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Synthesis and properties of hyperbranched fluorescence/phosphorescence hybrid copolymers for white polymer light emitting devices

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ABSTRACT

A series of hyperbranched fluorescence/phosphorescence hybrid copolymers with 9,9-dioctylfluorene and bis(1-phenyl-isoquinoline)(acetylacetonato)iridium(III) (**Ir(piq)₂acac**) as the branches and the three-dimensional structured spiro[3.3]heptane-2,6-dispirofluorene (**SDF**, 10 mol%) as the core have been synthesized by adjusting the feeding ratios of **Ir(piq)₂acac** (0.02–0.05 mol%). The copolymers showed good thermal and spectral stability, and amorphous film morphology because of the hyperbranched structures. The 2,7-substituted fluorenes of **SDF** were incorporated into the π -system of the polyfluorene branches, and remained the Förster resonance energy transfer (FRET) efficiency from fluorene segment to **Ir(piq)₂acac** unit. The copolymers exhibited efficient electroluminescent characters, and white-light emission was achieved in **PFSDf-Ir4** (**Ir(piq)₂acac** 0.04 mol%)-based single layer device with CIE coordinates at (0.30, 0.34), a maximum luminance of 6777.3 cd/m² (at 18.3 V), and a maximum current efficiency of 4.0 cd/A.

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1. Introduction

White polymer light-emitting devices (WPLEDs) have received great attention towards their potential applications in large-area full-color and flexible displays combined with a color filter, backlights and solid lighting sources.^{1–4} Among the common approaches used to generate white light in WPLEDs, single white-emitting polymer bearing either three primary colors (red (R), green (G) and blue (B)) or two complementary colors (generally blue (B) and orange (O)) emitting units incorporated into or attached to the backbone has advantages including relieved phase separation, controlled proportion of different emitting moieties, and easy fabrication process etc.⁵

The phosphorescent materials such as iridium complexes can realize theoretical 100% internal quantum efficiency due to the ability to harvest both singlet and triplet excitons to light.^{6,7} Therefore, phosphorescence molecules (usually as the narrow-band-gap chromophores) embedded into the fluorescence polymer chains (usually as the wide-band-gap emitters) could

effectively improve the electroluminescent (EL) performance of the WPLEDs.^{8–10} Furthermore, because the phosphorescence chromophores disperse into the polymer at the molecular level, the system can be regarded as homogeneous. The required content of the phosphorescence emitter was low (usually in the range of one ten thousandth to one thousandth (molar ratio)) because of the efficient energy transfer process.⁵ Thus, the triplet–triplet (T–T) annihilation of iridium complexes could be well-suppressed, and efficient EL performance could be expected.

Polyfluorenes (**PFs**) are shown to be the most promising blue light-emitting materials because of high photoluminescence quantum efficiency, and relatively good chemical and thermal stabilities.^{11,12} When orange-light-emitting iridium complex is dispersed to **PFs**, white light emission could be obtained by incomplete Förster resonance energy transfer (FRET) from the fluorene segment to the Ir complex unit.^{13,14} However, linear copolymers suffer from intermolecular interactions, which reduce the efficiency of the device.¹⁵ On the other hand, hyperbranched polymers with three-dimensional structure can prevent the aggregation of polymer chains, make the material form amorphous films with good quality, and increase the glass transition temperature (T_g) of the polymers.^{16–21} Recently, a number of

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hyperbranched electroluminescent polymers with the three principle colors (red,²² green^{23,24} and blue¹⁸) have been synthesized, and both emission efficiency and thermal stability were effectively improved with respect to their linear analogies.^{15,25–27} However, white-light-emitting hyperbranched polymers have rarely been reported.

In this paper, hyperbranched fluorescence/phosphorescence hybrid copolymers with 9,9-dioctylfluorene and bis(1-phenyl-isoquinoline)(acetylacetonato)iridium(III) (**Ir(piq)₂acac**) branches and spiro[3.3]heptane-2,6-dispirofluorene (**SDF**) core (10 mol%) were constructed. The three-dimensional-structured **SDF** exhibits great morphological stability and intense fluorescence,²⁸ and furthermore, its steric hindrance can prevent rotation of the adjacent aryl groups, which reduces close packing and intermolecular interactions between the chromophores in the solid-state.^{29,30} In order to obtain white-light emission, the orange light-emitting unit **Ir(piq)₂acac** was introduced with different contents from 0.02 mol% to 0.05 mol%. Such a highly branched framework may provide a highly efficient white-light electroluminescence.

2. Results and discussion

2.1. Synthesis and characterization

The synthesis of **Ir(Brpiq)₂acac** even reported used 1-chloroisoquinoline, 4-bromophenylboronic acid and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ as the orange light-emitting unit. The hyperbranched copolymers with 9,9-dioctylfluorene and **Ir(piq)₂acac** as the branches and **SDF** as the core were prepared by Suzuki polycondensation with yields ranging from 49% to 59% (Scheme 1). The feed molar ratios of the branching point **SDF** were 10% and **Ir(piq)₂acac** were varied from 0.02% to 0.05% relative to the fluorenyl units, and the corresponding hyperbranched copolymers were named as **PFSDf-Ir2** (**Ir(piq)₂acac** 0.02 mol%), **PFSDf-Ir3** (**Ir(piq)₂acac** 0.03 mol%), **PFSDf-Ir4** (**Ir(piq)₂acac** 0.04 mol%) and **PFSDf-Ir5** (**Ir(piq)₂acac** 0.05 mol%), respectively. All of the copolymers are readily soluble at room temperature in common organic solvents such as CHCl_3 , THF and toluene. The synthetic and structural results of the copolymers were summarized in Table 1. The ¹H NMR spectra of the copolymers were quite similar (Fig. S2, the proton signals of **Ir(piq)₂acac** were not detected because of its low content), revealing the similar backbone structures of the copolymers. Taking **PFSDf-Ir4** as an example (Fig. S3), the actual content of **SDF** was calculated by comparing the peak integral intensities of the proton signals of the spiro[3.3]heptane of **SDF** (δ 3.0–3.5) and the aromatic ring of fluorene (δ 7.4–8.0) of the copolymer (8.80:1), which was close to the feed ratio (8.25:1). The number-average molecular weights (M_n s) of the copolymers were all around 13000 with the polydispersity indexes (PDIs) ranging from 1.56 to 3.35. All of the copolymers exhibit good thermal stability with the onset decomposition temperatures (T_d , measured at a 5% weight loss) from 407 to 423 °C. DSC data reveals the glass transition temperatures (T_g s) of copolymers were all around 155 °C (Fig. S4, Supplementary data).

2.2. Photophysical properties

Fig. 1 shows the UV-visible absorption of **Ir(Brpiq)₂acac** and photoluminescence (PL) spectra of hyperbranched polyfluorene-spiro[3.3]heptane-2,6-dispirofluorene (**PFSDf**, **SDF** 10 mol%) copolymer in CHCl_3 solution at a concentration of 1.0×10^{-5} mol/L. There are two strong absorption peaks seated at 243 nm and 297 nm, which are mainly attributed to the spin-allowed ligand-centered (¹LC) state transitions. The weak absorption peaks seated at 345 nm are mainly assigned to the spin-allowed metal-to-ligand charge-transfer (¹MLCT) state transitions. The un conspicuous

absorption peak around 472 nm is mainly belonged to the spin-inhibited metal-to-ligand charge-transfer (³MLCT) state and ligand-centered (³LC) state transitions.³¹ It is obvious that the emission of copolymer **PFSDf** and the absorption spectrum of the Ir complex show good spectra overlap. Therefore, efficient FRET from the **PFSDf** to the Ir complex, and white-light emission can be expected by the combination of blue light-emitting from **PFSDf** and orange light-emitting from **Ir(piq)₂acac** through finely adjusting the content of Ir complex.

The normalized UV–vis absorption and PL spectra of the copolymers in CHCl_3 solution (10^{-5} mol/L) and thin film states are shown in Fig. 2. In dilute solution, all of the copolymers exhibit typical absorption and emission bands of **PF** with an absorption maximum around 373–379 nm, and emission peaks at 420, 440, and a shoulder peak at 474 nm. The presence of vibronic structure in the emission spectra indicates that the hyperbranched copolymers have rigid and well-defined backbone structures. The absorption and emission bands of **Ir(piq)₂acac** were not detected due to its comparatively low content (0.02–0.05 mol%) in the copolymers. In dilute solution, the energy transfer was exclusively intrachain.³²

In films, the copolymers exhibit UV–vis absorption bands at around 375 nm similar to those in dilute solution. In the PL spectra, the maximum emission bands of the copolymers are at about 420 and 440 nm, showing no obvious bathochromic shift with respect to those in dilute solution. This result indicates that the hyperbranched molecular structure can prevent the aggregation and the interaction of the copolymer chains efficiently. The emission band of **Ir(piq)₂acac** centered at 613 nm still can't be observed due to the low content of **Ir(piq)₂acac**, as a result of both intra- and interchain FRET from fluorene unit to **Ir(piq)₂acac**.^{22,33}

2.3. Film forming properties

The morphology of the spin-coated films of the copolymers was estimated by atomic force microscopy (AFM) at a tapping mode, and the images are shown in Fig. 3. All the films show smooth surface with small root-mean-square (RMS) values of 1.295, 1.670, 2.316 and 2.884 nm for **PFSDf-Ir2**, **PFSDf-Ir3**, **PFSDf-Ir4** and **PFSDf-Ir5**, respectively. The results indicate that the hyperbranched structure with three-dimensional-structured **SDF** branch point could provide a homogeneous morphology of spin-coating films, which could be favorable for the PLED fabrication.

2.4. Electroluminescence properties

Using the copolymers as emitting materials, single-layer PLEDs were fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/Copolymers (50 nm)/TPBi (35 nm)/LiF (1 nm)/Al (150 nm). The electroluminescent spectra of the devices are shown in Fig. 4a and the characteristics were summarized in Table 2.

Generally, all of the copolymers exhibit much broader EL spectra than their PL counterparts. At the voltage of 16 V, **PFSDf-Ir2** and **PFSDf-Ir3** both exhibit blue-light emitting and the broad peaks locate at the 452 nm and 484 nm, respectively. The spectrum of **PFSDf-Ir4** covers the visible light region with 400–700 nm and the main peaks locate at 425 and 548 nm, respectively. White-light emission is obtained with CIE coordinates located at (0.31, 0.35) (Fig. 4b). The emission peak of **PFSDf-Ir5** mainly locates at 533 nm and yellow-light emission is achieved. For all of the copolymers, the emission band around 540 nm may be from the excimer of **PFSDf** formed under the electric field.^{5,22,34–36} As the electrons and holes can be trapped on the Ir complex,²² the formation of the excimer may be induced by **Ir(piq)₂acac** under electric excitation.³⁵ As a result, the excimer emission intensity increased with the **Ir(piq)₂acac** contents. In **PFSDf-Ir5**, the emission from the **PFSDf**

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