



## Novel orange-red light-emitting polymers with cyclometaled iridium complex grafted in alkyl chain

Lei Ying, Jianhua Zou, Anqi Zhang, Bing Chen, Wei Yang\*, Yong Cao

*Institute of Polymer Optoelectronic Materials and Devices, Key Laboratory of Specially Functional Materials, Ministry of Education, South China University of Technology, Guangzhou 510640, China*

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### ABSTRACT

Novel poly(fluorene-*alt*-carbazole) (PFCz) based copolymers with 3,6-carbazole-*N*-alkyl grafted iridium complex using 2,3-diphenylpyrazine as ligand (IrBpz) were synthesized by Suzuki polycondensation. The emission of host polymer, PFCz, was completely quenched when the copolymer with 1 mol% of iridium complex. An orange-red emission with CIE coordinate of (0.56, 0.42) was observed from PhPLEDs made by this copolymer-iridium complex showed a maximum luminous efficiency (LE) of 5.58 cd/A and a maximal luminance of 8625 cd/m<sup>2</sup>. White light with CIE coordinate of (0.33, 0.27) was observed from white PhPLEDs (WPhPLEDs) made by the copolymer containing 0.4 mol% iridium complex. A LE of 2.30 cd/A with luminance of 2068 cd/m<sup>2</sup> was observed from WPhPLEDs.

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### 1. Introduction

Phosphorescent polymer light-emitting diodes (PhPLEDs) have been attracted the attention of scientist during last decade because their internal quantum efficiency is theoretically 100% and they can be fabricated by low-cost wet process techniques [1,2]. In General, the emissive layer of PhPLEDs was fabricated by conjugated polymers blended with phosphorescent dyes [3]. These PhPLEDs exhibited high luminous efficiency (LE) and high brightness, however, these PhPLEDs are unstable because phase separation and triplet-triplet annihilation at the bias of high current densities. In order to resolve this problem, an alternative approach is to fabricate PhPLEDs by conjugated polymers chemically bonded with phosphorescent dyes, i.e. to copolymerize phosphorescent dyes in conjugated polymer backbone [4] or to graft phosphorescent dyes into polymer side chain by a long alkyl chain [5]. These conjugated polymers containing phosphorescent dyes allow for the formation of well-designed solid-state materials while the phase separation or dopant aggregation could be restrained and the PhPLEDs with high LE and brightness are expected.

Among PhPLEDs, white PhPLEDs (WPhPLEDs) are of particular interests because their potential applications in full-color flat panel displays and solid state lighting sources [6]. Various approaches including a simultaneously incorporating three primary colors (red, green and blue) [7] or two complementary colors [8] into one polymer main chain have been reported to realize WPhPLEDs

by one conjugated polymers containing phosphorescent dyes in polymer main chain. Recently, our group reported the poly(2,7-fluorene-*alt*-3,6-carbazole) (PFCz) derivatives with phosphorescent iridium complexes in polymer side chain [9]. In these new materials, the emission from the host PFCz is completely quenched by the incorporated iridium complexes, and emissions of these polymers are mainly relied on the incorporated iridium complexes [10].

In this paper, we reported the synthesis of PFCz-IrBpz, an iridium(III)bis(2,3-diphenylpyrazine-*N,C*<sup>2'</sup>)-2,4-pentadiketone (IrBpz) as a phosphorescent dyes chemically bonded with PFCz side chain by alkyl side chain. We demonstrated that the PhPLEDs with CIE coordinate of (0.56, 0.42) and a LE of 5.58 cd/A due to the emission of IrBpz from PFCz-IrBpz was observed by carefully tune the content of IrBpz in PFCz. Moreover, WPhPLEDs with CIE coordinate of (0.33, 0.27) and a LE of 2.30 cd/A was achieved from PFCz-IrBpz via further tuning the content of IrBpz in PFCz to realize the emission from PFCz and IrBpz.

### 2. Results and discussion

#### 2.1. Synthesis of monomers and polymers

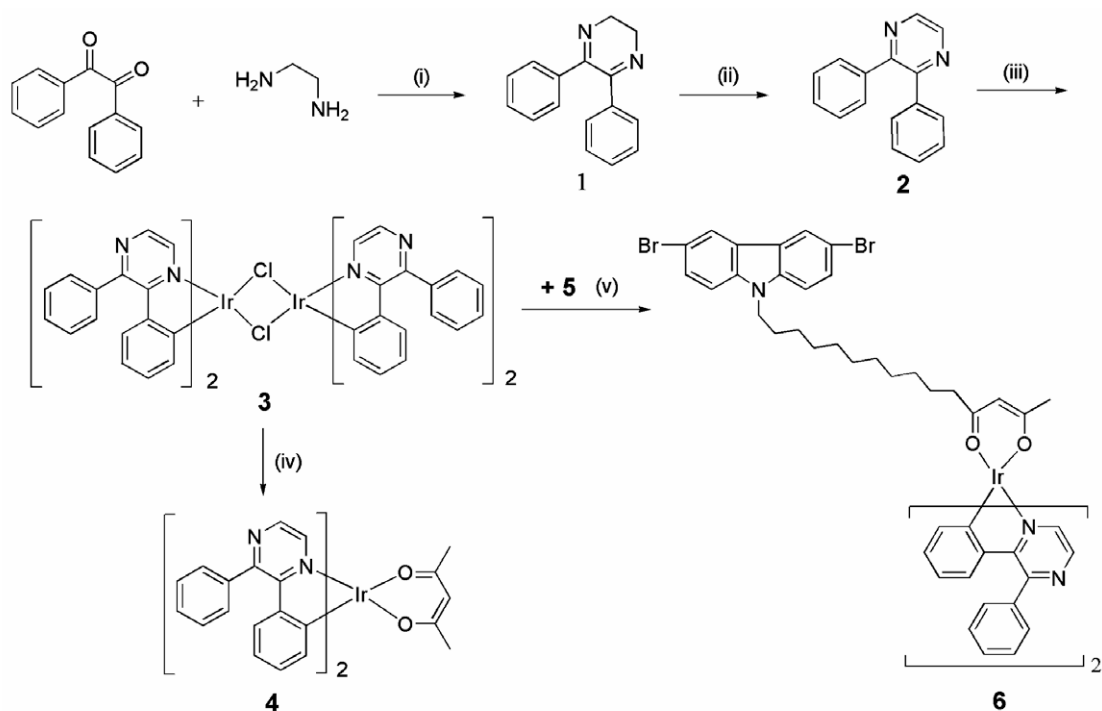
The ligand 2,3-diphenylpyrazine (**2**) was prepared in high yield from dehydration of 2,3-diphenyl-5,6-dihydropyrazine (**1**) with FeCl<sub>3</sub> in dehydrate ethanol. By treatment of the bisenolate of 2,4-pentanedione with 3,6-dibromo-9-(10'-bromodecane)carbazole with sodium hydro in absolute THF, the β-diketone was successfully tethered into the side chain of carbazole-*N* of compound **5** by long alkyl chain with 70% yield. The reaction of the

\* Corresponding author. Fax: +86 20 87110606.

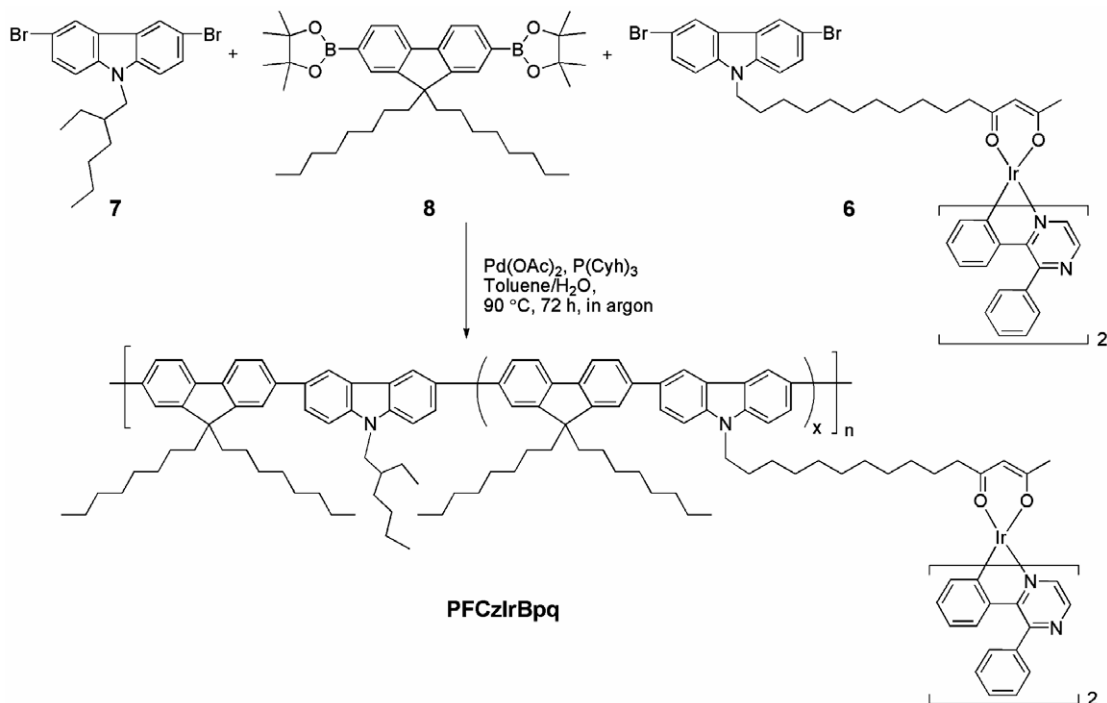
E-mail address: [pswyang@scut.edu.cn](mailto:pswyang@scut.edu.cn) (W. Yang).

$\beta$ -diketone ligand **5** with the crude chloro-bridged iridium dimer **3** in 2-ethoxyethanol under reflux for 16 h given the 3,6-dibromocarbazole-*N*-decamethylene-tethered iridium complex (**6**) a yield of 38%. The model iridium complex **4** was synthesized in similar yield from this approach, and the yield was still as low as 42%. The synthetic routes of these compounds are shown in Scheme 1.

The reason for the low yield might be attributed to the side reaction of generated hydrodebrominated derivatives, which has been previously evidenced by Evans et al. [11]. Although the yield was much lower than expectation, the  $^1\text{H}$  NMR spectrum of the 3,6-dibromocarbazole-*N*-decamethylene-tethered iridium complex (**6**) was well accordance with the target molecular structure while only a trace of impurities was found. Molecular structure of **6** was



(i) Reflux in dehydrated ethanol for 6 h in nitrogen; (ii) iron (III) chloride, stirred for 30 min at 60 °C in dehydrated ethanol; (iii) NaCl,  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  / 2-ethoxyethanol, 120 °C for 24 h; (iv) 2,4-Pentadione,  $\text{Na}_2\text{CO}_3$ , 2-ethoxyethanol, 120 °C for 16 h; (v) 3,6-Dibromo-*N*-(12,14-pentadecyldiketone)carbazole,  $\text{Na}_2\text{CO}_3$ , 2-ethoxyethanol, 120 °C for 16 h.



Scheme 1. Synthetic route for the compounds and polymers.

further verified by the data from both ESI-MS and elemental analysis. In addition, a  $^1\text{H}$ - $^1\text{H}$  COSY spectrum enables the near-complete assignment of all aromatic protons for the 3,6-dibromo-carbazole-*N*-decamethylene-tethered iridium complex (**6**) in deuterated chloroform except the detailed splitting of protons in pyrazine ligand (adjacent to the aromatic phenyl carbon atoms which coordinated with iridium core), which might caused by face-to-face conformation of the iridium complex. Combining the integral values of each of the peaks in the one-dimensional  $^1\text{H}$  NMR spectrum and the coherence peaks of protons coupled over two (geminal) or three (vicinal) bonds in  $^1\text{H}$ - $^1\text{H}$  COSY spectrum, the assignment along with the protons chemical shifts of complex **6** is attained and the results are shown in Fig. 1.

The copolymers were prepared from 3,6-dibromo-9-(iridium(III)bis(2,3-diphenylpyrazine- $\text{N},\text{C}^2$ ))-12,14-pentadecyldiketone)carbazole (**6**), 3,6-dibromo-9-(2-ethylhexyl)-carbazole [12] (**7**), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene [13] (**8**) by Suzuki polycondensation (Scheme 1). At the end of the polymerization, phenylboric acid and bromobenzene are added subsequently to remove the possible ended bromo- or boric ester groups in the resulted polymers. The feed ratio of Ir complex in the polycondensation are 0, 0.2, 0.4, 0.6, 1 and 2 mol%, and the corresponding copolymers are named PFCz, PFCzIrBpz-02, PFCzIrBpz-04, PFCzIrBpz-06, PFCzIrBpz-1 and PFCzIrBpz-2, respectively. Average molecular weights ( $M_n$ ) of these copolymers are from 8200 to 10 200 with the polydispersity (PDI) in the range of

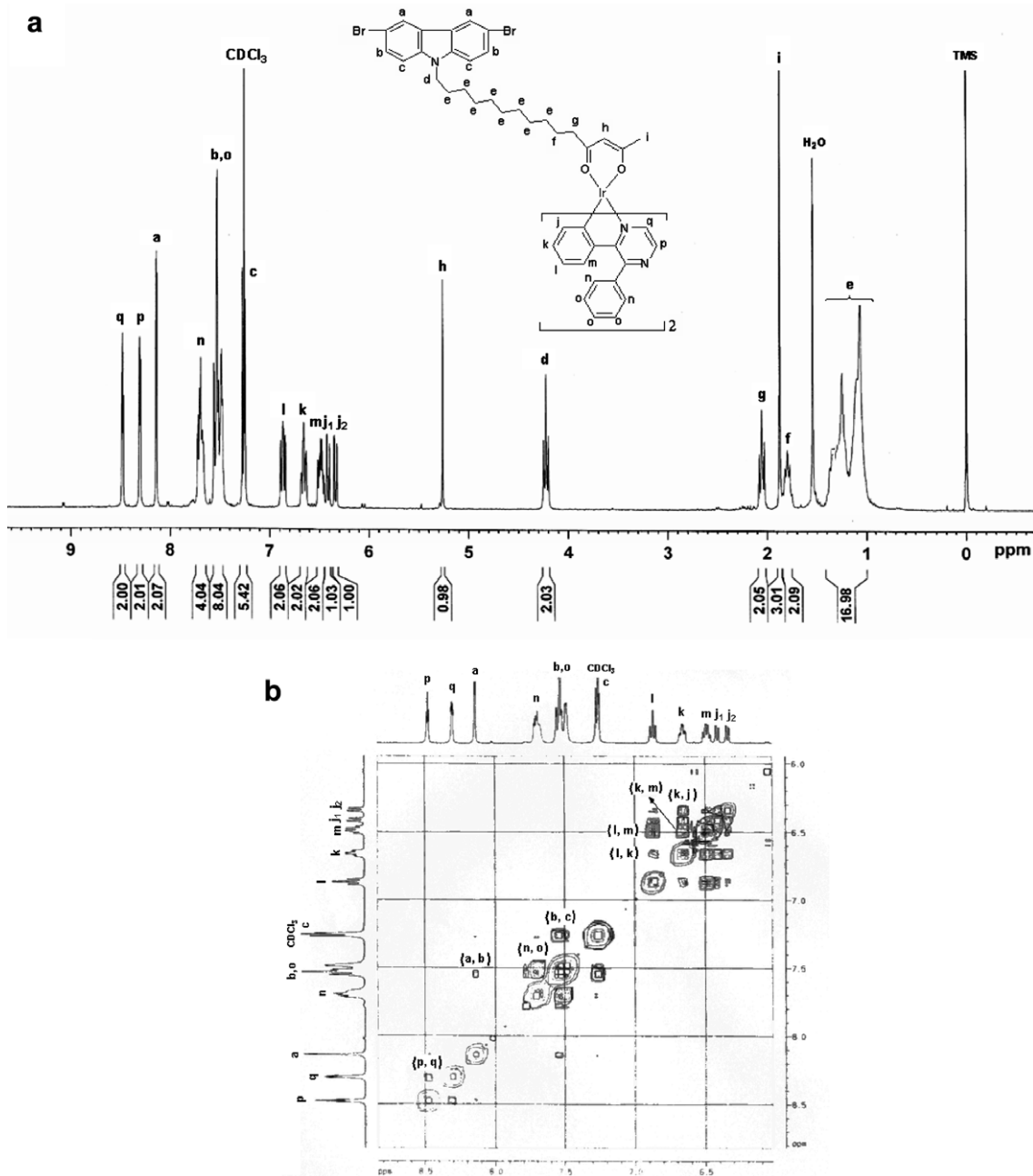


Fig. 1.  $^1\text{H}$  NMR (a) and  $^1\text{H}$ - $^1\text{H}$  COSY (b) of monomer **6**.

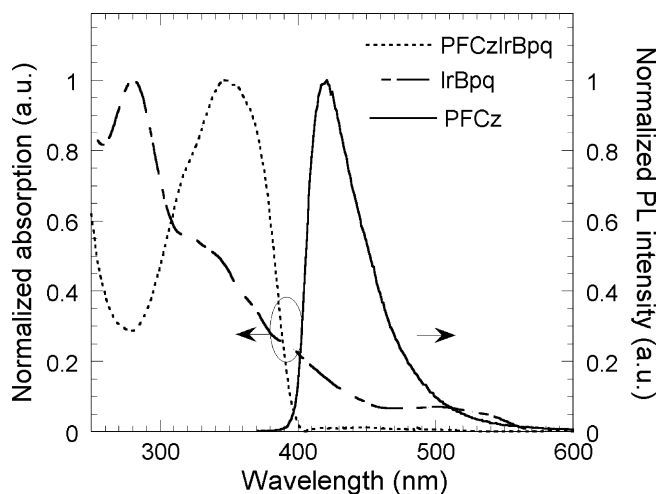
**Table 1**  
Molecular weight and electrochemical properties of polymers.

Polymer	$M_n$ ( $\times 10^3$ )	PDI	$E_{ox}$ (V)	HOMO (eV)	LUMO (eV)	$E_g^{opt}$ (eV)
PFCzIrBpz-02	9.3	1.8	1.02	-5.42	-2.30	3.12
PFCzIrBpz-04	8.2	2.0	1.00	-5.40	-2.27	3.13
PFCzIrBpz-06	8.5	1.7	1.03	-5.43	-2.31	3.12
PFCzIrBpz-1	10.2	1.8	1.10	-5.45	-2.33	3.12
PFCzIrBpz-2	9.0	1.6	1.12	-5.47	-2.35	3.12

1.6–2.0, which is consistent with the Suzuki polycondensation procedure [14] (see Table 1).

## 2.2. Photophysical and electrochemical properties

Fig. 2 shows the UV–vis absorption spectra of copolymer PFCzIrBpz and Ir complex (IrBpz) and the PL spectrum of PFCz. It was found that all of these copolymers have very similar UV–vis spectra, and the characteristic absorption of IrBpz cannot be observed because of their fairly low content level in copolymers. The model Ir complex (IrBpz) has broad absorption band ranged from 270 nm to 570 nm. An intense absorption band below 350 nm is attributed to the spin-allowed singlet state  $^1\pi-\pi^*$  transition of cyclometalated ligands. A weak absorption band around 410 nm is assigned to the spin-allowed singlet metal-to-ligand charge-transfer ( $^1MLCT$ ) transition. The strong absorption peaked at 512 nm for IrBpz is originated from triplet metal-to-ligand charge-transfer ( $^3MLCT$ ) transition. Fig. 2 shows clearly that there is a good spectral overlap between the PL emission of the host copolymer PFCz and the absorption spectra of the guests (IrBpz) which was shown clearly in Fig. 1. This good spectra overlap indicated an efficient Förster energy transfer from the PFCz host to Ir complex guests is expected [14].



**Fig. 2.** UV–vis of IrBpz and PL of IrBpz and PFCz.

The electrochemical behaviors of copolymers were investigated by cyclic voltammetry (CV) in 0.1 M of tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) acetonitrile ( $CH_3CN$ ) solution. The CV curves were referred to an Ag quasireference electrode, which was calibrated using the ferrocene/ferrocenium redox couple (0.35 V vs. Ag/AgCl) as an internal standard prior to measurements. The photophysical and electrochemical properties of Ir complexes and the redox potentials of copolymers derived from the onset in the cyclic voltammetry are summarized in Table 1. The HOMO energy levels of polymers can be estimated using the empirical equation  $E_{HOMO} = -e(E_{ox} + 4.40)$  (eV) [15]. However, since the redox peaks cannot be recorded corresponding to Ir complex in the copolymers, so the LUMO energy levels ( $E_{LUMO}$ ) is estimated from both of the absorption onset (the optical energy gap,  $E_g^{opt}$ ) and  $E_{HOMO}$ . The oxidation for IrBpz observed at 0.96 V, thus the HOMO energy level of IrBpz was calculated as -5.26 eV, which was slight lower than that of PEDOT:PSS (-5.20 eV) but higher than that of host PFCz (-5.47 eV). The LUMO energy level ( $E_{LUMO}$ ) was estimated to be -3.08 eV based on  $E_{HOMO}$  and corresponding optical band gap ( $E_g^{opt}$ ). In considering that the iridium complex (IrBpz) was tethered to PFCz side chain by a long alkyl spacer, thus its  $E_{HOMO}$  and  $E_{LUMO}$  would not distinctly change. In this case, both of the  $E_{HOMO}$  and  $E_{LUMO}$  would fall within that of PFCz, so that the grafted IrBpz is expected to function as both hole and electron trapping center.

The photoluminescent (PL) spectra of the copolymers were shown in Fig. 3. All of the emissions of copolymers are dominant at 420 nm with a small shoulder at 585 nm. The emission peaked at 420 nm is attributed to the emission of host PFCz, while the 585 nm peaks are ascribed to the emission of grafted IrBpz complex. The relative intensities at 420 nm remain almost independent with the Ir complex (IrBpz) contents in the copolymers and the emission at 585 nm increased gradually with the grafted IrBpz contents. The PL quantum efficiencies of PFCz–IrBpz and PFCzIrBpz are in the range of 45–60%.

## 2.3. Electroluminescent properties

In order to balance the carrier's transporting, 30 wt% of 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) was blended with the copolymers to make in the emissive layer because copolymer exhibited a good hole transport property due to the incorporated carbazole moiety into main chain of polymer, and PBD is well-know electron transporting molecule [16]. The electroluminescent (EL) spectra observed from the devices with a configuration of ITO/

**Table 2**  
Electroluminescent properties of polymers.

Polymer	At maximal luminous efficiency				$L_{max}$ (cd/m <sup>2</sup> )	CIE (x, y)
	Bias (V)	$J$ (mA/cm <sup>2</sup> )	QE (%)	LE (cd/A)		
PFCzIrBpz-02	6.4	1.7	0.18	0.23	136	(0.20, 0.12)
PFCzIrBpz-04	5.4	8.7	1.84	2.30	2068	(0.33, 0.27)
PFCzIrBpz-06	6.0	12.8	2.80	3.50	4416	(0.48, 0.38)
PFCzIrBpz-1	5.6	7.7	4.46	5.58	8625	(0.56, 0.42)
PFCzIrBpz-2	5.2	8.0	2.91	3.64	5025	(0.56, 0.43)

Device structure: ITO/PEDOT/polymer + PBD (30 wt%)/Ba/Al.

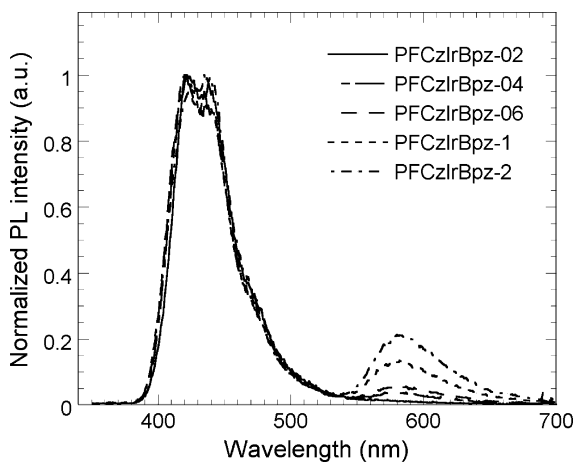


Fig. 3. PL spectra of copolymers.

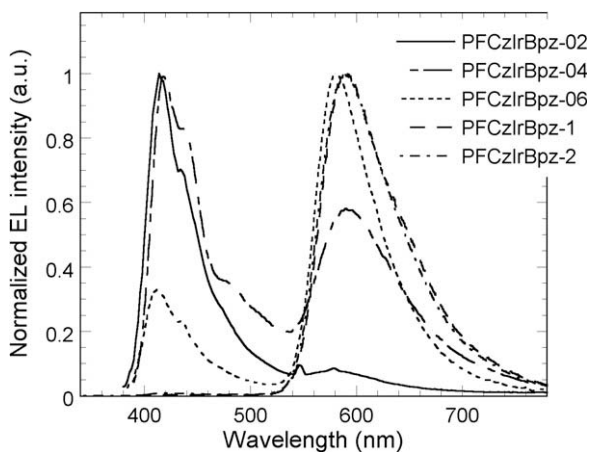


Fig. 4. EL spectra of polymers.

PEDOT:PSS (40 nm)/polymer + PBD (30 wt%) (80 nm)/Ba (4 nm)/Al (150 nm) were shown in Fig. 4. Unlike the PL spectra, the emission from host PFCz was completely quenched when the content of IrBpz reaches 1 mol%. The substantial differences in PL and EL indicated that the operational mechanisms in PL and EL were different. The HOMO and LUMO of the grafted iridium complex IrBpz were within the band gap of the host copolymer (PFCz) (whose HOMO and LUMO are  $-5.47$  and  $-2.27$  eV, respectively). Therefore, the injected hole from the anode and the electron from the cathode should be readily trapped by the grafted Ir complex sites [17]. In other words, the grafted Ir complexes functioned as both hole and electron trapping centers and dominated electrical excitation processes in the devices. The EL spectra shown in Fig. 4 further demonstrated that when the content of the grafted IrBpz is larger than 1 mol%, the EL emission from host PFCz was completely quenched. However, the dominated electrical excitation processes in the devices can be tuned if the content of the grafted iridium complex were controlled at a certain level [10]. Two simultaneously emissions both from PFCz (blue emission) and IrBpz (orange-red emission) are expected.

In order to obtain white light from PFCz–IrBpz via combination blue emission from PFCz and orange-red emission from IrBpz, we synthesized PFCzIrBpz04, where the content of IrBpz is as low as 0.4 mol%. The EL spectra observed from PhPLEDs made by PFCzIrBpz-04 shown two peaks. The blue emission was from PFCz fluorescent and the orange-red emission, peaked at 585 nm) was

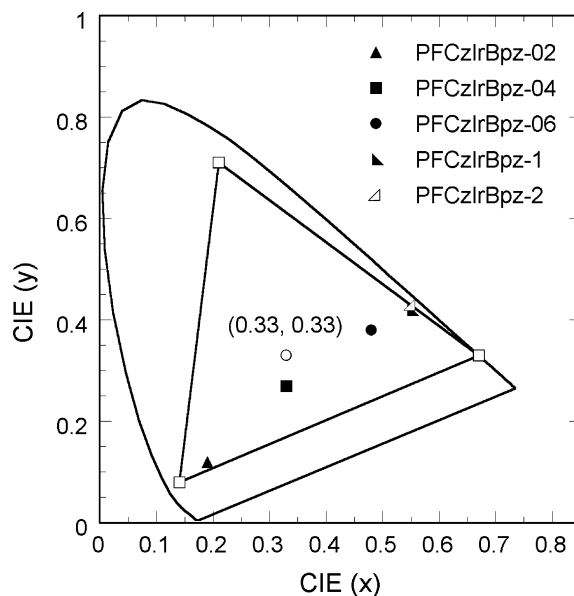


Fig. 5. CIE coordinates (x, y) of polymers.

from IrBpz phosphorescent. Observed white light has CIE of (0.33, 0.27) which is very close to that from pure white light (0.33, 0.33). The observed CIE coordinates were shown in Fig. 5.

The devices performances were summarized in Table 2. The applied voltages from these devices made by various copolymers were relatively low. This was probably due to the incorporated carbazole moiety in main chain of polymer resulting in high HOMO as compared with polyfluorene homopolymers. The best device performance was observed from PhPLEDs made by PFCzIrBpz-1. The light observed from this device has a CIE coordinate of (0.56, 0.42). The devices exhibited a maximum LE of 5.58 cd/A with brightness of 8625 cd/m<sup>2</sup> at current density of 7.7 mA/cm<sup>2</sup>. The device performance became poor when a high content of IrBpz was incorporated with copolymers. However, the white light was observed from PhPLED made by PFCzIrBpz-04. The white light has CIE coordinate of (0.33, 0.27). The WPhPLEDs exhibited a LE<sub>max</sub> of 2.30 cd/A and brightness of 2068 cd/m<sup>2</sup> at current density of 8.7 mA/cm<sup>2</sup>. We also observed a stable color when PhPLEDs and WPhPLEDs were biased at different current densities. For the fabricated WPhPLEDs based on PFCzIrBpz-04 as active layer, the CIE coordinates varied from (0.33, 0.27) to (0.34, 0.25) while the corresponding current density increased from 5 mA/cm<sup>2</sup> to 100 mA/cm<sup>2</sup>. These results demonstrated that the graft of phosphorescent complexes by long alkyl side chain into polymer backbone is an effective approach to obtain stable white light from WPhPLEDs, particularly, at the bias of high current density [18].

### 3. Conclusion

Electrophosphorescent polymers grafted iridium complex by a long alkyl chain were synthesized by Suzuki polycondensation. The orange-red light with a CIE coordinate of (0.56, 0.42) was observed from PhPLEDs made by copolymer with 1 mol% IrBpz into PFCz. The PhPLEDs exhibited a LE of 5.6 cd/A. White light with a CIE coordinate of (0.33, 0.27) was observed from WPhPLEDs made by a copolymer of PFCzIrVpz-04, in which the content of IrBpz was tuned to be 0.4% into PFCz. WPhPLEDs exhibited a LE of 2.30 cd/A and stabilized white light at the bias of high current densities. All these results demonstrated that semiconducting polymer containing metal complex is an efficiency approach to realize high performance PhPLEDs and WPhPLEDs.

## 4. Experimental

### 4.1. Materials and characterization

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Co. and were used as received. 3,6-Dibromo-9-(2-ethylhexyl)-carbazole [15], 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene [15], 3,6-dibromo-9-(12,14-pentadecyldiketone)carbazole [13] and poly(fluorene-*alt*-carbazole) (PFCz) were synthesized according to similar reported procedures.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX 300 spectrometer operating respectively at 300 and 75 MHz, with tetramethylsilane (TMS) as a reference. The H,H-COSY spectrum was recorded and processed in the absolute value mode 10. The spectral width was 5208.33 Hz; 8 accumulations,  $1\text{ K} \times 400$  data points ( $t_2 \times t_1$ ). The data point array was  $F_2 \times F_1 = 1\text{ K} \times 1\text{ K}$  for Fourier transformation after zero filling. The probe temperature was regulated at 298 K. Direct injection mass spectra were recorded by the electron spray impact (ESI) method on a LCQ DECA XP Liquid Chromatography–Mass Spectrometer (Thermo Co.). Molecular weight determination was obtained using a Waters GPC 2410 in tetrahydrofuran via a calibration curve of polystyrene standards. Elemental analyses were performed on Vario EL Elemental analysis instrument (Elementar Co.). Samples were pressed as homogeneous tablets (= 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 ISO80 (Labsphere) with 325 nm excitation of HeCd laser (Mells Griot). Cyclic voltammetry was carried out on a potentiostat/galvanostat model at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in acetonitrile ( $\text{CH}_3\text{CN}$ ). Element analyses were performed on Vario EL Elemental analysis instrument (Elementar Company).

### 4.2. Device fabrication and characterization

Polymers were dissolved in *p*-xylene and filtered with a 0.45  $\mu\text{m}$  PTFE filter. Patterned ITO coated glass substrates were cleaned with acetone, detergent, distilled water and 2-propanol followed by in an ultrasonic bath. After treated with oxygen plasma, 50 nm of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS, Batron-P 4083, Bayer AG) was spin-coated onto the ITO substrates followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of polymers was coated onto the resulting PEDOT:PSS layer by spin-casting inside a glove box filled with nitrogen. The film thickness of the active layers was around 75–80 nm, as determined with an Alfa Step 500 surface profiler (Tencor). Current–Voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source meter. EL spectra were obtained by Oriel Instaspec IV CCD spectrograph. Luminance was measured by a calibrated silicon photodiode and calibrated by a photometer (PR705, Photo Research). The external quantum efficiency was determined by a calibrated silicon photodiode in an integrating sphere (ISO80, Labsphere).

### 4.3. Synthesis of monomers

#### 4.3.1. Synthesis of 2,3-diphenyl-5,6-dihydropyrazine (**1**)

First, with the use of 300 ml of dehydrated ethanol as a solvent, 21.0 g (100 mmol) of benzyl and 6.1 g (101 mmol) of ethylenediamine are held at reflux in a nitrogen atmosphere for 6 h. Then the solution is condensed to one fifth, and a produced precipitation is collected. By washing the obtained precipitation with cool ethanol,

the light-yellow powder is obtained (yield: 78%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.43–7.37 (m, 4H), 7.34–7.20 (m, 6H), 3.70 (s, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 160.30, 137.78, 129.64, 128.39, 127.91, 45.84. Elemental Anal. Calc. for  $\text{C}_{16}\text{H}_{14}\text{N}_2$ : C, 82.02; H, 6.02; N, 11.96. Found: C, 82.32; H, 5.92; N, 11.76%.

#### 4.3.2. Synthesis of 2,3-diphenylpyrazine (Bpz, **2**)

2,3-Diphenyl-5,6-dihydropyrazine (**4**, 10 g, 27 mmol) was put into a 500 ml three neck flask, and 100 ml of dehydrate ethanol was added to be dissolved. Then, iron (III) chloride (8.8 g, 54 mmol) of was added thereto, and this mixture was heated and stirred for 30 min at 60 °C to be reacted. After the reaction, 300 ml of water was added to the reaction mixture and the precipitated solid was filtered followed by dissolved in toluene. After this mixture was washed with saturated saline, the solid was obtained by concentrating the solvent and purified by silica column chromatography. The eluent was concentrated to obtain 6.3 g of an orange solid of product in the yield of 60%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.60 (s, 2H), 7.47–7.42 (m, 4H), 7.33–7.29 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 152.84, 142.11, 138.62, 129.66, 128.69, 128.30. Elemental Anal. Calc. for  $\text{C}_{16}\text{H}_{12}\text{N}_2$ : C, 82.73; H, 5.21; N, 12.06. Found: C, 82.62; H, 5.39; N, 11.98%.

#### 4.3.3. Synthesis of chloride-bridged dimer [ $\text{Ir}(\text{Bpz})_2\text{Cl}$ ]<sub>2</sub> (**3**)

First, with the use of a mixture of 30 ml of 2-ethoxyethanol and 10 ml of water as a solvent, 1.86 g of the ligand 2,3-diphenylpyrazine (**5**) and 0.96 g of iridium chloride ( $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ ) are mixed in 100 ml of flask with magnetic stirrer. Then the mixture was held at reflux for 17 h in a nitrogen atmosphere to obtain a dinuclear complex [ $\text{Ir}(\text{Bpz})_2\text{Cl}$ ]<sub>2</sub> (brown powder, yield: 35%). The product was used directly for the next step without further purification.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.80 (d,  $J = 3.24$  Hz, 4H), 8.26 (d,  $J = 3.18$  Hz, 4H), 7.75 (d,  $J = 3.48$  Hz, 8H), 7.40 (m, 12H), 6.74 (d,  $J = 7.95$  Hz, 4H), 6.58 (td,  $J = 1.26$  Hz and 6.72 Hz, 4H), 6.46 (t,  $J = 7.98$  Hz, 4H), 6.02 (t,  $J = 7.26$  Hz, 4H).

#### 4.3.4. Synthesis of iridium(III)bis(2,3-diphenylpyrazine-*N,C*<sup>2'</sup>)-2,4-pentadiketone ( $\text{IrBpz}$ , **4**)

Chloride-bridged dimer [ $\text{Ir}(\text{Bpz})_2\text{Cl}$ ]<sub>2</sub> (**3**) (0.45 g, 0.345 mmol), 2,4-pentadiketone (0.09 g, 0.885 mmol), and sodium carbonate (0.1 g) were mixed and refluxed in 2-ethoxyethanol (30 ml) for 16 h under a nitrogen atmosphere. The solution was cooled to room temperature and filtered before washing with water and hexane. The crude products were purified by silica chromatography (40% dichloromethane and 60% petroleum ether) with yield of 42%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.50 (dd,  $J = 0.72$  Hz and 3.15 Hz, 2H), 8.33 (d,  $J = 3.15$  Hz, 2H), 7.69 (m, 4H), 7.52 (m, 6H), 6.86 (d,  $J = 8.07$  Hz, 2H), 6.67 (t,  $J = 7.38$  Hz, 2H), 6.49 (t,  $J = 8.04$  Hz, 2H), 6.36 (d,  $J = 7.62$  Hz, 2H), 5.29 (s, 1H), 1.87 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 185.60, 161.90, 153.31, 149.80, 142.62, 140.91, 139.91, 139.06, 132.49, 129.57, 129.49, 129.02, 128.88, 120.72, 100.73. Elemental Anal. Calc. for  $\text{C}_{37}\text{H}_{29}\text{IrN}_4\text{O}_2$ : C, 58.95; H, 3.88; N, 7.43. Found: C, 58.83; H, 3.60; N, 7.60%.

#### 4.3.5. Synthesis of 3,6-dibromo-9-(12,14-pentadecyldiketone)carbazole (**5**)

In a 50 ml two-neck flask with magnetic stirrer, sodium hydride (60% dispersion in mineral oil; 320 mg, 8.00 mmol) was washed thoroughly with tetrahydrofuran (THF) under protection of argon to remove the mineral oil, and 20 ml THF was then added to the flask. Subsequently, 2,4-pentanedione (0.80 ml, 7.8 mmol) was added dropwise over 20 min to a stirred suspension of the sodium hydride in THF (20 ml) at 0 °C. The resultant mixture was stirred for 30 min at 0 °C. *n*-Butyllithium (2.5 M in hexane; 4.9 ml, 7.8 mmol) was added dropwise over 20 min to the stirred mixture at 0 °C. The resultant solution was stirred for 25 min at 0 °C. A solu-

tion of 3,6-dibromo-9-(10'-bromodecane)carbazole (1.62 g, 2.58 mmol) in THF (5 ml) was added dropwise over 10 min to the stirred solution at 0 °C. The resultant mixture was stirred for 1 h at 0 °C and for a further 1 h at room temperature, after which it was quenched with aqueous ammonium chloride (10 wt%, 8 ml). The mixture was acidified with concentrated hydrochloric acid to pH 1 and the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were washed with saturated aqueous sodium bicarbonate, dried with anhydrous magnesium sulfate and evaporated under reduced pressure. The crude product was purified by silica chromatography using petroleum ether/ethyl acetate as eluent to give the tethered ligand as white solid in yield of 70%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 15.51 (s, 1H, enolone 3-H3), 8.13 (d, *J* = 1.89 Hz, 2H), 7.54 (dd, *J* = 1.89 Hz and 8.70 Hz, 2H), 7.27 (d, *J* = 8.70 Hz, 2H), 5.48 (s, 0.8H, enolone 3-H), 4.23 (t, *J* = 7.14 Hz, 2H), 3.56 (s, 0.4 H, dione 3-H2), 2.49 (t, *J* = 7.32 Hz, 0.4 H, dione 5-H2), 2.24 (t, *J* = 7.41 Hz, 1.6 H, enolone 5-H2), 2.23 (s, 0.6 H, dione 1-H3), 2.05 (s, 2.4H, enolone 1-H3), 1.81 (m, 2H), 1.57 (m, 2H), 1.42–1.25 (m, 14H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 194.32, 191.41, 139.31, 129.00, 123.44, 123.25, 111.93, 110.40, 99.76, 43.34, 38.27, 29.42, 29.39, 29.34, 29.28, 29.21, 29.18, 28.83, 27.19, 25.68, 24.99. Elemental Anal. Calc. for C<sub>27</sub>H<sub>33</sub>Br<sub>2</sub>NO<sub>2</sub>: C, 57.56; H, 5.90; N, 2.49. Found: C, 57.29; H, 6.00; N, 2.52%.

#### 4.3.6. Synthesis of 3,6-dibromo-9-(iridium(III)bis(2,3-diphenylpyrazine-N,C<sup>2'</sup>))-12,14-pentadecylidone)carbazole (**6**)

Chloride-bridged dimer [Ir(Bpz)<sub>2</sub>Cl]<sub>2</sub> (**3**) (0.45 g, 0.345 mmol), 3,6-dibromo-9-(12,14-pentadecylidone)carbazole (**5**, 0.54 g, 0.885 mmol), and sodium carbonate (0.1 g) were mixed and refluxed in 2-ethoxyethanol (30 ml) for 16 h under a nitrogen atmosphere. The solution was cooled to room temperature and filtered before washing with water and hexane. The crude products were purified by silica chromatography (40% dichloromethane and 60% petroleum ether) with yield of 38%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.48 (dd, *J* = 2.04 Hz and 3.06 Hz, 2H), 8.30 (dd, *J* = 1.14 Hz and 3.12 Hz, 2H), 8.14 (d, *J* = 1.86 Hz, 2H), 7.70 (m, 4H), 7.56–7.47 (m, 8H), 7.25 (d, *J* = 8.70 Hz, 2H), 6.85 (dt, *J* = 1.20 Hz and 5.94 Hz, 2H), 6.66 (tt, *J* = 0.90 Hz and 7.20 Hz, 2H), 6.52–6.45 (m, 2H), 6.42 (dd, *J* = 0.72 Hz and 7.56 Hz, 1H), 6.34 (dd, *J* = 0.66 Hz and 7.53 Hz, 1H), 5.26 (s, 1H), 4.23 (t, *J* = 7.14 Hz, 2H), 2.05 (t, *J* = 7.32 Hz, 2H), 1.88 (s, 3H), 1.80 (m, 2H), 1.37–1.06 (m, 16H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 189.17, 185.72, 161.96, 161.82, 153.31, 153.21, 150.26, 149.99, 142.54, 140.80, 140.74, 139.90, 139.34, 139.05, 139.02, 132.85, 132.57, 129.56, 129.53, 129.35, 129.02, 128.88, 128.75, 123.47, 123.28, 120.68, 120.63, 111.95, 110.41, 43.36, 41.77, 31.89, 29.44, 29.40, 29.36, 29.32, 29.29, 29.07, 28.88, 28.83, 27.33, 27.18, 22.66, 14.11. Elemental Anal. Calc. for C<sub>59</sub>H<sub>54</sub>Br<sub>2</sub>IrN<sub>5</sub>O<sub>2</sub>: C, 58.22; H, 4.47; N, 5.75. Found: C, 58.46; H, 4.70; N, 5.60%. ESI-MS (*m/z*): 1218.4.

#### 4.3.7. General procedure for Suzuki polycondensation of copolymers PFCzIrBpz, taking PFCzIrBpz-1 as an example

3,6-Dibromo-9-(2-ethylhexyl)carbazole (**7**, 268.7 mg, 0.495 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**8**, 321.3 mg, 0.5 mmol), 3,6-dibromo-9-(iridium(III)bis(2,3-diphenylpyrazine-N,C<sup>2'</sup>))-12,14-pentadecylidone)carbazole (**6**, 6.6 mg, 0.005 mmol), palladium(II) acetate (Pd(OAc)<sub>2</sub>, 1.5 mol% equivalent) and tricyclohexylphosphine (P(Cy)<sub>3</sub>, 4 mol% equivalent) were dissolved in the mixture of toluene (8 ml), after stirred for 0.5 h, deionized H<sub>2</sub>O (2 ml) and Et<sub>4</sub>NOH (35 wt%) aqueous solution (0.2 ml) was added. The mixture was heated to 90 °C and stirred for 48 h under argon atmosphere. Then the reaction was capped by adding phenyl boric acid (25 mg) by stirring for 12 h to remove the bromine end groups, and then bromobenzene (1 ml) was added as a mono functional

end-capping reagent by heating for another 12 h to remove the resident boronic ester end groups. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene as eluent to remove small molecular fraction and residue catalyst (yield 69%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.54 (br, 2H), 7.86 (br, 2H), 7.78 (br, 2H), 7.73 (br, 2H), 7.56 (m, 2H), 7.24 (m, 2H), 4.32 (m, 2H), 2.10 (m, 1H), 1.95 (m, 4H), 1.52–0.78 (m, 44H).

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