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A novel high-efficiency white hyperbranched polymer derived from polyfluorene with green and red iridium(III) complexes as the cores

Jing Sun<sup>a,b</sup>, Hua Wang<sup>a,b</sup>, Huixia Xu<sup>a,b</sup>, Tiaomei Zhang<sup>a,b</sup>, Lu Li<sup>d</sup>, Jie Li<sup>a,b</sup>, Yuling Wu<sup>a,b</sup>, Bingshe Xu<sup>a,b,\*</sup>, Xinwen Zhang<sup>c,\*</sup>, Wenyong Lai<sup>c</sup>

<sup>a</sup> Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan 030024, P. R. China

<sup>b</sup> Research Center of Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, P. R. China

<sup>c</sup> Key Laboratory for Organic Electronics & Information Displays, Nanjing University of Posts and Telecommunications, Nanjing 210023, P. R. China

<sup>d</sup> Institute of New Materials Technology Research, Chongqing University of Arts and Sciences, Chongqing 404100, P. R. China

#### ABSTRACT

A new kind of single triple-color hyperbranched polymer PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n was designed and synthesized, in which green and red iridium(III) complexes acted as cores and blue polyfluorene acted as backbone. PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) had higher quantum efficiency than PF-Ir(piq)<sub>2</sub>(pytzph)5. The energy transfer from green core bis(2-phenylpyridine)[3-(2-pyridyl)-5-phenyl-1,2,4-triazole]iridium(III) [Ir(ppy)<sub>2</sub>(pytzph)] with high triplet energy level ( $E_T$ =2.58 eV) to red core bis(1-phenylisoquinolinato)[3-(2-pyridyl)-5-phenyl-1,2,4-triazole]iridium(III) [Ir(piq)<sub>2</sub>(pytzph)] ( $E_T$ =2.12 eV) could realize by intermediate poly(9,9-dioctylfluorene) (PF) segments. A typical single emitting-layer device with the configuration of ITO/PEDOT:PSS (40 nm)/PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 exhibited for the white polymers, PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 exhibited

<sup>\*</sup>Corresponding author. E-mail address: xubs@tyut.edu.cn (Xu BS);

<sup>\*\*</sup>Corresponding author. E-mail address: iamxwzhang@njupt.edu.cn (Zhang XW)

excellent electroluminescent properties with a Commission Internationale Ed I'eclairage (CIE) coordinate of (0.32, 0.34) and a maximum luminous efficiency of 11.49 cd/A.

**Keywords:** Triple-color white-light emitting polymer, Hyperbranched structure, Green and red iridium(III) complexes, Photophysical properties, Film-forming, Electroluminescent properties

#### 1. Introduction

White organic light-emitting diodes (WOLEDs) have received great attentions because of their potential applications in full-color displays, backlights, and lighting [1–5]. In the last decades, the deposited white-light small organic molecule diodes were investigated utilizing doping systems, however, it was not effective for large-area displays owing to the inevitable phase separation and complicated fabrication process [6–7]. Meanwhile, the polymer blending systems [8–11] with strong cross-linking by wet-process were developed for large-area displays, which still faced the problem of phase separation that could decrease the electroluminescent (EL) performance. Therefore, single white-light polymers with excellent EL performance were investigated, such as single linear polymers [12–14], single multi-branched fluorescent polymers [15–18] and single polymers with various fluorescent units [19–21]. Among these polymers, single multi-branched fluorescent polymers with globular features had improved EL properties by reducing intermolecular interaction; and single fluorescent/phosphorescent linear polymers which, with a wonderful prospect, incorporated heavy metal complexes into the  $\pi$ -conjugation polymers via covalent bonds, could simultaneously utilize the spin-symmetric triplets and spin-antisymmetric singlets with the ratio of 3:1, as theoretically and experimentally demonstrated [22–23].

Recently, single-color hyperbranched polymers with phosphorescent iridium(III) complexes as emitting cores were reported [24–26]. Hyperbranched structure had large steric hindrance, which effectively suppressed triplet-triplet annihilation, at the same time phosphorescent iridium(III) complexes were incorporated into the main chain that improved energy transfer efficiency. Therefore, hyperbranched structure was utilized to synthesize double-color white-light polymers [27–28]. Aimed at the control of energy transfer process and charge trapping in the EL process, white-light hyperbranched polymers were obtained. Meanwhile, the mixing of singlet and triplet energy levels could improve the utilization ratio of excitons. However, double-color white-light hyperbranched polymers

with red phosphorescent cores and blue fluorescent branches had imbalanced white-light EL spectra because of a loss of green emission.

Herein, we designed and synthesized a kind of triple-color hyperbranched polymer, using two novel iridium(III) complexes, i. e., green-light  $Ir(ppy)_2(pytzph)$  with high triplet energy ( $E_T$ ) level and red-light  $Ir(piq)_2(pytzph)$  with low- $E_T$ , as cores and polyfluorene (PF) as blue branches through Suzuki reaction. The green-light iridium(III) complexes could not only act as green-light emission but also a ladder for the triplet energy transfer in the hyperbranched polymer. Furthermore, photophysical properties and EL performance were investigated [29–33].

#### 2. Results and Discussion

#### 2.1. Design and Synthesis

The synthesis routes and chemical structures of phosphorescent iridium(III) complexes [34-35] are outlined in Scheme 1. In order to investigate the photophysical properties of emitting cores in the hyperbranched polymers, model complexes bis(2-phenylpyridine)[3-(2-pyridyl)-5-phenyl-1,2,4-triazole]iridium(III) [(Ir(ppy)<sub>2</sub>(pytzph)] and bis(1-phenylisoquinoline)[3-(2-pyridyl)-5-phenyl-1,2,4-triazole]iridium(III) [(Ir(piq)<sub>2</sub>(pytzph)] were synthesized that exhibited excellent photophysical properties owing to electron-transporting 1,2,4-triazole auxiliary ligand. The reaction monomer of phosphorescent iridium(III) complexes, green bis(2-(4-bromophenyl)pyridine)[3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazoleliridium(III) [Ir(ppyBr)<sub>2</sub>(pytzphBr)] bis(1-(4-bromophenyl) and red isoquinolinato)[3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazole]iridium(III) [Ir(piqBr)<sub>2</sub>(pytzphBr)], were synthesized on the basis of the synthesis route of heteroleptic iridium(III) complexes [36-38] with high yield (72% and 61%). The ligands (ppyBr and piqBr) and the compounds [Ir(ppyBr)2(pytzphBr), Ir(piqBr)2(pytzphBr), Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph)] were verified by <sup>1</sup>H NMR spectroscopy, <sup>13</sup>C NMR spectroscopy, elemental analysis and TOF-MS spectrometry.

Scheme 2 illustrates the synthesis routes and chemical structure of hyperbranched polymers, named PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=0, n=5; m=5, n=5 and m=25, n=5) were synthesized from 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**M1**), 9,9-dioctyl-2,7-dibromofluorene (**M2**), Ir(ppyBr)<sub>2</sub>(pytzphBr) (**M3**) and Ir(piqBr)<sub>2</sub>(pytzphBr) (**M4**) by one-pot Suzuki polycondensation. The feed ratios of the monomers were 1000: 998.5: 0: 1(m=0, n=5), 1000: 997: 1: 1(m=5, n=5) and 1000: 991: 5: 1(m=25, n=5), respectively. All synthesized polymers have higher yield (45%~69%)

with excellent solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), and toluene, which favors subsequent wet-processes for device fabrication. The chemical structures of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n were confirmed by <sup>1</sup>H NMR spectroscopy.

The number-average molecular weights  $(M_n)$  and weight-average molecular weights  $(M_w)$  of these hyperbranched polymers were determined by gel permeation chromatography (GPC). The  $M_n$  and  $M_w$  of synthesized polymers ranged from 10.41 to 13.62 and from 22.23 to 36.70, respectively, with polydispersity indices (PDIs) from 2.14 to 2.69. The data above indicate that both hyperbranched polymers have appropriate molecular weight and narrow distribution of molecular weight. The thermal properties were also studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. The hyperbranched polymers have high stability that the thermal decomposition temperature ( $T_d$ ) exceeds 390°C and the glass-transition temperature ( $T_g$ ) are 151, 133 and 140°C, respectively, higher than that of linear polymers [39–40] owing to their large steric hindrance of hyperbranched structure. The good thermal stability is in favor of forming excellent polymer films and realizing stability in the fabrication process of WOLEDs.

Scheme 1. Synthesis routes of red and green phosphorescent iridium(III) complexes.

Scheme 2. Synthesis routes of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

Table 1 Molecular weights and thermal properties of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

# 2.2. Optical Properties

In order to investigate the possibility of energy transfer in such three component emissions from single hyperbranched polymers, UV-vis absorption spectra and PL spectra of fluorescent PF and two phosphorescent chromophores [Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph)] are measured as shown in Fig. 1. The absorption band of Ir(piq)<sub>2</sub>(pytzph) between 410 and 550 nm is assigned to  $S_0 \rightarrow {}^3MLCT$  transitions, which overlaps PF emission band among 410~550 nm. Similarly, the absorption spectrum of green Ir(ppy)<sub>2</sub>(pytzph) overlaps PF emission band at the region of 410~460 nm, smaller than the overlapped band of Ir(piq)<sub>2</sub>(pytzph). Therefore, more effective energy transfer occurs from blue PF segments to red Ir(piq)<sub>2</sub>(pytzph) than to green Ir(ppy)<sub>2</sub>(pytzph). All these results illustrate effective Förster energy transfer in the triple-color system that ensures high-quality white-light emission.

**Fig. 1.** The UV-vis absorption spectra and PL spectra of PF, Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) in diluted CHCl<sub>3</sub> solution.

The UV-vis absorption spectra and photoluminescence (PL) spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n in diluted CHCl<sub>3</sub> solution and solid films are shown in Fig. 2, and detailed data are summarized in Table 2. In diluted CHCl<sub>3</sub> solution, all hyperbranched polymers exhibit similarly the maximum absorption peaks at about 385 nm, assigned to the  $\pi$ - $\pi$ \* transitions of PF backbones (Fig. 2a). The absorption band of iridium(III) complexes have not been detected owing to the comparatively low content in these polymers and large distance between adjacent molecules in diluted CHCl<sub>3</sub> solution. In films (Fig. 2b), compared with in solution, the maximum absorption bands have a little red-shift and broader absorption band because the interaction between adjacent molecular chains enhances aggregation that results in inter- and intra-chains transition of delocalized  $\pi$ -election [25]. In PL spectra (Fig. 2a and 2b), the maximum emission peaks in diluted CHCl<sub>3</sub> solution of hyperbranched polymers are at 416, 439 nm and a shoulder peak at 470 nm, however, maximum emission peaks in films are located at 421, 437, 464, 498 and 616 nm. The emission peak at 437 nm is fairly stable in both solution and film owing to the large steric hindrance in the hyperbranched structure. While the emission peaks at 415 nm in solution has 5 nm red-shift compared to the film, meanwhile, the red emission at 616 nm appears in film. This phenomenon could be explained as follows. In diluted solution, adjacent molecules are dispersed in solvent forming disordered arrangement and Förster energy transfer is dominated by intra-molecular interaction. In films, the molecules are at high aggregation states which result in Förster energy transfer dominated by inter-molecular interaction. Compared with that of Ir(piq)<sub>2</sub>(pytzph), the red emission peak (616 nm) from PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n has 18 nm red-shift owing to the large conjugacy for effective inter-molecular and intra-molecular Förster energy transfer [28]. Though the content of green iridium complexes increases in PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5, the green emission peak is still absent. Because green cores act not only as green emission units, but also as a channel of energy transfer from Ir(ppy)<sub>2</sub>(pytzph) to Ir(piq)<sub>2</sub>(pytzph). The fluorescence quantum efficiencies (QYs) in films are also investigated, as shown in Table 2. The QYs of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n(m=5, n=5 and m=25, n=5) are higher than that of PF-Ir(piq)<sub>2</sub>(pytzph)5 owing to the introduction of Ir(ppy)<sub>2</sub>(pytzph). Because Ir(ppy)<sub>2</sub>(pytzph) could capture the  $\pi$ -electron from singlet PF segments, at the same time interrupt the conjugacy of the PF segment and prevents energy transfer back from  $Ir(piq)_2(pytzph)$  to PF which is far away from the red  $Ir(piq)_2(pytzph)$  core [41,42].

**Fig. 2.** The UV-vis absorption spectra and PL spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n in 10<sup>-6</sup> mol/L CHCl<sub>3</sub> solution (a) and films (b).

 Table 2 The UV-vis and luminescence data, and electrochemical properties of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

Fig. 3. Phosphorescent spectra of Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) at 77 K in 2-methyltetrahydrofuran.

Fig. 3 shows phosphorescent spectra of Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) at 77 K, which could be used to calculate triplet energy levels [43,44]. The maximum emission peak of Ir(ppy)<sub>2</sub>(pytzph) locates at 481 nm with  $E_T$  of 2.58 eV. Similarly,  $E_T$  of Ir(piq)<sub>2</sub>(pytzph) is 2.12 eV, lower than that of Ir(ppy)<sub>2</sub>(pytzph), which could restrain energy transfer back from Ir(piq)<sub>2</sub>(pytzph) to Ir(ppy)<sub>2</sub>(pytzph) and improve the utilization of excitons. Energy transfer sketch of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph) is shown in Fig. 4. Some excitons from excited PF segments transfer to Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) by intersystem crossing (ISC) as a result of the spin-orbit coupling of heavy metals in PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) (Fig. 4a). Excitons from excited Ir(ppy)<sub>2</sub>(pytzph) would directly transfer to the triplet energy level of PF (2.15 eV) by Dexter energy transfer [45,46], and then excitons would be trapped by Ir(piq)<sub>2</sub>(pytzph) which could utilize both singlet and triplet excitons to realize red emission. Meanwhile, most excited PF segments would realize blue emission, and some excited Ir(ppy)<sub>2</sub>(pytzph) would achieve triple-color white-light emission. While in PF-Ir(piq)<sub>2</sub>(pytzph)5 (Fig. 4b), excitons from excited PF segments are directly transfer to Ir(piq)<sub>2</sub>(pytzph)5 by ISC which could realize red emission. Most excited PF segments would realize blue emission is achieved.

**Fig. 4.** Energy transfer sketch in PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) (a) and PF-Ir(piq)<sub>2</sub>(pytzph)5 (b).

# 2.3. Thin film morphologies

The morphologies of PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 film and annealed film coated on ITO glasses were investigated by atomic force microscopy (AFM), as shown in Fig. 5a, b. The film and annealed film show small roughness with the root mean square (RMS) of 2.21 nm and 1.79 nm ( $5 \times 5 \mu m^2$ ), respectively. The annealed film has smaller RMS than the film owing to the molecular peristalsis in the process of annealing treatment. Though the Ir(ppy)<sub>2</sub>(pytzph) has three-dimensional configuration, the film morphologies has not been influenced owing to the low content and the hyperbranched structure [47]. In addition, the UV-vis absorption spectra and PL spectra of the annealed PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 films are shown in Fig 5c. The maximum absorption peak of the

annealed film is located at 381 nm with a 4 nm blue-shift than the film, and the emission peaks are located at 432, 450, 483, 517 and 615 nm. Compared to the film without annealing treatment, the emission peak at 421 nm disappears because the molecular peristalsis occurs in the process of annealing treatment that results in the ordered arrangement of the molecules.

**Fig. 5.** AFM 3D images  $(5\times5 \ \mu\text{m}^2)$  of PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 film (a) and film annealed at 100°C for 15 min (b) coated on ITO glasses; and the UV-vis absorption spectra and PL spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 film and film annealed at 100°C for 15 min (c) coated on quartz glasses.

#### 2.4. Electroluminescent Properties

To investigate electroluminescent (EL) performances in devices of synthesized hyperbranched polymers, typical single-layer white-light emitting devices with a configuration of indium-tin oxide (ITO)/ poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (80 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated. The LUMO level of TPBi (-2.8 eV) could match with the LUMO level of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (around -2.96 eV) that makes the electrons injection and transmission easier. The HOMO level of the PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (around -5.84 eV) is reduced 0.64 eV than PEDOT:PSS (-5.2 eV) with a small injection barrier. The EL spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n nearly cover the whole visible light region, are shown in Fig. 6a, b and c, and the maximum emission peaks and CIE coordinates are listed in Table 3. In EL spectra, all emission peaks of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n are located at about 432, 460, 492 and 520 nm with a red emission at 624 nm. However, the emission peaks of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) at 488 nm and 520 nm enhance with increasing driving voltage, which could be attributed to the introduction of Ir(ppy)<sub>2</sub>(pytzph). With increasing voltage, blue emission of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) decreases proving that more effective energy transfer exists, but PF-Ir(piq)<sub>2</sub>(pytzph)5 has no obvious difference. In EL process, carriers are injected from both cathode and anode and charge trapping mechanism dominates gradually [48,49]. At low driving voltages, effective Förster energy transfer could occur from PF to Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) in PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5), and captured excitons in Ir(ppy)<sub>2</sub>(pytzph) could also transfer to Ir(piq)<sub>2</sub>(pytzph) through PF segments, which results in weakened green emission at low driving voltages. In PF-Ir(piq)<sub>2</sub>(pytzph)5, effective Förster energy transfer is just from PF to Ir(piq)<sub>2</sub>(pytzph). As the driving voltage increases, direct charge trapping of Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph)

enhances because of abundant injected electrons and holes. Therefore, charge trapping of green core is dominated that green-emission by radiative transition could be observed. The CIE coordinates of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=0, n=5; m=5, n=5 and m=25, n=5) are shown in Fig. 6d. PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 has a better CIE coordinate around (0.32, 0.34), closer to the standard white emission (0.33, 0.33) than PF-Ir(piq)<sub>2</sub>(pytzph)5 owing to the introduction of green-emission. Similarly, PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5 also has a better CIE around (0.31, 0.34) located in the white-emission region.

**Fig. 6.** EL spectra at different driving voltages of PF-Ir(piq)<sub>2</sub>(pytzph)5 (a), PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 (b) and PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (o), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph)5 (c); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (c), PF-Ir(piq)<sub>2</sub>(pytzph

 $Ir(ppy)_2(pytzph)5$ - $Ir(piq)_2(pytzph)5$  ( $\triangle$ ) and PF- $Ir(ppy)_2(pytzph)25$ - $Ir(piq)_2(pytzph)5$  ( $\Box$ ).

**Fig. 7.** Luminance-current density-current efficiency (L-J-CE) curves of the devices from PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

Table 3 EL performances of the synthesized PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

The luminance-current density-current efficiency (L-J-CE) curves of the devices are shown in Fig. 7 and the detailed data are listed in Table 3. PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) have better EL performance. PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 achieves the best EL performance with a turn-on voltage of 5.6 V, the maximum luminance of 13 415 cd/m<sup>2</sup> and the maximum current efficiency (CE<sub>max</sub>) of 11.49 cd/A. The fabricated devices in this work do not contain additional hole-transporting layers in addition to PEDOT:PSS and remains a little injection barrier which results in the high turn-on voltage. The maximum luminance of PF-Ir(piq)<sub>2</sub>(pytzph)5 is just 5 976 cd/m<sup>2</sup>, with CE<sub>max</sub> 1.29 cd/A, which proves that the introduction of phosphorescent green iridium(III) complexes in hyperbranched structure could effectively improve the EL performance. At the same time, in hyperbranched structure, iridium(III) complexes are encircled by PF branches, which effectively suppresses concentration quenching and triplet-triplet (T-T) annihilation. Therefore, the "roll-off" phenomenon could be restrained. However, the concentration of Ir(ppy)<sub>2</sub>(pytzph) in PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5 is too high that the EL efficiencies decline with increasing current density to some extent.

Compared with double-color hyperbranched polymers [27], triple-color phosphorescent hyperbranched polymers exhibit optimized EL performance by the introduction of phosphorescent green-light Ir(ppy)<sub>2</sub>(pytzph). These results indicate that triple-color phosphorescent hyperbranched polymers would be promising candidates for display and

solid-state lighting purpose. Therefore, investigations of triple-color phosphorescent hyperbranched polymers are on the way to improve EL performance further.

#### 3. Conclusion

In conclusion, we have succeeded in synthesizing a kind of triple-color hyperbranched polymers, incorporating green Ir(ppy)<sub>2</sub>(pytzph) and red Ir(piq)<sub>2</sub>(pytzph) as the cores and blue PF segments as the backbones. The large steric hindrance of hyperbranched structure effectively restrains triplet-triplet (T-T) annihilation of phosphorescent iridium(III) complexes and largely improves the energy transfer efficiency. Single-layer devices of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)m were fabricated with excellent EL performance. PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 exhibits better white EL spectra with a CIE coordinate of (0.32, 0.34), and the maximum CE of 11.49 cd/A. These excellent results demonstrate that triple-color phosphorescent hyperbranched polymers could achieve preferable EL performance that should be deeply investigated in the future.

# 4. Experimental Section

#### 4.1. Materials

All the raw materials were purchased from Energy Chemical companies and used without further purification. The solvents used for the synthesis of the intermediates and end-products were purified by routine procedures under nitrogen protection. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**M1**), 9,9-dioctyl-2,7-dibromofluorene (**M2**) were synthesized according to Reference [50,51].

#### 4.1.1. Synthesis of 2-(4-bromophenyl)-pyridine (L1).

2-Bromopyridine (1.57 g, 10 mmol) and 4-bromophenylboronic acid (2.01 g, 10 mmol) were added into the solution of toluene (20 mL) and ethanol (5 mL), and stirred under nitrogen atmosphere. Then tetrakis (triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (34.68 mg, 0.03 mmol) and an aqueous solution of 2 mol/L Na<sub>2</sub>CO<sub>3</sub> (8 mL) was added to the stirred mixture. The reaction mixture was then stirred at 70 °C for 8 h. After cooling to room temperature, the reaction mixture was extracted using dichloromethane/water, and then the organic layer was separated and concentrated. Finally, the crude product was purified by column chromatography using the eluent hexane/ethyl acetate (7:1). The resulting transparent solid product was achieved with a yield of 72% (1.48 g). M<sub>p</sub>:  $63\sim64$  °C. <sup>1</sup>H NMR: (600 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)= 6.9 (d, J=4.8 Hz, 1 H), 7.88 (dt, J<sub>1</sub>=8.4 Hz, J<sub>2</sub>=2.4 Hz, J<sub>3</sub>=1.8

Hz, 2 H), 7.75 (dd,  $J_1$ =7.8 Hz,  $J_2$ =1.8 Hz, 1 H), 7.70 (dt,  $J_1$ =7.8 Hz,  $J_2$ =0.6 Hz, 1 H), 7.60 (dt,  $J_1$ =8.4 Hz,  $J_2$ =2.4 Hz,  $J_3$ =1.8 Hz, 2 H), 7.25 (ddd,  $J_1$ =7.2 Hz,  $J_2$ =4.8 Hz,  $J_3$ =1.2 Hz, 1 H). <sup>13</sup>C NMR: (600 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)= 156.38, 149.91, 138.38, 137.00, 132.00, 128.59, 123.57, 122.56, 120.42. Element Anal. Calcd (%): C, 56.44; H, 3.44; N, 5.98. Found (%): C, 56.28; H, 3.33; N, 5.99.

#### 4.1.2. Synthesis of 1-(4-bromophenyl)-isoquinoline [38] (L2).

1-Chloroisoquinoline (1.63 g, 10 mmol), 4-bromophenylboronic acid (2.00 g, 10 mmol) and tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (34.68 mg, 0.03 mmol) were dissolved in the mixed solution of degassed toluene (20 mL) and ethanol (5 mL). Then an aqueous solution of 2 mol/L Na<sub>2</sub>CO<sub>3</sub> (8 mL) was added to the stirred mixture. Subsequently, the resulting mixture was slowly heated to 94°C and stirred overnight. After cooling to room temperature, the reaction mixture was washed with water, dried under anhydrous magnesium sulfate. Finally, the solvent was removed and the residue was purified by column chromatography (silica gel, dichloromethane/hexane=1:4). A white needle crystal was isolated with a yield of 78% (2.21 g). M<sub>p</sub>: 80~85°C. <sup>1</sup>H NMR: (600 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)= 8.61 (d, J=5.4 Hz, 1 H), 7.98 (d, J=3 Hz, 2 H), 7.74-7.53 (m, 7 H). <sup>13</sup>C NMR: (600MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)= 159.6, 142.4, 138.7,137.0, 131.7, 130.3, 127.5, 127.3, 126.7, 123.2, 120.3. Element Anal. Calcd (%): C, 63.40; H, 3.55; N, 4.93. Found (%): C, 63.47; H, 3.75; N, 4.86.

4.1.3. Synthesis of 3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazole (L5).

2-Cyanopyridine(2.08 g, 20 mmol) and hydrazine monohydrate (1.06 g, 21 mmol) were dissolved in ethanol (~5 mL) in nitrogen. Then the mixture solution was stirred for 12 h in ice-bath. After that, the solvent was removed by reducing pressure. Subsequently, the crude products were washed by diethyl ether and dried, then the needle solid was achieved without further purification, named (pyridine-2-yl)amidrazone. (Pyridine-2-yl)amidrazone (1.36 g, 10 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.59 g, 15 mmol) were added into the mixture solution (60 mL) of THF and N,N-dimethylacetamide (DMAC) (1:2). The mixture was stirred at 0°C for 15 min. Then 4-bromobenzoyl chloride (2.19 g, 10 mmol) was added and the reaction mixture was stirred for another 12 h. Then, the crude products were washed by water, filtered and dried. Finally, the white solid was added into anhydrous ethylene glycol (30 mL) and heated to 190°C for 4 h under nitrogen atmosphere. After cooling to room temperature, the reaction solution was filtered, washed by water and dried. A white cotton-shaped solid without further purification was achieved with a yield of 63% (1.89 g). M<sub>p</sub>: 239~242°C. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)= 12.18 (s, 1 H), 8.72 (d, J=4.2 Hz,

1 H), 8.29 (d, J=8.4 Hz, 1 H), 8.09 (d, J=8.4 Hz, 2 H), 7.90 (dt, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=1.8 Hz, 1 H), 7.61 (d, J=8.4 Hz, 2 H), 7.43 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=3.6 Hz, 1 H). <sup>13</sup>C NMR: (400 MHz, CDCl<sub>3</sub>): δ(ppm)=162.58, 155.02, 149.51, 145.94, 137.59, 131.80, 129.88, 128.07, 125.16, 123.63, 121.66. Element Anal. Calcd (%): C, 51.85; H, 3.01; N, 18.60. Found (%): C, 51.25; H, 3.33; N, 18.39.

#### 4.1.4. Synthesis of 3-(2-pyridyl)-5-phenyl-1,2,4-triazole (L5').

(Pyridine-2-yl)amidrazone (1.36 g, 10 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.59 g, 15 mmol) were added into the mixture solution (60 mL) of THF and N,N-dimethylacetamide (DMAC) (1:2) under nitrogen atmosphere. The mixture was stirred at 0°C for 15 min. Then benzoyl chloride (1.41 g, 10 mmol) was added and the reaction mixture was stirred for another 15 h. Then, the crude products were washed by water, filtered and dried. Finally, the white solid was added into anhydrous ethylene glycol (30 mL) and heated to 190°C for 5 h under nitrogen atmosphere. After cooling to room temperature, the reaction solution was filtered, washed by water and dried. A white needle-shaped solid without further purification was achieved with a yield of 67% (1.48 g). M<sub>p</sub>: 215~219°C. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)=12.71(s, 1 H), 8.77 (d, J=4.8 Hz, 1 H), 8.34 (d, J=8 Hz, 1 H), 8.23 (d, J=6.8 Hz, 2 H), 7.91 (dt, J<sub>1</sub>=7.6 Hz, J<sub>2</sub>=1.6 Hz, 1 H), 7.52-7.41 (m, 4 H). <sup>13</sup>C NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)=163.38, 155.22, 149.66, 146.43, 137.76, 130.97, 129.58, 128.80, 126.68, 125.18, 121.95. Element Anal. Calcd (%): C, 70.26; H, 4.54; N, 25.21. Found (%): C, 70.75; H, 4.68; N, 24.78.

# 4.1.5. Synthesis of bri(2-(4-bromophenyl)pyridine)[3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazole]iridium (III) (Ir(ppyBr)<sub>2</sub>(pytzphBr): M3).

Iridium trichloride hydrate (352 mg, 1.0 mmol), 2-(4-bromophenyl)-pyridine (515 mg, 2.2 mmol), 2ethoxyethanol (21 mL) and water (7 mL) were added into a two-neck flask (50 mL) under nitrogen atmosphere. The mixture was stirred and refluxed for 15 h. After cooling to room temperature, more water was added and yellow precipitate came into being. The yellow chloride-bridged dimer complexes were filtered and washed by water and ethanol, and then dried. The chloride-bridged dimer complexes (228 mg, 0.2 mmol) were mixed with 3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazole (135 mg, 0.44 mmol) and Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4 mmol) in degassed 2ethoxyethanol (16 mL). The mixture was stirred at 135 °C under nitrogen atmosphere for 24 h. After cooling to room temperature, more water was added into the mixture. Then the green precipitate was washed by water, filtered and dried. Finally, the precipitate was purified by column chromatography (silica gel, dichloromethane/petroleum ether=1:10) to get green powder with a yield of 39% (150 mg). <sup>1</sup>H NMR: (600 MHz, (CD<sub>3</sub>)<sub>2</sub>OS):  $\delta$ (ppm)= 8.23 (t, J=6.6 Hz, 2 H), 8.16 (d, J=7.8 Hz, 1H), 8.06 (t, J=6.6 Hz, 1 H), 7.90 (t, J=7.8 Hz, 2 H), 7.86 (d, J=8.4 Hz, 3 H), 7.82 (d, J=8.4 Hz, 1 H), 7.65 (d, J=5.4 Hz, 1 H), 7.60 (t, J=7.2 Hz, 2H), 7.24 (d, J=8.4 Hz, 2H), 7.41(t, J=6 Hz, 1 H), 7.25 (t, J=7.2 Hz, 1 H), 7.17-7.21 (m, 2H), 7.12 (dd, J<sub>1</sub>=8.4 Hz, J<sub>2</sub>=1.8 Hz, 1 H), 6.21 (d, J=1.8 Hz, 1 H), 6.15 (d, J=1.3 Hz, 1 H). Element Anal. Calcd (%): C, 43.86; H, 2.31; N, 8.77. Found (%): C,44.35; H, 2.60; N, 8.49. TOF-MS, measured, 956.75, calcd, 955.91.

4.1.6. Synthesis of bri(1-(4-bromophenyl)-isoquinoline)[3-(2-pyridyl)-5-(4-bromophenyl)-1,2,4-triazole]iridium (III) (Ir(piqBr)<sub>2</sub>(pytzphBr): M4).

Iridium trichloride hydrate (352 mg, 1 mmol), 1-(4-bromophenyl)-isoquinoline (622 mg, 2.2 mmol), degassed 2ethoxyethanol (21 mL) and water (7 mL) were all added into a two-neck flask (50 mL). The mixture was stirred and refluxed under nitrogen atmosphere for 15 h, and then cooled to room temperature. A red precipitate of the chloride-bridged dimer complexes were collected after adding more water. Subsequently, the red solid was filtered, washed by ethanol and dried. The chloride-bridged dimer complexes (316 mg, 0.2 mmol), 3-(2-pyridyl)-5-(4bromophenyl)-1,2,4-triazole (135 mg, 0.44 mmol) and Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4 mmol) were dissolved in degassed 2ethoxyethanol (16 mL). The mixture was stirred at 130°C for 24 h. After cooling to room temperature, the red solution was washed by water and filtered, then the precipitate was dried. Finally, the red precipitate was purified by column chromatography (silica gel, dichloromethane/ petroleum ether=1:8) to get red powder with a yield of 34% (144 mg). <sup>1</sup>H NMR: (600 MHz, (CD<sub>3</sub>)<sub>2</sub>OS):  $\delta$ (ppm)= 9.01-8.96 (m, 2 H), 8.35 (d, J=8.4 Hz, 1 H), 8.32 (d, J=9 Hz, 1 H), 8.21 (d, J=8.4 Hz, 1 H), 8.11-8.05 (m, 3 H), 7.92-7.88 (m, 4 H), 7.86 (d, J=9 Hz, 1 H), 7.73 (d, J=6 Hz, 1 H), 7.66 (d, J=6.6 Hz, 1 H), 7.65 (d, J= 7.8 Hz, 1 H), 7.59 (d, J=6.6 Hz, 1 H), 7.56 (d, J=6 Hz, 1 H), 7.53 (d, J=8.4 Hz, 1 H), 7.43 (ddd, J<sub>1</sub>=7.2 Hz, J<sub>2</sub>=5.4 Hz, J<sub>3</sub>=1.2 Hz, 1 H), 7.32 (dd, J<sub>1</sub>=9 Hz, J<sub>2</sub>=2.4 Hz, 1 H), 7.25 (dd, J<sub>1</sub>=9 Hz, J<sub>2</sub>=2.4 Hz, 1 H), 6.39 (d, J=1.8 Hz, 1 H), 6.29 (d, J=2.4 Hz, 1 H). Element Anal. Calcd (%): C, 48.79; H, 2.48; N, 7.94. Found (%): C, 49.27; H, 2.86; N, 6.53. TOF-MS, measured, 1056.98, calcd, 1055.94.

 $4.1.7. \ Synthesis \ of \ bri(2-phenylpyridine) [3-(2-pyridyl)-5-phenyl-1,2,4-triazole] iridium \ (III) \ (Ir(ppy)_2(pytzph): M3'). \ M3') \ (III) \ (Ir(ppy)_2(pytzph): M3') \ (III) \ (III) \ (Ir(ppy)_2(pytzph): M3') \ (III) \ (Ir(pytzph): M3') \ (III) \ (III) \ (III) \ (Ir(pytzph): M3') \ (III) \ (III) \ (Ir(pytzph): M3') \ (III) \ (III) \ (Ir(pytzph): M3') \ (III) \ (I$ 

Iridium trichloride hydrate (352 mg, 1.0 mmol), 2-phenylpyridine (341 mg, 2.2 mmol), 2-ethoxyethanol (21 mL) and water (7 mL) were added into a two-neck flask (50 mL) under nitrogen atmosphere. The mixture was stirred and refluxed for 12 h. After cooling to room temperature, more water was added and yellow precipitate came into being. The yellow chloride-bridged dimer complexes were filtered, washed by water and ethanol, and then dried. The chloride-bridged dimer complexes (214 mg, 0.2 mmol) was mixed with 3-(2-pyridyl)-5-phenyl-1,2,4-triazole

(98 mg, 0.44 mmol) and Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4 mmol) in degassed 2-ethoxyethanol (16 mL). The mixture was stirred at 130°C under nitrogen atmosphere for 20 h. After cooling to room temperature, the green crude products were washed by water, filtered and dried. Then the precipitate was purified by column chromatography (silica gel, dichloromethane/petroleum ether=1:12) to get the green powder with a yield of 51% (147 mg). <sup>1</sup>HNMR: (600 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)=8.17 (dd, J<sub>1</sub>=7.8 Hz, J<sub>2</sub>=15.6 Hz, 3 H), 8.03 (dt, J<sub>1</sub>=1.8 Hz, J<sub>2</sub>=7.8 Hz, 1 H), 7.93 (dd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=8.4 Hz, 1 H), 7.87-7.82 (m, 3 H), 7.80 (dd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=7.8 Hz, 1 H), 7.76 (d, J=4.8 Hz, 1 H), 7.63-7.58 (m, 2 H), 7.37-7.30 (m, 3 H), 7.26 (t, J=7.2 Hz, 1 H), 7.18 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 7.13 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.95 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=6 Hz, J<sub>3</sub>=7.2 Hz, 1 H), 6.75 (ddd, J<sub>1</sub>=0.6 Hz, J<sub>2</sub>=1.8 Hz, J<sub>3</sub>=8.4 Hz, 2 H). Element Anal. Calcd (%): C, 58.24; H, 3.49; N, 11.64. Found: C, 57.87; H, 3.89; N, 10.98. TOF-MS, measured, 723.04, calcd, 722.18.

4.1.8. Synthesis of bri(1-phenylisoquinoline)[3-(2-pyridyl)-5-phenyl-1,2,4-triazole]iridium (III) (Ir(piq)<sub>2</sub>(pytzph): **M4'**).

Iridium trichloride hydrate (352 mg, 1 mmol), 1-phenylisoquinoline (451 mg, 2.2 mmol), degassed 2ethoxyethanol (21 mL) and water (7 mL) were all added into a two-neck flask (50 mL). The mixture was stirred and refluxed under nitrogen atmosphere for 12 h, and then cooled to room temperature. A red precipitate of the chloride-bridged dimer complexes was collected after adding more water. Subsequently, the red solid was filtered, washed by ethanol and dried. The chloride-bridged dimer complexes (254 mg, 0.2 mmol), 3-(2-pyridyl)-5-phenyl-1,2,4-triazole (98 mg, 0.44 mmol) and Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4 mmol) were dissolved in degassed 2-ethoxyethanol (16 mL). The mixture was stirred at  $130^{\circ}$ Cfor 20 h. After cooling to room temperature, the red solution was washed by water and filtered, then the precipitate was dried. Finally, the red precipitate was purified by column chromatography (silica gel, dichloromethane/petroleum ether=1:4) to get the red powder with a yield of 56% (184 mg). <sup>1</sup>H NMR: (600 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm)=9.04-8.95 (m, 2 H), 8.33 (t, J=7.8 Hz, 2 H), 8.20 (d, J=1.8 Hz, 1 H), 8.06-7.99 (m, 3 H), 7.92 (d, J=7.2 Hz, 2 H), 7.88-7.81 (m, 4 H), 7.64 (dd, J<sub>1</sub>=6.6 Hz, J<sub>2</sub>=10.8 Hz, 2 H), 7.56 (dd, J<sub>1</sub>=6.6 Hz, J<sub>2</sub>=18.6 Hz, 2 H), 7.49 (d, J=6 Hz, 1 H), 7.37-7.29 (m, 3 H), 7.26 (t, J=7.2 Hz, 1 H), 7.09 (dt, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=8.4 Hz, 1 H), 7.02 (dt, J<sub>1</sub>=1.2 Hz, J<sub>2</sub>=7.8 Hz, 1 H), 6.90 (t, J=6.6 Hz, 1 H), 6.76 (t, J=7.8 Hz, 1 H), 6.33 (d, J=7.2 Hz, 1 H), 6.25 (d, J=7.2 Hz, 1 H). Element Anal. Calcd (%): C, 62.83; H, 3.56; N, 10.22. Found: C, 61.72; H, 3.89; N, 10.78. TOF-MS, measured, 821.95, calcd, 822.21.

4.2. General procedure for polymerization.

Under nitrogen atmosphere, the reactive monomers **M1**, **M2**, **M3** and **M4** with different ratios (1000:998.5:0:1, 1000:997:1:1 and 1000:991:5:1) were dissolved in toluene (20 mL). The mixture was stirred for 30 min at room temperature. Then catalyst of Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol%) was added to the reaction mixture and the mixture was continually stirred. Subsequently, methyl trioctyl ammonium chloride (Aliquat 336) and aqueous solution of 2 mol/L K<sub>2</sub>CO<sub>3</sub> (10 mL) were added, and then the mixture was slowly heated to the refluxing temperature for 60 h. After that, the polymers were capped by adding benzeneboronic acid (20 mg) with extra reaction for 12 h, and then bromobenzene (0.2 mL) was added with continuous reaction for another 12 h. Finally, the whole reaction solution was cooled to room temperature and washed by water, and then the organic layer was evaporated to a certain concentration and poured into the stirred methanol (300 mL). Subsequently, the precipitate was collected by filtration and purified by soxhlet extraction with acetone to remove the small molecules and catalyst residue. The crude products were purified by column chromatography (silica gel, dichloromethane/THF=15:1), and the pure solid powder was achieved.

# PF-Ir(piq)<sub>2</sub>(pytzph)5

**M1**(642.6 mg, 1 mmol), **M2** (547.6 mg, 0.9985 mmol), and **M4** (1.05864 mg, 0.001 mmol) were used for polymerization with a yield of 49% (381 mg). <sup>1</sup>HNMR: (600 MHz, CDCl<sub>3</sub>): δ(ppm)=7.84 (1 H, Ar-H), 7.73-7.63 (2 H, Ar-H), 2.13 (2 H, CH<sub>2</sub>), 1. 26-1.04 (10 H, 5 CH<sub>2</sub>), 0.90-0.73 (5 H, CH<sub>2</sub>, CH<sub>3</sub>).

#### PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5

**M1**(642.6 mg, 1 mmol), **M2** (546.8 mg, 0.997 mmol), **M3** (0.95591 mg, 0.001 mmol), and **M4** (1.05864 mg, 0.001 mmol) were used for polymerization with a yield of 64% (499 mg). <sup>1</sup>H NMR: (600 MHz, CDCl<sub>3</sub>): δ(ppm)= 7.84 (1 H, Ar-H), 7.73-7.64 (2 H, Ar-H), 2.11 (2 H, CH<sub>2</sub>), 1.28-1.04 (10 H, 5 CH<sub>2</sub>), 0.86-0.73 (5 H, CH<sub>2</sub>, CH<sub>3</sub>). *PF-Ir*(*ppy*)<sub>2</sub>(*pytzph*)25-*Ir*(*piq*)<sub>2</sub>(*pytzph*)5

**M1**(642.6 mg, 1 mmol), **M2** (543.5 mg, 0.991 mmol), **M3** (4.77955 mg, 0.005 mmol), and **M4** (1.05864 mg, 0.001 mmol) were added in the polymerization with a yield of 57% (445 mg). <sup>1</sup>H NMR: (600 MHz, CDCl<sub>3</sub>): δ(ppm)= 7.84(1 H, Ar-H), 7.74-7.62(2 H, Ar-H), 2.12(2 H, CH<sub>2</sub>), 1.26-1.06(10 H, 5 CH<sub>2</sub>), 0.92-0.76(5 H, CH<sub>2</sub>, CH<sub>3</sub>).

#### 4.3. Instruments and characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured using Bruker DXR 600 MHz or 400 MHz spectrometers with tetramethylsilane as internal reference in deuterated chloroform or dimethyl sulfoxide. Elemental analyses were

conducted on a Vario EL elemental analyzer, and TOF-MS analysis was performed on Bruker MALDI-TOF. The molecular weights of the PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n were determined by waters GPC 2410 using THF as eluent. TGA curves were recorded on a Netzsch TG 209 F3 at a heating rate of 10°Cmin under nitrogen flow. DSC curves were measured on TA Q2000 under nitrogen flow at a heating rate of 10°Cmin. UV-vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer in diluted CHCl<sub>3</sub> solution of 10<sup>-6</sup> mol/L and thin solid films coated on quartz plate by spin-coating process from 12 mg/mL toluene solution. The PL spectra were recorded on a Fluoromax-4 spectrophotometer in 10<sup>-6</sup> mol/L CHCl<sub>3</sub> solution or thin solid films with 365 nm excitation. The phosphorescent PL spectra were also measured by a Fluoromax-4 spectrophotometer at 77 K in 2-methyltetrahydrofuran. Cyclic voltammetry (CV) data were measured on the Autolab/PG STAT302 electrochemical workstation with a three-electrode cell in acetonitrile (0.1 mol/L) solution of tetrabutylammonium perchlorate as electrolyte at a scan rate of 50 mV/s at room temperature under nitrogen atmosphere. A film of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n was coated onto the working electrode of Pt plate and calomel electrode acted as the reference electrode at room temperature.

#### 4.4. Device fabrication

The electroluminescent devices with the configuration of ITO/PEDOT:PSS (40 nm)/polymers (80 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated with the following general procedure. ITO patterned glass substrates were pre-cleaned, followed by  $O_2$  plasma treatment for 8 min. In the glove boxes, PEDOT:PSS layer was spin-coated at 2000 rpm for 60 s, and then annealed for 20 min at 120°C The toluene solution (12 mg/mL) of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n was spin-coated onto the uniform PEDOT:PSS layer, yielding a 80 nm single emitting layer. Subsequently, the substrates were annealed at 100°C for 15 min. Finally, a 40 nm thick TPBi electron transporting layer, a 0.8 nm thick LiF layer and a 100 nm thick Al layer were deposited at pressures below  $10^{-4}$  Pa, separately. The current-voltage-luminescence characteristics of the devices were recorded using a combination of a Keithley source meter (model 2602) and a luminance meter. The EL spectra and CIE coordinates of the devices were analyzed with a spectra-scan PR655 spectrophotometer. All measurements were performed at room temperature.

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	$M_n$	$M_{\rm w}$		Feed ratio (mol%)		T <sub>d</sub>	$T_{g}$
Polymers	(×10 <sup>3</sup> )	(×10 <sup>3</sup> )	PDI	Ir(ppy) <sub>2</sub> (pytzph)	Ir(piq) <sub>2</sub> (pytzph)	(°C)	(°C)
PF-Ir(piq) <sub>2</sub> (pytzph)5	13.62	36.70	2.69	0	0.05	399	151
PF-Ir(ppy) <sub>2</sub> (pytzph)5-							
Ir(piq)2(pytzph)5	10.41	22.23	2.14	0.05	0.05	419	133
PF-Ir(ppy)2(pytzph)25-							
Ir(piq)2(pytzph)5	12.46	29.12	2.34	0.25	0.05	419	140

# Table 1 Molecular weights and thermal properties of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

 Table 2
 The UV-vis and luminescence data, and electrochemical properties of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

	So	Solution <sup>a</sup> (nm) Film(nm)			QY <sup>b</sup>	$E_g$	НОМО	LUMO
Polymers	$\lambda_{abs}$	$\lambda_{PL}$	$\lambda_{abs}$	$\lambda_{PL}$	(%)	(eV)	(eV)	(eV)
PF-Ir(piq) <sub>2</sub> (pytzph)5	387	417/439/468	386	422/438/464/494/618	10	2.90	-5.79	-2.89
PF-Ir(ppy) <sub>2</sub> (pytzph)5								
-Ir(piq) <sub>2</sub> (pytzph)5	385	416/439/469	385	421/437/464/494/616	19	2.88	-5.84	-2.96
PF-Ir(ppy) <sub>2</sub> (pytzph)25								
-Ir(piq) <sub>2</sub> (pytzph)5	386	417/439/470	386	420/437/465/498/618	15	2.90	-5.79	-2.89

<sup>a</sup> The solution was 10<sup>-6</sup> mol/L in CHCl<sub>3</sub>.

<sup>b</sup> The QYs were measured in films spin-coated from toluene solution.

		V <sub>turn-on</sub>	L <sub>max</sub>	CE <sub>max</sub>	
Polymers	$\lambda_{EL}(nm)$	(V)	$(cd/m^2)$	(cd/A)	CIE
PF-Ir(piq) <sub>2</sub> (pytzph)5	432/464/492/524/624	7.5	5 976	1.29	(0.20, 0.25)
PF-Ir(ppy) <sub>2</sub> (pytzph)5					
-Ir(piq) <sub>2</sub> (pytzph)5	432/460/488/520/624	5.6	13 415	11.49	(0.32, 0.34)
PF-Ir(ppy) <sub>2</sub> (pytzph)25					
-Ir(piq) <sub>2</sub> (pytzph)5	432/460/492/520/626	8.2	6 030	7.81	(0.31, 0.34)

Table 3 EL performances of	f the synthesized F	PF-Ir(ppy) <sub>2</sub> (pytzph)m-Ir	(piq) <sub>2</sub> (pytzph)n.
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Scheme 1. Synthesis routes of red and green phosphorescent iridium(II) complexes.



Feed Ratio(M1:M2:M3:M4): PF-Ir(piq)<sub>2</sub>(pytzph)5=1000:998.5:0:1; PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5=1000:991:5:1

PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5=1000:997:1:1





**Fig. 1.** The UV absorption spectra and PL spectra of PF, Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) in diluted CHCl<sub>3</sub> solution.



**Fig. 2.** The UV-vis absorption spectra and PL spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n in 10<sup>-6</sup> mol/L CHCl<sub>3</sub> solution (a) and films (b).



Fig. 3. Phosphorescent spectra of Ir(ppy)<sub>2</sub>(pytzph) and Ir(piq)<sub>2</sub>(pytzph) at 77 K in 2-methyltetrahydrofuran.





**Fig. 4.** Energy transfer sketch in PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n (m=5, n=5 and m=25, n=5) (a) and PF-Ir(piq)<sub>2</sub>(pytzph)5 (b).





**Fig. 5.** AFM 3D images  $(5 \times 5 \ \mu\text{m}^2)$  of PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 film (a) and film annealed at 100°C for 15 min (b) coated on ITO glasses; and the UV and PL spectra of PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 film and film annealed at 100°C for 15 min (c) coated on quartz glasses.





**Fig. 6.** EL spectra at different driving voltages of PF-Ir(piq)<sub>2</sub>(pytzph)5 (a), PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 (b); and the CIE coordinates (d) of PF-Ir(piq)<sub>2</sub>(pytzph)5 (○), PF-Ir(ppy)<sub>2</sub>(pytzph)5-Ir(piq)<sub>2</sub>(pytzph)5 (△) and PF-Ir(ppy)<sub>2</sub>(pytzph)25-Ir(piq)<sub>2</sub>(pytzph)5 (□).



**Fig. 7.** Luminance-current density-current efficiency (L-J-CE) curves of the devices from PF-Ir(ppy)<sub>2</sub>(pytzph)m-Ir(piq)<sub>2</sub>(pytzph)n.

- Triple-color white-light polymers were designed and synthesized.
- Polyfluorene acts as the backbone in the hyperbranched polymers.
- Green Ir(ppy)<sub>2</sub>(pytzph) and red Ir(piq)<sub>2</sub>(pytzph) act as the cores in the hyperbranched polymers.
- The introduction of green Ir(ppy)<sub>2</sub>(pytzph) has improved the electroluminescent performance.