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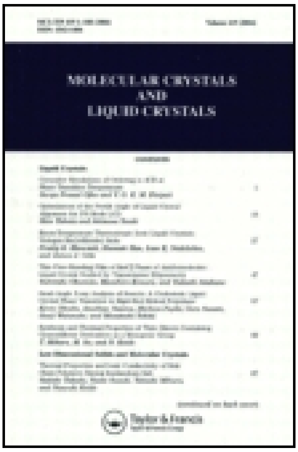

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Effects of Symmetry of Ir (III) Complex on the Photophysical Properties and Device Performances

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The optical, electrochemical properties of two isomers of $Ir(mpp)_2acac$ *(mpp = anion of 3-methyl-2-phenyl-pyridine and acac = acetylacetonate) and the device performance of polymer light emitting devices using two isomers as a triplet emitter have been studied. The two isomers show the symmetric and asymmetric coordination of two mpp ligands to Ir(III), which is confirmed from the* ^1H *NMR spectra. The ligand based absorption is red shifted by 35 nm in asymmetric* $Ir(mpp)_2acac$ *compared to the symmetric* $Ir(mpp)_2acac$*. The MLCT absorption peak positions are similar in both cases, but the extinction coefficients of the asymmetric* $Ir(mpp)_2acac$ *are higher than those of symmetric* $Ir(mpp)_2acac$*. The two isomers exhibit similar PL emission spectra but PL lifetimes of two isomers are different. The lifetime of the symmetric* $Ir(mpp)_2acac$ *is 1.74 μs, whereas that of the asymmetric* $Ir(mpp)_2acac$ *is 0.9 μs. The asymmetric* $Ir(mpp)_2acac$ *shows higher electrochemical oxidation potential than that of the symmetric* $Ir(mpp)_2acac$*. The polymer light emitting devices are fabricated by blending 8 wt% of* $Ir(mpp)_2acac$ *in the PVK. The polymer light emitting device with symmetric* $Ir(mpp)_2acac$ *shows a maximum external quantum efficiency* (η_{ext}) *of 0.48% at 73 mA/cm*^{2} *and a luminance of 12,300 cd/m*^{2}*. The polymer light emitting device with asymmetric* $Ir(mpp)_2acac$ *shows a maximum external quantum efficiency of 0.32% at 100 mA/cm*^{2} *and a luminance of 7,500 cd/m*^{2}*. This results show that the symmetry of metal complex can affect the photophysical properties as well as the device performance.*

Keywords symmetry; Ir(III) complex; isomer; polymer light emitting devices

Introduction

The phosphorescent dye blended polymer (organic) light emitting devices have drawn enormous attention for the realization of the full color displays [1–14]. Developments of new device structures [15] and materials [16–17] are one of the main research topics to improve the device performance. As far as the materials are considered, developing new phosphorescence dye, especially, 5*d* transition metal complexes have become the

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most essential part of improving the device performance of electrophosphorescent polymer (organic) light emitting devices. Due to the strong spin orbit coupling [18], these complexes exhibit efficient emissions from the triplet metal-to-ligand charge-transfer (^{3}MLCT) state in the microsecond range. The polymer (organic) light emitting devices furnish high quantum efficiency and brilliant luminance when these complexes are used as the emissive dopants in suitable host material. Both the singlet and triplet excitons on the host can be transferred to these complexes with the subsequent emission from the ^{3}MLCT states [19]. And also, the emission color can be tuned by the proper ligand selection and modification of metal complexes [20–23].

Until now, most of phosphorescent dye blended polymer (organic) light emitting devices use the Os(II) [24–26], Pt(II) [22, 27–28] and Ir(III) [3–5, 20, 21, 23, 29–32] complexes coordinated to pyridines or arylpyridine derivative as triplet dopant. These complexes mostly exhibit a symmetric configuration of the coordinating atoms around the metal ion. The metal complexes show different symmetric configuration by the coordination environment and this difference of symmetry at metal complexes results in different optical and electrical properties. However, there has been few reports [33–35] about the consideration of the symmetry of the coordination environment and the effects of symmetry to its photophysical properties as well as device performance.

In this work, optical, electrochemical and electroluminescence properties of both symmetric and asymmetric bis-orthometalted Ir(III) complexes, Ir(mpp)$_2$acac (mpp = the anion of 3-methyl-2-phenyl-pyridine and acac = acetylacetonate), have been reported. Polymer light emitting devices are fabricated by blending 8 wt% Ir(mpp)$_2$acac in polymer host PVK and the device performances have been investigated. The two isomers show the difference in the absorbance, PL lifetime, electrochemical properties as well as device performance.

Experimental

Synthesis

The syntheses were carried out in an argon atmosphere by using the schlenk arrangement. The products were stored in vacuum to avoid air contact. All the starting materials and solvents are reagent grade. The solvents are appropriately purified whenever required.

The symmetric Ir(mpp)$_2$acac [36] is synthesized (Fig. 1) by heating 0.1 m mol of the dinuclear complex [Ir(mpp)$_2$Cl]$_2$ and 0.2 m mol of acetylacetone in 2-ethoxyethanol at 100°C in the presence of 50 mol of sodium carbonate for 15h. The yellow residue is filtered, washed with water, ether and *n*-hexane and then dried in vacuum at 80°C. The dried product is purified by silica column using dichloromethane as the eluent. After rotary evaporation of the solvent and vacuum drying, the complex was sublimated at 260°C and 10^{-6} torr. Analytical, found: C% 55.44, N%, 4.31 H%, 4.19; calculated: C% 55.50, N% 4.4, H% 4.3. ^{1}H NMR (300 MHz, CDCl$_3$) ppm: 8.51(d, 2H, J = 7.5 Hz), 7.84(d, 2H, J = 7.8 Hz), 7.52(d, 2H, J = 8.2 Hz), 7.02(t, 2H, J = 5.67 Hz), 6.80(t, 2H, J = 4.4 Hz), 6.64(t, 2H, J = 6.7 Hz), 6.26(d, 2H, J = 7.5 Hz), 5.17(s, 1H), 2.84(s, 6H), 1.74(s, 6H).

The asymmetric Ir(mpp)$_2$acac is synthesized (Fig. 1) by using the same materials in the similar proportion in 2-ethoxyethanol at a temperature of 20–30°C higher than the boiling point of 2-ethoxyethanol for 48h. The final product is isolated by using above purification method. Analytical, found: C% 55.47, N% 4.30, H% 4.18; calculated: C% 55.50, N% 4.4, H% 4.3. ^{1}H NMR (300 MHz, CDCl$_3$) ppm: 8.85(d, 1H, J = 4.0 Hz), 8.51(d, 1H, J = 6 Hz), 7.82(t, 2H, J = 9.3 Hz), 7.60(d, 1H, J = 7.5 Hz), 7.52(d, 1H, J = 8.4 Hz), 7.16(t, 1H, J =

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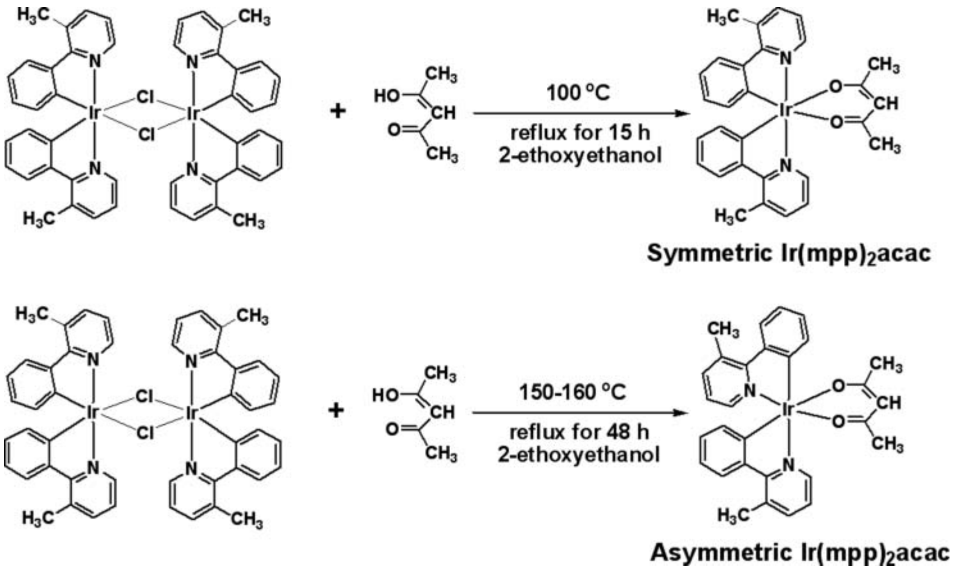

Figure 1. Synthetic scheme and the molecular structure of symmetric and asymmetric Ir(mpp)$_2$acac.

6.6 Hz), 7.02(t, 1H, J = 7.5 Hz), 6.79(t, 2H, J = 7.8), 6.66–6.59 (m, 2H), 6.26 (d,1H, J = 7.5 Hz), 6.07(d, 1H J = 7.5), 5.17(s, 1H), 2.84(s, 6H), 1.74(s, 6H). Figure 1 show synthetic scheme and the molecular structure of symmetric and asymmetric Ir(mpp)$_2$acac.

Fabrication of PLED

The glass substrate pre-coated with indium-tin-oxide was cleaned by an ultrasonic bath of acetone, followed by methanol and isopropyl alcohol and then was dried in vacuum oven at 100°C. Surface treatment was carried out by exposing ITO to UV-ozone plasma. The hole-injecting layer, a 40 nm thick film of PEDOT:PSS (Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate)), and 8 wt% symmetric and asymmetric Ir(mpp)$_2$acac doped PVK are spin coated successively on ITO from 1,2 dichloroethane solutions. A 20 nm thick BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) layer was deposited as the exciton-blocking and electron transporting layer followed by a 30 nm Alq$_3$ (tris-(8-hydroxyquinoline)aluminium(III)) as an electron transporting layer by thermal evaporation at 10^{-6} torr. Finally Mg:Ag (100 nm) and Ag(20 nm) were deposited as the cathode through a shadow mask by thermal evaporation. The fabricated polymer light emitting devices have the configuration of ITO/PEDOT:PSS (40 nm)/PVK : symmetric or asymmetric Ir(mpp)$_2$acac (8 wt%) (20–30 nm)/BCP (20 nm)/Alq$_3$ (30 nm)/Mg:Ag (100 nm)/Ag (20 nm).

Measurements

^{1}H NMR spectra were recorded at 300 MHz with a JEOL JNM-LA 300 WB FT-NMR spectrometer. Chemical shifts were referenced to internal SiMe$_4$. Element analyses were performed by using a Thermo Quest Italia S.p.A. EA1110 CHNS-O analyzer. Absorption spectra were monitored with a Hewlett-Packard HP8452A UV-visible diode array spectrophotometer equipped with a Hewlett-Packard HP Vectra Qs 16 computer and corrected for background absorption. Photoluminescence spectra were detected by ACTON spectrometer connected to a photomultiplier tube (Acton Research PD-438) with Xenon lamp as excitation source. Emission lifetimes ware measured with the storage sampling oscilloscope (Tektronics TDS 520B) by exciting the samples at 355 nm with a Q-switched Nd-YAG pulsed laser.

Cyclic voltammetry was performed with an Autolab potentiostat by Echochemie under nitrogen in a one-compartment electrolysis cell consisting of a platinum wire working electrode, a platinum wire counter electrode, and $Ag^+/AgCl$ reference electrode. Cyclic voltammograms were monitored at a scan rate of 0.05 V/s and recorded in dichloromethane (Aldrich 99.8%) distilled twice over $CaSO_4$. The concentration of the complex was maintained at 0.5 mM or less and each solution contained 0.1 mM of tetrabutylammonium hexafluorophosphate (Aldrich) as the electrolyte. The oxidation of ferrocene in such a system takes place at 0.37 V. The HOMO level with reference to ferrocene gives the energy corresponding to vacuum level.

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Results and Discussion

Figure 2 show the ^1H NMR spectra of symmetric and asymmetric $Ir(mpp)_2acac$. The ^1H NMR spectrum of the symmetric $Ir(mpp)_2acac$ shows seven coupled spins for the seven

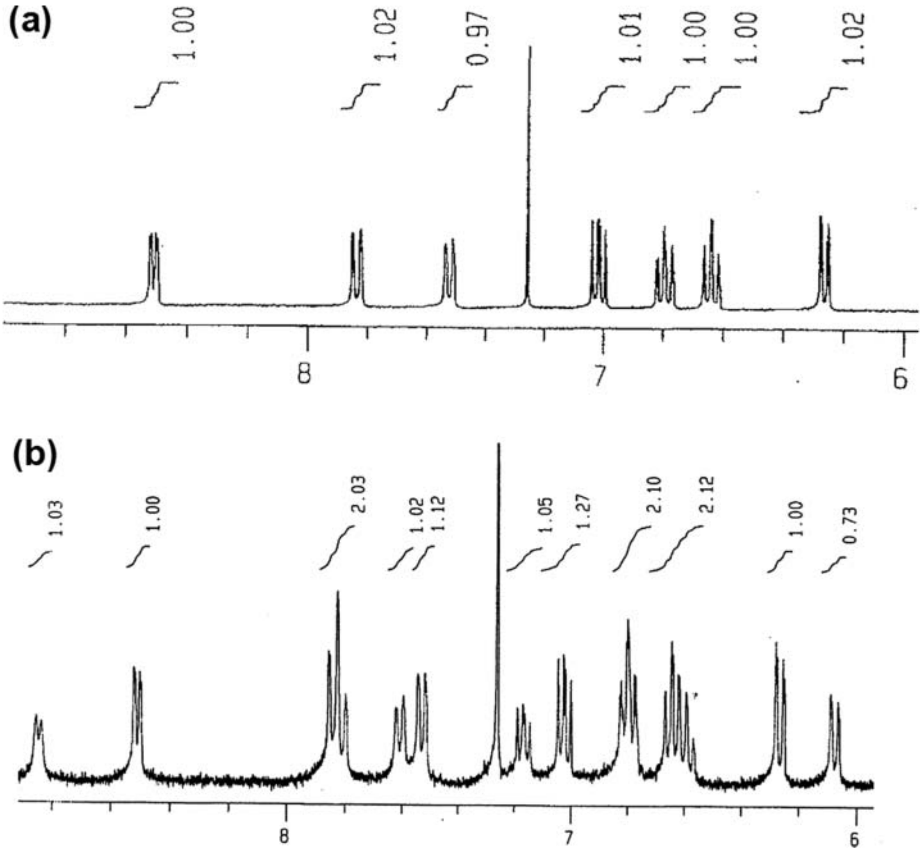

Figure 2. ^1H NMR spectra of (a) symmetric and (b) asymmetric $Ir(mpp)_2acac$.

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aromatic protons of mpp in the region, δ 8.47–6.20. The structures of similar molecules containing two coordinating carbons in the *cis* positions and the two nitrogen atoms in the *trans* positions have been established [20]. But the asymmetric Ir(mpp)$_2$acac shows 11 coupled spins in the region δ 8.85–6.06. It indicates a different arrangement of the coordinated C and N in the metal complex. In the symmetric and asymmetric Ir(mpp)$_2$acac, the methyl protons of mpp are equivalent and show similar chemical shifts at δ 2.84. The similar feature is also observed for the methyl protons of acac appearing at δ 1.74 in both the complexes. The methine proton of acac appears at δ 5.17 for the two isomers.

The room temperature absorption, PL spectra of the symmetric and asymmetric Ir(mpp)$_2$acac in 10^{-5}M dichloromethane solution are shown in Fig. 3. Figure 3 shows that the ligand-centered absorption at 258 nm is red shifted to 293 nm in the asymmetric Ir(mpp)$_2$acac. Though the MLCT peaks [37] appear at the same wavelengths, the extinction coefficients of the asymmetric Ir(mpp)$_2$acac is higher than that of the symmetric Ir(mpp)$_2$acac. However, both isomers show almost similar PL spectrum in solution.

The isomers show quasi-reversible electrochemical oxidation processes. The HOMO levels of symmetric and asymmetric Ir(mpp)$_2$acac referenced to vacuum is 5.13 and 5.29 eV, respectively (Fig. 4). Since the PL emissions of the two isomers are observed to be close, it indicates that the HOMO-LUMO gap to be similar in both the cases. It is envisaged that the ligand π^* orbital in the asymmetric Ir(mpp)$_2$acac is lowered in energy. This is supported by the red shift of the ligand-centered band in the asymmetric Ir(mpp)$_2$acac in the absorption spectra.

The lifetimes (Fig. 5) are obtained from the transient PL spectra of PMMA films blended with 6 wt% of symmetric and asymmetric Ir(mpp)$_2$acac. The lifetime of the

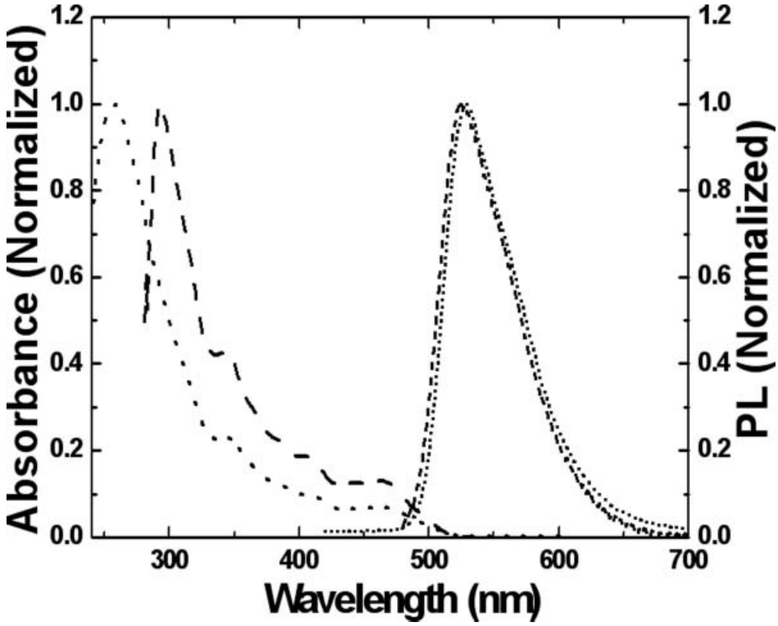

Figure 3. Absorption, PL spectra of symmetric and asymmetric Ir(mpp)$_2$acac in 10^{-5} M dichloromethane solution. Absorption of symmetric Ir(mpp)$_2$acac (dot line), absorption of asymmetric Ir(mpp)$_2$acac (dash line), PL of symmetric Ir(mpp)$_2$acac (short dot line), PL of asymmetric Ir(mpp)$_2$acac (short dash line).

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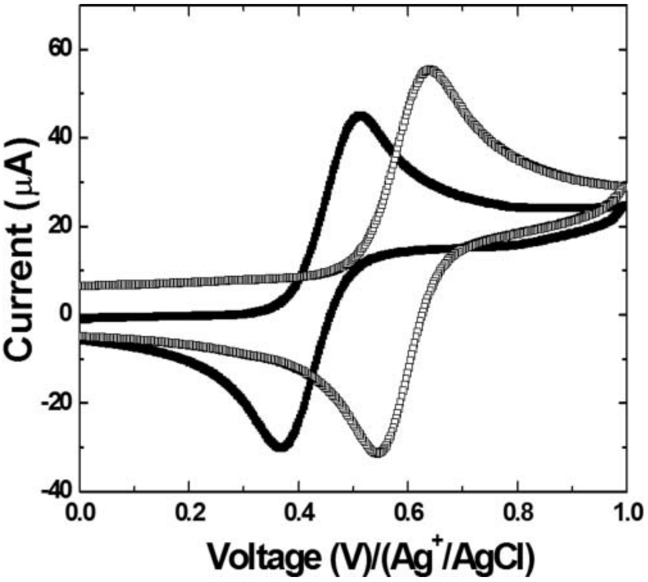

Figure 4. Cyclic voltametry of symmetric (filled squares) and asymmetric (open squares) Ir(mpp)$_2$acac.

symmetric Ir(mpp)$_2$acac is found be 1.74 μs and asymmetric Ir(mpp)$_2$acac is 0.9 μs. The absorption, PL, cyclic voltametry and lifetime results show the effect of the symmetry of metal complex on the optical and electrochemical properties. Table 1 summarizes the optical and electromechanical properties of symmetric and asymmetric Ir(mpp)$_2$acac.

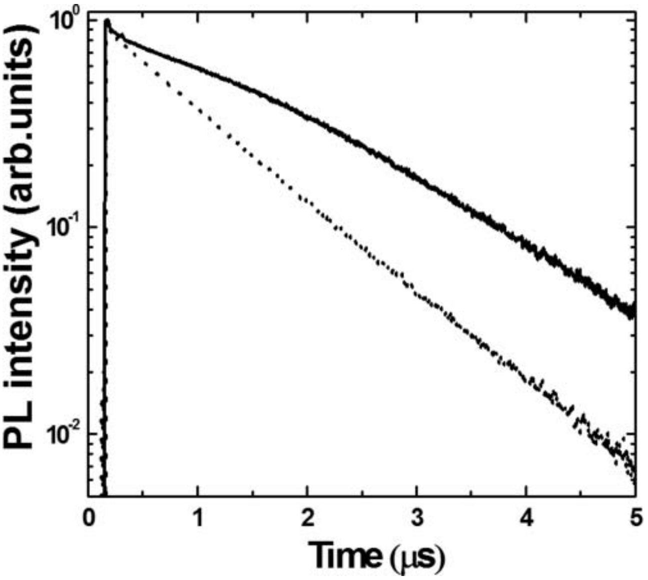

Figure 5. Time resolved PL spectra of 6 wt% symmetric (solid line) and asymmetric (dot line) Ir(mpp)$_2$acac doped PMMA films at room temperature.

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Table 1. Optical, electrochemical and electroluminescence properties as well as PLED performances using the symmetric and asymmetric $Ir(mpp)_2acac$ as triplet emitter

	Symmetric $Ir(mpp)_2acac$	asymmetric $Ir(mpp)_2acac$
HOMO (eV)	5.13	5.29
λ_{max} PL (nm)	530	525
Lifetime (μs)	1.74	0.9
λ_{max} EL (nm)	534	535
Quantum efficiency (η_{ex}) (%)	0.48	0.32
Power efficiency (η_p)(lm/W)	0.42	0.27
Luminance (cd/m^2)	12,300	7,500

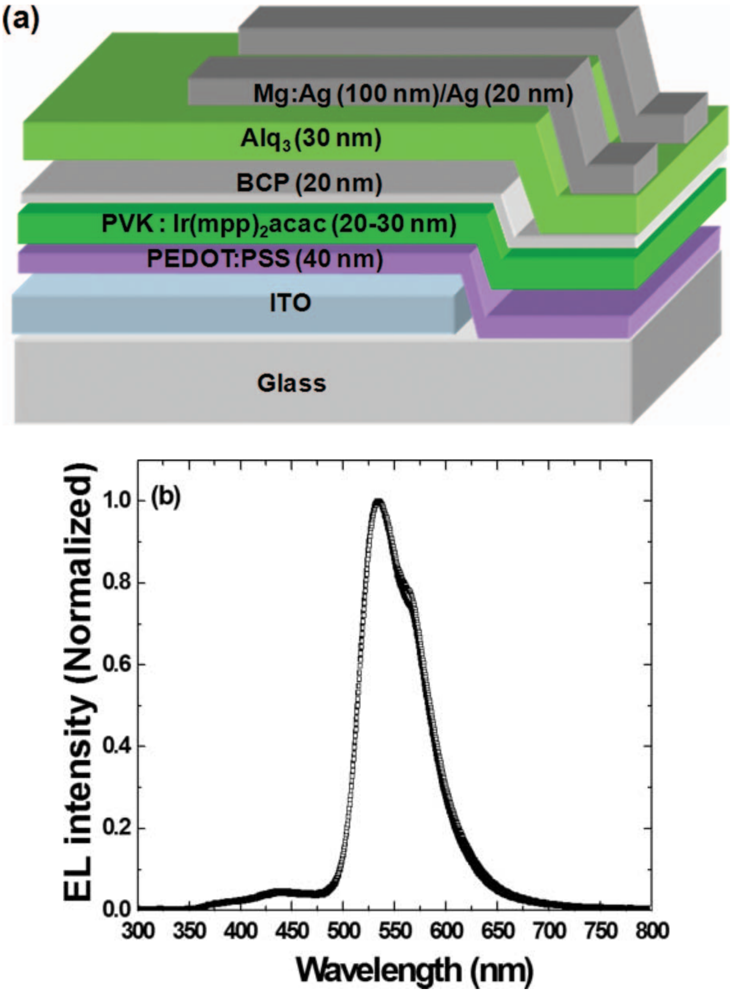

Figure 6. (a) Device configuration and (b) EL spectra of symmetric (filled squares) and asymmetric (open squares) $Ir(mpp)_2acac$ blended PVK devices.

Figure 6 shows (a) the schematic illustration of the device configuration and (b) the EL spectra of the polymer light emitting devices using two isomers as a triplet dopant. The two isomers show EL emission peaks around 535 nm that have little red shift from the solution spectra. The emission at 440 nm could be due to the emission from the hole-blocking BCP [9].

An external quantum efficiency of 0.48% at 73 mA/m^2 (Fig. 7 (a)) and a luminance of 12,300 cd/m^2 at 1,050 mA/m$_2$ (Fig. 7 (b)) was obtained from the polymer light emitting

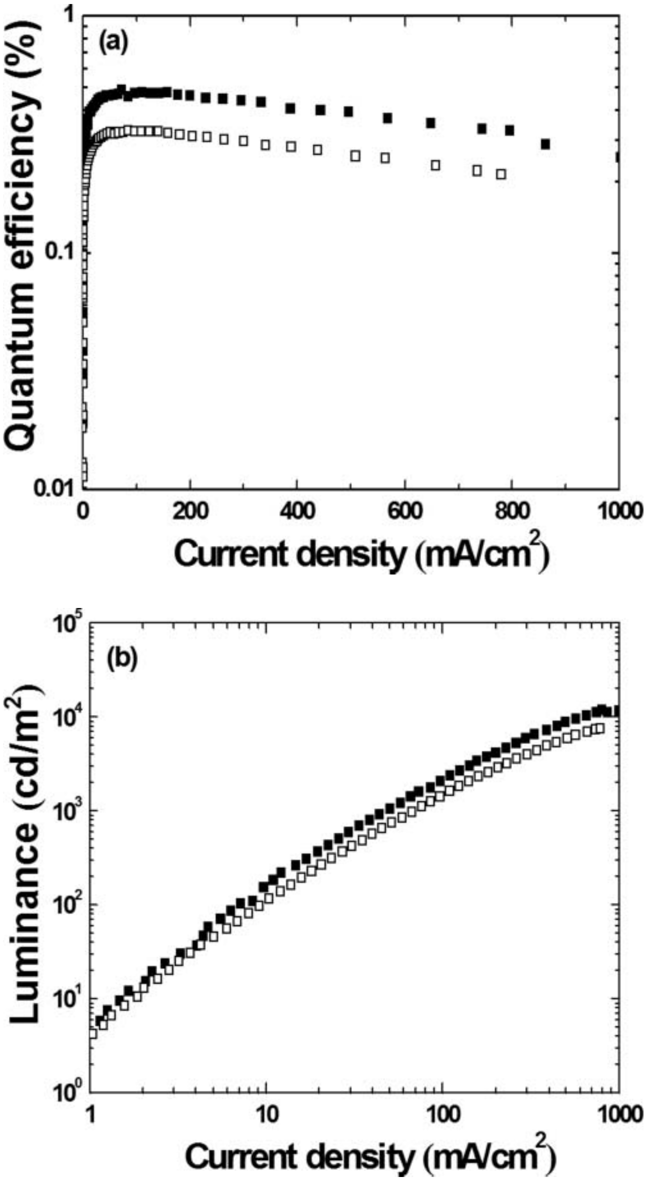

Figure 7. (a) External quantum efficiency and (b) Luminance versus current density of 8 wt% symmetric (filled squares) and asymmetric (open squares) Ir(mpp)$_2$acac blended PVK devices.

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diode with the symmetric Ir(mpp)$_2$acac. The maximum external quantum efficiency and luminance obtained from the polymer light emitting device with asymmetric Ir(mpp)$_2$acac is 0.32% at 100 mA/m^2 and 7,500 cd/m^2 at 750 mA/m^2. The turns on voltage for both the devices are almost similar value. The polymer light emitting device with symmetric Ir(mpp)$_2$acac furnishes 30% higher external quantum efficiency than that of polymer light emitting device with asymmetric Ir(mpp)$_2$acac. The present situation offers an intriguing case of device performance involving dopants with the same composition but different isomeric forms. More study is necessary to reach at any conclusive remark for such differences in the device efficiencies furnished by the two isomers. Table 1 summarizes the PLED performances using the symmetric and asymmetric Ir(mpp)$_2$acac as triplet emitter.

Conclusions

Symmetric and asymmetric Ir(mpp)$_2$acac is synthesized and their optical, electrochemical and electroluminescence properties have been studied. The asymmetric Ir(mpp)$_2$acac shows a 35 nm red shift of the ligand based absorption and higher intensities of the MLCT transitions. Electrochemical oxidation of the asymmetric Ir(mpp)$_2$acac takes place at higher potential. The PL lifetime of the asymmetric Ir(mpp)$_2$acac is almost the half of that of the symmetric Ir(mpp)$_2$acac. The polymer light emitting devices are fabricated by using symmetric and asymmetric Ir(mpp)$_2$acac complexes as the triplet dopants in PVK. The symmetric Ir(mpp)$_2$acac furnished 30% better device performance than that of the asymmetric Ir(mpp)$_2$acac. This result shows the effect of the molecular symmetry on the photophysical properties as well as the device performance.

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