

# High-efficiency blue light-emitting electrophosphorescent device with conjugated polymers as the host

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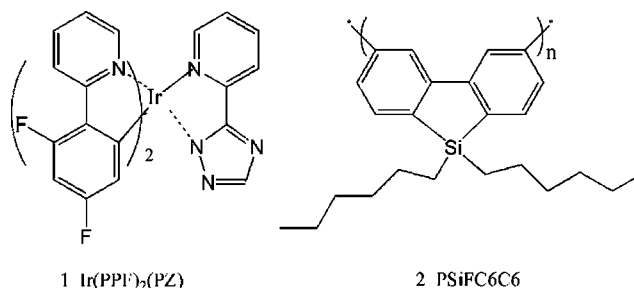
Highly efficient blue polymer phosphorescent organic light-emitting diode (PHOLED)-containing iridium(III) bis (2,4-difluorophenyl-2-pyridine) (2-(4H-1, 2, 4-triazol-3-yl)pyridine) [Ir(PPF)<sub>2</sub>(PZ)] complex embedded into wide-gap poly (9,9'-alkyl-3, 6-silafluorene) (PSiFC6C6) has been fabricated. Despite the significant quenching of photophosphorescence emission of the iridium complexes by a PSiFC6C6 host polymer, organic light-emitting diodes containing Ir(PPF)<sub>2</sub>(PZ) doped into the polymer host PSiFC6C6 emit high-efficiency blue light peaked at 462 nm. The maximal external quantum and luminance efficiencies were, respectively, 4.8% photons/electrons and 7.2 cd/A at 644 cd/m<sup>2</sup> and with Commission Internationale de l'Eclairage coordinates of (0.15,0.26). © 2006 American Institute of Physics. [DOI: 10.1063/1.2167788]

Organic phosphorescence has been one of the most important developments in the field of organic light-emitting diodes (OLEDs) in recent years.<sup>1,2</sup> Highly efficient organic phosphorescent OLEDs (PHOLEDs) based on cyclometalated iridium complexes are widely investigated.<sup>3,4</sup> These complexes contain a heavy metal atom with strong spin-orbit coupling that enhances intersystem crossing and mixes the singlet and triplet states. Of three primary red-green-blue colors, blue is the most important since many applications, such as full-color flat-panel displays and solid-state lightings are based on high-efficiency and long lifetime blue devices. Although blue light-emitting electrophosphorescent devices with small molecule hosts of high triplet energy level, such as N,N'-dicarbazolyl-4,4'-biphenyl, N, N'-dicarbazolyl-3,5-benzene,<sup>5</sup> 3,5-bis(9-carbazolyl) tetraphenylsilane,<sup>6</sup> yet the use of ultrahigh-energy gap organosilicon compounds<sup>7</sup> demonstrates high quantum efficiency (above 10%) for blue PHOLEDs, the studies of blue PHOLED with polymer host [polymer light-emitting devices (PLEDs)] are substantially behind small molecule PHOLED.<sup>8-12</sup> One of the main reason is short of suitable polymer hosts. In most of phosphorescent PLEDs, poly (N-vinylcarbazole) (PVK) has been used as wide-gap host.<sup>13-15</sup> Due to the exciplex emission of PVK (with emission around 420–430 nm), PVK is not really good host for blue-emitting complexes.<sup>13</sup> The highest external quantum efficiency of 1.3% has been reported for blue polymer PHOLEDs (PPHOLED) with iridium(III) bis[(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>] picolinate (FIrpic) doped into a PVK host.<sup>14</sup> The reported similar efficiency of the device made from bisorthometalated (phosphine) cyano iridium complex Ir(ppy)<sub>2</sub>P(n-Bu)<sub>3</sub>CN doped into PVK was 1.45%.<sup>15</sup>

In this letter, we report a high-efficiency blue light-emitting device made from a new wide-gap conjugated polymer PSiFC6C6 which was synthesized recently in our laboratory<sup>16</sup> and was used as host doped with a novel blue iridium complex iridium(III) bis (2,4-difluorophenyl-2-pyridine) (2-(4H-1, 2, 4-triazol-3-yl)pyridine) [Ir(PPF)<sub>2</sub>(PZ)]

shown in Scheme 1. High external quantum efficiency of 5% and good Commission Internationale de l'Eclairage (CIE) coordinate (0.15, 0.26) have been realized. To the best of our knowledge, this is the highest reported so far for polymer blue phosphorescent devices.

Recently, blue light-emitting iridium complex with triazolate-based ancillary ligand [iridium bis(4,6-difluorophenylpyridinato)-3-(trifluoromethyl)-5-(pyridin-2-yl)-1,2,4-triazolate (FIrtaz) and iridium bis(4,6-difluorophenylpyridinato)-5-(pyridin-2-yl)-1H-tetrazolate (FIrN4)] were reported.<sup>6</sup> Compared with the previously reported FIrN4 and FIrtaz the elimination of the CF<sub>3</sub> group in triazine ligand in our new complex Ir(PPF)<sub>2</sub>(PZ) leads to a stronger  $\sigma$ -donor character of the ligand. In results, the reaction of complex formation can be conducted with better yields under much milder conditions. Details of synthesis of Ir(PPF)<sub>2</sub>(PZ) will be reported elsewhere. The absorption spectra in dilute solution and in solid state of Ir(PPF)<sub>2</sub>(PZ) are shown in Fig. 1. The strong absorption bands at 254 nm and 281 nm, respectively, in the solution and in the film are assigned to  $\pi^* \leftarrow \pi$  transitions on the 2-phenylpyridine ligands. Figure 1 also shows the photoluminescence (PL) spectrum of Ir(PPF)<sub>2</sub>(PZ) complex, PSiFC6C6, and PVK hosts. PL spectra were obtained using Fluorolog-3 spectrophotometer (Jobin Yvon). The PL emission spectrum of the complex Ir(PPF)<sub>2</sub>(PZ) in acetone solution shows that the peak of the maximum emission is 462 nm with 350 nm excitation. The PL maximum emission peak of PSiFC6C6 and



SCHEME 1. Structures of 1, Ir(PPF)<sub>2</sub>(PZ), and 2, PSiFC6C6.

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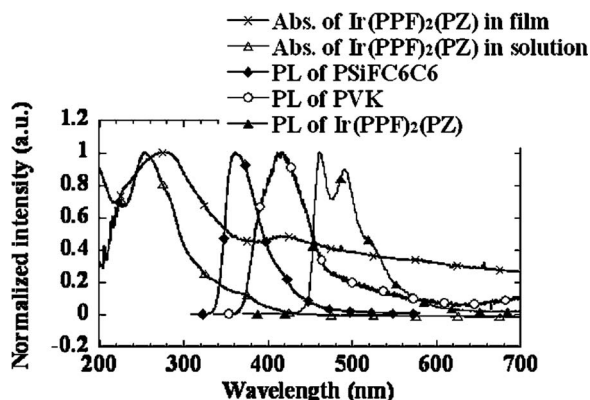


FIG. 1. Ultraviolet-visible absorption spectra in dichloromethane solution and in film and PL spectra of  $\text{Ir}(\text{PPF})_2(\text{PZ})$  in acetone solution and PL spectra of the PSiFC6C6 and PVK host in film.

PVK in the film is 360 nm and 415 nm under at 273 nm and 350 nm excitation, respectively. Figure 1 indicates that the PL emission spectrum of the host polymer PSiFC6C6 shows much better overlap with the absorption spectrum of  $\text{Ir}(\text{PPF})_2(\text{PZ})$  than that with PVK host. Therefore, we could expect more efficient Förster energy transfer from PSiFC6C6 host to the complex guest than that from PVK, if the overlap between PL of the host and absorption of the guest is a dominating factor in the energy transfer process. In contrast to our expectation, we will show later that in PL process that the PL of Ir complexes in PSiFC6C6 host has been almost completely quenched probably due to low-lying triplet level of host.

Blue light-emitting PPHOLEDs device from  $\text{Ir}(\text{PPF})_2(\text{PZ})$  complex doped into PSiFC6C6 as an emitting layer was fabricated in the structure of indium tin oxide (ITO)/PEDOT/PVK/[PSiFC6C6+ $\text{Ir}(\text{PPF})_2(\text{PZ})$ ]/Ba/Al. A 50 nm thick layer of PEDOT was spincoated onto precleaned ITO-glass substrates. Then, a 40 nm thick layer of PVK was spincoat on the top of PEDOT. A mixture of  $\text{Ir}(\text{PPF})_2(\text{PZ})$  with PSiFC6C6 was spincoated from chlorobenzene solution. The device fabrication and characterization was followed procedure described in previous publication.<sup>8</sup>

The PL spectra of the iridium complex doped into PSiFC6C6 and PVK film in different concentrations are shown in Fig. 2(a). For PSiFC6C6 host, the emission from the iridium complex under photo excitation almost cannot be observed for the films with the guest concentration as high as 8 wt %. The PL spectra were dominated by the emission of the host PSiFC6C6. However, when PVK was used as a host, the emission of the guest was clearly observed at very low dopant concentration indicating the efficient energy transfer from the host to the guest. Furthermore, the intensity of the host emission decreases with the increasing dopant concen-

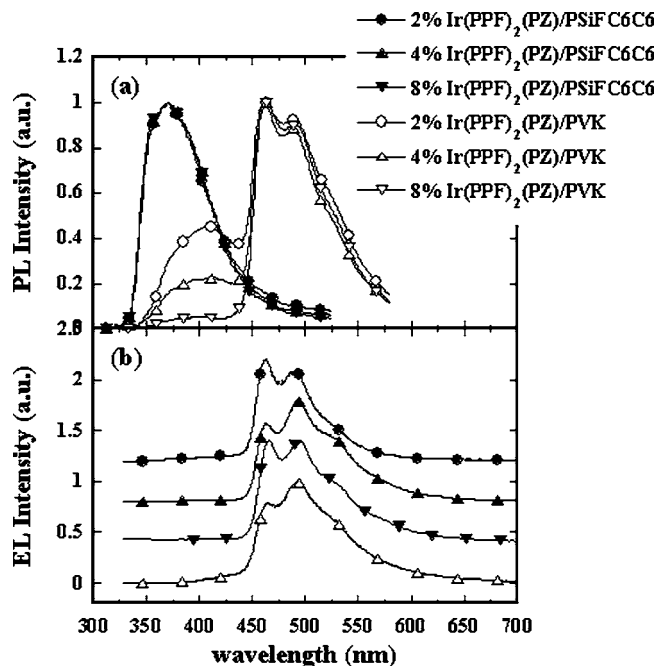


FIG. 2. (a) PL spectra of the iridium complex  $\text{Ir}(\text{PPF})_2(\text{PZ})$  with different concentration doped into PSiFC6C6 and PVK, respectively. (b) EL spectra of devices  $\text{Ir}(\text{PPF})_2(\text{PZ})$  doped into PSiFC6C6 and PVK.

tration in the PVK [Fig. 2(a)]. The emission of PVK host was almost completely quenched when the  $\text{Ir}(\text{PPF})_2(\text{PZ})$  concentration in PVK reached 8 wt %.

In contrast to completely quenching of PL emission of iridium complex under photo excitation, the electroluminescence (EL) of devices with  $\text{Ir}(\text{PPF})_2(\text{PZ})$  doped into PSiFC6C6 shows efficient energy transfer from PSiFC6C6 host to the Ir complexes [Fig. 2(b)]. The EL emission of iridium complexes is dominant at a dopant concentration as low as 2%. Recently, Jiang *et al.*<sup>17</sup> reported a similar phenomenon for efficient green devices composed of  $\text{Ir}(\text{Bu-ppy})_3$  doped into PFO polymer. The great difference between the EL and PL spectra was attributed to the charge-trapping mechanism in EL process rather than Förster transfer under photoexcitation.<sup>18</sup> We speculate that the triplet energy level of PSiFC6C6 host is lower than that of the  $\text{Ir}(\text{PPF})_2(\text{PZ})$  guest. As a result, the back energy transfer from the Ir complex to the polymer host is energetically favorable in PL process. The fact that photophosphorescence of iridium complexes was completely quenched in the PSiFC6C6 host, but not in the PVK host with no low-lying triplet level,<sup>19</sup> is consistent with the speculation.

In contrast to photoexcitation, the EL efficiency of the devices from iridium complexes doped into PSiFC6C6 is much higher than that from PVK devices (see Table I). For

TABLE I. Device performances.

Blend	Cathode	Voltage (V)	$I$ (mA)	$L$ (cd/m <sup>2</sup> )	$\text{QE}_{\text{max}}$ (%)	LE (cd/A)	the first emission peak (nm)	CIE	
								x	y
$\text{Ir}(\text{PPF})_2(\text{PZ})(2\%)$ -PSiFC6C6	Ba/Al	10.0	1.3	644.3	4.8	7.2	461.9	0.15	0.26
$\text{Ir}(\text{PPF})_2(\text{PZ})(4\%)$ -PSiFC6C6	Ba/Al	14.0	1.1	683.5	5.9	9.5	463.5	0.19	0.39
$\text{Ir}(\text{PPF})_2(\text{PZ})(8\%)$ -PSiFC6C6	Ba/Al	10.0	1.5	639.2	4.3	6.4	466.0	0.18	0.37
$\text{Ir}(\text{PPF})_2(\text{PZ})(4\%)$ -PVK(PBD20%)	Ba/Al	10.0	11.4	78.2	0.5	0.8	465.1	0.20	0.36

Note: QE=Quantum efficiency; LE=luminance efficiency.

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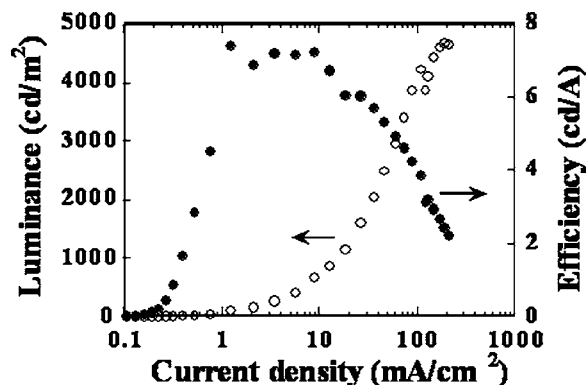


FIG. 3.  $L$  and  $LE$  vs  $J$  of the device ITO/PEDOT/PVK/Ir(PPF)<sub>2</sub>(PZ) × (2%) - PSiFC6C6/Ba/Al.

the device of 2 w/w% Ir(PPF)<sub>2</sub>(PZ) doped into PSiFC6C6 host, the external quantum and luminous efficiencies were respectively 4.8% photons/electrons (ph/el) and 7.2 cd/A at 644.3 cd/m<sup>2</sup>, with CIE coordinates of (0.15,0.26) which is a best number reported so far for blue polymer PHOLEDs. Figure 3 shows luminance-current density ( $L$ - $J$ ) and luminous efficiency-current density curves ( $LE$ - $J$ ) of such devices. With dopant concentration increasing up to 4%, the device efficiencies were raised to the external quantum efficiency of 5.9% ph/el and luminous efficiency of 9.5 cd/A at 683.5 cd/m<sup>2</sup>, but the CIE coordinates were changed to (0.19,0.39) because that 0-1 vibronic peak (peaked at 491 nm) dominates the EL spectra.

In conclusion, iridium complex with 2,4-difluorophenyl-2-pyridine and 2-(4H-1, 2, 4-triazol-3-yl)pyridine, Ir(PPF)<sub>2</sub>(PZ) was synthesized. The photoexcitation and emission of the complex was investigated through the measurement of absorption and PL spectra. Despite the significant phosphorescence quenching of PL emission by PSiFC6C6 host polymer, PLED-containing Ir(PPF)<sub>2</sub>(PZ) doped into the polymer host PSiFC6C6 show high EL-efficiency blue light with the emission peaked at 462 nm. For the device of 2 w/w% Ir(PPF)<sub>2</sub>(PZ) doped into PSiFC6C6 host, the external quantum and luminous efficiencies were

respectively 4.8% ph/el and 7.2 cd/A at 644.3 cd/m<sup>2</sup>, with CIE coordinates of (0.15,0.26) which is best blue emitter reported so far for polymer PHOLEDs.

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