

Synthesis and Properties of Electrophosphorescent Conjugated Polymers Containing Iridium Complexes in Polymer Backbone

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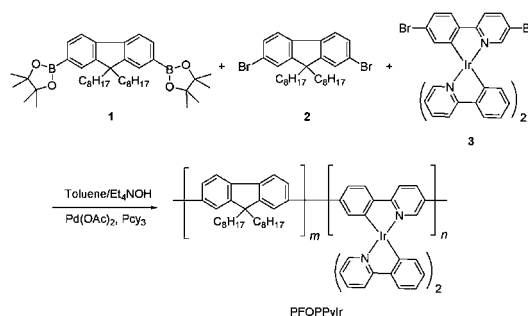
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A novel series of electrophosphorescent conjugated polyfluorenes (PFOPPyIr) based on (4,4'-dibromophenylpyridinato-*N,C*²)bis(2-phenylpyridinato-*N,C*²)iridium(III) were synthesized, in which the polymer main chains consist phenylpyridine ligand and fluorene segment with extended conjugation. The optical and electroluminescent properties of PFOPPyIr were investigated. A luminance efficiency of 3.80 cd/A and luminance of 1248 cd/m² were achieved.

Electrophosphorescent polymers with heavy metal complexes, such as iridium complex, in polymer main or side chains have attracted considerable attention because of their potential of getting higher efficiency by utilization of both singlet and triplet excitations combined with good solution processibility.¹ In addition, incorporating heavy metal complexes into polymer main or side chains can also reduce the aggregation and phase segregation that commonly happened in polymer/metal complex blending system in PLEDs. Incorporating iridium complexes into conjugated polymer main chains has been reported by several groups.^{2,3} For example, Sandee et al. incorporated green and yellow iridium complexes into a series of conjugated oligo- and polyfluorene by Suzuki polymerization.^{2b} Zhen et al. synthesized a series of fluorene- and carbazole-based polymers with incorporation of green-red iridium complex into polymer main chains.^{2c,2d} All these electrophosphorescent polymers are coordination polymers, where the polymer main chains are connected via coordination bond. The resulted polymer is not fully conjugated since the conjugation is broken on the metal site implying relatively low conductivity of this type polymer and high operating voltage.^{2c}

In this paper, we describe the novel conjugated PFOPPyIr polymers, in which fluorene segments and phenylpyridine ligands were incorporated into polymer backbones and iridium complexes attached to polymer backbones could not interrupt the fluorene-phenylpyridine conjugation. It is expected such copolymers should have relatively high conductivity due to the large conjugation length compared with these coordination polymers. Along with the relatively narrowed energy band gaps, lower operating voltage for devices from such copolymers was expected.

The polymers were synthesized by Suzuki polymerization reaction as shown in Scheme 1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**1**) and 2,7-dibromo-9,9-dioctylfluorene (**2**) were synthesized according to the literature methods.³ (4,4'-Dibromophenylpyridinato-*N,C*²)bis(2-phenylpyridinato-*N,C*²)iridium(III) (**3**)^{3a} was synthesized by the reaction of 4,4'-dibromophenylpyridine and (ppy)₂-Ir(μ -Cl)₂Ir(ppy)₂ under refluxing in glycerol. The structures of **1**, **2**, and **3** were confirmed by NMR spectroscopy and elemental



Scheme 1. Synthetic route of PFOPPyIr ($n = 0.5, 1, 2, 5,$ and 8 mol %, $m + n = 1$).

analysis. Pd-catalyzed coupling polymerization of **1**, **2**, and **3**, carried out in the presence of Et₄NOH under refluxing in toluene solution in argon atmosphere for 48 h, afforded PFOPPyIr as yellow fiber after pouring into methanol. The feed ratio of monomer **3** was 0.5, 1, 2, 5, and 8 mol %, respectively, and the corresponding polymers were named PFOPPyIr05, PFOPPyIr1, PFOPPyIr2, PFOPPyIr5, and PFOPPyIr8. All these polymers are soluble in THF, toluene, chloroform, etc. The molecular weight measured from gel permeation chromatography (GPC) against polystyrene standard showed the number-average molecular weight (M_n) from 6200 to 14600 with polydispersity (M_w/M_n) index from 1.3 to 2.4.

The optical properties of PFOPPyIr were investigated in solid film states. Absorption spectra in thin solid films are similar for all copolymers of different Ir content. For each polymer, the absorption spectrum displays a dominant band at around 384 nm in thin solid films. The band is assigned to π - π^* transitions of the PFO segments and the extended ppy ligands. This suggests that π - π^* transition of fluorene chains and the iridium complex cannot separated and that the fluorene chains and the extended ppy ligands form one conjugated entity with a common π - π^* singlet state (Figure 1a).

The PL spectra of PFOPPyIr in thin solid films were shown in Figure 1b. The films were excited at 325 nm in which the absorption of ¹MLCT and ³MLCT bands of phosphorescent segment do not fall;⁴ therefore, there should have no direct excitation from the phosphorescent segment. As shown in Figure 1b, the emission from PFO segment at around 464 nm decreased with increasing the content of iridium complex, while the emission from Ir complex segments (at around 597 nm) increased, which becomes dominant at more than 1 mol % of iridium complex in polymers. At about 5 mol % of iridium complex (PFOPPyIr5), the blue emission from PFO segments was almost completely quenched; only emission from iridium complexes could be observed. The transfer mechanism was assigned

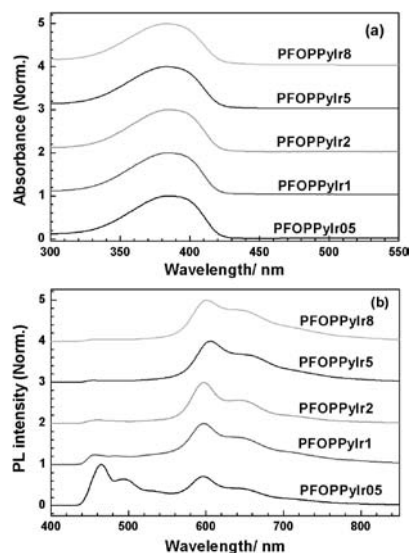


Figure 1. UV-vis (a) and PL (b) spectra of PFOPPyIr in thin solid film.

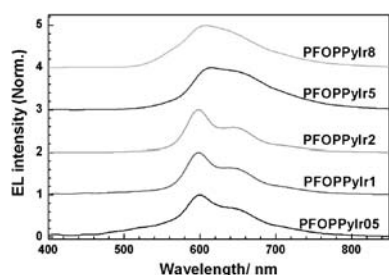


Figure 2. Normalized EL spectra of devices based on PFOPPyIr.

to the Förster energy transfer (FRET) from the PFO segments to the iridium cores.⁵

The electroluminescent properties of the polymers were investigated, and the EL devices based on PFOPPyIr with the device structures of ITO/PEDOT:PSS/PFOPPyIr/Ba/Al were fabricated. Figure 2 shows the electroluminescence spectra of these polymers, which peaked at around 600 nm. The emission from these devices is dominated by phosphorescent emission of iridium complexes which are almost identical in peak position and line-width for all polymers. Compared with PL spectra, even at 0.5 mol % of Ir complexes, the EL emission from PFO segments at around 460 nm was almost completely quenched. These results indicate that the dominant mechanisms for the EL emission in PFOPPyIr is charge trapping rather than FRET.^{2,3,6,7}

Among these polymers, PFOPPyIr2 showed the best device performance. The luminous efficiency (LE)–current density (J)–luminance (L) curves were shown in Figure 3. For PFOPPyIr2, the devices turn on at 6.4 V and a peak luminance of 1248 cd/m^2 was achieved at 15.2 V. These results indicate that operating voltage is substantially lower than those of the devices from copolymer of coordination type where conjugation of the copolymer was terminated by Ir complexes.^{2b,2c} The maximum EQE and maximum LE of the devices from PFOPPyIr2 are 2.79% and 3.80 cd/A , respectively.

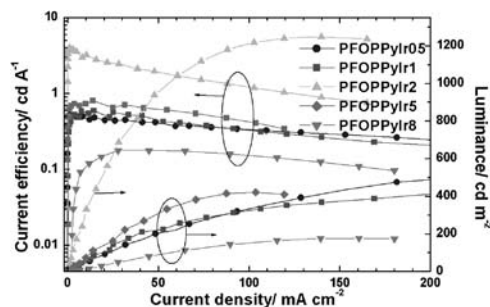


Figure 3. The luminous efficiency (LE)–current density (J)–luminance (L) curves based on PFOPPyIr.

In conclusion, a series of electrophosphorescent conjugated polyfluorene with Ir complexes in the polymer main chains with extended conjugation of fluorene and phenylpyridine ligand was synthesized. The optical properties of these copolymers were studied. The electroluminescent properties of these polymers were investigated, and the EL device based on PFOPPyIr2 with the device structure of ITO/PEDOT:PSS/PFOPPyIr2/Ba/Al has the maximum EQE of 2.79%, the maximum of LE of 3.80 cd/A and the maximum luminance of 1248 cd/m^2 . We have shown that the operating voltage of such device is much lower than that from the coordination polymer type. This is important for hand-held device application which requires low power consumption.

The authors are deeply grateful to the MOST of China (No. 2002CB613403) and the National Natural Science Foundation of China (No. 50433030) for financial support.

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