Novel light-emitting electrophosphorescent copolymers based on carbazole with an Ir complex on the backbone

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Novel light-emitting phosphorescent polymers based on 3,6-carbazole with an iridium complex on the backbone were synthesized by Suzuki polycondensation of A-A and B-B type monomers. Three difluoro-substituted phenylpyridine iridium complexes with different ancillary ligands (FIrptz, FIrpic and FIrtmd) were introduced into the poly(3,6-carbazole) (PCz) backbone, causing distinct differences in the photo- and electroluminescence properties. The PL efficiency of PCz-FIrtmd5 is as high as 62% compared with the value of 9% of the fluorene-*alt*-carbazole-based copolymer (PFCz-FIrtmd5), which indicated that the 3,6-carbazole unit was suitable to serve as the host for a green electrophosphorescent polymer. The ancillary ligand of bicycloiridium complexes also affects the device performance based on chelating copolymers. The best device performances were obtained from copolymer PCz-FIrtmd5 with the maximal luminous efficiency of 4.4 cd A^{-1} and a luminance of 453 mA cm^{-2} at a current density of 10.3 mA cm^{-2} with the configuration: ITO/PEDOT/polymer + PBD(30 wt%)/Ba/Al.

Introduction

Phosphorescent organic light-emitting diodes (PHOLED)s composed of phosphorescent iridium complexes have been attracting much attention because of their relatively short phosphorescent lifetime and high luminous efficiency.[1–4] Phosphorescent dye-doped polymer light-emitting devices are extremely attractive due to their ease of fabricated by printing techniques and the potential applications in large-area flat panel displays.[5,6] Phosphorescent polymers dye-doped chemically into the polymer chain can decrease phase segregation, which leads to fast decay of efficiency with increasing current density. Lee *et al.*[7] synthesized a non-conjugated polyethylene main chain with phenylpyridine attached to the side chains as a ligand and with pendant *N*-vinylcarbazole as a host unit. A high external quantum efficiency of 4.4% ph el^{-1} (photons per electron) was achieved at a current density of 6.4 mA cm^{-2}. A similar approach of using a non-conjugated main chain with a pendant diketone was reported by Tokito *et al.*[8] High external quantum efficiencies of 5.5%, 9% and 3.5% in red, green and blue PLEDs respectively were achieved. Phosphorescent conjugated polymers based on a polyfluorene backbone with a diketone pendant attached to the 9-carbon position of fluorene were reported by Chen *et al.*[9] An external quantum efficiency of 1.59% ph el^{-1} with the peak emission at 610 nm was achieved. A device consisting of a fluorene-*alt*-carbazole copolymer grafted with an Ir complex shows the highest external quantum efficiency of 4.9% ph el^{-1} and a peak emission at 610 nm.[10] Recently, phosphorescent conjugated polymers that possess M–C or π-bonds in the backbone have attracted substantial attention. A series of yellow and red conjugated well-defined oligo- and polyfluorenyl bis-cyclometalated Ir complexes was synthesized by Sandee *et al.*with the maximal external quantum efficiencies of 0.12% ph el^{-1} and 1.5% ph el^{-1} respectively.[11] In our early work,[12,13] yellow and red electrophosphorescent copolymers with Ir complexes on the backbone of poly(fluorene-*alt*-carbazole) (PFCz) and polyfluorene (PFO) were synthesized by Suzuki polycondensation to achieve maximal external quantum efficiencies of 4.6% and 7.0% ph el^{-1} respectively. In this case, high-efficiency energy transfer from the polymer host to the Ir complex in the polymer main chain *via* efficient intramolecular energy transfer would be expected. Of the phosphorescent polymers, the reported blue and green light-emitting polymers are very rare especially for main chain-type conjugated polymers, as the complex in conjugation with a neighboring conjugated segment in the polymer backbone makes the luminous wavelength of copolymers red-shift. Iridium complexes with fluoro-substituted phenylpyridine as a ligand were doped into organic small molecules for greenish blue OLEDs.[14–17]

In this paper, 3,6-carbazole with a wide band-gap was used as a host unit and three different ancillary ligand fluoro-substituted phenylpyridine Ir complexes (FIrptz, FIrpic and FIrtmd) were introduced into the polymer backbone by bromo-substituted Ir complex monomers at the 5-position of pyridine in the ligand.

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Experimental

Materials

All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. The solvents (THF, toluene) were purified by routine procedures and distilled in dry argon before being used. All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co. and used as received.

Preparation of the monomers

5-Bromo-2-(2,4-difluorophenyl)pyridine (FppyBr) (1). 1 was synthesized by the following procedure: 2,5-dibromopyridine (10 mmol), 2,4-difluorophenylboronic acid (10 mmol) and tetrakis(triphenylphosphine)palladium (0.1 mmol) were dissolved in toluene (15 ml) and ethanol (5 ml). Then an aqueous solution of 2 M Na_2CO_3 (6 ml) was added to the mixture. The resulting mixture was stirred at 100 °C for 24 h. The reaction mixture was concentrated by evaporation of solvents and the residue was dissolved in dichloromethane, washed with water and dried under anhydrous sodium carbonate. After the evaporation of solvent, the obtained product was purified by column chromatography (silica gel) (yield: 75%). ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm): 8.76 (d, J = 2.28 Hz, 1H), 8.05–7.97 (m, 1H), 7.88 (dd, J = 8.49 Hz and 2.40 Hz, 1H), 7.67 (dd, J = 8.49 Hz and 1.92 Hz, 1H), 7.01 (td, J = 8.30 Hz and 2.49 Hz, 1H), 6.93 (td, J = 10.03 Hz and 2.49 Hz, 1H). Elemental anal. Calcd for $C_{11}H_6BrF_2N$ (%): C, 48.97; H,2.24; N, 5.19. Found (%): C, 49.03; H, 2.12; N, 5.04. GC-MS (270, M^+)

5-Methyl-3-(pyridin-2-yl)-4*H*-1,2,4-triazole (Hptz) (2)[18]. 2-Cyanopyridine (50 mmol) and hydrazine monohydrate (50 mmol) was mixed and 20 ml ethanol was added to obtain a clear solution. After standing overnight at the room temperature, the almost colorless crystals of 2-pyridine carboxamidrazone could be filtered off. The product was washed with diethyl ether and dried in air. The obtained solid was added to a mixture of 30 ml acetic acid and acetic anhydride (1 : 1) at 0 °C and the solution was stirred at room temperature for 2 h. The solution was then concentrated under vacuum and purified by repeated crystallization from diisopropyl ether. Yield: 60%. ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm): 12.91 (s, 1H), 8.76 (d, J = 4.26 Hz, 1H), 8.20 (d, J = 7.92 Hz, 1H), 7.86 (td, J = 7.73 Hz and 1.65 Hz, 1H), 7.39 (t, J = 6.23 Hz, 1H), 2.54(s, 3H). Elemental anal. Calcd for $C_8H_8N_4$ (%): C, 60.00; H,5.03; N, 34.98. Found (%): C, 60.21; H, 4.89; N, 34.86. GC-MS (160, M^+)

Chloride-bridged dimer complex **$(FppyBr)_4Ir_2Cl_2$ (3)** was synthesized by the procedure reported.[19]

Iridium(III) bis[5-bromo-2-(2,4-difluorophenyl)pyridine]picolinate (BrFIrpic) (4). $(FppyBr)_4Ir_2Cl_2$ (**3**) (0.2 mmol) and picolinic acid (0.5 mmol) were refluxed under an inert gas atmosphere in dichloromethane for 24 h. After cooling to room temperature, the reaction mixture was dissolved in dichloromethane, washed with water and dried under anhydrous sodium carbonate. After the evaporation of solvent, the obtained product was purified by column chromatography (silica gel) (yield: 63%). ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm): 8.82 (d, J = 2.07 Hz, 1H), 8.40 (d, J = 7.98 Hz, 1H), 8.20–8.12 (m, 2H), 8.02 (td, J = 7.73 Hz and 1.32 Hz, 1H), 7.90 (d, J = 8.79 Hz, 2H), 7.75 (d, J = 4.92 Hz, 1H), 7.49 (t, J = 5.85 Hz, 1H), 7.33 (d, J = 2.04 Hz, 1H), 6.55–6.37 (m, 2H), 5.82 (dd, J = 8.46 Hz and 2.22 Hz, 1H), 5.56 (dd, J = 8.37 Hz and 2.19 Hz, 1H). Elemental anal. Calcd. for $C_{28}H_{14}Br_2F_4IrN_3O_2$ (%): C, 39.45; H, 1.66; N, 4.93. Found (%): C, 39.62; H, 1.69; N, 4.78. EIMS: m/z 853 $(M + 1)^+$.

Iridium(III) bis[5-bromo-2-(2,4-difluorophenyl)pyridine]-2,2,6,6-tetramethyl-3,5-heptanedione (BrFIrtmd) (5). 5 was synthesized according to the published procedure.[19] ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm): 8.39 (d, J = 2.22 Hz, 2H), 8.10 (dd, J = 8.88 Hz and 2.28 Hz, 2H), 7.88 (dd, J = 8.79 Hz and 2.13 Hz, 2H), 6.37 (td, J = 10.97 Hz and 2.31 Hz, 2H), 5.76 (dd, J = 8.67 Hz and 2.31 Hz, 2H), 5.59 (s, 1H), 0.95 (s, 18H). Elemental anal. Calcd $C_{33}H_{29}Br_2F_4IrN_2O_2$ (%): C, 43.38; H, 3.20; N, 3.07. Found (%): C, 43.52; H, 3.11; N, 2.97. EIMS: m/z 914 $(M + 1)^+$.

Iridium(III) bis[5-bromo-2-(2,4-difluorophenyl)pyridine]-5-methyl-3-(pyridin-2-yl)-1,2,4-triazole (BrFIrptz) (6). $(FppyBr)_4Ir_2Cl_2$ (**3**) (0.078 mmol), Hptz (**2**) (0.2 mmol), and 100 mg of sodium carbonate were refluxed under inert gas atmosphere in 2-ethoxyethanol for 16 h. After cooling to room temperature, the colored precipitate was filtered off and was washed with water, followed by 2 portions of ether and hexane. The crude product was flash chromatographed using a silica (dichloromethane : acetone = 1 : 1) column followed by recrystallization with methanol to obtain the green powder product after solvent evaporation and drying (yield: 67%). ^{1}H NMR (300 MHz; DMSO-d_6) δ (ppm): 8.23–8.12 (m, 4H), 8.08 (d, J = 4.26 Hz, 2H), 7.67 (d, J = 5.49 Hz, 1H), 7.48 (d, J = 2.01 Hz, 1H), 7.43–7.38 (m, 2H), 6.95–6.80 (m, 2H), 5.81 (dd, J = 8.16 Hz and J = 2.31 Hz, 1H), 5.61 (dd, J= 8.64 Hz and J = 2.34 Hz, 1H), 2.24 (s, 3H). Elemental anal. Calcd for $C_{30}H_{17}Br_2F_4IrN_6$ (%): C, 40.49; H,1.92; N, 9.45. Found (%): C, 40.63; H, 1.80; N, 9.37. EIMS: m/z 890 $(M + 1)^+$.

3,6-Dibromo-9-ethylhexylcarbazole (7), **3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (8)**[20] and **2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (9)**[21,22] were prepared according to the published methods.

Preparation of the polymers

General procedures of Suzuki polycondensation, taking PCz-FIrpic1 as an example. 3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (265.5 mg, 0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (214 mg, 0.49 mmol), BrIrpic (6.6 mg, 0.01 mmol) and palladium(II) acetate (2 mg) were dissolved in a mixed solution of toluene–THF (1 : 1, 10 ml), stirred for 0.5 h, and then Et_4NOH (20%) aqueous solution (4 ml) was added. The mixture was heated to 100 °C and stirred for 42 h under argon atmosphere. Then the polymer was capped by adding 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (45 mg) by continuous stirring for 12 h, and then bromobenzene (0.25 ml) followed by continuously reacting for another 12 h. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene to removethe small molecular complex and catalyst residue (yield: 50%). Elemental anal. Calcd. (%): C, 85.80; H, 8.16; N, 5.08. Found (%): C, 86.51; H, 7.84; N, 4.89.

PCz-FIrpic3. Monomer feed ratio: 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.47 mmol) and BrIrpic (0.03 mmol) (yield: 50%). Elemental anal. Calcd. (%): C, 84.19; H,7.88; N, 5.14. Found (%): C, 85.07; H, 7.12; N, 4.97.

PCz-FIrpic5. Monomer feed ratio: 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.45 mmol) and BrIrpic (0.05 mmol) (yield: 46%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.92 (s, Ar–H), 8.56 (s, 2H), 7.96 (s, Ar–H), 7.91 (d, 2H), 7.76–7.62 (m, Ar–H), 7.54–7.36 (m, 2H), 4.29–4.08 (m, 2H), 2.10 (m, 1H), 1.50–1.18 (m, 8H), 0.96–0.78 (m, 6H). Elemental anal. Calcd. (%): C, 82.66; H,7.61; N, 5.20. Found (%): C, 83.51; H, 7.34; N, 4.84.

PCz-FIrtmd3. Monomer feed ratio: 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.47 mmol) and BrIrtmd (0.03 mmol) (yield: 50%). Elemental anal. Calcd. (%): C, 82.66; H,7.83; N, 4.87. Found (%): C, 83.47; H, 7.54; N, 4.31.

PCz-FIrtmd5. Monomer feed ratio: 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.45 mmol) and BrIrtmd (0.05 mmol) (yield: 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.89 (s, Ar–H), 8.54 (s, 2H), 7.93 (s, Ar–H), 7.89 (d, 2H), 7.78–7.65 (m, Ar–H), 7.52–7.41 (m, 2H), 4.30–4.06 (m, 2H), 2.08 (m, 1H), 1.49–1.28 (m, 8H), 1.18 (s, tmd-CH_3), 0.92–0.75 (m, 6H). Elemental anal. Calcd. (%): C, 80.28; H,7.55; N, 4.76. Found (%): C, 81.06; H, 7.14; N, 4.35.

PFCz-FIrtmd5. Monomer feed ratio: 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (341 mg, 0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.45 mmol) and BrIrtmd (0.05 mmol) (yield: 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.74 (s, Ar–H), 8.52 (s, 2H), 7.85–7.72 (m, 6H), 7.53 (d, 2H), 7.24 (d, 2H), 4.28–4.05 (m, 2H), 2.16 (m, 1H), 1.95 (m, 4H), 1.58–1.03 (m, 32H), 0.93–0.74 (m, 12H). Elemental anal. Calcd. (%): C, 82.84; H,8.73; N, 2.11. Found (%): C, 83.21; H, 8.27; N, 1.86.

PCz-FIrptz3. Monomer feed ratio: 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (0.5 mmol), 3,6-dibromo-9-ethylhexylcarbazole (0.47 mmol) and BrIrptz (0.03 mmol) (yield: 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.92 (s, Ar–H), 8.57 (s, 2H), 8.14 (m, Ar–H), 7.91 (d, 2H), 7.76–7.62 (m, Ar–H), 7.49 (m, 2H), 4.25 (m, 2H), 2.11 (m, 2H), 1.52–1.22 (m, 8H), 0.97–0.78 (m, 6H).

Measurements

^{1}H NMR spectra were recorded on a Bruker 300 MHz Spectrometer operating at 300 MHz in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide-d_6 (DMSO-d_6) solution with tetramethylsilane as a reference. Mass spectra (MS) of the ligands were obtained by a CE Instruments Trace 2000 Series GC/MS, and the MS of the Ir complexes were recorded on a LCQ DECA XP Liquid Chromatograph–Mass Spectrometer (Thermo Group). The molecular weight of the polymers was determined by using a Waters GPC 2410 in tetrahydrofuran (THF). Number-average (M_n) and weight-average (M_w) molecular weights were estimated by using a calibration curve of polystyrene standards. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). The iridium content analyses were determined by using a Philips (Magix PRO) sequential X-ray fluorescence spectrometry (XRF), with a rhodium tube operated at 60 kV and 50 mA, a LiF 200 crystal and a scintillation counter. Tris(acetylacetonate)iridium(III) (Ir content of 38%, from Alfa Aesar Co.) was used as an internal reference specimen. Samples and specimens were pressed into homogeneous tablets (Φ = 30 mm) of compressed (375 MPa) powder of the copolymers. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. The PL quantum yields were determined in an Integrating Sphere IS080 (LabSphere) with 325 nm excitation of a HeCd laser (Melles Griot). PL spectra of the copolymer were obtained on a Fluorolog-3 Spectrometer (Jobin-Yvon) with 90° angle detection.

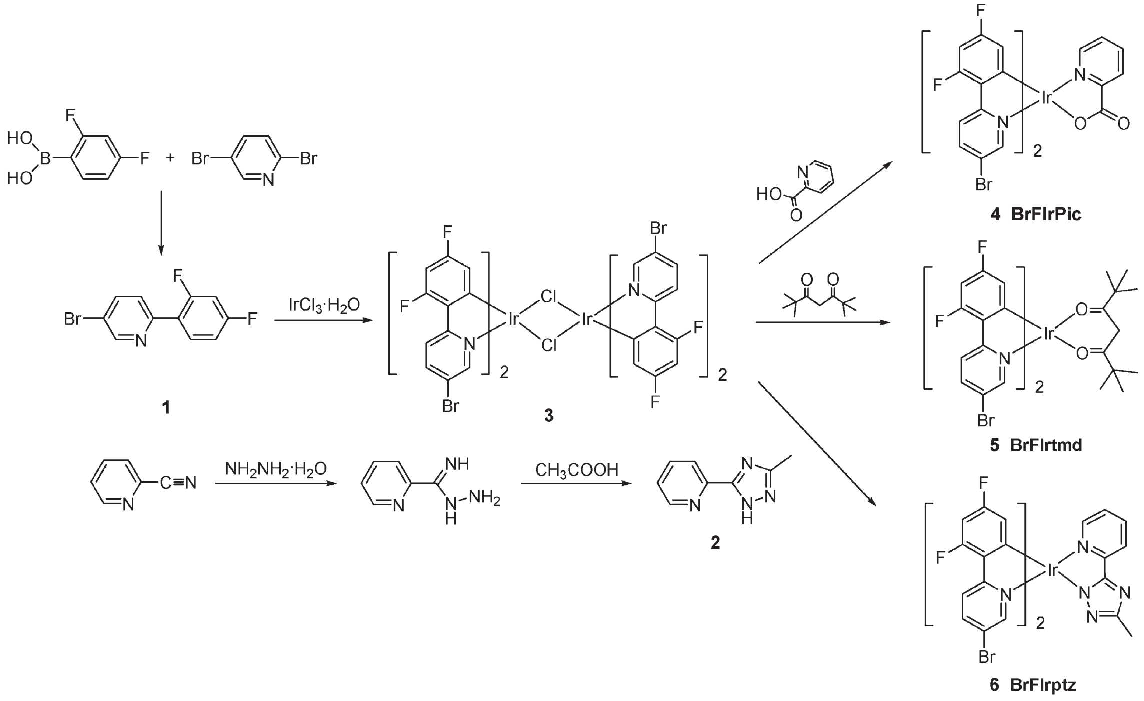
LED fabrication and characterization

Copolymers 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 isopropanol, subsequently 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 copolymer was coated onto the anode by spin casting inside a dry box. 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 on the top of an EL polymer layer in a vacuum of 1×10^{-4} Pa. Device performances were measured inside a dry box. Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source meter. EL spectra were collected by a PR 705 photometer (Photo Research). Luminance was measured by a calibrated silicon diode and calibrated by a PR 705 photometer. The external quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

Results and discussion

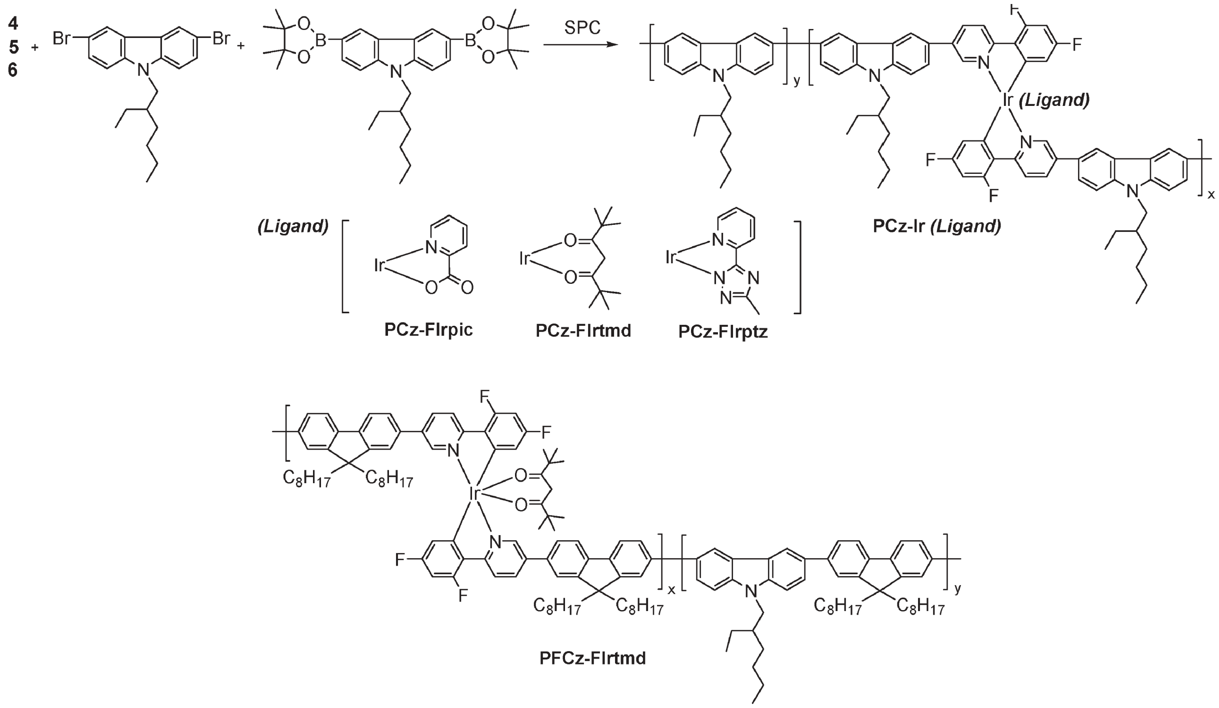
Synthesis and characterization

The synthetic routes to the monomers are depicted in Scheme 1. 5-Bromo-2-(2,4-difluorophenyl)pyridine was synthesized *via* a Suzuki coupling reaction of 2,5-dibromopyridine and



Scheme 1 Synthetic route to monomers.

2,4-difluorophenylboronic acid in high yield. The iridium complexes were synthesized as chloride-bridged iridium dimers with picolinate (Hpic), 2,2,6,6-tetramethyl-3,5-heptanedione (Htmd) and 5-methyl-3-(pyridin-2-yl)-4*H*-1,2,4-triazole (Hptz) ligands. The copolymers with different complexes were prepared from 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole, 3,6-dibromo-9-ethylhexylcarbazole and the complexes by Suzuki polycondensation (SPC; Scheme 2). The feed ratios of complexes in the polycondensation were 1 mol%, 3 mol% and 5 mol%, and the corresponding copolymers were named PCz-FIrpic1, PCz-FIrpic3, PCz-FIrpic5, PCz-FIrtmd3, PCz-FIrtmd5 and PCz-FIrptz3, respectively. In order to investigate the effect of the host segment on the luminous performances of the copolymers, the copolymer



Scheme 2 Synthetic route to copolymers.

Table 1 Molecular weights and compositions of the polymers

Polymer	M_n ($\times 10^3$)	PDI	Complex content (mol%)	
			in feed ratio	in copolymer[a]
PCz-FIrpic1	8.17	1.60	1	0.4
PCz-FIrpic3	8.01	1.52	3	1.3
PCz-FIrpic5	5.06	2.19	5	2.6
PCz-FIrptz3	6.01	1.31	3	2.7
PCz-FIrtmd3	4.53	1.81	3	1.6
PCz-FIrtmd5	6.07	1.44	5	3.2
PFCz-FIrtmd5	11.20	1.67	5	3.5

[a] Calculated from the contents of carbon, hydrogen, nitrogen and iridium complex in copolymers.

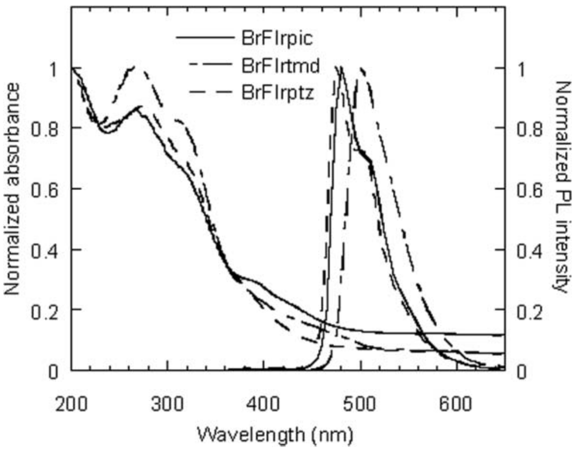


Fig. 1 UV-visible absorption and PL spectra of the complexes in CH_2Cl_2 solution (0.01 M).

PFCz-FIrtmd5 with a fluorene-*alt*-carbazole unit as a host was prepared to make a comparison. The iridium contents in the copolymers were estimated by X-ray fluorescence spectrometry (XRF), and the molar ratios of Ir complexes incorporated into the copolymers were calculated by combining XRF data with the elemental analyses of carbon, hydrogen and nitrogen (Table 1). The results indicate that the actual Ir complex contents in the copolymers are substantially lower than the feed ratios of complex monomers, and increase with the increasing feed ratios. Meanwhile, the Ir complex contents in these copolymers are also different even at the same feed ratios of complex monomers. The FIrptz complex content is 2.7 mol% in the PCz-FIrptz3 polymer, while the FIrtmd complex content is 1.6 mol% in the PCz-FIrtmd3 polymer at the same feed ratio of 3 mol%, which implies that BrFIrptz complex monomer has a higher reaction activity compared with BrFIrtmd.

The number-average molecule weights (M_n) of carbazole-based copolymers are less than 10 000 with the polydispersity index (PDI) from 1.31 to 2.19 (Table 1). These results are comparable with those of the other copolymers synthesized by Suzuki polycondensation between diborate and two different kinds of dibrominated monomers.[12,13]

Photophysical properties

UV-vis absorption and PL spectra of the Ir complexes BrFIrpic, BrFIrtmd and BrFIrptz in dichloromethane solution are shown in Fig. 1. The intense absorption peaks below 300 nm are attributed to the spin-allowed singlet state $^1(\pi–\pi^*)$ transition of cyclometalated ligands and the weak absorption peaks around 320 nm can be assigned to the spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT) transition.[23] The absorption peaks around 390–400 nm are due to the triplet metal-to-ligand charge-transfer (^{3}MLCT) transition for the three complexes. In the PL spectra, the maximum wavelengths of BrFIrpic, BrFIrptz and BrFIrtmd are at 480 nm, 475 nm and 500 nm respectively. The UV-vis absorption and PL spectra are almost red-shifted by 10 nm compared with the pristine complexes without bromo-substitution in the ligands.[14–16]

Fig. 2a shows the UV-vis absorption spectra of the copolymers PCz-FIrpic. The absorption spectrum of PCz-FIrpic1 is almost as the same as that of PCz, with two peaks at 260 nm and 310 nm,[23] owing to the low content of the complex. Compared with PCz-FIrpic1, the spectra of PCz-FIrpic3 and PCz-FIrpic5 are red-shifted by 20 nm, and the new absorption peak at 420 nm is due to the triplet metal-to-ligand charge-transfer (^{3}MLCT) transition of the complex unit. In Fig. 2b, the spectra of PCz-FIrtmd3 and PCz-FIrtmd5 are similar and the spectrum of PFCz-FIrtmd5 is red-shifted owing to the longer conjugated length of the backbone. In Fig. 2c, there is an obvious absorption peak at 420 nm due to

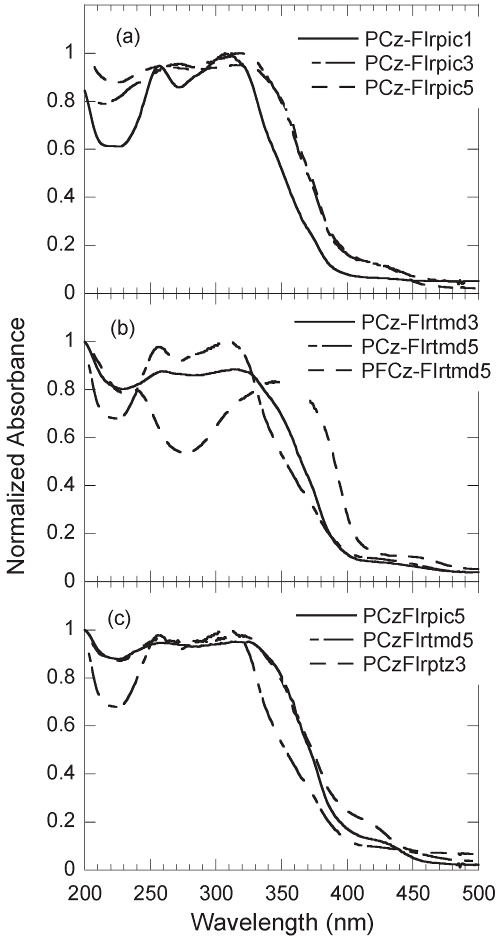


Fig. 2 UV-visible absorption spectra of the copolymers in film form.

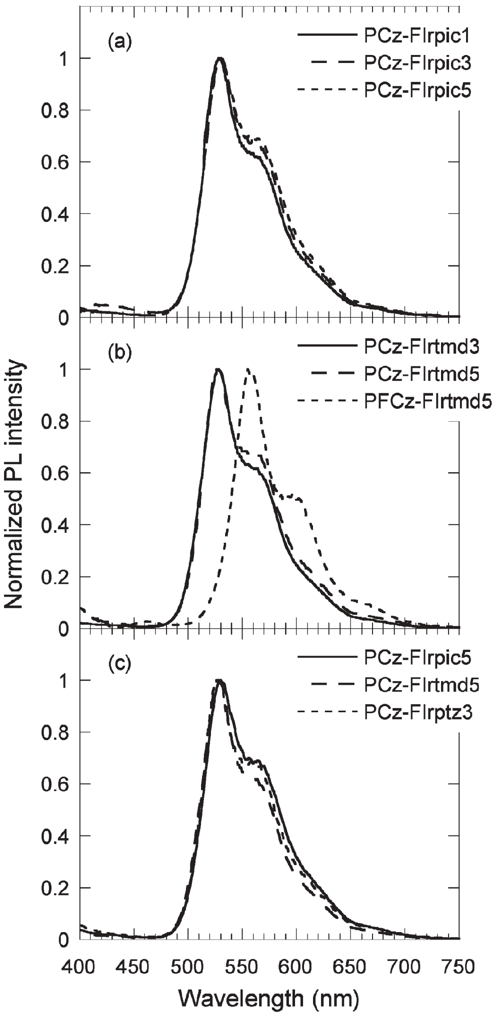


Fig. 3 PL spectra of the copolymers in film form.

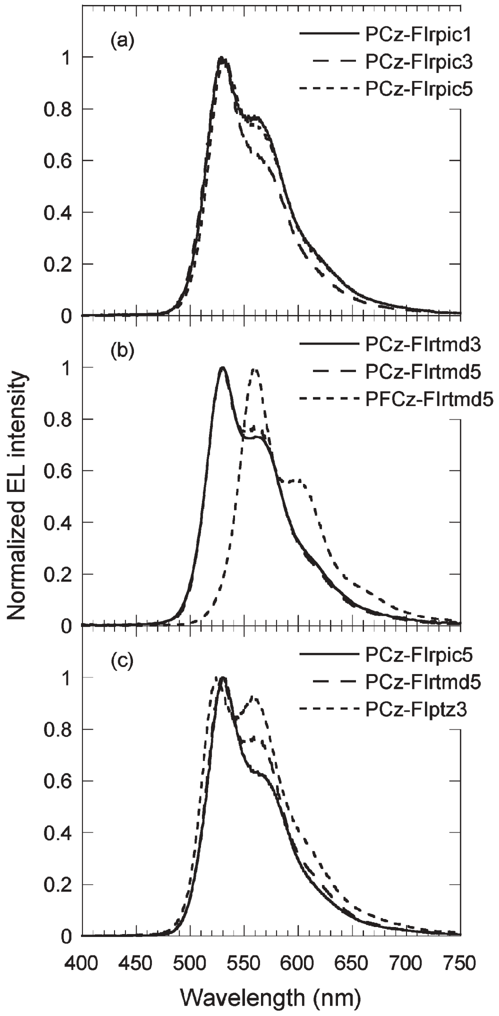


Fig. 4 EL spectra of the copolymers.

the ^{3}MLCT transition of the complex unit in PCz-FIrptz3. All absorptions of the complexes units in copolymers are red-shifted, which indicates that the complexes have been introduced into the conjugated polymer backbone. PL spectra of the copolymers are shown in Fig. 3. The energy transfer from the host segment to the Ir complex is efficient for Ir complex content as low as 1 mol% (Fig. 3a). The PL spectrum of PFCz-FIrtmd5 is red-shifted by 30 nm (Fig. 3b), because the extended ligand of the Ir complex unit in the PFCz-based copolymer has a longer conjugation length.[12,13] The optical properties of the polymers are listed in Table 2. The PL efficiency of PCz-FIrtmd5 is as high as 62%, whereas that of PFCz-FIrtmd5 is as low as 9%, which indicates that 3,6-carbazole is suitable for a host unit as a greenish blue Ir complex guest.

Table 2 Optical properties of the polymers

		Photoluminescence	
Polymer	$\lambda_{\mathrm{abs\ max}}$/nm	λ_{PL}/nm	Q_{PL} (%)
PCz-FIrpic1	260, 310	532, 574	26
PCz-FIrpic3	270, 320, 420	532, 574	20
PCz-FIrpic5	270, 320, 420	532, 574	25
PCz-FIrptz3	260, 330, 420	531, 569	27
PCz-FIrtmd3	260, 310, 430	531, 567	34
PCz-FIrtmd5	260, 310, 430	531, 568	62
PFCz-FIrtmd5	350, 450	560, 601	9

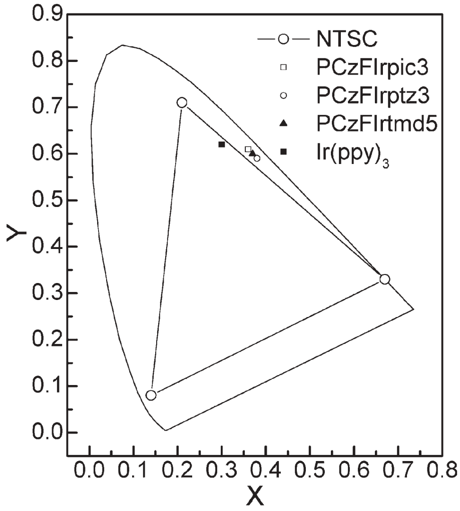


Fig. 5 CIE chromaticity diagram of the devices fabricated from the copolymers.

Table 3 Device performances of the polymers

Polymer	Maximum efficiency Bias/V	J/mA cm^{-2}	L/cd m^{-2}	QE$_{ext}$ (%)	LE/cd A^{-1}	CIE^b coordinates (x, y)
PCz-FIrpic1	9.8	13.5	106	0.40	0.79	0.37, 0.60
PCz-FIrpic3	9.0	11.0	69	0.32	0.63	0.36, 0.61
PCz-FIrpic5	7.8	38.5	552	0.71	1.43	0.36, 0.61
PCz-FIrptz3	8.8	10.5	119	0.58	1.14	0.38, 0.59
PCz-FIrtmd3	6.5	36.9	575	0.97	1.56	0.37, 0.60
PCz-FIrtmd5	7.8	10.3	453	2.22	4.40	0.37, 0.60
PFCz-FIrtmd5	7.5	33.1	237	0.63	0.72	0.48, 0.52

[a] Device structure: ITO/PEDOT/polymer + PBD(30 wt%)/Ba/Al. [b] Obtained at the current density of 12 mA cm^{-2}.

Electrophosphorescent properties

The single-layer devices were fabricated in the configuration: ITO/PEDOT/polymer + PBD(30 wt%)/Ba/Al. EL spectra of the copolymers PCz-FIrpic are shown in Fig. 4a, which shows that the spectra of the copolymers are identical and the energy transfer from the host segments to the Ir complex is efficient. The EL spectra of copolymers PCz-FIrtmd5 and PFCz-FIrtmd5 are shown in Fig. 4b; as in the PL emission, the EL spectrum of PFCz-FIrtmd5 is also red-shifted by 30 nm. Typical CIE coordinates of the devices based on PCz-FIrpic3 (0.36, 0.61), PCz-FIrptz3 (0.38, 0.59) and PCz-FIrtmd5 (0.37,0.60), along with Ir(ppy)$_3$ (0.29, 0.61) at a current density of 12 mA cm^{-2}, are presented in Fig. 5. Compared with Ir(ppy)$_3$ (yellowish green), the EL emissions of the copolymers are in the region of yellowish green or green yellow. The device performances of the copolymers are shown in Table 3; the best performance was observed for the device based on PCz-FIrtmd5, and a maximal luminous efficiency of 4.4 cd A^{-1} with a luminance of 453 mA cm^{-2} was achieved at a current density of 10.3 mA cm^{-2}. Compared with PCz-FIrtmd5, the device performances based on the PFCz-FIrtmd5 copolymer are much poorer. For the three Ir complexes with different ancillary ligands, the copolymers with the FIrtmd complex have better luminous performances, which indicates that the ancillary ligand also has a great effect on the device performance of chelating electrophosphorescent polymers.

In order to investigate the characteristics of this kind of chelating polymer, three device structures were used for comparison: ITO/PEDOT/polymer/Ba/Al (1), ITO/PEDOT/poly(N-vinylketone) (PVK)/polymer/Ba/Al (2) and ITO/PEDOT/polymer + 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (30 wt%)/Ba/Al (3). The external quantum efficiency and light intensity *versus* current density of the devices based on PCz-FIrtmd5 are shown, as an example, in Fig. 6. It is found that device 3 has a higher efficiency and light intensity than the others. The device performances are poor with PVK as a inserting layer, but the blended copolymers are better with PBD as an emission layer, which indicates that the poor electron-transporting capability of the copolymers is not equivalent to the good hole-transporting capability from PCz and PBD needs to be used for balance.[24]

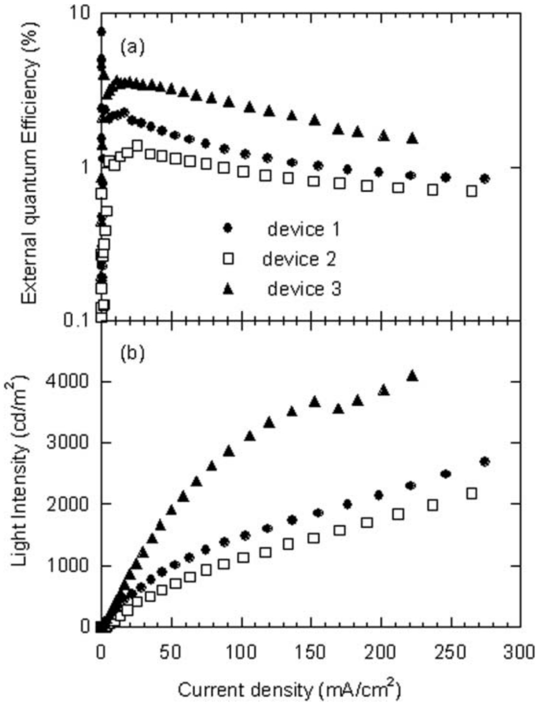


Fig. 6 Current density *vs.* efficiency (a) and luminance (b) characteristics of the PCz-FIrtmd5 based devices: ITO/PEDOT/polymer/Ba/Al (1), ITO/PEDOT/PVK/polymer/Ba/Al (2) and ITO/PEDOT/polymer + PBD(30 wt%)/Ba/Al (3).

Conclusion

Phosphorescent polymers can be synthesized by Suzuki polycondensation of A-A and B-B type monomers with 3,6-carbazole as a host unit and greenish blue light-emitting iridium complexes as guests. The ancillary ligand of the iridium complex has a great effect on the device performance. The best device performances were achieved from PCz-FIrtmd5 with the maximal luminous efficiency of 4.4 cd A^{-1} and a luminance of 453 mA cm^{-2} at a current density of 10.3 mA cm^{-2}.

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