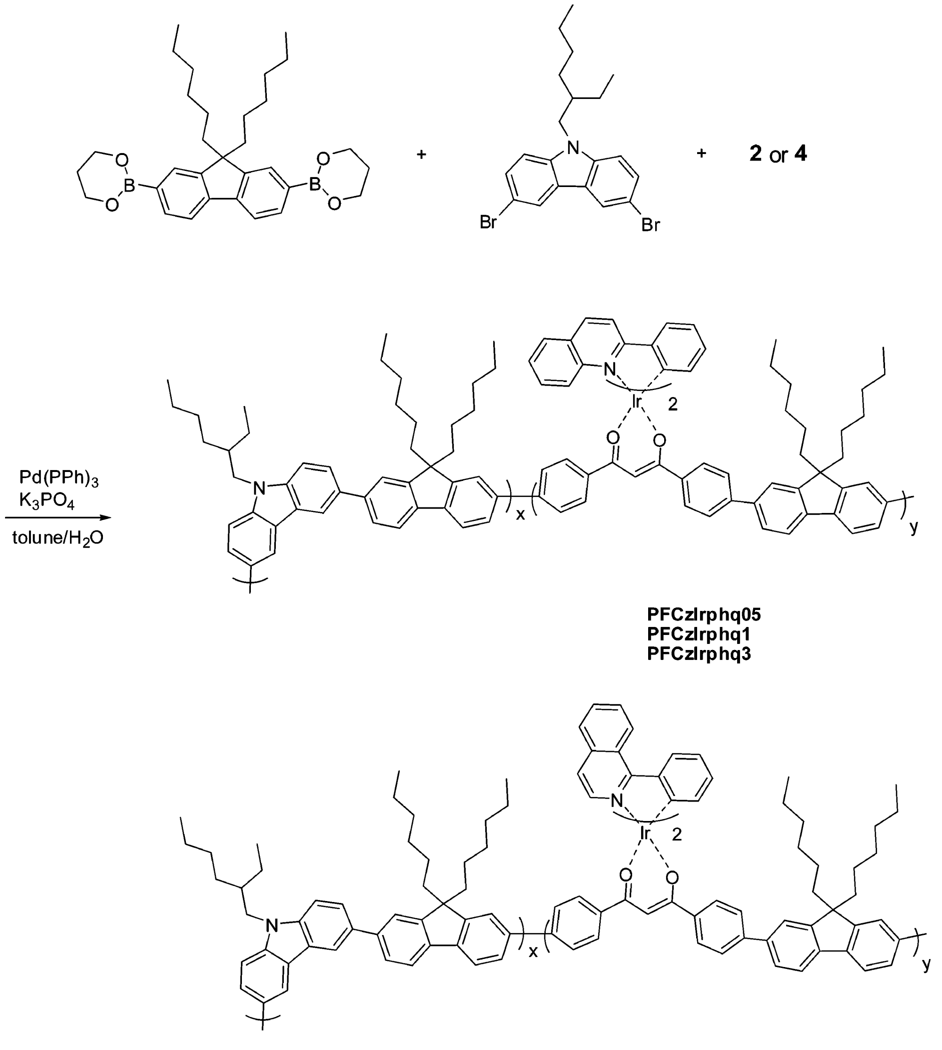
[16] Grell, C. H.; Shu, C. F. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3314.

Scheme 2. Synthesis of Copolymers



PFCzIrphq05
PFCzIrphq1
PFCzIrphq3

PFCzIrpiq05
PFCzIrpiq1
PFCzIrpiq3

Table 1. Structural and Thermal Properties of the Copolymers

	Ir complex (mol %)					
copolymer	feed ratio	copolymer[a]	M_n[b]	PDI	T_g (°C)	T_d (°C)
PFCz	0	0	10200	1.4	148	425
PFCzIrphq05	0.5		5811	1.4	159	420
PFCzIrphq1	1	0.7	5304	1.5	157	423
PFCzIrphq3	3	2.5	5777	1.5	157	393
PFCzIrpiq05	0.5		5800	1.5	152	414
PFCzIrpiq1	1	0.8	7200	1.3	163	419
PFCzIrpiq3	3	2.3	7400	1.4	175	397

[a] The iridium contents in copolymers were estimated by ^1H NMR. [b] Molecular weights were determined by GPC using polystyrene standards.

Table 2. Electrochemical Properties of Copolymers and Iridium Complexes

copolymer or complex	E_{ox}^{onset} (V)	HOMO[a] (eV)	E_{opt}[b] (eV)	LUMO (eV)
PFCz	1.12	−5.52	3.08	−2.44
PFCzIrphq05	1.07	−5.47	3.06	−2.41
PFCzIrphq1	1.06	−5.46	3.05	−2.41
PFCzIrphq3	1.05	−5.45	3.02	−2.43
PFCzIrpiq05	1.04	−5.49	3.08	−2.41
PFCzIrpiq1	1.04	−5.46	3.07	−2.39
PFCzIrpiq3	1.02	−5.49	3.02	−2.47
$(phq)_2$Irdbm	0.82[c]	−5.22		−2.60[d]
$(piq)_2$Irdbm	0.74[c]	−5.17		−2.62[d]

[a] Estimated from the onset oxidation potential. [b] Estimated from the onset of absorption edge. [c] Measured in CH_2Cl_2 solution. [d] Estimated from the onset reduction potential measured in THF.

stability of the copolymers. This is highly desirable for polymers used as emissive layers in light-emitting devices.

Electrochemical Properties. Cyclic voltammetry (CV) was employed to investigate the redox behavior of the copolymers and the monomeric iridium complexes (Supporting Information, Figure S1). All of the electrochemical data are given in Table 2. All copolymers show a partial reversible oxidation wave with an onset potential around 1.02−1.12 V. On the basis of low loading of iridium complexes in the copolymers, we believe that the voltamograms of copolymers are predominantly characteristic of the fluorene-*alt*-cabazole backbone. The HOMO levels of copolymers can be calculated by the formula $E_{HOMO}/\text{eV} = -e(E_{OX} + 4.4)$.[17,18] The difference between the HOMO levels and the optical energy gap (E_{opt}) can be used to estimate the LUMO energy levels of copolymers, where E_{opt} values were

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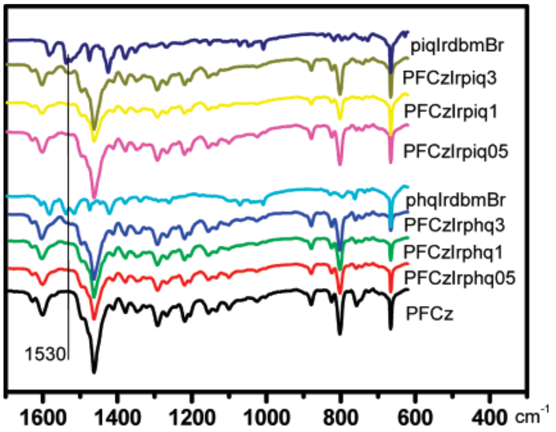

Figure 1. Comparison of infrared spectra of copolymers and iridium monomers.

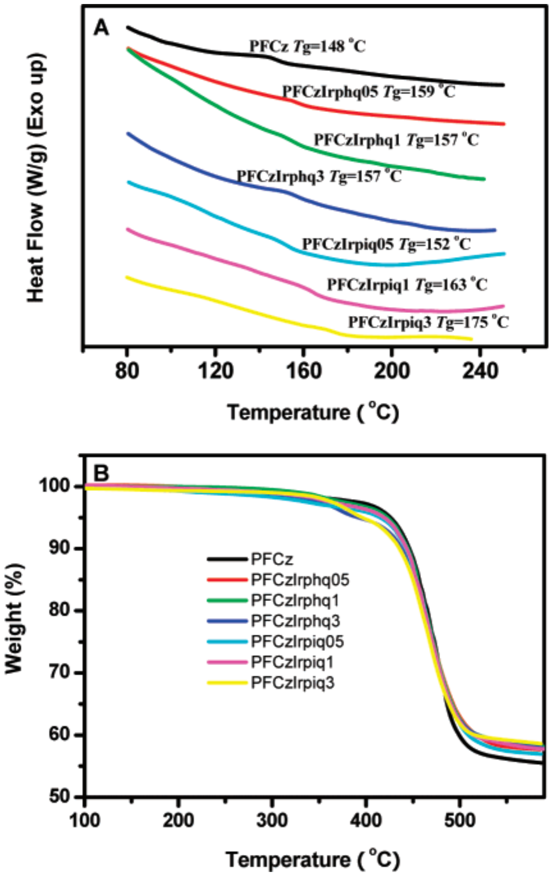

Figure 2. DSC (A) and TGA (B) thermograms of PFCz and copolymers.

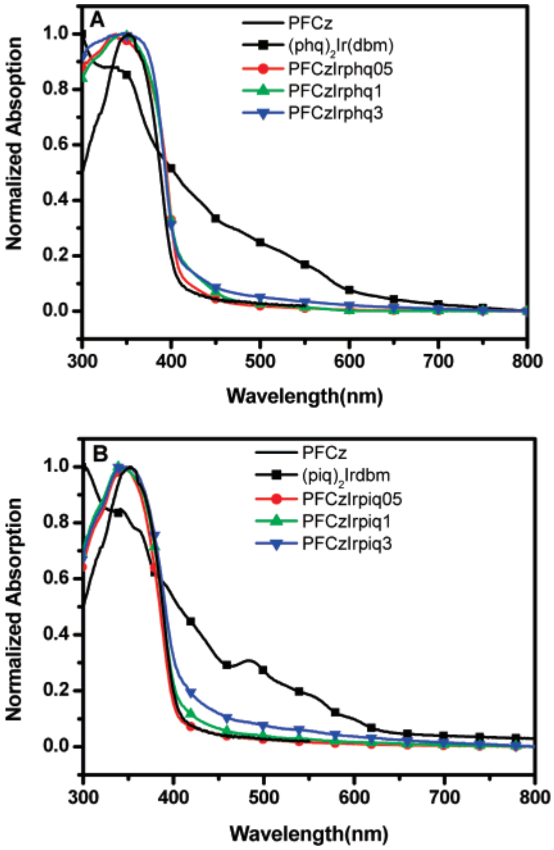

Figure 3. Absorption spectra of PFCzIrphq (A) and PFCzIrpiq (B) as films and the corresponding iridium complexes in CH_2Cl_2.

Table 3. Photophysical Data of Copolymers and Iridium Complexes

	λ_{abs}(max) (nm)[a]	λ_{PL}(nm)[a]	λ_{EL} (nm)[b]	Q_{PL} (%)[c]
PFCz	351	434		24.8
PFCzIrphq0.5	346	588	599	20.3
PFCzIrphq1	345	590	600	21.8
PFCzIrphq3	353	593	603	22.0
PFCzIrpiq0.5	349	619	628	23.8
PFCzIrpiq1	347	620	629	23.4
PFCzIrpiq3	350	623	630	21.0
$(phq)_2$Irdbm[d]	338, 476, 555	595		
$(piq)_2$Irdbm[d]	339, 483, 548	625		

[a] Measured as films. [b] Measured in the device ITO/PEDOT/copolymers /Ba/Al. [c] Measured relative to quinine bisulfate (in 1.0 M H_2SO_4) in chloroform solution. [d] Measured in CH_2Cl_2 solution.

deduced from the absorption onset of copolymers in the film. Considering that the HOMO and LUMO energy levels of the iridium complexes **1** and **3** fall within those of the host polymer PFCz (Table 2), the holes and electrons are expected to be trapped by the iridium complexes in the copolymers under electrical excitation.[19]

Photophysical Properties. Absorption spectra of the copolymers as well as of the monomeric complexes $(phq)_2$Ir(dbm) (**1**) and $(piq)_2$Ir(dbm) (**3**) for comparison are shown in Figure 3. The photophysical data are given in Table 3. For the two complexes, the intense absorption below 400 nm can be attributed to the transitions of ligand-centered states with mostly spin-allowed $^1\pi-\pi^*$ character from cyclometalated ligands. The weak absorptions from 400 to 600 nm can be likely associated with both the metal to ligand charge-transfer (MLCT) and $^3\pi-\pi^*$ transitions of iridium complexes.[20] The absorption spectra of the copolymers are almost the same as that of the PFCz host with a maximum absorbance around 350 nm. At the same time, with increasing contents of iridium complexes in copolymers, the weak absorption bands between 400 and 600 nm become observable, and the peak intensity gradually increased.

The photoluminescent (PL) spectra of copolymers and iridium complexes are shown in Figure 4. The good overlap between the emission spectrum of the host (PFCz) and the absorption spectra of the iridium complexes $(phq)_2$Ir(dbm) (**1**) and $(piq)_2$Ir(dbm) (**3**) implies efficient Förster energy transfer from the fluorene-*alt*-carbazole segments to the iridium complexes in the copolymers. The PL spectra of the copolymers were dominated

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(20) Schimid, B.; Garces, F. O.; Watts, R. J. *Inorg. Chem.* **1994**, *33*, 9.

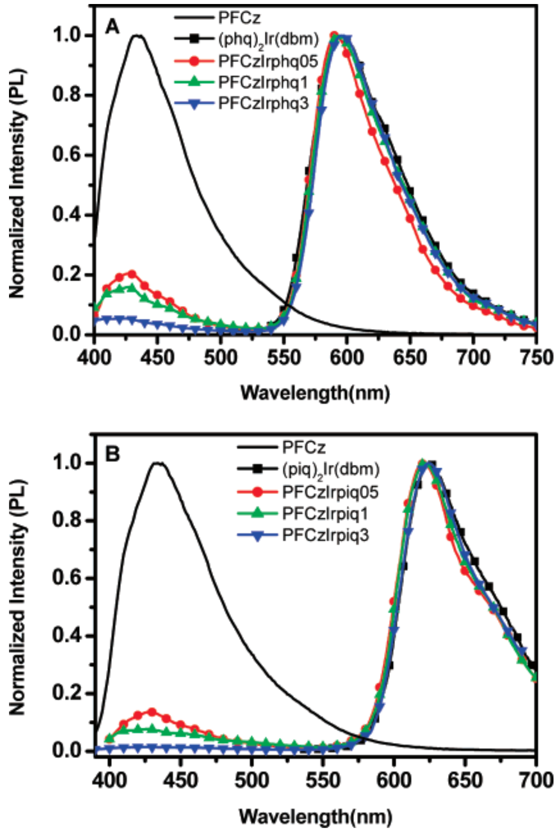

Figure 4. Photoluminescence spectra of the copolymers as films and the iridium complexes in CH_2Cl_2.

by emission from the iridium complexes, even at a feed ratio of Ir complexes as low as 0.5 mol %. As shown in Figure 4, emission around 420 nm from fluorene-*alt*-carbazole segments can be observed for those copolymers with low iridium complex feed ratios of 0.5 and 1 mol %; when the feed ratio reached 3 mol %, the emission around 420 nm was completely quenched by phosphorescent complexes. The significantly lower loading of iridium complexes required for complete quenching of host emission as compared to that needed in the guest−host blending systems indicates that intramolecular energy transfer is much more efficient than intermolecular energy transfer. It is noteworthy that the copolymers show almost the same emission spectra as the monomeric iridium complexes, with peak emissions at 590 and 620 nm for PFCzIrphq and PFCzIrpiq, respectively (Figure 4). In contrast, the PL emissions of chelating copolymers with iridium complexes conjugated with main chain segments via cyclometalating C^N ligands usually exhibit remarkable red shifts with respect to their monomeric complexes, due to the extended conjugated length in the ligand.[9,21] For example, emissions from the copolymers of fluorene conjugated with iridium complexes via naphthylpyridine cyclometalated ligands exhibited about 20 nm bathochromic shifts relative to emissions of their monomeric complexes.[21] Here the copolymerization through ancillary ligands provides a methodology to control the emission wavelengths of chelating copolymers.

Electroluminescent Properties. In order to understand the electroluminescent and charge-transporting properties of the copolymers, three types of light-emitting devices (device **a**, ITO/PEDOT (50 nm)/copolymer (80 nm)/Ba (4 nm)/Al (120 nm); device **b**, ITO/PEDOT (50 nm)/PVK (40 nm)/copolymer (80 nm)/Ba (4 nm)/Al (120 nm); device **c**, ITO/PEDOT (50 nm)/copolymer + 40% PBD (80 nm)/Ba (4 nm)/Al (120 nm)) were fabricated, where an additional PVK layer (in device **b**) was used to improve the hole-transport ability and PBD (in device **c**) was blended into the emitting layer to improve the electron-transport capability as in previous literature reports.[22] The EL spectra of devices from the copolymers PFCzIrphq and PFCzIrpiq exhibited emission peaks around 600 and 629 nm, respectively (Figure 5 and Table 3), with slight red shifts in comparison with their PL emission maxima. Unlike PL spectra in films (Figure 4), EL spectra of all of the copolymers show exclusive triplet emission, even at a feed ratio of iridium complex as low as 0.5 mol %. Complete quenching of the host PFCz emission at 420 nm in EL with lower contents of Ir complexes as compared to those in PL emission indicates that charge trapping (rather than Förster energy transfer in PL) is the dominant process under EL excitation.[23]

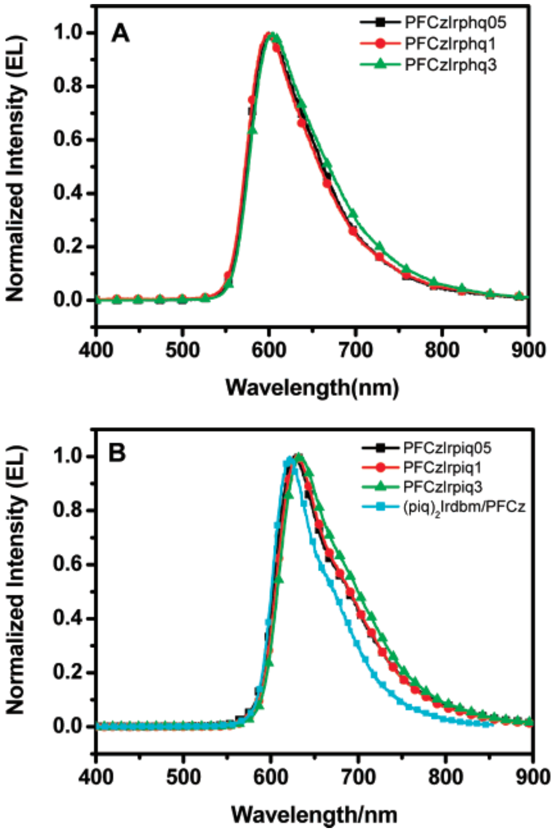

Figure 5. EL spectra of single-layer devices with PFCzIrphq (A) and PFCzIrpiq (B) in the configuration ITO/PEDOT/copolymers/Ba/Al.

Figures 6 and 7 show the luminance and external quantum efficiency as a function of current density for the devices using the copolymers as the emission layers. The performances of all the devices are summarized in Table 4. For the single-layer devices with PFCzIrpiq as the emitting layer (device **a**; Figure 6), the external quantum efficiencies increased from 0.05% to 0.24% when the feed ratio of iridium complex increased from 0.5 to 3 mol %. The same tendency can be observed for the devices from PFCzIrphq with efficiencies from 0.02 to 0.22%.

Comparing the performances of three types of devices, we note that device **c** with PBD doping shows efficiency over twice

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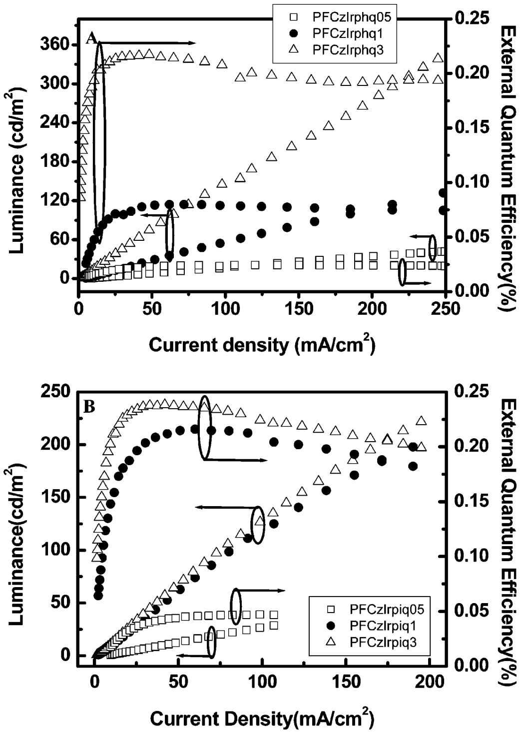

Figure 6. Luminance and external quantum efficiency vs current density using PFCzIrphq (A) and PFCzIrpiq (B) as emitting layers in single-layer devices.

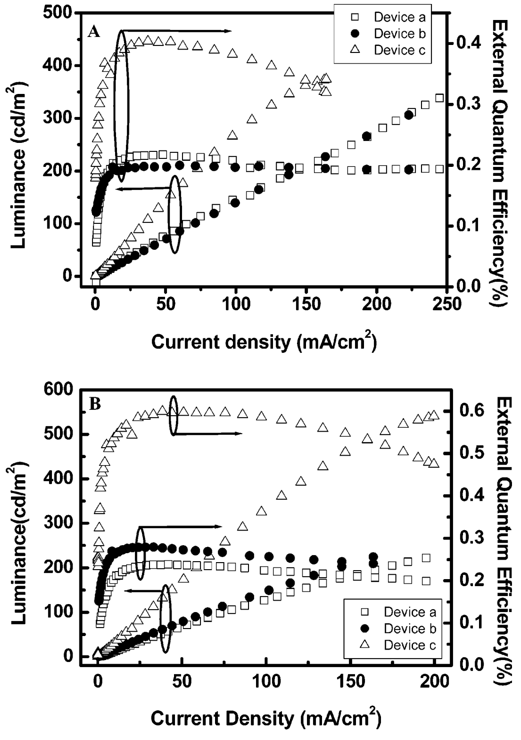

Figure 7. Luminance and external quantum efficiency vs current density using PFCzIrphq3 (A) and PFCzIrpiq3 (B) as emitting layers in devices **a**−**c**.

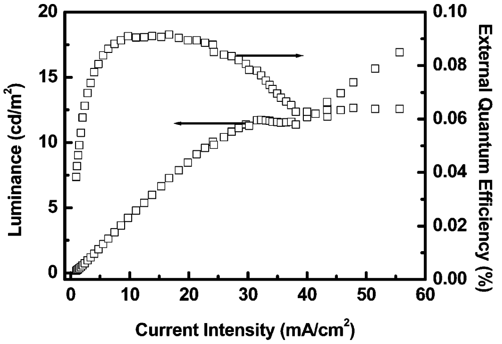

Figure 8. Luminance and external quantum efficiency vs current density for blending systems using the complex (piq)$_2$Ir(dbm) (**3**) as phosphorescent dopant.

Table 4. Device Performance of Copolymers

copolymer	L (cd/m^2)/ bias (V)[d]	EQE$_{\max}$ (%)	LE$_{\max}$ (cd/A)	J (mA/ cm^2)[e]
PFCzIrphq05[a]	41.8/24	0.024	0.017	120
PFCzIrphq05:PVK[b]	73.4/30	0.03	0.023	195
PFCzIrphq05:PBD[c]	92.5/16	0.10	0.075	24
PFCzIrphq1[a]	132/30	0.08	0.057	62
PFCzIrphq1:PVK[b]	126/33	0.09	0.06	21
PFCzIrphq1:PBD[c]	103/17	0.17	0.12	22
PFCzIrphq3[a]	349/26	0.22	0.16	48
PFCzIrphq3:PVK[b]	368/32	0.20	0.14	60
PFCzIrphq3:PBD[c]	400/16	0.41	0.29	37
PFCzIrpiq05[a]	107/29	0.05	0.03	98
PFCzIrpiq05:PVK[b]	67/35	0.08	0.04	150
PFCzIrpiq05:PBD[c]	28/18	0.13	0.07	32
PFCzIrpiq1[a]	247/26	0.22	0.12	60
PFCzIrpiq1:PVK[b]	326/31	0.28	0.16	54
PFCzIrpiq1:PBD[c]	344/17	0.53	0.30	39
PFCzIrpiq3[a]	221/24	0.24	0.14	42
PFCzIrpiq3:PVK[b]	225/30	0.28	0.16	33
PFCzIrpiq3:PBD[c]	541/15	0.60	0.34	39
(piq)$_2$Ir(dbm)-PFCz:PBD[c]	39/26	0.09	0.04	17

[a] Device **a**: ITO/PEDOT/copolymer/Ba/Al. [b] Device **b**: ITO/PEDOT/PVK/copolymer/Ba/Al. [c] Device **c**: ITO/PEDOT/copolymer + PBD (40%)/Ba/Al. [d] Maximum luminance and corresponding bias. [e] Current intensity for maximum external quantum efficiency and luminance efficiency.

as large as those of both devices **a** and **b** without PBD. In contrast, device **b** with an additional PVK layer only exhibits a slight improvement in comparison with device **a** without a PVK layer (Table 4 and Figure 7). This result suggests that the incorporation of carbazole units into the copolymers indeed improves the hole-transporting ability of the chelating copolymers. The best performance, with a maximum external quantum efficiency of 0.60% at a current density (J) of 39 mA/cm^2 and a maximum luminance of 541 cd/m^2 at 16 V, was achieved for the copolymer PFCzIrpiq3. Those data for the copolymer PFCzIrphq3 are 0.41% at $J = 47$ mA/cm^2 and 400 cd/m^2 at 16 V. However, these EL performances are inferior to those of other similar systems reported by Evans et al.,[24] where red-emitting phosphorescent iridium complexes based on the [Ir(btp)$_2$(acac)] fragment were either attached directly (spacerless) or attached through an octamethylene-tethered linkage at the 9-position of a 9-octylfluorene host. A red emission PLED device, with an external quantum efficiency of 2.0% ph/el at the luminance of 100 cd/m^2, was obtained. The relatively poor performances in our work may be attributed to the potential triplet energy back-transfer from the iridium complexes to the polymer backbone PFCz due to the spacerless linkage between them, as demonstrated by Evans et al.[24] We are now trying to design new phosphorescent copolymers with polymer backbones having high triplet energy to minimize the triplet energy back-transfer,[25] aiming to improve device performance.

To evaluate the effectiveness of electroluminescent copolymers, a device based on the blending system ITO/PEDOT (50

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(24) Evans, N. R.; Devi, L. S.; Mak, C. S. K.; Watkins, S. E.; Pascu, S. I.; Köhler, A.; Friend, R. H.; Williams, C. K.; Holmes, A. B. *J. Am. Chem. Soc.* **2006**, *128*, 6647.

(25) Sudhakar, M.; Djurovich, P. I.; Hogen-Esch, T. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7796.

nm)/3 mol % $(piq)_2Ir(dbm)$ (**3**) doped in PFCz + 40% PBD (80 nm)/Ba (4 nm)/Al (120 nm) was also fabricated for comparison with the device based on the copolymer PFCzIrpiq3 in the same device configuration. Devices from both the chelating copolymer PFCzIrpiq and doping system show almost identical EL spectra, with peak emissions around 628 nm (Figure 5B). Figure 8 shows the luminance and external quantum efficiency as a function of current density for the blending system. It is obvious that the device performance of the blending system is rather low and the efficiencies decrease dramatically beyond a current density of 30 mA/cm^2. The external quantum efficiencies of the device with the copolymer PFCzIrpiq3 as the emission layer are over 6 times higher and decay gently with an increase of current density up to 100 mA/cm^2. This indicates that the covalent linkage of phosphorescent complexes into the polymer main chain can effectively suppress the primary origins, leading to fast decay of efficiency for the blending system at high current density, such as concentration quenching and T−T annihilation.

Conclusions

In conclusion, we have synthesized and characterized a series of novel fluorene-*alt*-carbazole-based copolymers with iridium coordinating to β-diketonate units in the main chain. This is the first report about copolymers with iridium complexes linked to polymer main chains via ancillary ligands. It promises a facile preparation of the copolymers with various iridium complexes incorporated into the main chain. The high affinity of β-diketonate for most metal ions also makes the method versatile for constructing metal-containing polymers. TGA/DSC measurements indicate that the copolymerization of carbazole and iridium complex units with fluorene units increase the thermal stability. All copolymers show almost the same emission spectra as their monomeric complexes in the PL spectra. This makes the emission wavelength of phosphorescent copolymers controllable. EL studies reveal that the copolymers with iridium complexes in the main chain show highly efficient energy transfer of excitons from the fluorene-*alt*-carbazole host segments to the iridium complexes by a dominant intramolecular trapping mechanism. We note that all of the devices are almost free of efficiency decay even at the high current density, due to the covalent linkage of phosphorescent complexes into the polymer main chain. Despite its modest external quantum efficiency in PLEDs, this kind of copolymer opens the door for other more efficient structures.

Acknowledgment. We thank the National Natural Science Foundation of China (Project Nos. 20474047 and 20371036) and the Program for New Century Excellent Talents in University, the Ministry of Education of China, for financial support. We also thank the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for partial financial support.

Supporting Information Available: Figures and tables giving cyclic voltammograms of the copolymers and monomeric iridium complexes, electroluminescent device configurations, and detailed device performance data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070037T