Iridium Complex Grafted to 3,6-Carbazole-*alt*-tetraphenylsilane Copolymers for Blue Electrophosphorescence

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Received 9 December 2009; accepted 14 January 2010
DOI: 10.1002/pola.23934

ABSTRACT: We designed a 3,6-dibromo-9-hexyl-9*H*-carbazole derivative with the blue emissive iridium complex bis[2-(4,6-difluorophenyl)pyridyl-N,$C^{2'}$](picolinato)iridium(III) (FIrpic) linked at the alkyl terminal. Based on this monomer, novel 3,6-carbazole-*alt*-tetraphenylsilane copolymers grafted with FIrpic were synthesized by palladium-catalyzed Suzuki coupling reaction, and the content of FIrpic in the polymers could be controlled by feed ratio of the monomers. The polymer films mainly show blue emission from FIrpic, and the emission intensity from the polymer backbones is much weaker compared with the doped analogues, which demonstrates an efficient energy transfer from polymeric host to covalently bonded guest. The phase separation in the polymers was suppressed, which can be identified by atomic force microscopy and designed electroluminescent (EL) devices. EL devices based on the polymers exhibited blue phosphorescence from FIrpic. The luminous efficiency of preliminary devices reached 2.3 cd/A, and the efficiency roll-off at high current densities was suppressed. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1859–1865, 2010

KEYWORDS: host-guest systems; metal-polymer complexes; phase separation; synthesis

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INTRODUCTION Phosphorescent transition metal complexes, such as Re(I),[1] Ru(II),[2,3] Os(II),[4,5] Pt(II),[6] and Ir(III)[7–10] complexes, are regarded as the promising materials for highly efficient organic light-emitting diodes (OLEDs), because they can capture both singlet and triplet excitons and exhibit higher internal quantum efficiency up to 100% in principle.[4,6] Among these complexes, iridium complexes have attracted considerable attention due to their high phosphorescent efficiencies in OLEDs.

In a phosphorescent OLED (PHOLED), a suitable host material in which phosphorescent emitters are dispersed is necessary to prevent triplet–triplet annihilation, especially under high current densities.[11] OLEDs based on polymers (PLEDs) have their advantages of allowing low cost and efficient wet processing technologies,[12] such as spin coating and inkjet printing, which are more suitable for preparing large area displays. Many efforts on doping iridium complexes into polymer hosts were made in the past few years and highly efficient green and red PHOLEDs have been realized.[10,13–17] But host materials for blue iridium complexes are still a serious shortage, as the triplet energy of most conjugated polymers is lower than blue iridium complexes, which would result in backward energy transfer and quenching the emission of the phosphors.[18] It is a challenge to find wide band gap hosts for blue iridium complexes.

Recently we developed a 3,6-carbazole-*alt*-tetraphenylsilane based copolymer,[19] P36HCTPSi, which is a proper host for green and blue iridium complexes. As we know, the physical blends of the polymer host and complex guest run the risk of aggregation of the phosphors, phase separation and inefficient energy transfer. We hope these shortcomings could be overcome by combining the host and guest in one composite material. The attachment of functional pendants to polymer backbones has been discussed in detail in recent review articles.[20,21] In this article, we report novel 3,6-carbazole-*alt*-tetraphenylsilane copolymers grafted with blue emissive iridium complex bis[2-(4,6-difluorophenyl)pyridyl-N,$C^{2'}$](picolinato)iridium(III) (FIrpic). The content of the complex in the polymers could be controlled by feed ratio of monomers. The photophysical and electroluminescent (EL) properties of the polymers were investigated. The phase separation in polymers was restrained, and the efficiency roll-off at high current densities was suppressed in EL devices.

EXPERIMENTAL

Synthesis

Tetrahydrofuran (THF) and diethyl ether were dried and purified by fractional distillation over sodium in the presence of benzophenone. All starting materials were purchased from Aldrich and Acros and used directly.

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 1859–1865 (2010) © 2010 Wiley Periodicals, Inc.

*9-Hexyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (M1)*

To a solution of 3,6-dibromo-9-hexyl-9*H*-carbazole (2.51 g, 6.14 mmol) in anhydrous THF (65 mL) at −78 °C was added *n*-BuLi (9.8 mL, 24.50 mmol) dropwise. The reaction mixture was stirred for 2 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxabrorolane (10 mL, 48.03 mmol) was then added quickly to the solution. The reaction mixture was warmed to room temperature and stirred for 24 h. Some water was poured into the solution and then the organic layer was extracted with diethyl ether several times. The organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography eluting with ethyl acetate–cyclohexane mixture to give a white solid in 64% yield (1.99 g). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.66 (s, 2H, Ar-H), 7.91 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.39 (d, *J* = 7.9 Hz, 2H, Ar-H), 4.32 (t, *J* = 6.7 Hz, 2H, CH_2), 1.86–1.83 (m, 2H, CH_2), 1.39 (s, 24H, CH_3), 1.35–1.32 (m, 2H, CH_2), 1.30–1.24 (m, 4H, CH_2), 0.86 (t, *J* = 7.0 Hz, 3H, CH_3). MS: *m/z* calcd 503.3; found 504.4. Elemental Anal. Calcd. for $C_{30}H_{43}B_2NO_4$: C, 71.59%; H, 8.61%; N, 2.78%. Found: C, 71.76%; H, 8.40%; N, 2.70%.

Bis(4-bromophenyl)diphenylsilane (M2)

1,4-Dibromobenzene (4.72 g, 20 mmol) was dissolved in dry diethyl ether and cooled to −78 °C. To the solution was added *n*-BuLi (2.5 M, 8.4 mL, 1.05 equiv) dropwise. After stirred for 2 h, dichlorodiphenylsilane (2.1 mL, 10 mmol) was added dropwise in one portion. Then the reaction mixture was warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was poured into water and extracted with diethyl ether, then the combined organic solution was washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by recrystallization in ethanol as a white solid in 70% yield (3.46 g). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.46–7.44 (m, 8H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.33–7.30 (m, 8H, Ar-H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 140.38, 138.77, 135.56, 135.21, 133.78, 132.56, 130.66, 127.53. Elemental Anal. Calcd. for $C_{24}H_{18}Br_2Si$: C, 58.32%; H, 3.67%. Found: C, 58.66%; H, 3.66%.

FIrpicOH (1)

The cyclometalated chloride-bridged dimer $[(dfppy)_2Ir(\mu\text{-}Cl)]_2$ (101.1 mg, 0.081 mmol), 3-hydroxypyridine-2-carboxylic acid (34.8 mg, 0.25 mmol) and sodium carbonate (79.7 mg, 0.75 mmol) were refluxed at 120 °C in a nitrogen atmosphere in 2-ethoxyethanol (7.5 mL) for 40 h. After cooling to room temperature, a precipitate was filtered off and washed with water and ether. The crude product was applied to column chromatography on silica gel, eluting with acetone–dichloromethane mixture to provide the desired product in a bright yellow solid in 65% yield (77.2 mg). ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.57 (s, 1H, OH), 8.51 (d, *J* = 4.9 Hz, 1H, Ar-H), 8.30 (d, *J* = 8.2 Hz, 1H, Ar-H), 8.26 (d, *J* = 8.5 Hz, 1H, Ar-H), 8.09 (t, *J* = 7.3 Hz, 1H, Ar-H), 8.05 (t, *J* = 7.0 Hz, 1H, Ar-H), 7.69 (d, *J* = 5.2 Hz, 1H, Ar-H), 7.64 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.54–7.50 (m, 2H, Ar-H), 7.36 (t, *J* = 6.1 Hz, 1H, Ar-H), 7.26 (d, *J* = 4.0 Hz, 1H, Ar-H), 6.89–6.79 (m, 2H, Ar-H), 5.68 (dd, *J* = 8.5, 2.4 Hz, 1H, Ar-H), 5.50 (dd, *J* = 8.5, 2.4 Hz, 1H, Ar-H). MS: *m/z* calcd 710.7; found 711.7. Anal. Calcd for $C_{28}H_{16}F_4IrN_3O_3$: C, 47.32; H, 2.27; N, 5.91. Found: C, 47.34; H, 2.04; N, 5.84.

*3,6-Dibromo-9-(6-bromohexyl)-9*H*-carbazole (2)*

9-(6-Bromohexyl)-9*H*-carbazole (1.04 g, 3.16 mmol) was dissolved in THF (20 mL), to the solution was added *n*-bromosuccinimide (1.14 g, 6.32 mmol), then the reaction vessel was shielded from light by an aluminum foil and stirred for 24 h at 65 °C. The solution was poured into brine and extracted with dichloromethane then dried over anhydrous magnesium sulfate. The solution was concentrated and purified by recrystallization in dichloromethane and methanol as a white solid in 97% yield (1.49 g). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.15 (d, *J* = 1.8 Hz, 2H, Ar-H), 7.57 (dd, *J* = 8.7, 1.8 Hz, 2H, Ar-H), 7.29 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.29 (t, *J* = 6.9 Hz, 2H, CH_2), 3.38 (t, *J* = 6.9 Hz, 2H, CH_2), 1.89–1.75 (m, 4H, CH_2), 1.53–1.44 (m, 2H, CH_2), 1.44–1.31 (m, 2H, CH_2). Anal. Calcd for $C_{18}H_{18}Br_3N$: C, 44.30; H, 3.72; N, 2.87. Found: C, 44.54; H, 3.62; N, 2.75.

Monomer M3

Compounds **1** (76.0 mg, 0.11 mmol), **2** (52.6 mg, 0.11 mmol), potassium carbonate (K_2CO_3) (16.2 mg, 0.12 mmol) and 18-crown-6 (1.6 mg, 0.0061 mmol) were dispersed in 10 mL acetone. The reaction mixture was degassed and then stirred at 55 °C for 48 h. After cooling to room temperature, the solution was concentrated and the obtained concentration was purified by column chromatography eluting with acetone–dichloromethane mixture to give a bright yellow solid in 75% yield (90.2 mg). ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 8.58 (d, *J* = 5.5 Hz, 1H, Ar-H), 8.47 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.28 (d, *J* = 8.5 Hz, 1H, Ar-H), 8.23 (d, *J* = 8.5 Hz, 1H, Ar-H), 8.05 (t, *J* = 8.0 Hz, 1H, Ar-H), 8.00 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.76 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.66 (d, *J* = 5.5 Hz, 1H, Ar-H), 7.63 (d, *J* = 8.8 Hz, 3H, Ar-H), 7.54–7.51 (m, 3H, Ar-H), 7.47 (t, *J* = 7.0 Hz, 1H, Ar-H), 7.34 (t, *J* = 7.0 Hz, 1H, Ar-H), 7.28 (d, *J* = 5.2 Hz, 1H, Ar-H), 6.85–6.76 (m, 2H, Ar-H), 5.67 (dd, *J* = 8.5, 4.0 Hz, 1H, Ar-H), 5.45 (dd, *J* = 8.5, 3.7 Hz, 1H, Ar-H), 4.41 (t, *J* = 11.6 Hz, 2H, CH_2), 4.05 (t, *J* = 5.2 Hz, 2H, CH_2), 1.78–1.72 (m, 2H, CH_2), 1.70–1.65 (m, 2H, CH_2), 1.53–1.47 (m, 2H, CH_2), 1.35–1.29 (m, 2H, CH_2). MS: *m/z* calcd 1117.8; found 1118.0. Anal. Calcd for $C_{46}H_{33}Br_2F_4IrN_4O_3$: C, 49.43; H, 2.98; N, 5.01. Found: C, 50.30; H, 3.16; N, 4.86.

P36HCTPSi

Compounds **M1** (109.4 mg, 0.22 mmol), **M2** (107.5 mg, 0.22 mmol) and $Pd(dppf)Cl_2$ (5.0 mg, 0.0061 mmol) were dissolved in THF (4 mL) and 1 M K_2CO_3 aqueous solution (1 mL). The reaction mixture was degassed and then stirred at 75 °C for 3 days. At the end of the polymerization, phenylboronic acid (5 mol %), and bromobenzene (5 mol %) were added sequentially for end-capping. The mixture was poured into water and extracted with dichloromethane then dried over anhydrous magnesium sulfate. The solution was concentrated and purified by flash column chromatography to remove the catalyst. After removal of the organic solvent, the condensed crude product was dropped into about 60 mL methanol to precipitate plenty of solid. The solid was collected by filtration and then dried under vacuum at 40 °C to afford the desired polymer as a light gray solid in 64% yield (81.0 mg). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.38 (s, 2H, Ar-H), 7.75–7.67 (m, 14H, Ar-H), 7.48–7.35 (m, 8H, Ar-H), 4.37–4.21 (m, 2H, CH_2), 1.88–1.87 (m, 2H, CH_2), 1.39–1.29 (m, 6H, CH_2), 0.85–0.84 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.10, 140.55, 136.97, 136.48, 134.56, 132.11, 131.90, 129.58, 127.91, 126.70, 125.38, 123.53, 119.01, 109.14, 43.36, 31.58, 29.03, 26.99, 22.55, 14.02. M_n 13,053, M_w 15,850, M_w/M_n 1.21 (GPC, PS calibration).

PCzSiIr2.5

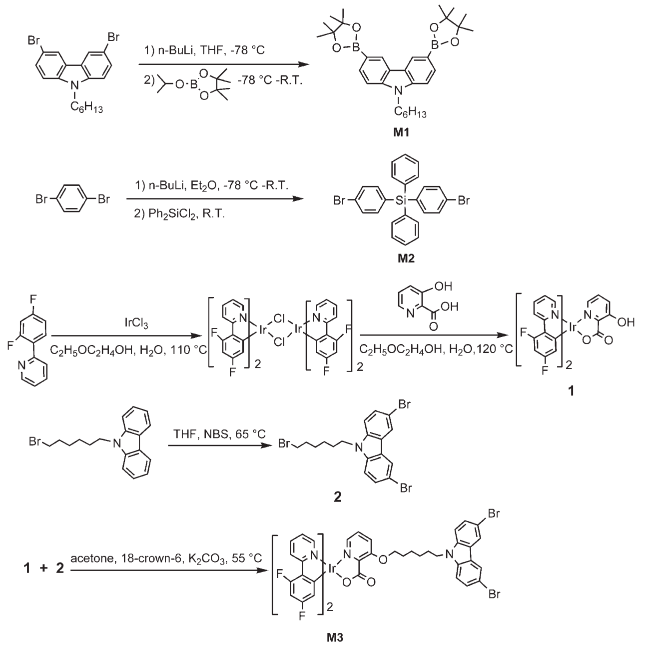
Compounds **M1** (98.8 mg, 0.20 mmol), **M2** (92.8 mg, 0.19 mmol), **M3** (10.8 mg, 0.01 mmol), and Pd(dppf)Cl_2 (5.8 mg, 0.0071 mmol) were dissolved in THF (4 mL) and 1 M K_2CO_3 aqueous solution (1 mL). The reaction mixture was degassed and then stirred at 75 °C for 3 days. The same purification procedure for P36HCTPSi was applied to give a light yellow solid in 59% yield (69.4 mg). The FIrpic content of the polymer was analyzed by NMR spectra. M_n 12,489, M_w 15,369, M_w/M_n 1.23 (GPC, PS calibration).

PCzSiIr5

Compounds **M1** (121.3 mg, 0.24 mmol), **M2** (107.2 mg, 0.22 mmol), **M3** (27.1 mg, 0.024 mmol), and Pd(dppf)Cl_2 (5.9 mg, 0.0072 mmol) were dissolved in THF (4 mL) and 1 M K_2CO_3 aqueous solution (1 mL). The reaction mixture was degassed and then stirred at 75 °C for 3 days. The same purification procedure for P36HCTPSi was applied to give a grayish green solid in 64% yield (100.2 mg). The FIrpic content of the polymer was analyzed by NMR spectra. M_n 9574, M_w 13,311, M_w/M_n 1.39 (GPC, PS calibration).

Characterization of Materials and Devices

^{1}H and ^{13}C NMR spectra were measured on AVANCZ 500 spectrometers at 298 K using $CDCl_3$ or dimethylsulfoxide-d6 (DMSO-d6) as solvent and tetramethylsilane (TMS) as standard in all cases. Elemental analysis was performed by Flash EA 1112, CHNS-O elemental analysis instrument. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a HPLC Waters 510 pump using a series of low-polydispersity polystyrene standards in THF (HPLC grade, Aldrich) at 308 K. Differential scanning calorimetry (DSC) was performed on a NETZSCH (DSC-204) unit at a heating rate of 10 °C/min under nitrogen. UV-visible absorption spectra were recorded on a UV-3100 spectrophotometer. PL spectra were carried out with a RF-5301PC fluorometer. Surface morphology was investigated using tapping-mode atomic force microscopy (AFM) (SPI3800N). AFM measurements were performed in air at room temperature. EL spectra and Commission Internationale De L'Eclairage (CIE) coordination of the devices were measured by a PR650 spectrometer. The current density–voltage–luminance characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.



SCHEME 1 The synthetic routes to three monomers **M1**, **M2**, and **M3**.

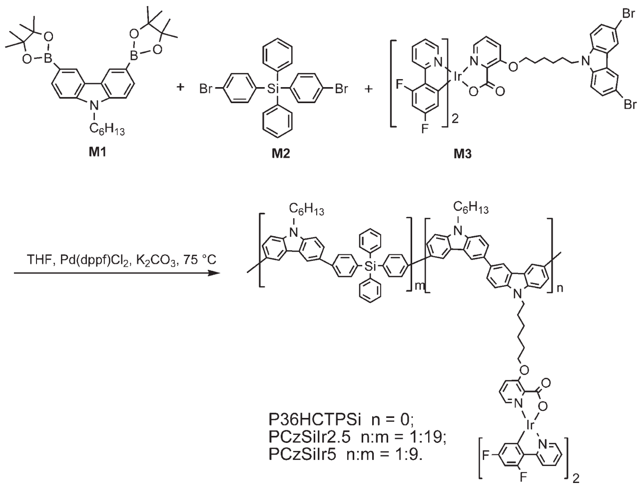
Fabrication of PLEDs

Devices consisting of ITO/PEDOT: PSS/LEL/TPBI/LiF/Al (ITO = iridium tin oxide, PEDOT: PSS = poly(3,4-ethylenedioxythiophene): poly(styrene sulfonic acid), LEL denotes light-emitting layer, TPBI = 2,2′,2″-(1,3,5-phenylene) tris(1-phenyl-1*H*-benzimidazole)) were fabricated as follows: PEDOT:PSS was spin coated onto the cleaned ITO-coated glass substrate from its aqueous solution and then heated at 120 °C for 20 min to remove the residual water solvent. The undoped polymer (PCzSiIr2.5 or PCzSiIr5) or doped polymer (tris(1-phenylisoquinoline) iridium(III) (Ir(piq)$_3$) doped PCzSiIr5) was used as LEL, which was prepared by spin coating its chlorobenzene solution with a concentration of 5 mg/mL atop PEDOT: PSS layer. After spin coating, the devices were transferred into a vacuum chamber immediately without exposure to the atmosphere (one doped device was annealed at 110 °C for 30 min in nitrogen atmosphere at first). Inside the chamber, 40-nm-thick TPBI, 0.5-nm-thick LiF, and 200-nm-thick Al were in sequence deposited by thermal evaporation at a pressure of 4.0 × 10^{-6} mbar. All processes after the preparation of PEDOT:PSS layer were performed in a nitrogen-filled glove box.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes to the monomers are shown in Scheme 1. 3,6-Dibromo-9-hexyl-9*H*-carbazole,[22] 9-(6-bromohexyl)-9*H*-carbazole,[23] and the cyclometalated chloride–bridged dimer [(dfppy)$_2$Ir(μ-Cl)]$_2$[24] were prepared according to the reported procedures. 3,6-Dibromo-9-hexyl-9*H*-carbazole was



SCHEME 2 The synthetic routes to three polymers P36HCTPSi, PCzSiIr2.5, and PCzSiIr5.

treated with *n*-BuLi at −78 °C in dry THF solution and the resulting lithiated species was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxabrorolane at room temperature to afford monomer **M1**. 1,4-Dibromobenzene was treated with *n*-BuLi at −78 °C in dry diethyl ether and the resulting lithiated species was quenched with dichlorodiphenylsilane and as such gave the monomer **M2**. The cyclometalated chloride–bridged dimer $[(\mathrm{dfppy})_2\mathrm{Ir}(\mu\text{-Cl})]_2$ was treated with 3-hydroxypyridine-2-carboxylic acid in 2-ethoxyethanol in the presence of sodium carbonate to yield compound **1**. The bromination of 9-(6-bromohexyl)-9*H*-carbazole with NBS supplied compound **2**. Subsequent reaction of compound **1** with compound **2** in acetone in the presence of K_2CO_3 and 18-crown-6 afforded the monomer **M3**. This 3,6-dibromo-9-hexyl-9*H*-carbazole derivative with FIrpic linked at the alkyl terminal can be used for building polymers by palladium-catalyzed Suzuki coupling reaction. The monomers were well characterized before polymerization.

As shown in Scheme 2, three polymers were synthesized by Suzuki coupling reaction. The copolymerization was undertaken using $Pd(dppf)Cl_2$ as the catalyst in a mixture of THF and 1 M K_2CO_3 aqueous solution. The complex content in polymers could be controlled by feed ratio of the monomers. Polymers P36HCTPSi, PCzSiIr2.5, and PCzSiIr5 with different feed ratios (**M1, M2,** and **M3** in a molar ratio of 1:1:0, 20:19:1, and 10:9:1 for P36HCTPSi, PCzSiIr2.5, and PCzSiIr5, respectively) were successfully synthesized.

The content of complex part in the polymers could be calculated from the ^{1}H NMR spectra. Figure 1 shows the ^{1}H NMR spectra of monomer **M3** and polymer PCzSiIr5, and the diagnostic protons are marked in the insets. For **M3**, the protons marked by A_1, B_1, B_2, and C_1 are much clearer than others and the integrals can be obtained accurately, which is beneficial for determining the complex content in the polymers. The integral ratio of A_1:B_1:B_2:C_1 of **M3** is 2:1:1:2, and the integral ratio of B_1:B_2:C_1 in PCzSiIr5 is quite good consistent with that of **M3**. Combining earlier result with the chemical structure of PCzSiIr5, the molar ratio of monomer **M1:M3** in PCzSiIr5 can be calculated from the integrals of $A_1+A_2+A_3$ and C_1 with a value of 10.3:1, which is very close to the feed ratio of 10:1. So it is considered that the copolymers contain similar complex content with the feed ratios.

The resulting copolymers are readily soluble in common organic solvents, such as chloroform, toluene, and THF but not soluble in ethanol and acetone. The number-average molecular weights were determined to be 13,053, 12,489, and 9574 for P36HCTPSi, PCzSiIr2.5, and PCzSiIr5, with polydispersities of 1.21, 1.23, and 1.39, respectively. The glass transition temperatures (T_g) of PCzSiIr2.5 and PCzSiIr5 determined by differential scanning calorimetry (DSC) are around 220 °C, almost identical to that of P36HCTPSi (217 °C). This result implies the introduction of iridium complex in such small amounts does not significantly alter the thermal properties of the polymers.

Film Morphology

The film surface topographies of PCzSiIr5 and P36HCTPSi doped by FIrpic at the same mole percent of PCzSiIr5 (5%) were investigated by AFM and shown in Figure 2. The PCzSiIr5 film shows a flat surface with a vertical root-mean-square roughness of 0.36 nm, while the blend film shows obvious aggregation with a size of ~85 nm and a bigger root-mean-square roughness of 0.52 nm. This comparison indicates that phase separation exists in the blend system owing to the immiscibility of P36HCTPSi and FIrpic,[25] while the polymer with FIrpic covalently bonded to the backbones is free from phase separation.

Optical Properties

The UV-visible absorption spectra of the polymers in dilute THF solutions are shown in Figure 3. The main absorption peaks of three polymers are similar, all show the absorption maximum at 305 nm and a shoulder at 262 nm, which can be assigned to the $\pi-\pi^*$ transitions of the polymer

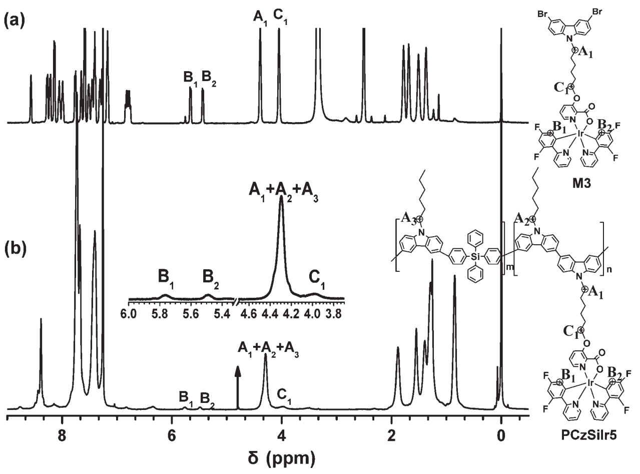


FIGURE 1 ^{1}H NMR spectra of (a) monomer **M3** (in DMSO) and (b) polymer PCzSiIr5 (in $CDCl_3$). Inset: Chemical structures of **M3** and PCzSiIr5 and amplified NMR spectrum of PCzSiIr5 with the chemical shift from 3.8 to 6.0 ppm.

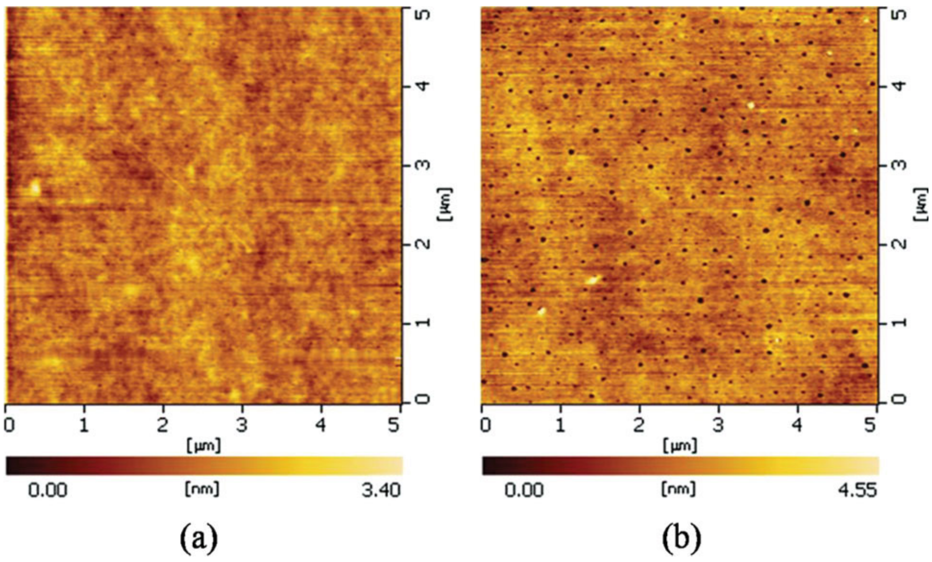


FIGURE 2 Tapping-mode AFM topographic images of (a) PCzSiIr5 film and (b) P36HCTPSi film doped by 5 mol % FIrpic on quartz glass.

backbones. It is noteworthy that the absorption intensities of the polymers between 250 and 280 nm increase with the complex content, which is consistent with that the strong absorption of π–π* transition of 2-(2,4-difluorophenyl)pyridine ligands in FIrpic is also located between 250 and 280 nm.[26] Furthermore, the absorbance between 370 and 450 nm, which is the characteristic MLCT absorption band of FIrpic, also increases with the content of FIrpic (inset of Fig. 3), and the intensities are relatively low because of the small amount of FIrpic in polymers and the low molar extinction coefficients of the MLCT absorptions.

Figure 4 shows the normalized PL spectra of the neat and doped films of the polymers. As it can be seen, the emission intensity from polymer main chains decreases as the FIrpic content increases in both neat and doped films, and the typical blue emissions from FIrpic (with the maximum peak at 472 nm) are much stronger than those of polymer backbones as the molar concentration of FIrpic up to 5%. Further, the emission ratio of FIrpic/polymer chains is much higher in neat films than that of the doped analogues, suggesting energy transfer is more efficient in polymers PCzSiIr2.5 and PCzSiIr5. The strong emission intensity from FIrpic in neat polymer films demonstrates energy transfer from polymer backbones to FIrpic is facilitated through both inter- and intra-chain channels in solid state. These are the first aromatic-chain polymers with covalently bonded blue iridium complex in the side chains, which show effective energy transfer from the polymer backbones to FIrpic in solid state.

Electroluminescent Properties

To investigate the EL properties of polymers PCzSiIr2.5 and PCzSiIr5, two PLEDs with configurations of ITO/PEDOT:PSS/PCzSiIr2.5/TPBI/LiF/Al and ITO/PEDOT:PSS/PCzSiIr5/TPBI/LiF/Al were fabricated. It is expected that phase separation could be avoided in such devices. The normalized EL spectra of two phosphorescent PLEDs are shown in Figure 5. As we can see, the main emission attributes to FIrpic, while the emission of polymer backbones is very weak, especially for PCzSiIr5. In contrast to the PL spectra, EL spectra of both PLEDs show much weaker emission from the polymer

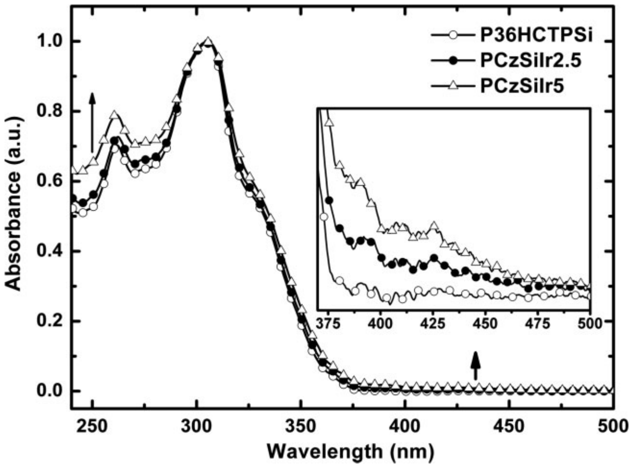


FIGURE 3 The UV-visible absorption spectra of the polymers in THF solutions. Inset: Amplified absorption spectra with the wavelength from 370 to 500 nm.

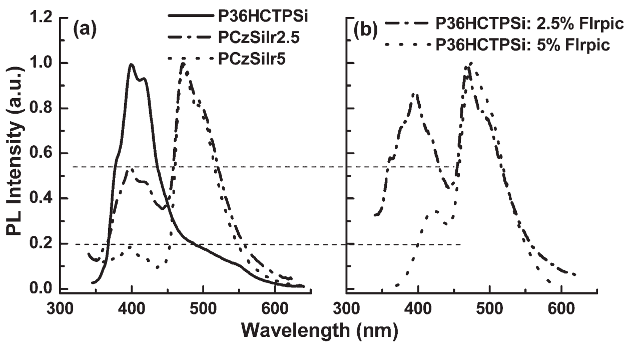


FIGURE 4 The PL spectra of (a) the polymers in films and (b) P36HCTPSi film doped by FIrpic at the mole percent of 2.5 and 5% with the excited wavelength of 330 nm.

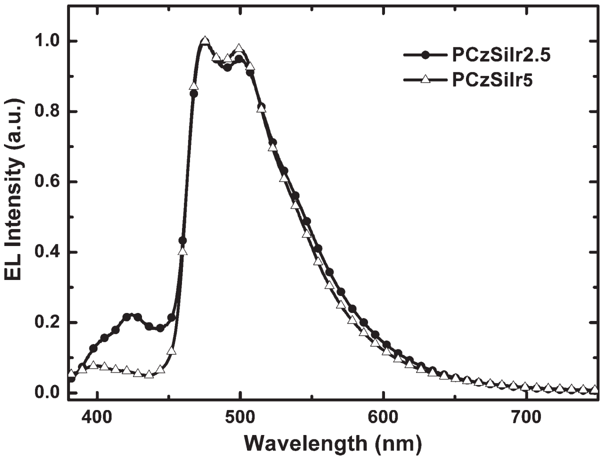


FIGURE 5 Normalized EL spectra of two devices with configurations of ITO/PEDOT:PSS/PCzSiIr2.5/TPBI/LiF/Al and ITO/PEDOT:PSS/PCzSiIr5/TPBI/LiF/ Al at the voltage of 12 V.

backbones, suggesting that not only energy transfer but also charge trapping and direct formation of excitons in FIrpic molecules are responsible for the observed EL.[27,28] According to the HOMO and LUMO levels of P36HCTPSi and FIrpic (which are −5.5 and −2.3 eV for P36HCTPSi and −5.8 and −2.9 eV for FIrpic,[19] respectively), only electrons can be trapped in FIrpic molecules, and this might be the reason for the weak emission of polymer backbones in the PLEDs.

The current density–voltage–luminance (*J*–*V*–*L*) characteristics of the PLEDs are shown in Figure 6. PCzSiIr5 shows a lower turn-on voltage for 1 cd/m^2 (7.2 V) than that of PCzSiIr2.5 (8.2 V), and the current density is a little higher. The LUMO of FIrpic is lower than that of P36HCTPSi, this facilitates the injection of electrons from TPBI into the LEL and might be the reason for the lower turn-on voltage and the higher current density of PCzSiIr5 device. PLEDs with PCzSiIr2.5 and PCzSiIr5 as LEL exhibit the maximum luminous efficiency of 0.9 and 2.3 cd/A, with the maximum luminance of 667 and 1022 cd/m^2, respectively. It is notable that the efficiency does not show remarkable decrease to 100 mA/cm^2, especially for PCzSiIr2.5 device. The suppressed efficiency roll-off at high current densities indicates polymers with covalently linked complex are beneficial for suppressing phase separation and preventing triplet-triplet annihilation.

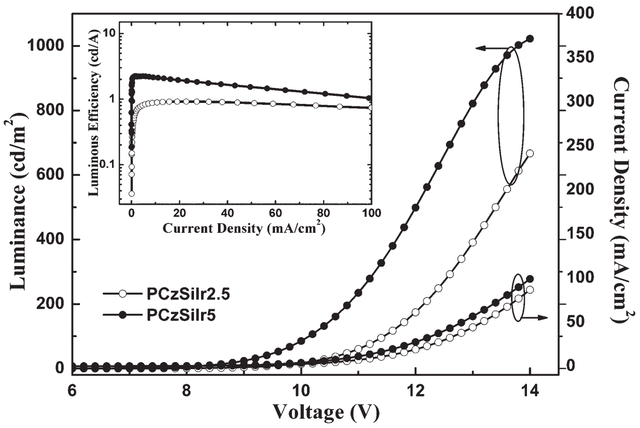


FIGURE 6 The current density–voltage–luminance (*J*–*V*–*L*) characteristics of two devices with configurations of ITO/PEDOT:PSS/PCzSiIr2.5/TPBI/LiF/Al and ITO/PEDOT:PSS/PCzSiIr5/TPBI/LiF/Al. Inset: Luminous efficiency as a function of the current density of the two devices.

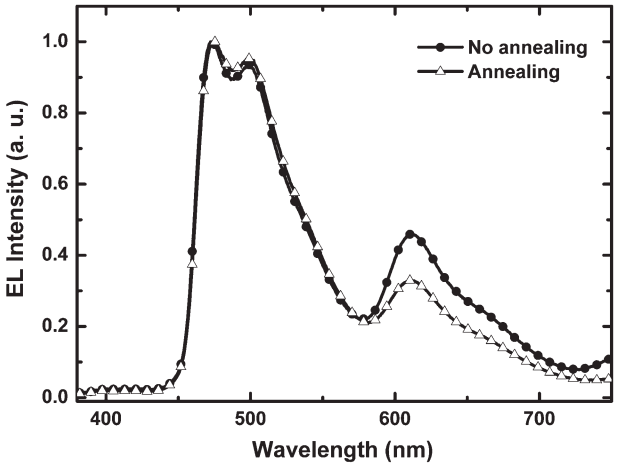


FIGURE 7 Normalized EL spectra of two devices with the same structure of ITO/PEDOT:PSS/PCzSiIr5:1 wt % Ir(piq)$_3$/TPBI/LiF/Al at the voltage of 7 V. One of the devices was annealed at 110 °C for 30 min after the Ir(piq)$_3$ doped polymer film was prepared by a spin coating method, while there was no annealing for the other device.

To further investigate the difference between the FIrpic-linked polymers and the doped systems, we designed two phosphorescent PLEDs with the same structure of ITO/PEDOT:PSS/PCzSiIr5: 1 wt % Ir(piq)$_3$/TPBI/LiF/Al. After the Ir(piq)$_3$ doped polymer film was prepared by a spin coating method, one of the devices was annealed at 110 °C for 30 min, while there was no annealing for the other device. In the PLEDs, FIrpic is used as the "internal standard" to compare with the other introduced red dye Ir(piq)$_3$. Figure 7 shows the normalized EL spectra of the two devices. It can be seen that the blue emissive parts (from FIrpic) of two devices are almost the same, while the red emission (from Ir(piq)$_3$) intensity of the device with annealing decreased greatly in comparison with the device without annealing. It is considered that there is no or not strong phase separation in film of PCzSiIr5 before and after annealing. When doping another compound (Ir(piq)$_3$) to the film, even with a low content of only 1 wt %, the film may suffer from phase separation, especially in the process of annealing, which would result in triplet–triplet annihilation because of the phosphor's aggregation. This result further demonstrates that covalent link is more proper than physical blend to restrict phase separation and achieve effective energy transfer.

CONCLUSIONS

In summary, a method to introduce the blue emissive FIrpic into the polymer side chains was developed, and 3,6-

carbazole-*alt*-tetraphenylsilane copolymers grafted with FIrpic in the side chains were synthesized. Energy transfer from the polymer backbones to iridium complex in solid state was realized. Expected suppression of phase separation compared with the doped analogues was identified by AFM and designed EL devices. PLEDs based on the polymers showed blue phosphorescence from the iridium complex with a maximum luminous efficiency of 2.3 cd/A. The efficiency roll-off at high current densities was suppressed in the devices.

We thank both the National Science Foundation of China (grant numbers: 20834006 and 60906021) and the Ministry of Science and Technology of China (grant number: 2009CB623605).

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