

Polymer Phosphorescence Device using a New Green Emitting Ir(III) Complex

Chang-Lyoul Lee, Rupasree Ragini Das, Yong-Young Noh, and Jang-Joo Kim

Abstract

We have synthesized a new green Ir(III) complex *fac*-tris-(3-methyl-2-phenyl pyridine)iridium(III) Ir(mpp)₃ and fabricated phosphorescent polymer light-emitting device using it as a triplet emissive dopant in PVK. Ir(mpp)₃ showed absorption centered at 388 nm corresponding to the ¹MLCT transition as evidenced by its extinction coefficient of the order of 10³. From the PL and EL spectra of the Ir(mpp)₃ doped PVK film, the emission maximum was observed at 523 nm, due to the radiative decay from the ³MLCT state to the ground state, confirming a complete energy transfer from PVK to Ir(mpp)₃. The methyl substitution has probably caused a red shift in the absorption and emission spectrum compared to Ir(ppy)₃. The device consisting of a 2 % doped PVK furnished 4.5 % external quantum efficiency at 72 cd/m² (current density of 0.45 mA/cm² and drive voltage of 13.9 V) and a peak luminance of 25,000 cd/m² at 23.4 V (494 mA/cm²). This work demonstrates the impact of the presence of a methyl substituent at the 3-position of the pyridyl ring of 2-phenylpyridine on the photophysical and electroluminescence properties.

Keywords : electrophosphorescence, Ir(mpp)₃, energy transfer, MLCT.

1. Introduction

Orthometalating ligands are of great importance in designing Ir(III)-based phosphorescence for high performance full color display organic light emitting devices (OLEDs). Orthometalation enhances electron density at the metal center due to σ donation through the M-C bond [1], which not only affects the ground state reactivities but also has significant effects on MLCT (metal-to-ligand charge-transfer), LF (ligand field) and LL (ligand localized) excited states. Proper selection of a ligand can tune these states and furnish required luminescence properties. A chemical rough tuning brings about major changes in the luminescence character of a

complex [2], whereas the fine-tuning by the introduction of substituents is capable of causing small alterations in absorption and emission spectra without grossly changing the basic nature of the transitions responsible for these spectra. But it can reduce the deactivation of the emitting state and increase the quantum yield. In order to evaluate and emphasize the effect of the nature and position of the substituent upon both the ground- and excited-state properties, the present report aims at designing a new tris-orthometalated Ir (III) complex as a triplet emitter by using a modified 2-phenylpyridine. For this purpose, we have chosen 3-methyl-2-phenylpyridine (Hmpp). The methyl substitution at this position renders the ligand to exist in the form of two atropisomers at room temperature and would influence the extent of delocalization between the pyridyl and phenyl ring. This in turn shifts the metal- and ligand-centered states on complexation to Ir(III) as compared to Ir(ppy)₃. Methyl substitution in the pyridine ring of 2-phenyl pyridine is supposed to bring about a fine tuning of the HOMO and emitting ³MLCT states with a subsequent impact on the energy transfer from the host to the guest in OLEDs. We

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have investigated the effect of such substituent on the energy levels, PL (photoluminescence) and EL (electroluminescence) properties of $\text{Ir}(\text{mpp})_3$ as a triplet emissive dopant in PVK and the device performance as a whole.

2. Experimental

2.1 Synthesis of $\text{Ir}(\text{mpp})_3$

The complex *fac*-tris(3-methyl-2-phenylpyridinato- N,C^2') $\text{Ir}(\text{III})$, *fac*- $\text{Ir}(\text{mpp})_3$ was synthesized following the literature procedure with a slight alteration [3]. To a solution of 0.1 mmol (~0.49 g) of $\text{Ir}(\text{acac})_3$ (Aldrich) in degassed glycerol (5 mL) at 80 °C, 1.2 mmol (0.019 mL) of 3-methyl-2-phenylpyridine (Acros Organics) was added drop by drop in an argon environment. The reaction mixture was stirred for 4 h at 80 °C and then the temperature was gradually raised to 220 °C and heated for 24 h. After cooling, 100 mL of 1M HCl was added and filtered. Pure complex was isolated from the crude product by silica column using dichloromethane as the mobile phase. After purification, the compound was obtained as a bright yellow powder in ~55 % yield. The compound was then further purified by sublimation at a temperature of 290 °C and a pressure of 10^{-6} torr. Anal. Calcd: C, 62.05; H, 4.3; N, 6.03. Found: C, 62.35; H, 4.24; N, 5.17. M.P. 335 °C. ^1H NMR (300 MHz, CD_2Cl_2), ppm: 7.94 (d, 1H, $J = 7.86$), 7.45 (d, 1H, $J = 7.32$), 7.40 (d, 1H, $J = 7.95$), 6.87 (t, 1H, $J = 8.25$), 6.77 (m, 3H), 2.80 (s, 3H). Mass spectral analysis showed a parent peak at m/e 696 ($\text{Ir}(\text{mpp})_3$) $^+$ with fragments at m/e 528, 360, and 169 ($\text{Ir}(\text{mpp})_2$) $^+$, ($\text{Ir}(\text{mpp})$) $^+$, and mpp^+ . The analytical and NMR data confirm the formula *fac*- $\text{Ir}(\text{mpp})_3$. The HOMO, $^3\text{MLCT}$, and $^1\text{MLCT}$ levels were assigned the values, 4.93 eV, 2.56 eV, and 1.74 eV, respectively from the UPS, absorption, and emission data.

2.2 OLED fabrication

Fig. 1 shows the device structure, chemical structure and energy level of the materials used in the fabrication of the light emitting devices. The fabricated multilayer polymer light emitting devices have the structure of ITO/PEDOT (40 nm)/PVK- $\text{Ir}(\text{mpp})_3$ (30 nm)/TAZ (30 nm)/Alq₃ (20 nm)/Mg:Ag (100 nm)/Ag (20

nm). The glass substrate pre-coated with indium-tin-oxide was cleaned by an ultrasonic bath of acetone, followed by 2-propanol. Surface treatment was carried out by exposing ITO to a UV-ozone plasma. The hole transporting material, PEDOT and the emitting $\text{Ir}(\text{mpp})_3$ doped PVK were spin coated successively on ITO from dichloroethane solutions. The subsequent layers were deposited by high vacuum thermal evaporation. TAZ was used as a hole blocking material as well as an exciton blocking material because of its large band gap [4]. Finally a Mg-Ag layer (100-nm) capped by 20 nm of Ag were deposited as the cathode through a shadow mask by thermal evaporation. The Mg-Ag deposition ratio was 10:1. The light output was measured by a calibrated silicon photodiode and the current-voltage characteristics were measured by using a Kithley 237 Source Measurement Unit. All the measurements were performed at room temperature in air.

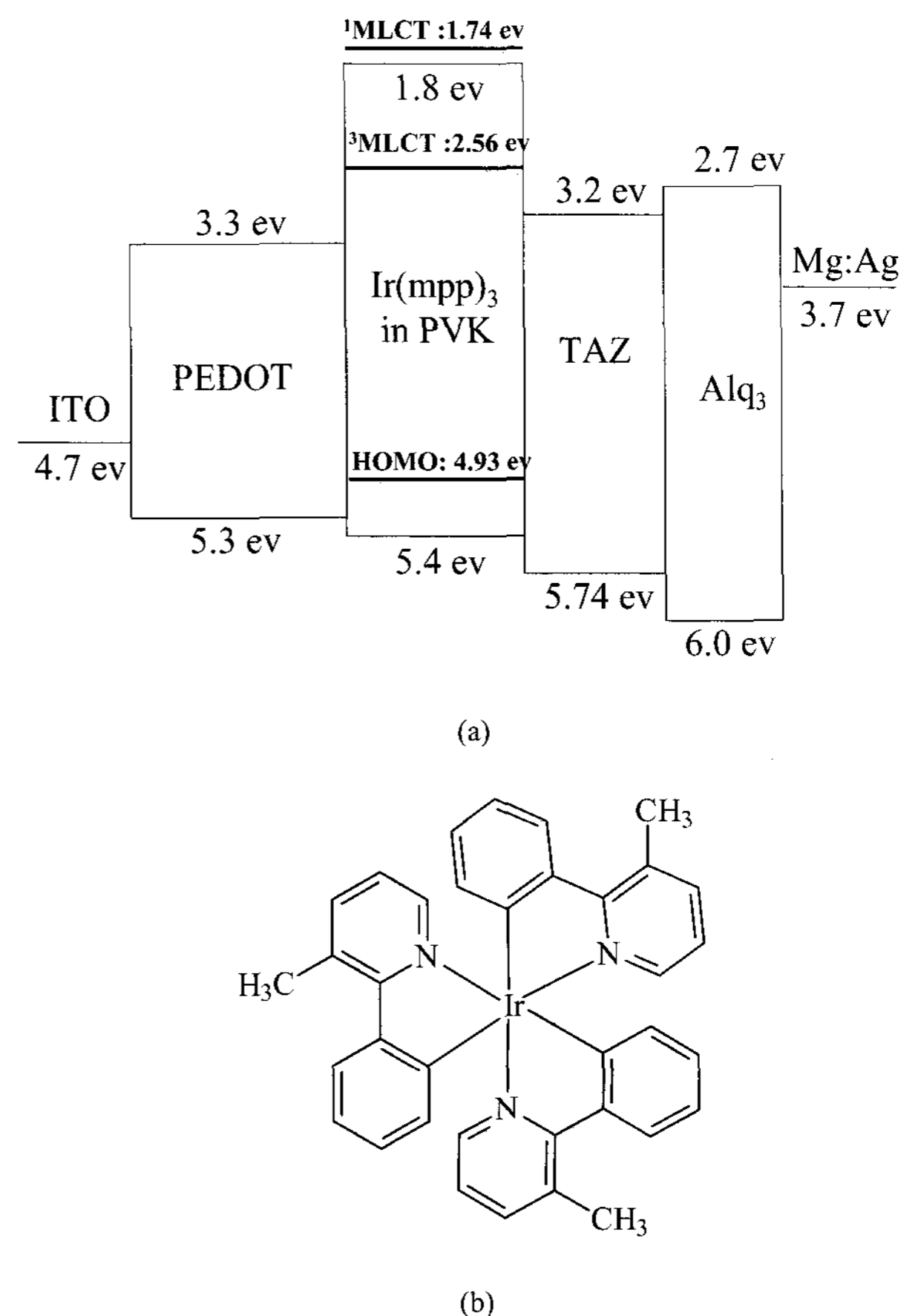


Fig. 1. (a) Proposed energy levels of the materials used in the fabrication of the light emitting devices with PVK - $\text{Ir}(\text{mpp})_3$. (b) Molecular structures of the phosphorescent dye, $\text{Ir}(\text{mpp})_3$.

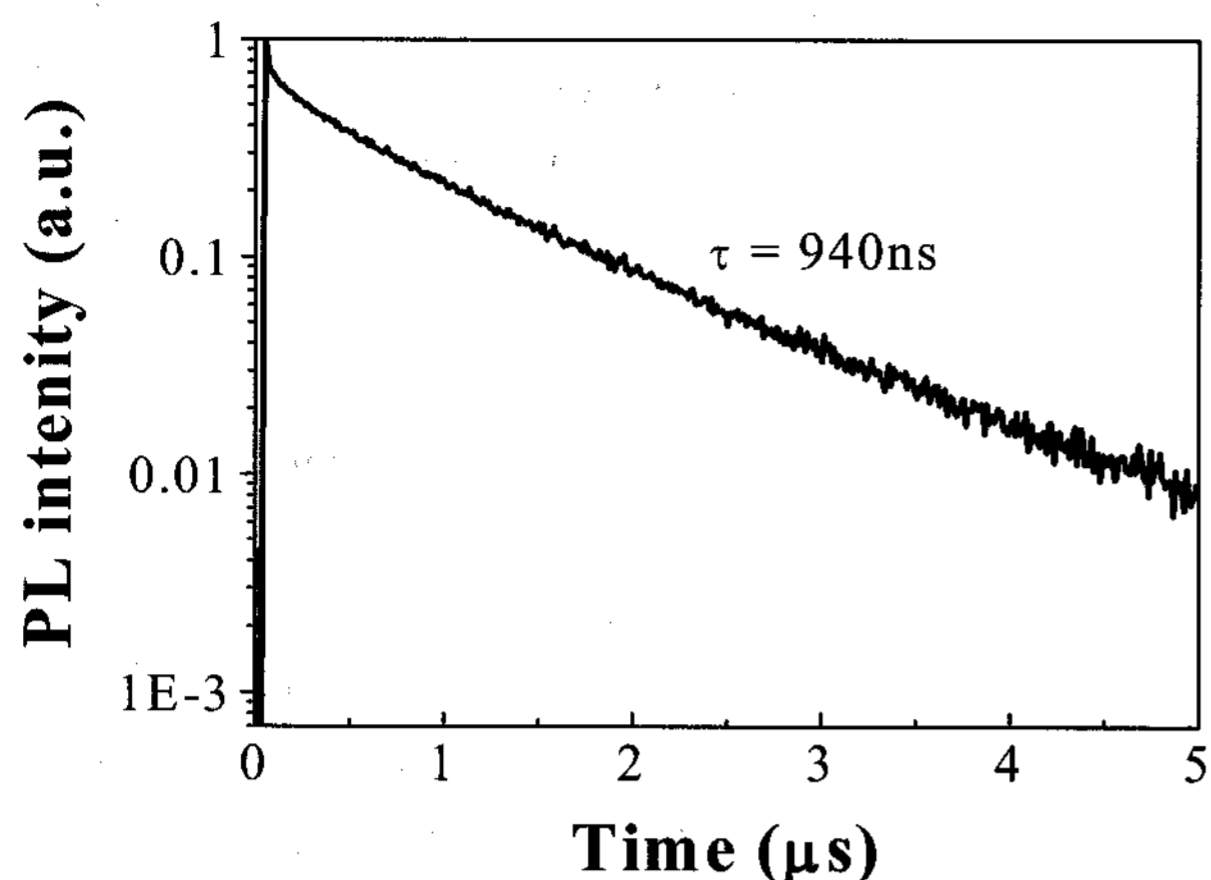


Fig. 2. Time resolved Photoluminescence spectra of Ir(mpp)₃ (6 %) doped PMMA thin film.

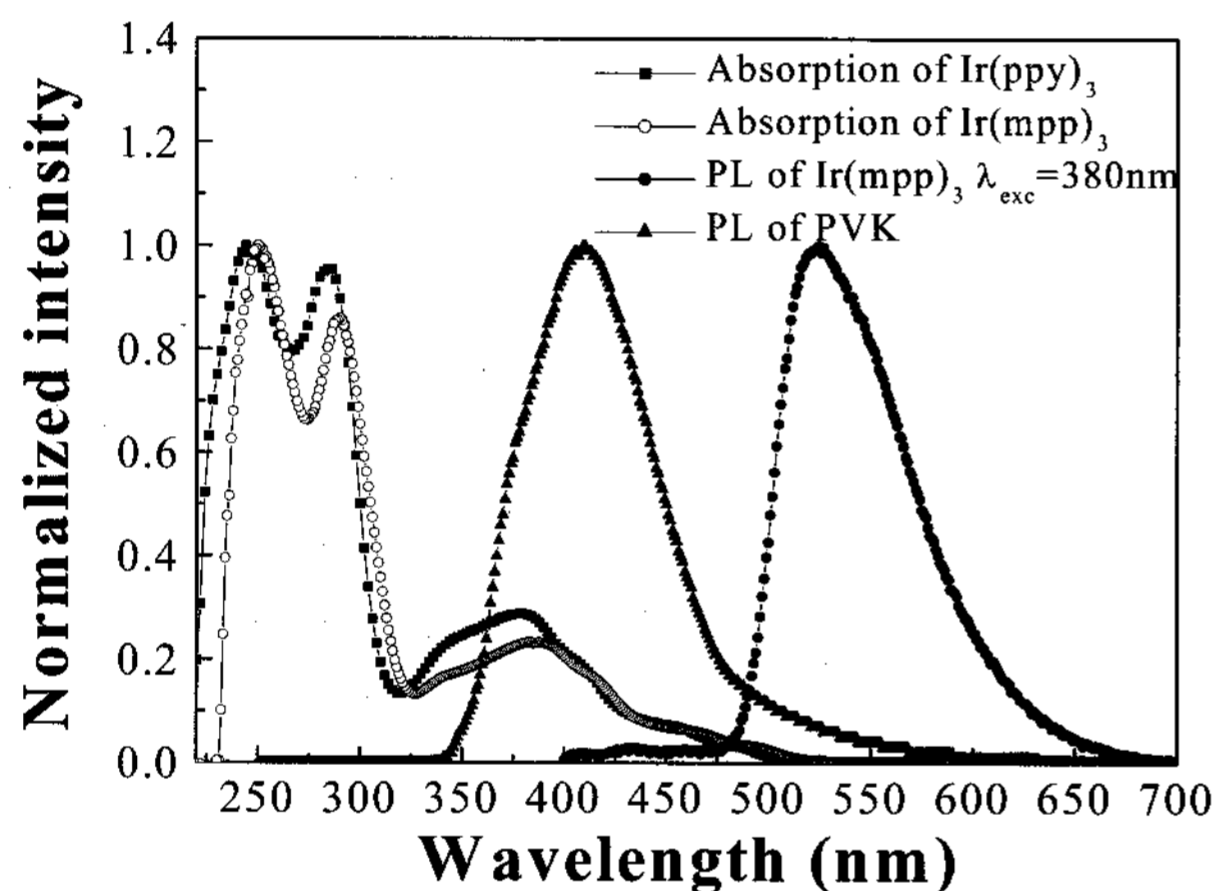


Fig. 3. The absorption and photoluminescence photoluminescence (PL) spectra of 10^{-4} M Ir(mpp)₃ and Ir(ppy)₃ in dichloroethane and emission spectra of host (PVK) at room temperature in air equilibrated condition.

3. Results and Discussion

Time resolved PL response (Fig. 2) provides evidence for the phosphorescence of Ir(mpp)₃ by demonstrating a single exponential curve. The lifetime of Ir(mpp)₃ was found to be $\sim 0.94 \pm 0.1$ μ s, using a film of PMMA doped with 6% Ir(mpp)₃ and was found to be less than that of Ir(ppy)₃ ($\sim 1.5 \pm 0.1$ μ s) under the same condition. The lifetime of several methyl and phenyl substituted complexes of bipyridine and phenanthroline complexes of Ir(III) are studied and inferred that the lifetime of a luminescent Ir(III) complex is a measure of the contribution of the ligand centered and MLCT

centered states to the emissive state [5]. It is envisaged that the activating methyl group facilitates a higher contribution of the MLCT state to the lowest energy emitting state. The decrease in radiative lifetime is also correlated to an increased transition to a highly allowed charge-transfer state from which the emitting state presumably borrows the intensity. The effect of substituents in decreasing the lifetime and quenching rate constant of the luminescence state, and increasing quantum efficiency has also been observed[5].

Fig. 3 shows the absorption and PL spectra of 10^{-4} M Ir(mpp)₃ and Ir(ppy)₃ in dichloroethane and emission spectra of host (PVK) at room temperature in air equilibrated condition. This figure shows good spectrum overlap between the polymer host emission and the singlet metal-to-ligand charge-transfer (¹MLCT) state of Ir(mpp)₃ (388 nm). The peak centered at 388 nm in the absorption spectra corresponds to the ¹MLCT transition as evidenced by the extinction coefficient of the order of 10^3 . A decrease in the extinction coefficient as compared to Ir(ppy)₃ [6] can be attributed to the opposing effects of methyl group on the σ -donor and π -acceptor abilities [7]. The electronic effect of methyl substitution on the aromatic ring should bring an increase in the σ -donor strength of the pyridyl ring and added electron density on Ir(III), facilitating MLCT transition. The steric effect of the methyl group forcing the two aromatic rings out of co-planarity twists the ligand mpp and reduces delocalization and the π -acceptor ability of the molecule, making charge transfer more difficult. Thus the influence of the two opposing effects are demonstrated by higher HOMO (4.93 eV) and ³MLCT (2.56 eV) and ¹MLCT (1.74 eV) values of Ir(mpp)₃ compared to Ir(ppy)₃. The complex shows strong luminescence in the solution state at room temperature in air-equilibrated conditions. The complex exhibits a large Stoke shift and the absorption and emission spectra show little overlap. This shows that the compound has little self-absorption. Ir(mpp)₃ shows emission peak at 523 nm (full width at half maximum, FWHM = 73 nm), a 10 nm bathochromic shift compared to the ppy complex. Similar bathochromic shifts are also revealed in the absorption spectra. The emission of the complex, centered at 523 nm is due to the radiative decay from the triplet manifold to the ground state. The emission is red shifted compared to Ir(ppy)₃. The steric interactions are anticipated to affect the energies of the excited states involving π -symmetry ligand orbitals

owing to decreased delocalisation between the rings and hence the emission wavelength [8]. The methyl substitution has probably caused a red shift in the absorption and emission spectrum compared to Ir(ppy)_3 . The absence of any vibrational progression in the PL spectra helps assigning the $^3\text{MLCT}$ state as the dominant emitting state at room temperature in equilibrium with the other neighbouring states.

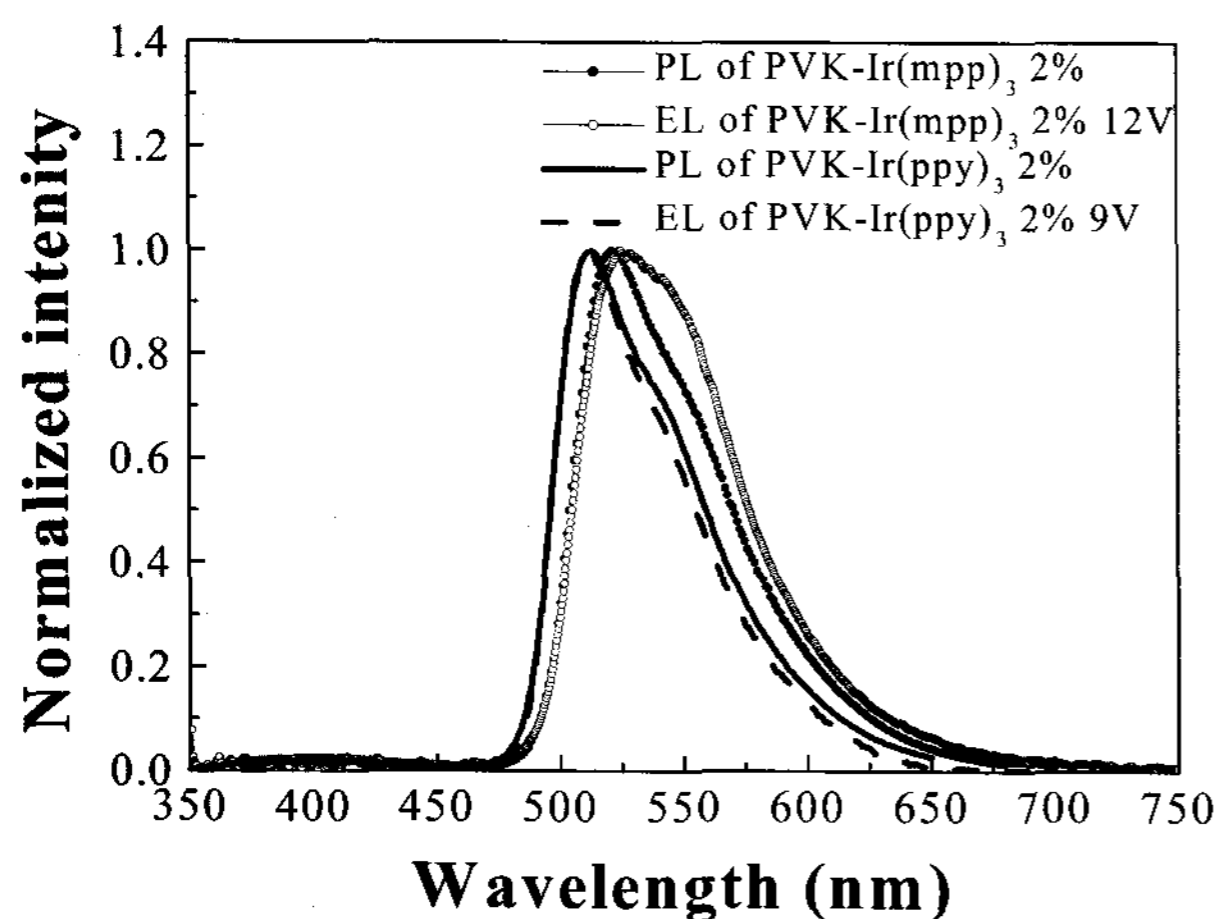


Fig. 4. Photoluminescence spectra of Ir(mpp)_3 (2 %) and Ir(ppy)_3 (2 %) doped PVK thin films and electroluminescence spectra of PVK- Ir(mpp)_3 (2 %) and PVK- Ir(ppy)_3 (2 %) devices.

Fig. 4 demonstrates the PL and EL spectra of a 2 % doped PVK- Ir(mpp)_3 and PVK- Ir(ppy)_3 films. A good spectrum overlap of Ir(mpp)_3 absorption and PVK emission satisfies the preliminary condition of energy transfer from PVK to Ir(mpp)_3 . PL emission behaviour of PVK- Ir(mpp)_3 film is similar to that of PVK- Ir(ppy)_3 film [9]. A thin film of PVK doped with Ir(mpp)_3 , in the doping range of 2-8 % gives emission maxima at 523 nm when excited by 335 nm (PVK absorption maximum). From the absorption and emission spectra of host PVK and guest Ir(mpp)_3 in Figure 3, we calculated the Förster radii for the singlet-singlet energy transfer between the polymer and Ir(mpp)_3 . Förster radius between the polymers and Ir(mpp)_3 is 33.1 Å, larger than 30 Å, (Ir(ppy)_3 showed 33.1 Å with PVK) indicating the possibility of efficient energy transfer by Förster mechanism [10]. In this calculation, the quantum efficiency of the guest material is not involved. Between electroluminescence and phospholuminescence, energy transfer to Ir(mpp)_3 is more efficient in the former than

in the latter. Weak host emission at 410 nm is observed in phospholuminescence of the doped PVK thin film but in electroluminescence, only Ir(mpp)_3 emission is observed. This is because, one more mechanism participates to generate the excitons in Ir(mpp)_3 in electroluminescence. In phospholuminescence, excitons in Ir(mpp)_3 are created by only the energy transfer mechanism (Förster and/or Dexter) from PVK excitons. However, in EL, energy transfer and carrier trapping make excitons in Ir(mpp)_3 . Direct exciton formation on Ir(mpp)_3 by hole electron recombination will give a more efficient Ir(mpp)_3 emission in electroluminescence.

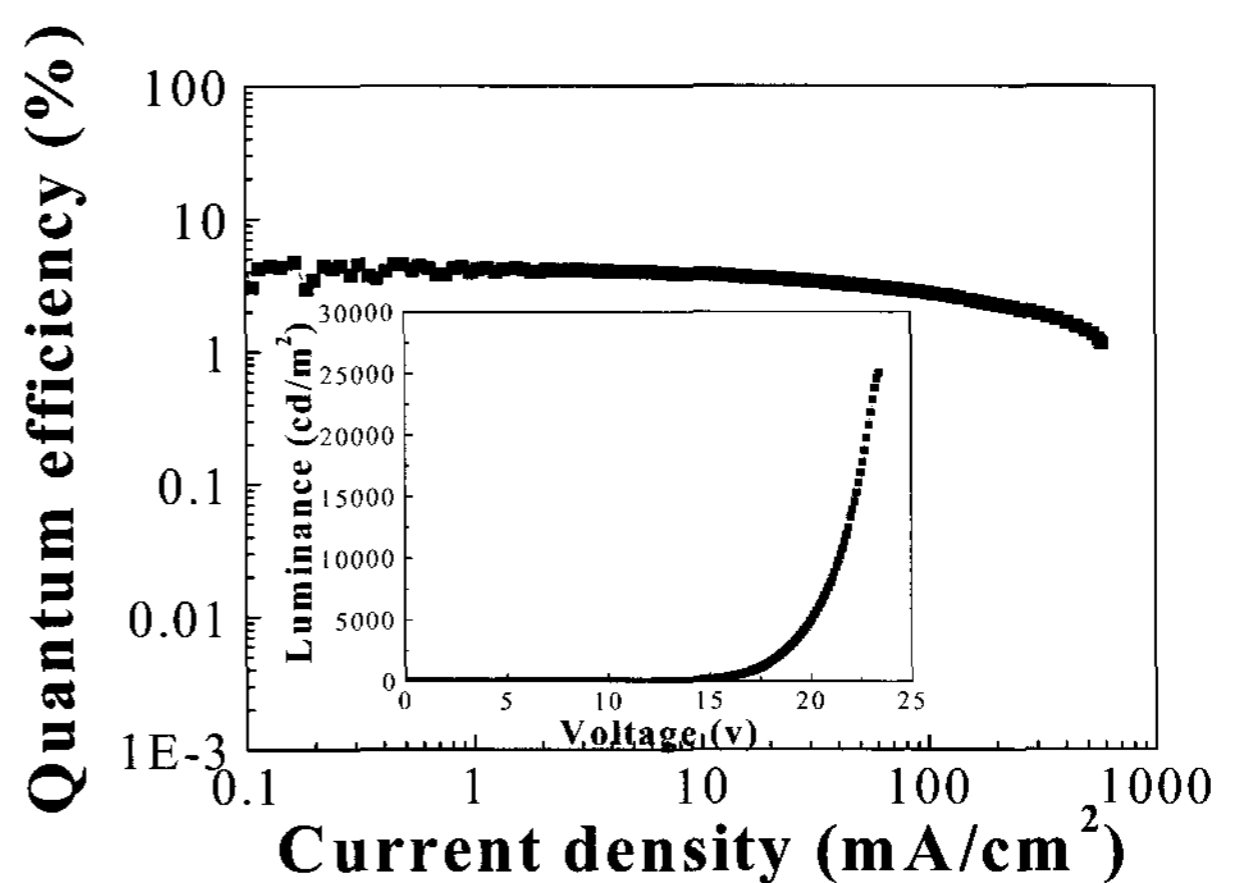


Fig. 5. External quantum efficiency of Ir(mpp)_3 in PVK versus current density. The inset figure shows luminance as a function of voltage of the device when doped with 2 % Ir(mpp)_3 in PVK.

Fig. 5 shows the external quantum efficiency as a function of the current density for PVK- Ir(mpp)_3 device. The inset figure shows the luminance of the PVK- Ir(mpp)_3 device as a function of driving voltage. A 2 % doped device furnishes maximum external quantum efficiency and power efficiency of 4.5 % and 3.6 lm/W at 72 cd/m^2 (current density of 0.45 mA/cm^2 and drive voltage of 13.9 V) and a peak luminance of 25,000 cd/m^2 at 23.4 V (474 mA/cm^2). The turn on voltage of the device is 10 V. The optimization of thickness of component layers and doping concentration can result in significant increase in the luminance, quantum efficiency and power efficiency.

In summary, we synthesized a new green Ir(III) complex and fabricated electrophosphorescent organic light emitting devices. This study manifests the effect of the presence of a methyl substituent at the 3-position of

the pyridyl ring of 2-phenylpyridine on the energy levels and electroluminescence behaviour of the complex Ir(mpp)₃. The delocalization between the pyridyl and phenyl ring affect the HOMO and MLCT energy levels. There is a bathochromic shift in the ¹MLCT and PL and EL peaks compared to Ir(ppy)₃. From the PL and EL spectra of the doped film, we can confirm that energy transfer from PVK to Ir(mpp)₃ takes place efficiently. A 2 % doped PVK based device shows 4.5 % external quantum efficiency and a peak luminance of 25,000 cd/m². Our findings show quite fascinating features of the phosphorescent emitter and can be concluded to be the result of direct impact of the fine tuning of the orthometalating ligand, coordinated to Ir(III).

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