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Synthesis of new iridium complexes and their electrophosphorescent properties in polymer light-emitting diodes

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Several new iridium complexes with *p*-substituted 2-phenylpyridine (R-PPy) ligands have been synthesized and characterized. The complexes were incorporated into phosphorescent polymer light-emitting devices using soluble poly[1,4-bis(6'-cyano-6'-methylheptyloxy)phenylene] (CNPPP) as the host and the resultant materials compared with $Ir(PPy)_3$ -doped devices. Green electrophosphorescence was observed, with peak emission at about 495 and 515 nm. Among the devices fabricated, highly efficient polymer light-emitting diodes were obtained with CNPPP doped with *fac*-tris[2-(4-*tert*-butylphenyl)pyridinato]iridium. An external quantum efficiency of 4.4% (photoluminescence/electroluminescence) and a luminous efficiency of 10 cd A⁻¹ were obtained at 120 cd m⁻². These values remain at 4.2% and 10 cd A⁻¹, respectively, at 2500 cd m⁻². The improvement is attributed to improved interaction between the guest and host, and to better and more complete energy transfer from the host singlet to the guest triplet state. These results demonstrate that efficient electrophosphorescence is not limited to small molecule organic light-emitting diodes, it can also be achieved in devices made with polymer hosts.

Introduction

Recently, high efficiency organic light-emitting diodes (OLEDs) have been fabricated using electrophosphorescent molecules such as 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinatoplatinum (PtOEP),^{1,2} *fac*-tris(2-phenylpyridinato)iridium [Ir(PPy)₃]^{3–5} and bis{2-[2'-benzo(4,5-*a*)thienyl]pyridinato-*N*,*C*³}-iridium acetylacetonate [(Btp)₂Ir(acac)].^{6,7} This has heralded a breakthrough in improving external quantum efficiency and luminous efficiency in OLEDs. Unlike fluorescence-based light-emitting diodes (LEDs), the quantum efficiency of phosphorescence-based LEDs are not limited and can theoretically reach 100% by using both singlet and triplet excitons. As a result, they have attracted attention worldwide, and are considered to be promising candidates for realizing commercial full color LED displays.

Much effort has been focused on developing highly efficient phosphorescent guest materials, selecting appropriate host materials and designing efficient device structures. At present, most of the phosphorescent guest materials investigated are complexes of heavy metals, as strong spin–orbit coupling leads to singlet–triplet state mixing, thus resulting in high efficiency electrophosphorescence in LEDs. Ortho-metalated complexes with d⁶ and d⁸ metal ions such as $Pt(\pi)$,² $Os(\pi)$,⁸ and $Ir(\pi)$ ^{3–7,9} have been extensively investigated for electrophosphorescent device applications. An energy efficiency of 40 lm W⁻¹ and an external quantum efficiency of 15% were reported in OLEDs using an iridium complex as the phosphorescent emitter.³

Research into host materials has mainly focused on small molecules. Typically, small molecule blue emitters such as tris(8-hydroxyquinolinato)aluminium (Alq₃),¹ 4,4'-dicarbazolebiphenyl (CBP),^{3,4} 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP),^{3,4} 1,3-bis(*tert*-butylphenyl)-1,3,4-oxadiazole (OXD7),⁷ 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ)^{3,7} have been used in electrophosphorescent devices. In contrast, there are only a few reports on phosphorescence-based LEDs using a polymer as the host material. Peak quantum efficiencies of 1.9 and 3.5% have been reported

for a Ir(PPy)3-doped polyvinylcarbazole device¹⁰ and a

PtOEP-doped polyfluorene device, respectively.¹¹ The quantum efficiencies for phosphorescent dye-doped polymer lightemitting diodes (PLED) prepared so far are much lower than those of dye-doped OLEDs using small molecules as host.

It is of interest to use polymers instead of organic small molecules as host materials, since PLEDs have the potential to be used for large area displays which can be made using simpler processes and at a lower cost. In order to improve performance of phosphorescence-based PLEDs and decrease phase segregation between host and guest, it is very important to design highly efficient phosphorescent guest materials.¹² In this paper, we report the synthesis of three new iridium complexes (Scheme 1) which show high phophorescence efficiencies, and report their optical and electroluminescent (EL) properties. We found that altering the length of the of alkyl substitution on the phenylpyridine ligands could lead to significant differences in EL performance.

Experimental details

Reagents

p-tert-Butylbromobenzene, 2-bromopyridine, n-butyllithium, 4-bromophenol, and anhydrous zinc chloride were purchased from Aldrich. Tetrakis(triphenylphosphine)palladium was obtained from TCI Co. Bromobenzene and anhydrous aluminium chloride were used as received. Anhydrous tetrahydrofuran was distilled over sodium–benzophenone under nitrogen prior to use, CS₂ was distilled over calcium chloride. 4-(3',7'-Dimethyloctyloxy)bromobenzene, decanoyl chloride, 1-bromo-4-decylbenzene, and 2,5-dichloro-1,4-bis-(6'-cyano-6-'methylheptyloxy)benzene were prepared following published procedures.^{13–16}

Syntheses

1-Bromo-4-decanoylbenzene (1). In a 250 ml three-necked round-bottom flask, 39.0 g (0.25 mol) of bromobenzene and 36.5 g (0.27 mol) of anhydrous aluminium chloride were added to 100 mL of dry CS_2 , and the mixture was cooled to 5–10 °C.



Scheme 1 Synthetic routes to and chemical structures of the materials used herein.

45.0 g (0.24 mol) of decanoyl chloride were added dropwise with vigorous stirring over 2 h. The resulting deep brown mixture was refluxed for 2 h. The mixture was cooled to room temperature and cautiously poured into a mixture of 250 g of crushed ice and 150 mL of concentrated hydrochloric acid in a beaker. The organic layer was extracted with ether. The resulting ether layer was washed successively with dilute sodium hydroxide (1%, w/w) and water, and dried over magnesium sulfate. The ether was evaporated to give a orange oil, which yielded a colorless liquid product (b.p. 141–143 °C/ 0.1 mmHg) after vacuum distillation.

1-Bromo-4-decylbenzene (2). 31.1 g (0.1 mol) of 1-bromo-4-decanoylbenzene, 15 mL (0.3 mol) of hydrazine monohydrate, and 18.5 g (0.33 mol) of potassium hydroxide were dissolved in 80 mL of 2-hydroxyethyl ether. The mixture was heated to 130 °C and stirred for 2 h, then the excess hydrazine hydrate was removed. The resulting mixture was reacted for 2 h at 200 °C, cooled to room temperature, and slowly poured into 100 mL of 18% (w/w) aqueous hydrochloric acid to give an oil and an aqueous layer. The oil was removed and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The ether and the oil layer were mixed together, washed with water, dried over magnesium sulfate, and the ether evaporated. The residue was distilled under 0.1 mmHg of vacuum and the colorless liquid product collected at 134–136 °C. GC-MS, *m/e*: 297 (M⁺, 2.6), 298 ([M + 1]⁺, 25), 296 ([M - 1]⁺, 25), 171 ([M + 1 - C₉H₁₉]⁺, 100), 169 ([M - 1 - C₉H₁₉]⁺, 100%).

2-(4-*tert***-Butylphenyl)pyridine (3).** 1-Bromo-4-*tert*-butylbenzene (5.33 g, 25.0 mmol) was dissolved in 50 mL of THF, and the solution was cooled to between -70 and -80 °C under nitrogen. n-Butyllithium solution (1.6 M in n-hexane, 15.6 mL, 25.0 mmol) was added dropwise over 10 min and the mixture was stirred for 15 min. Then, a solution of zinc chloride (3.40 g, 25.0 mmol) in THF (50 mL) was added dropwise at between -45 and -50 °C for 15 min and the mixture stirred for 30 min. After warming the reaction mixture to room temperature, a solution of 2-bromopyridine (3.95 g, 25.0 mmol) and tetrakis(triphenylphosphine)palladium (0.90 g, 0.078 mmol) in THF (15 mL) was added, followed by stirring for 1.5 h, and a yellow solution was obtained. The reaction mixture was neutralized to pH 8 with solution of aqueous sodium carbonate (10%, w/w), then the oil was removed and the aqueous layer was extracted with diethyl ether (2 × 25 mL). The ether and the oil layer were mixed together, washed with water, dried over magnesium sulfate, and evaporated to give an orange–red crude product. The crude product was purified by column chromatography (silica gel, n-hexane–ethyl acetate 3:1) to provide 3.10 g of a yellow liquid in 58.7% yield. GC-MS, *m/e*: 211 (M⁺, 23.1), 196 ([M – CH₃]⁺, 100), 154 ([M – C₄H₉]⁺, 4.5%).

2-[4'-(3",7"-Dimethyloctyloxy)phenyl]pyridine (4). This compound was synthesized according to the procedure used for the preparation of compound **3**. A yellow liquid product was obtained in 54.2% yield. GC-MS, m/e: 311 (M⁺, 7.9), 171 ([M + 1 - C₁₀H₂₁]⁺, 100), 154 (M - OC₁₀H₂₁]⁺, 6.6%).

2-(4'-Decylphenyl)pyridine (5). This compound was synthesized according to the procedure used for the preparation of compound **3**. A yellow liquid product was obtained in 51.1% yield. GC-MS, m/e: 295 (M⁺, 21.1), 182 ([M - C₈H₇]⁺, 67.1), 167 ([M - C₉H₁₉]⁺, 100%).

fac-Tris[2-(4'-*tert*-butylphenyl)pyridinato]iridium, Ir(BuPPy)₃ (6). 200 mg (0.4 mmol) of tris(acetylacetonato)iridium [Ir(acac)₃] and 646 mg (3.06 mmol) of 2-(4-*tert*-butylphenyl)pyridine (BuPPy) were added to 20 mL of degassed glycerol in a three-necked flask, and the mixture refluxed under a nitrogen atmosphere for 12 h. The reaction mixture was cooled to room temperature and then poured into 120 mL of dilute aqueous hydrochloric acid (0.1 M) to give a red-brown precipitate. The precipitate was filtered off, washed with water and methanol, and purified by column chromatography (silica gel, dichloromethane) to give 0.205 g of an orange product in 62.3% yield. Elemental analysis found: C, 65.22; H, 6.00; N, 4.93; calcd: C, 65.66; H, 5.88; N, 5.11%. *fac*-Tris{2-[4'-(3",7"-dimethyloctyloxy)phenyl]pyridinato}iridium, Ir(DecOPPy)₃ (7). This compound was synthesized according to the procedure used for the preparation of compound 6. An orange-yellow product was obtained in 50% yield. Elemental analysis found: C, 67.09; H, 7.56; N, 3.77; calcd: C, 67.35; H, 7.50; N, 3.71%.

fac-Tris[2-(4'-decylphenyl)pyridinato]iridium, Ir(DecPPy)₃ (8). This compound was synthesized according to the procedure used for the preparation of compound 6. A green–yellow product was obtained in 50% yield. Elemental analysis found: C, 70.08; H,7.99; N, 3.83; calcd: C, 70.35; H, 7.87; N, 3.92%.

Poly[1,4-bis(6'-cyano-6'methylheptyloxy)phenylene], CNPPP (9).¹⁶ Zinc powder (2.88 g, 44.2 mmol), nickel chloride (0.08 g, 0.63 mmol), bipyridine (0.095 g, 0.6 mmol), triphenylphosphine (1.90 g, 7.3mmol) and 2,5-dichloro-1,4-bis(6'-cyano-6-'methylheptyloxy)benzene (4.03 g, 13.5 mmol) were added to a three-necked flask. Under a nitrogen atmosphere, DMF (40 ml) was added to the flask *via* syringe. The mixture was stirred at 80 °C for 48 h, cooled to room temperature, then poured into the solution of 75 mL methanol and 10 ml concentrated HCl. The resulting mixture was stirred to give precipitate. The precipitate was dissolved in THF to form a pale yellow solution. A white precipitate was obtained by adding the solution to water. The product was purified by reprecipitation from THF with acetone.

Instrumentation

All GC-MS data were obtained using a Finnigan Trace GC-MS-2000 Series system. All NMR spectra were acquired with a Bruker Dex-400NMR instrument, using CDCl₃ as a solvent. Elemental analysis was performed on a Harrios elemental analyzer. The UV-Visible absorption spectra of films containing iridium complexes were recorded using an HP-8453 UV-Visible system. Photoluminescence (PL) and electroluminescence (EL) spectra were obtained with an Oriel InstaSpec IV CCD system. The PL quantum efficiencies of the blends as solid thin films on quartz substrates were measured with a LabSphere IS80 integrating sphere, together with a UDT S370 digital photometer, according to the method described by Greenham *et al.*¹⁷ Excitation for the measurement of PL spectra and PL efficiency was achieved using the 325 nm line from a He–Cd laser (Melles Griot).

Device fabrication and characterization

The polymer light-emitting diodes were fabricated on commercial indium tin oxide (ITO) substrates with a sheet resistance of 15 Ω \Box^{-1} (Nanbo, Shengzhen, China). Before spin coating, the ITO substrates were cleaned using acetone, detergent, deionized water, and 2-propanal, then treated with oxygen plasma for 10 min. The LED structure is illustrated in Scheme 2. A 40 nm layer of polyvinylcarbazole (PVK) was spin cast on top of the ITO substrate. The PVK layer functions as a hole-injection layer. A 70 nm phosphorescent dye-doped emitting layer was spin coated on top of the PVK layer. The thickness of the PVK and emitting layers were measured using a Tencor Alpha-step 500 surface profiler. Devices were made with a thin layer of barium as the cathode, deposited using



Scheme 2 Schematic representation of the PLED structure.

vacuum vapor deposition at a pressure below 3×10^{-4} Pa. Immediately after deposition of Ba, a 200 nm capping layer of aluminium was deposited on top of the Ba metal layer. The cathode area defines the active area of the device, which is typically 0.15 mm² for the devices in this study. The deposition speed and the thickness of the barium and aluminium layers were monitored with a Sycon Instruments Model STM-100 thickness/rate meter. All steps except the PVK-coating were performed in N₂-filled dry boxes with oxygen and water contents of less than 1 ppm. *I–V* Characteristics were measured with a computerized Keithley 236 source measuring unit. The luminance of the devices was measured with a calibrated photodiode.

Results and discussion

Synthesis of iridium complex

The synthesis of the ligands and iridium complexes is depicted in Scheme 1. The 2-arylpyridine ligands were synthesized *via* Pd-catalyzed cross-coupling using the modified method reported previously.¹⁸ The use of zinc (intermediate electronegativity) rather than lithium (low electronegativity) leads to favorable results in Pd-catalyzed coupling between aryl and pyridyl. The reaction was carried out in one step with a yield of over 50%. Iridium complexes were prepared according to the procedure reported previously.¹⁹ The reaction between arylpyridines and tris(acetylacetonato)iridium in refluxing glycerol can afford cycloiridium complexes. The yields of about 55% were obtained by varying the ratio of 2-arylpyridine to tris(acetylacetonato)iridium, using a higher ratio than that reported for *fac*-tris(2-phenylpyridinato)iridium in the literature.¹⁹ The elemental analysis results for the complexes are consistent with the structures shown in Scheme 1.

Optical and photoluminescent properties

Fig. 1 shows the UV-Visible absorption spectra of three complexes in solid films on quartz substrates. All three iridium complexes have almost identical UV-Visible absorption spectra, similar to that of $Ir(PPy)_3$, at a wavelength from 200 to 800 nm. An intense absorption band is observed in the ultraviolet parts of the spectra from 200 to 400 nm. The intense absorption band around 290 nm can be assigned to a spin-allowed ${}^{1}\pi-\pi^{*}$ transition on the cyclometalated ligands, and the broad absorption band at lower energy (380 nm) is typical for spin-allowed metal to ligand charge-transfer (${}^{1}MLCT$) transitions, as has been discussed in the literature. 19 The 380 nm peak for Ir(DecOPPy)_3 and Ir(BuPPy)_3. This indicates that modification of the PPy molecule by adding alkyl or alkoxy



Fig. 1 UV-Visible absorption spectra of films of the iridium complexes.



Fig. 2 (a) PL spectra of Ir(BuPPy)₃-doped CNPPP films on quartz substrates. (b) EL spectra of Ir(BuPPy)₃-doped CNPPP devices.

groups to the phenyl ring has little influence on the absorption properties of the corresponding iridium complexes.

Fig. 2(a) shows the normalized photoluminescence (PL) spectra of Ir(BuPPy)3-doped CNPPP devices with dopant concentrations of 0, 1, 2, 4, and 8 wt%. The photoluminescence profile contains two peaks: one is centered at 430 nm, resulting from the emission of the CNPPP host and the other, observed at 515 nm, is due to Ir(BuPPy)₃ triplet emission.²⁰ The emission at 430 nm decreases significantly as the dopant concentration is increased. At dopant concentrations of 4 wt% or more, the PL profiles are dominated by the 515 nm triplet emission. The observed concentration dependence of the PL profile resembles that observed for Ir(PPy)3-doped CNPPP films.¹² The results indicate that Forster transfer from CNPPP singlets takes place. In order gain a greater understanding of the energy transfer in such blend films, the absolute PL quantum efficiencies of thin (100 nm) blend films were measured in the integrating sphere, according to the method proposed by Greenham et al.¹ Table 1 lists the PL efficiencies of blend films containing the four Ir complexes in 4 wt% dopant concentrations (the point at which the emission of the Ir complex becomes dominant over that of CNPPP). For the purposes of comparison, the PL efficiencies of undoped CNPPP film and pure Ir complexes were also measured (Table 1). As expected, the PL efficiencies of the Ir complexes are only ca. 1%, due to concentration quenching. This value is consistent with the results reported for Ir complexes with other ligands.²¹ As can be seen from Table 1, the PL efficiency varies with alkyl chain length; Ir(BuPPy)₃doped CNPPP shows the highest PL quantum efficiency among the four blends, which is consistent with the electroluminescence (EL) results (see below). There are several possible explanations for the dependence of the PL properties on the alkyl chain length, and further photophysics studies are necessary to obtain a clearer picture.

 Table 1 PL efficiencies of pure Ir complexes and CNPPP, and blends thereof, measured in the integrating sphere

Material	Dopant concentration/wt%	PL efficiency (%)
Ir(PPy)3-CNPPP	4	32.1
Ir(BuPPy) ₃ -CNPPP	4	41.7
Ir(DecPPy) ₃ -CNPPP	4	28.4
Ir(DecOPPy) ₃ -CNPPP	4	12.3
CNPPP	0	26.3
$Ir(PPy)_3$		1.1
Ir(BuPPy) ₃	_	1.0

Device performance

Polymer LEDs were fabricated from the Ir complex-doped CNPPP films. A schematic representation of the device structure is shown in Scheme 2. Since the highest occupied molecular orbital (HOMO) level of alkoxy-substituted PPPs is 5.7 eV,¹⁵ a 40 nm polyvinylcarbazole film was placed between the indium tin oxide and the emitting layer to facilitate hole injection. A thin layer of Ba with a 200 nm Al capping layer was used as the cathode. The thickness of the Ir complexpolymer blend was 70-80 nm in all cases. Fig. 2(b) shows the corresponding EL spectra obtained from the devices with different Ir(BuPPy)₃ dopant concentrations. In contrast to the PL spectra [Fig. 2(a)], which show a significant contribution from the CNPPP host at low dopant concentrations, no difference can be seen between the EL emission profiles for devices with dopant concentrations between 1 and 8 wt%. The spectra of the devices contain only emissions from the Ir complexes, even at dopant concentrations as low as 1 wt%. This result clearly indicates that Forster transfer is not the only mechanism responsible for EL performance. O'Brien et al.¹¹ suggested that there is a significant contribution from carrier trapping. Recently, Lane et al. investigated Pt complex-doped polyfluorene and concluded that Forster transfer of singlet excitons was weak and the dominant emission mechanism in their doped polymer LEDs was charge trapping followed by recombination on the Pt complex.²² McGhee et al. reported a large difference between the PL and EL spectra of Eu complex-CNPPP devices at low dopant concentrations.²³ They attributed this behavior to the difference in recombination zone for photo- and electrical excitation.

Fig. 3. compares the EL spectra of devices prepared with CNPPP doped with different Ir complexes at 4 wt% dopant concentration. No emission peak at 420 nm corresponding to



Fig. 3 EL spectra of devices containing CNPPP doped with various iridium complexes.

Guest	V/V	Device performance				
		I/mA	Luminance/ cd m ⁻²	QE (%)	EL efficiency/ cd A^{-1}	
Ir(PPy) ₃ Ir(BuPPy) ₃ Ir(DecOPPy) ₃ Ir(DecPPy) ₃	30 30 28 26	4.7 3.8 7.5 2.7	1668 2501 1717 1022	2.27 4.22 1.46 1.39	5.4 10.0 3.5 3.3	

the host is observed, indicating that efficient energy transfer from CNPPP to the iridium complexes occurs at a dopant concentration of 4 wt% for all these devices. The $Ir(BuPPy)_3$ device emits green light centered at 515 nm, with exactly the same peak position and emission spectrum as for the $Ir(PPy)_3$ device. It is interesting to note that the attaching decyl and decyloxy groups at the *p*-position of the phenyl ring of 2-phenylpyridine shifts the emission peak significantly into the blue region. Both the $Ir(DecOPPy)_3$ and $Ir(DecPPy)_3$ devices emit blue–green light centered at 495 nm.

Table 2 shows the device performance of the three new complexes along with $Ir(PPy)_3$ in 4 wt% dopant concentration. Attaching a butyl group at the *p*-position of the phenyl ring of 2-phenylpyridine improves the device performance. The Ir(BuPPy)₃-doped CNPPP device shows a generally higher quantum efficiency (QE) than the Ir(PPy)3-doped device at each dopant concentration. For the 4 wt% Ir(BuPPy)₃ device, an external quantum efficiency of 4.2% (PL/EL) and a luminous efficiency of 10 cd A^{-1} were obtained at 2500 cd m^{-2} . while for the Ir(PPy)3-doped device fabricated under the same experimental conditions, the values are only 2.3% and 5.4 cd A^{-1} , respectively, at 1770 cd m^{-2} (Table 2). Devices prepared using Ir(DecOPPy)₃ and Ir(DecPPy)₃ show much lower efficiencies than the Ir(PPy)3 device, as can be seen from Table 2. It is important to note that the reduction rate of the QE under higher bias voltages (and currents) for the devices with different substitutions of the phenyl ring in 2-phenylpyridine differ remarkably. It is well known that the external QE in Ir(PPy)₃-TAZ devices³ reaches its maximum (15%) at very low current densities ($<10^{-2}$ mA cm⁻²) and decays very quickly with increasing current density due to triplet-triplet annihilation.³ Fig. 4 compares the luminous efficiencies of devices prepared from Ir(PPy)₃-, Ir(BuPPy)₃-, and Ir(DecOPPy)₃doped CNPPP at a dopant concentration of 2 wt%. The Ir(BuPPy)₃ device again shows the best performance at high current densities. For one of the best Ir(BuPPy)3-doped CNPPP devices with a dopant concentration of 4 wt%, the



Fig. 4 Luminous efficiency vs. bias for devices prepared with blend films with 2 wt% dopant concentration.

external QE and EL efficiency were 4.4% and 10 cd A^{-1} , respectively, at 120 cd m⁻². The efficiencies remain at 4.2% and 10 cd A^{-1} , respectively, at 2500 cd m⁻². A maximum external QE of 5.1% and an EL efficiency of 12 cd A^{-1} were observed at 800 cd cm⁻² and at a current density of 6.8 mA cm⁻². According to Greenham *et al.*,²⁴ the internal quantum efficiency can be estimated from the optical power emitted in the forward direction. Assuming the refractive index of the substituted polyphenylene as 1.6, as observed for most conjugated polymers,²⁵ the maximal internal quantum efficiency is 22% for the Ir(BuPPy)₃-doped CNPPP devices. Better blending and more homogeneous distribution of the guest molecules in the host polymer matrix may account for the improved energy transfer and the suppression of triplet–triplet annihilation.

Overall, these are very encouraging results. Although the external quantum efficiency for phosphorescent dye-doped PLEDs is still much lower than the corresponding OLEDs,^{3,26} significant improvement in QE reduction rate with increasing current density breaks the barrier to phosphorescent PLEDs being used for passive displays operated at low duty cycles. These results also demonstrate that efficient electrophosphorescence is not specific to small molecule OLEDs, it can also be achieved in devices made with a polymer host. At this stage of our experiments we don't know why the longer 2-phenylpyridine chain substitution in Ir(DecOPPy)₃ and Ir(DecPPy)₃) leads to lower QEs than both Ir(PPy)₃ and Ir(BuPPy)₃. However, this fact clearly indicates that there are many factors which affect the energy transfer process in such systems. An overlap of the emission spectrum of the host and the absorption spectrum of the guest is considered to be an important condition to obtain high efficiency in phosphorescent dyedoped LEDs. In this study, all of these iridium complexes have the same overlap between the emission spectrum of the CNPPP host and their absorption spectra, similar to that for Ir(PPy)₃. Nevertheless, the device performance is very different in each case. These results suggest that the energy transfer from the blue light-emitting host to the phosphorescent dye is a complicated process. Overlap of the emission of the host and the absorption of the guest (Fig. 1) is a necessary condition, but not a sufficient one. Other processes need to be considered. One such is the matching of the LUMO and HOMO levels between the host and guest in the singlet and triplet states. Another is phase segregation between the crystalline guest molecules and the amorphous host polymer. We have designed a series of experiments to identify the underlying mechanism and these are currently in progress.

Conclusions

We have synthesized and characterized three new iridium complexes with different substituted PPy ligands. The EL performance of these three complexes was compared with that of Ir(PPy)₃ in the same device configuration and using the same fabrication conditions. We found that device performance is quite sensitive to the substitution on the 2-phenylpyridine ligand. Highly efficient PLEDs were obtained with Ir(BuPPy)3-doped CNPPP. An external QE of 4.4% PL/ EL and a luminous efficiency of 10 cd A^{-1} were obtained at 120 cd m⁻². These values remain at 4.2% and 10 cd A⁻¹, respectively, at 2500 cd m⁻². We attribute these improvements over other similar devices to improved interaction between the guest and host, and to better and more complete energy transfer from the host singlet to the guest triplet state. These results demonstrate that efficient electrophosphorescence is not only a feature of small molecule OLEDs, it can also be achieved in devices made with a polymer host. This approach allows high efficiency electrophosphorescent devices fabricated via simpler and more cost-efficient processes, such as ink-jet printing and screen printing.

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