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# The efficient green emitting iridium(III) complexes and phosphorescent organic light emitting diode characteristics

Kwon Soon-Ki<sup>a</sup>, Thangaraju Kuppusamy<sup>a</sup>,

Kim Seul-Ong<sup>a</sup>, Youngjin Kang<sup>c</sup> and Kim Yun-Hi<sup>b\*</sup>

<sup>a</sup>*School of Material Science and Engineering & Engineering Research Institute (ERI),*

<sup>b</sup>*Department of Chemistry and Research Institute of Natural Science (RINS),*

*Gyeongsang National University, Jinju – 660 701, South Korea*

<sup>c</sup>*Division of Science Education, Kangwon National University, Chuncheon, 200-701, South Korea*

## 1. Introduction

Organic light emitting diodes (OLEDs) have attracted enormous attention in the recent years due to their potential application in the solid state lighting and full color flat panel displays because of their high efficiency, low fabrication cost, ease of fabricating large area devices, and wide range of emission colors (Shen et al. 1997; Tang & VanSlyke 1987). When compared to fluorescent OLEDs where only singlet state excitons can emit the light and luminescence is reduced due to triplet formation, the phosphorescent organic light emitting diodes (PHOLEDs) are efficient as both singlet and triplet excitons can be harvested for the light emission (Baldo et al. 1998; Baldo et al. 1999; Adachi et al. 2001; Ikai et al. 2001; Lo et al. 2002). The various phosphorescent light emitting materials have been synthesized and intensively studied worldwide. A promising phosphorescent metal complex should have a short lifetime in the excited state and high phosphorescent efficiency for the highly efficient OLEDs. Among the various phosphorescent emitters, iridium complexes remain the most effective material due to their ability to achieve maximum internal quantum efficiency, nearly 100%, and high external quantum efficiency in the devices (O'Brien et al. 2003; Duan et al. 2003; Xie et al. 2001; Noh et al. 2003; Wang et al. 2001; Neve et al. 2001). The most widely used homoleptic green emitting iridium(III) complex, *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)<sub>3</sub>], derivatives have shown a number of advantages such as ease of tuning emission energy by functionalizing the 'ppy' ligand with electron donating and electron withdrawing substituents and high phosphorescent quantum efficiency at room temperature (Grushin et al. 2001; Jung et al. 2004; Lee et al. 2009). The structural modifications of ppy ligand with various substituents have been carried out for the fine tuning of emission colors in the green region and to improve the device efficiencies for the lighting and display applications.

During our investigations the following substitutions have been examined. The influence of substitutions of (i) methyl groups, (ii) bulky trimethylsilyl groups, (iii) trimethylsilyl groups, and (iv) rigid and bulky cycloalkene units in the homoleptic green emitting iridium(III) complex  $[\text{Ir}(\text{ppy})_3]$  on the electrochemical, photo-physical, and electroluminescence properties has been investigated (Jung et al. 2004; Jung et al. 2006; Jung et al. 2009; Kang et al. 2008).

## 2. Substitution of Methyl groups on photophysical and electrophosphorescence characteristics of Iridium(III) complex

We attached the methyl groups as substituents on the ppy ligand of  $\text{Ir}(\text{ppy})_3$  to prepare a series of *fac*- $[\text{Ir}(\text{dmppy})_3]$  complexes [ $\text{Hdmppy} = n\text{-methyl-2-(n'methylphenyl)pyridine}$  and  $\text{H} = n, n'$ ] and studied their electrochemical, photophysical and electroluminescence properties in devices (Jung et al. 2004). The methyl moiety was chosen due to (i) the phosphorescence emission of  $\text{Ir}(\text{ppy})_3$  derivatives is strongly affected by the triplet energy of the ortho-chelating  $\text{C}\wedge\text{N}$  ligands. Hence the methyl substituents on the ppy rings could play a key role in alteration of the triplet energy and (ii) although a methyl group is a weaker electron-donating group than other functional groups (e.g. OMe,  $\text{NR}_2$  etc), it can influence on the highest occupied molecular orbital (HOMO) and/or the lowest unoccupied molecular orbital (LUMO) level as well as  $^3\text{MLCT}$  state of the iridium(III) complex. The molecular structures of  $\text{Ir}(\text{dmppy})_3$  derivatives are shown in Fig.1.

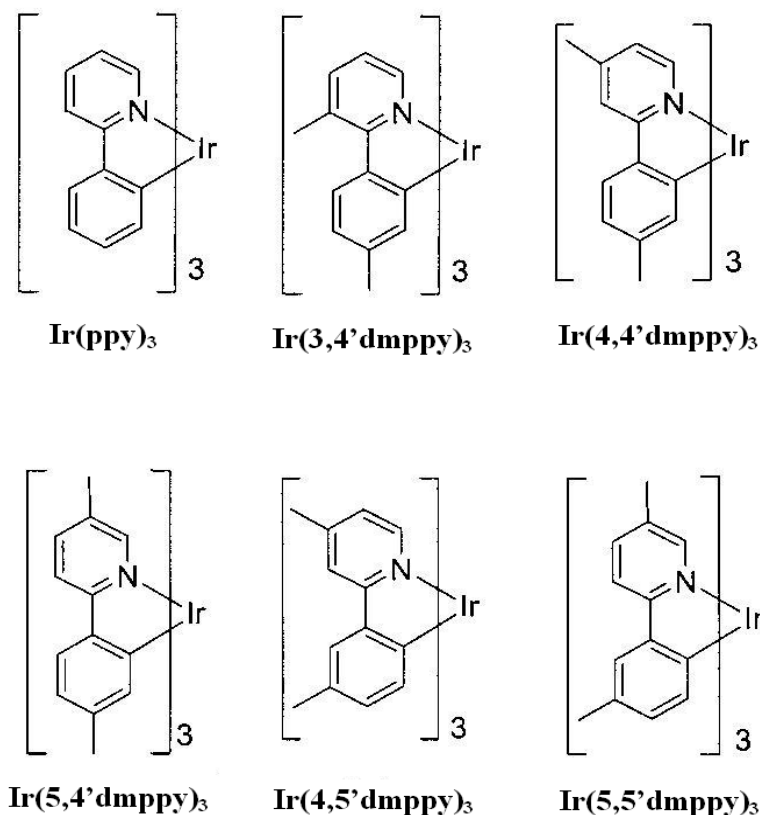


Fig. 1. The molecular structures of methyl substituted  $\text{Ir}(\text{dmppy})_3$  derivatives.

## 2.1 Structural, Electrochemical, Photophysical properties

The methyl substituted Ir(dmppy)<sub>3</sub> derivatives were synthesized by the Suzuki coupling reaction of 2-bromo-n-methylpyridine with the corresponding n'-methylphenylboronic acid in the presence of K<sub>2</sub>CO<sub>3</sub> and [Pd(PPh<sub>3</sub>)<sub>4</sub>] catalyst as reported by our research group (Jung et al. 2004). We found that the *fac*- isomer was formed as the major component, although some *mer*- isomer was formed with low yields and can be isolated. All Ir(dmppy)<sub>3</sub> derivatives are very stable up to 300°C without degradation in air. All the Ir(dmppy)<sub>3</sub> complexes were characterized by mass spectrometry and elemental analysis. The crystal structures of Ir(4,4'dmppy)<sub>3</sub> and Ir(4,5'dmppy)<sub>3</sub> complexes exhibit only the *fac*- configuration, with a distorted octahedral geometry around the Ir atom as shown in Fig. 2 and Fig. 3, respectively.

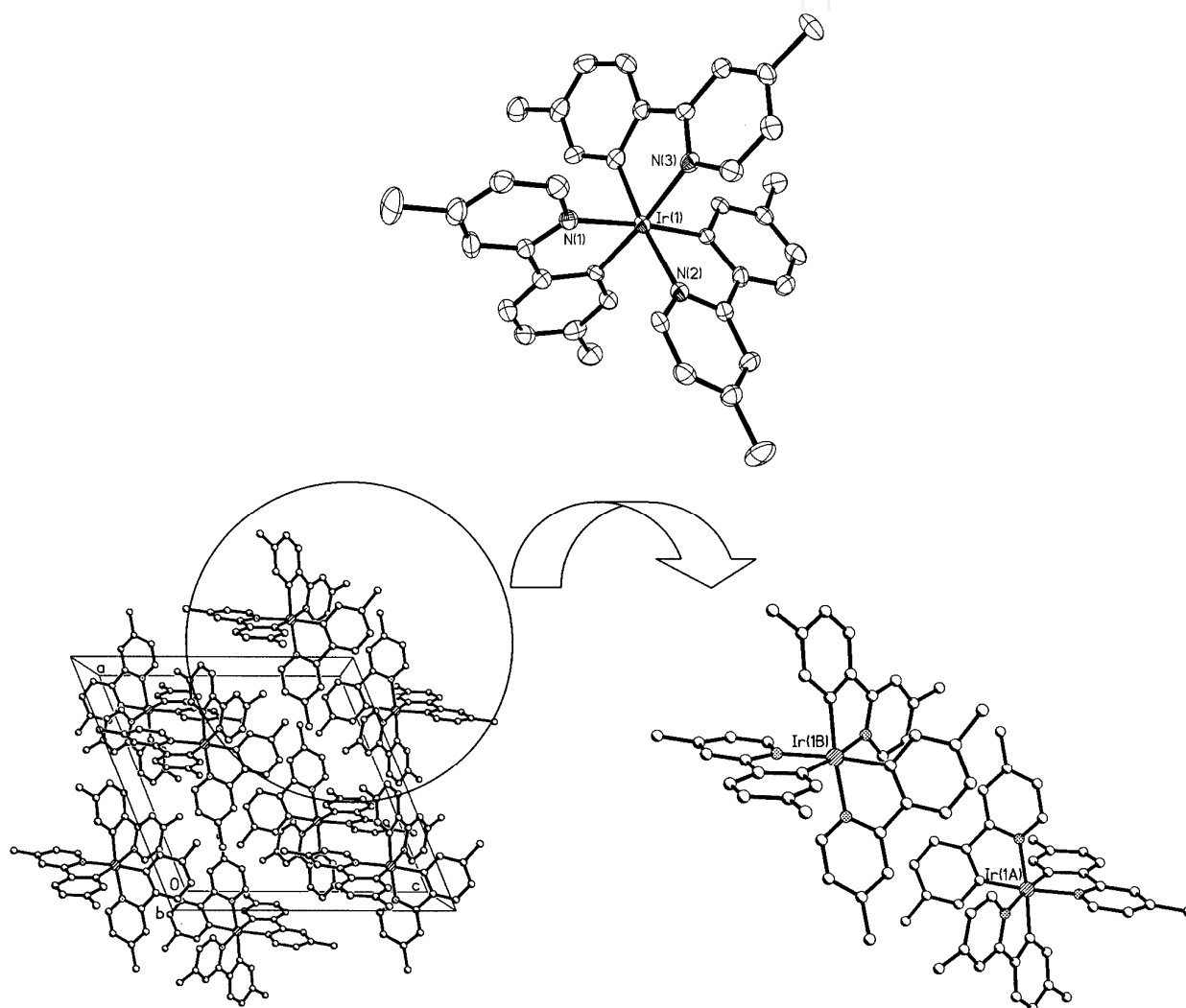


Fig. 2. Top: Molecular structure of Ir(4,4'dmppy)<sub>3</sub> with atom labeling schemes and 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity; bottom: crystal packing diagram between two adjacent molecules of Ir(4,4'dmppy)<sub>3</sub> showing the lack of a  $\pi$ - $\pi$  stacking interaction in the solid state.

The dihedral angle between the phenyl and pyridine rings in Ir(4,4'dmppy)<sub>3</sub> complex (8.81°) is approximately three times larger than that of Ir(4,4'dmppy)<sub>3</sub> (3.4°), indicating a decreased

conjugation of 4,4'-ppy ligands. The UV-visible absorption and emission spectra of all Ir(dmppy)<sub>3</sub> derivatives are shown Fig. 4. From the absorption data of all Ir(dmppy)<sub>3</sub> complexes, ligand-centred  $\pi$ - $\pi^*$  transitions were observed between 250 nm and 310 nm and However, <sup>1</sup>MLCT and <sup>3</sup>MLCT peaks of all the complexes appeared at lower energies except Ir(4,4'dmppy)<sub>3</sub> complex which showed at higher energies. This shows that the methyl groups on the dmppy rings have a significant effect on the electronic transitions energies. The emission spectra of all complexes show the phosphorescent emission between 509 nm and 534 nm in solution and thin films at room temperature (Ichimura et al. 1987; King et al. 1985). The absorption and emission data of all the Ir(dmppy)<sub>3</sub> derivatives in CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Table. 1.

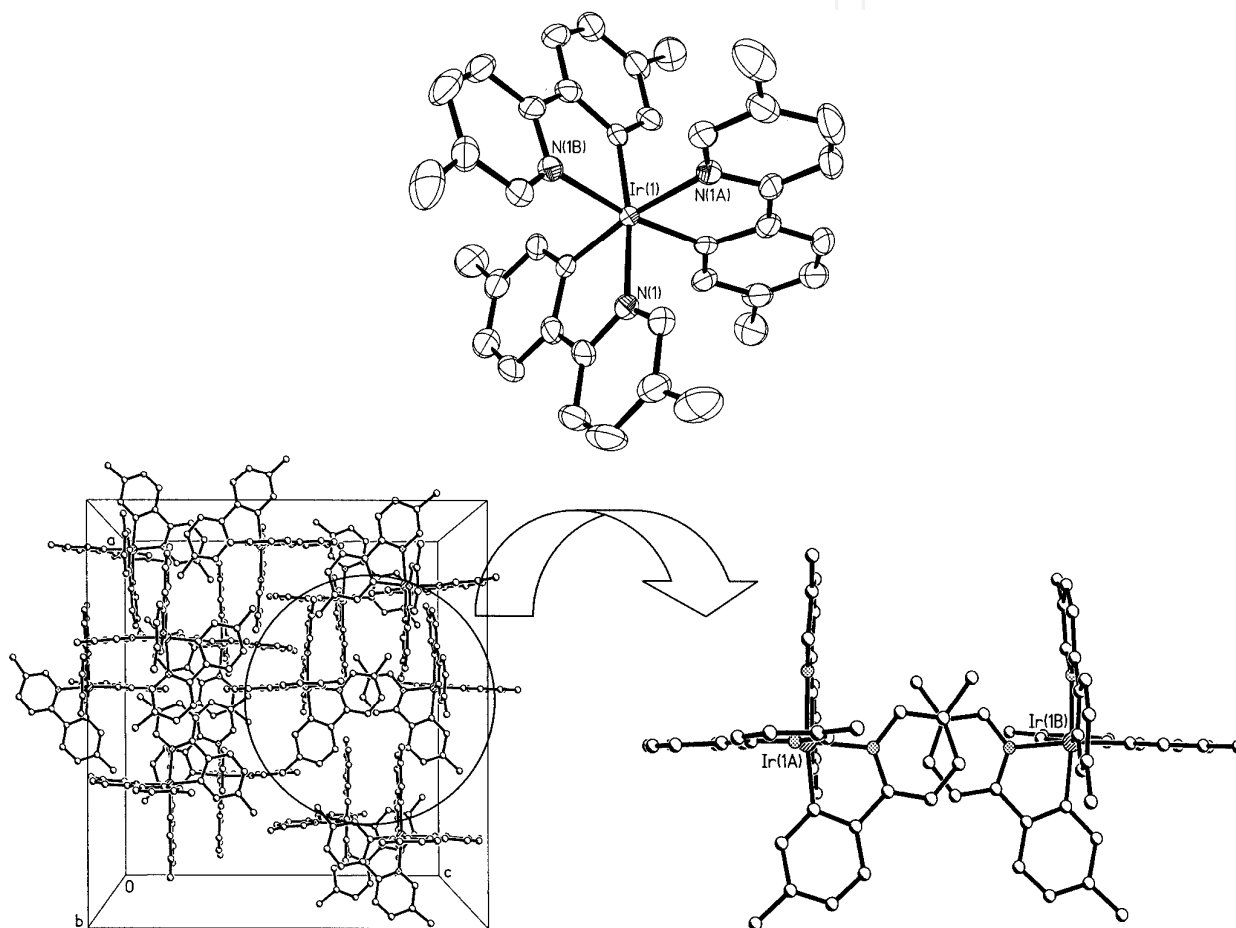


Fig 3. Top: Molecular structure of Ir(4,5'dmppy)<sub>3</sub> with atom labeling schemes and 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity; bottom: crystal packing diagram between two adjacent molecules of Ir(4,5'dmppy)<sub>3</sub> showing the intermolecular interaction in the solid state.

The blue-shifted absorption and emission spectra of Ir(4,4'dmppy)<sub>3</sub> complex compared with other complexes and Ir(ppy)<sub>3</sub> can be attributed to the reduction of conjugation between phenyl and pyridine rings as well as the lack of intermolecular interactions in the solid state (Sapochak et al. 2001). This is due to steric factors with a contribution from the strong electron donating effect of methyl groups. It has been reported that the donating effect from the methyl groups at either the 4'- or 6'- positions does not have any significant influence on

the HOMO energy levels, while methyl groups at the 3'- or 5'- positions effectively donate electrons to dmppy moiety.

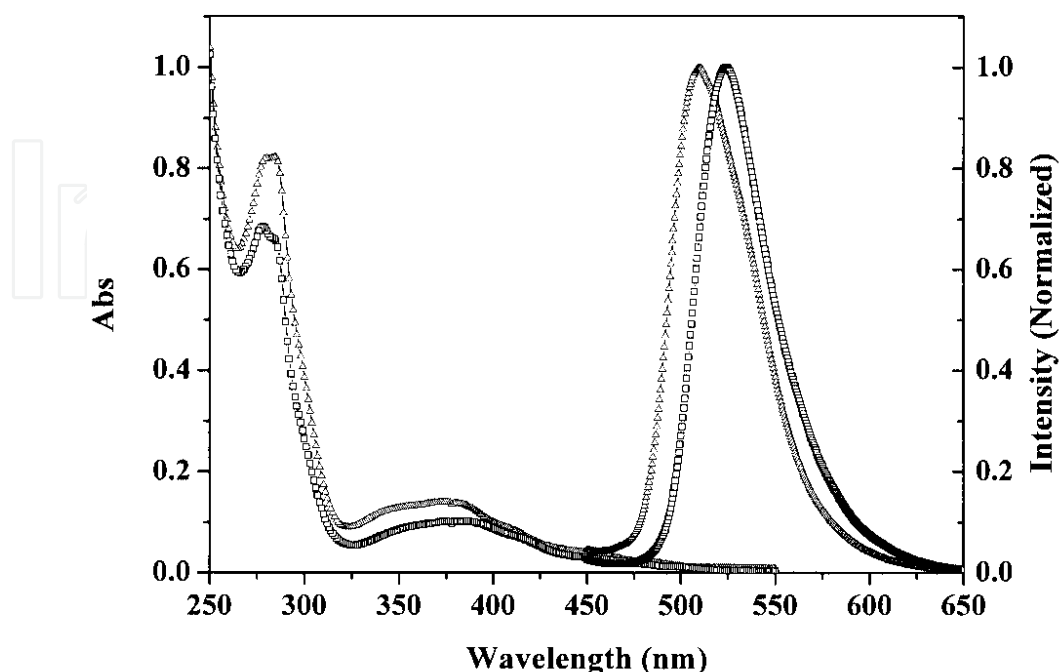


Fig. 4. Absorption and emission spectra of Ir(4,4'dmppy)<sub>3</sub> (triangles) and Ir(5,4'dmppy)<sub>3</sub> (squares) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

Ir Complex	UV-Vis Absorption nm(ε)	Emission (λ <sub>max</sub> )		Φ <sub>PL</sub>	Redox E <sub>1/2</sub> (V)
		Sol.	Film		
Ir(ppy) <sub>3</sub>	283(4.9),380(4.1),405(4.0),455(3.5),490(3.1)	514	516	0.40	0.71
Ir(3,4'dmppy) <sub>3</sub>	284(4.9),384(4.1),408(4.0),455(3.6),493(3.2)	522	529	0.41	0.51
Ir(4,4'dmppy) <sub>3</sub>	278(4.9),374(4.2),407(4.0),452(3.6),484(3.3)	509	512	0.52	0.54
Ir(4,5'dmppy) <sub>3</sub>	284(4.9),391(4.1),414(4.0),456(3.6),493(3.2)	524	534	0.32	0.49
Ir(5,4'dmppy) <sub>3</sub>	284(4.9),383(4.1),412(4.0),459(3.5),490(3.2)	524	536	0.34	0.52
Ir(5,5'dmppy) <sub>3</sub>	284(4.9),384(4.0),414(3.9),458(3.4),497(3.0)	524	532	0.29	0.47

Table 1. Photophysical and electrochemical data of Ir(dmppy)<sub>3</sub> complexes.

## 2.2 Electroluminescence properties

The phosphorescent organic light emitting diodes (PHOLEDs) based on Ir(dmppy)<sub>3</sub> complexes were fabricated by the vacuum deposition technique with the following configuration: ITO/copper phthalocyanine (CuPc, 10 nm) as hole injection layer/4,4'-bis[(1-naphthyl)(phenyl)-amino]-1,1'-biphenyl (NPD, 40 nm) as hole transport layer/CBP:Ir(dmppy)<sub>3</sub> (8%) (20 nm) as emissive layer/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm) as a hole blocking layer/tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>, 40 nm) as an electron transport layer/LiF (1 nm) as electron injection layer/Al (100

nm) as cathode. All iridium complexes,  $\text{Ir}(4,4'\text{-dmppy})_3$ ,  $\text{Ir}(4,5'\text{-dmppy})_3$  and  $\text{Ir}(5,4'\text{-dmppy})_3$ , doped in 4,4'-bis(9-carbazolyl)-1,1'-biphenyl (CBP) host were used as emissive layer for the devices and the devices performances were compared with that of a similar structured  $\text{Ir}(\text{ppy})_3$  based device. The device structure and molecular structures of the materials used in the devices are shown in Fig. 5.

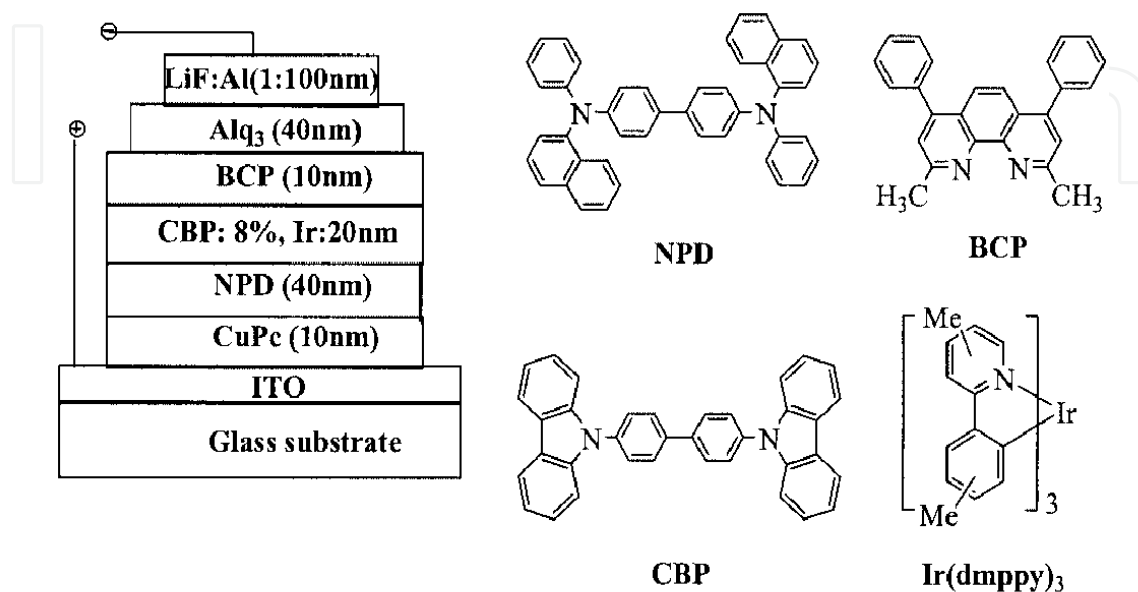


Fig. 5. Device structure and molecular structures of the materials used in the device.

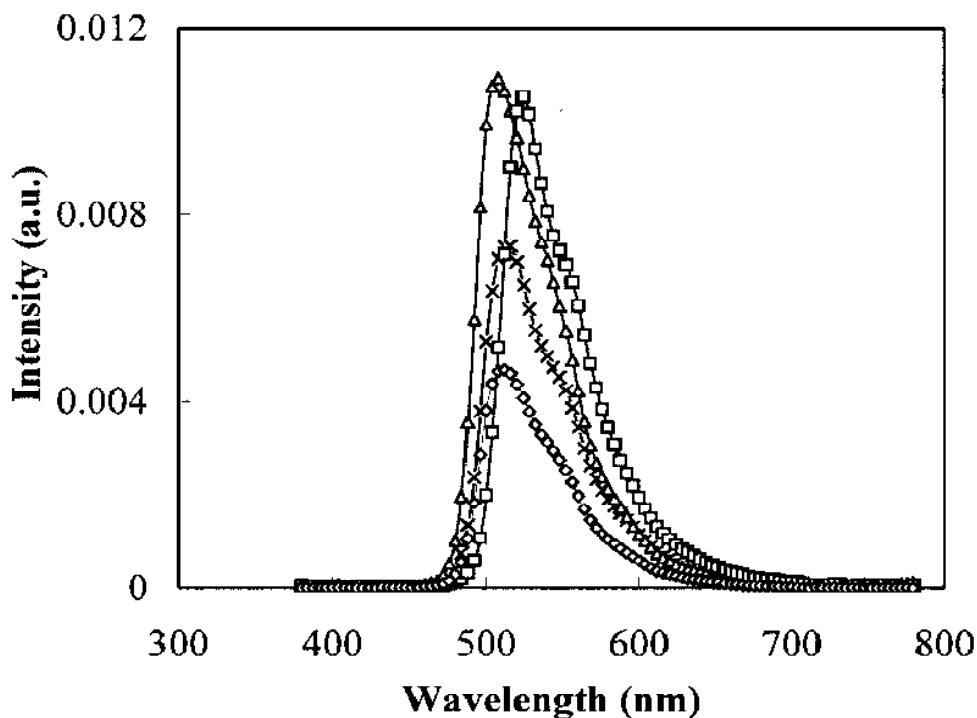


Fig. 6. Electroluminescence spectra of  $[\text{Ir}(\text{ppy})_3]$ , (X),  $\text{Ir}(4,4'\text{-dmppy})_3$  (triangles),  $\text{Ir}(4,5'\text{-dmppy})_3$  (squares) and  $\text{Ir}(5,4'\text{-dmppy})_3$  (diamonds) based devices.



The electroluminescence spectra of all devices showed green emission between 508 nm and 520 nm as shown in Fig. 6, which are quite similar to their PL emission spectra in solution. No host emission was observed, which indicates that the energy transfer from host to dopant is efficient in the EML of the device. The turn-on voltages (defined as 1 mA/cm<sup>2</sup>) and device performances of all three Ir(dmppy)<sub>3</sub> and Ir(ppy)<sub>3</sub> complexes based devices are given in Table 2. The observed higher operating voltages for Ir(4,4'dmppy)<sub>3</sub>- and Ir(5,4'dmppy)<sub>3</sub>- based devices relative to Ir(ppy)<sub>3</sub> based device could be caused by the effective hole trapping. The observed decreasing device efficiencies of all the devices with increasing current densities were attributed to triplet-triplet annihilation. The device based on Ir(4,4'dmppy)<sub>3</sub> complex exhibits higher device performance compared with those of other devices.

Device	Luminescence (Cd/m <sup>2</sup> ) At 20 mA/cm <sup>2</sup>	Operating Voltage (V)	External quantum efficiency (%)		
			at 1 mA/cm <sup>2</sup>	at 10 mA/cm <sup>2</sup>	At 50 mA/cm <sup>2</sup>
Ir(ppy) <sub>3</sub>	3156	4.9	6.0	5.4	4.7
Ir(4,4'dmppy) <sub>3</sub>	4543	5.6	11	8.2	6.8
Ir(4,5'dmppy) <sub>3</sub>	4470	5.1	10.9	7.6	5.8
Ir(5,4'dmppy) <sub>3</sub>	3551	4.6	8.6	6.5	5.0

Table 2. Electroluminescent data of Ir(ppy)<sub>3</sub> and Ir(dmppy)<sub>3</sub> complexes based devices.

### 3. Photophysical and electroluminescence characteristics of bulky trimethylsilyl substituted Iridium(III) complex

The bulky trimethylsilyl substituted iridium(III) complex, *fac*-tris[4-methyl-2-(4'-trimethylsilylphenyl)pyridine]iridium(III) [Ir(msippy)<sub>3</sub>], has been synthesized by our research group and studied its photo-physical and electroluminescence properties in device (Jung et al. 2006). This bulky trimethylsilyl substitution is expected to have inhibited triplet annihilation due to the intermolecular interactions. The molecular structure, UV-Vis and Photoluminescence (PL) spectra of Ir(msippy)<sub>3</sub> complex are shown in Fig. 7. In the UV-Vis spectrum of Ir(msippy)<sub>3</sub> in dichloromethane solution at room temperature, the strong absorption band around 286 nm, which is assigned to  $\pi - \pi^*$  transitions on the cyclometalated ligand, and broad absorption bands from 380 nm to 480 nm assigned to spin allowed and spin forbidden metal-to-ligand charge transfer (MLCT) transitions were clearly observed. PL spectrum of Ir(msippy)<sub>3</sub> in solution shows the emission at 510 nm, indicating the radiative decay from the triplet manifold to the ground state. PL quantum yield of  $\Phi = 0.43$  was observed for the Ir(msippy)<sub>3</sub>, which is slightly higher than that of widely used green emitting phosphorescent Ir(ppy)<sub>3</sub> complex ( $\Phi = 0.40$ ) (Jung et al. 2006; King et al. 1985). This bulky trimethylsilyl substituted Ir(msippy)<sub>3</sub> complex is expected to give better device performances compared with that of Ir(ppy)<sub>3</sub> complex. The electrochemical studies were carried out by cyclic voltametry. The HOMO, LUMO and band gap of the Ir(msippy)<sub>3</sub> are 5.15 eV, 2.67 eV, and 2.47 eV, respectively, from UV absorption data.



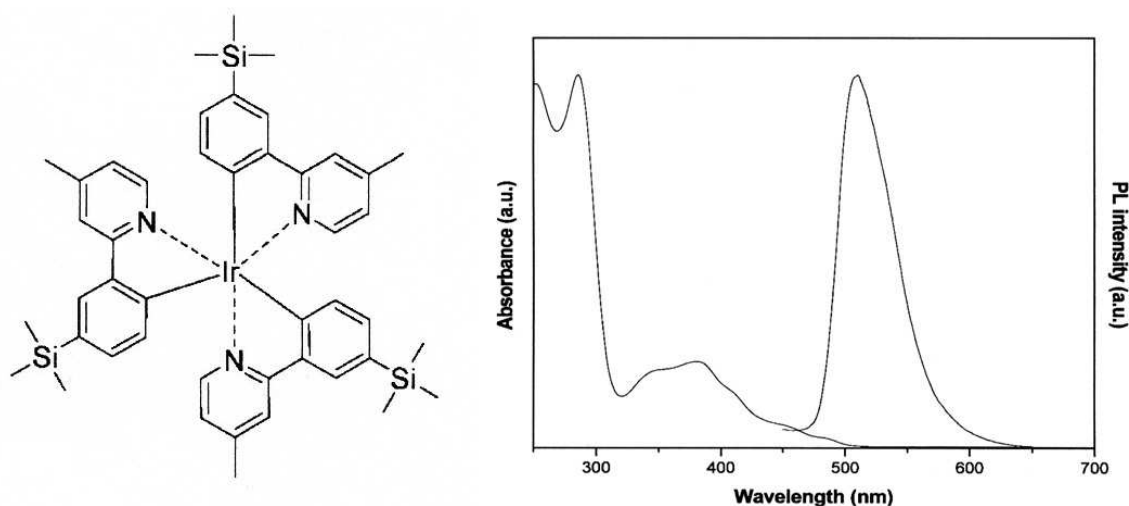


Fig. 7. The molecular structure (left), UV-Visible absorption and Photoluminescence spectra of Ir(msippy)<sub>3</sub> complex (right) in dichloromethane solution.

The phosphorescent organic light emitting diodes (PHOLEDs) were fabricated using the Ir(msippy)<sub>3</sub> complex as phosphorescent dopant by thermal evaporation process and characterized. The optimized device structure was indium-tin-oxide (ITO) (70 nm)/1,1-bis[di-4-tolylamino]phenyl]cyclohexane (TAPC) (50 nm) as a hole transporting layer/4,4',4''-tris(carbazole-9-yl)tri-phenylamine (TcTa) (10 nm) as exciton blocking layer/Ir(msippy)<sub>3</sub> or Ir(ppy)<sub>3</sub> (5%) doped in 4,4'-N,N'-dicarbazole)biphenyl (CBP) host as EML (30 nm) / 1,3,5-tris(m-pyrid-3-yl-phenyl)benzene (TmPyPB) (60 nm) as a hole blocking layer as well as electron transport layer/ LiF (1 nm) as an electron injection layer/ Al (120 nm) as cathode. The device structure and electroluminescence (EL) spectra of the fabricated PHOLEDs are shown in Fig. 8. PHOLEDs based on Ir(msippy)<sub>3</sub> shows the EL emission peak at 521 nm with shoulder peak around 549 nm, which confirms the yellowish-green emission originating from the triplet excited states of the Ir(msippy)<sub>3</sub> dopant in the EML of the device. No emission from host and/or adjacent layers was observed, indicating the charge carriers and excitons are confined well within the EML. It has also been reported that the energy and/or charge transfer from CBP host to Ir(msippy)<sub>3</sub> dopant is complete. The maximum external quantum efficiency (EQE) of 25.6% and current efficiency of 84.4 Cd/A were observed for Ir(msippy)<sub>3</sub> based device with CIE color coordinates of (0.31, 0.64). PHOLEDs based on Ir(ppy)<sub>3</sub> shows the green EL emission peak at 512 nm with shoulder peak around 539 nm originating from the triplet excited states of the Ir(ppy)<sub>3</sub> dopant in the EML of the device, which is consistent with earlier report (Zhang et al. 2005; Cheng et al. 2003; Kim et al. 2007). The small additional emissions from CBP host and TcTa layers were observed for the devices based on Ir(ppy)<sub>3</sub> complex, which indicates that the energy and/or charge transfer from host to dopant is incomplete. The PHOLEDs based on Ir(ppy)<sub>3</sub> showed a maximum EQE of 18.7 % and current efficiency of 60.3 Cd/A. The device performances are shown in Table 3.

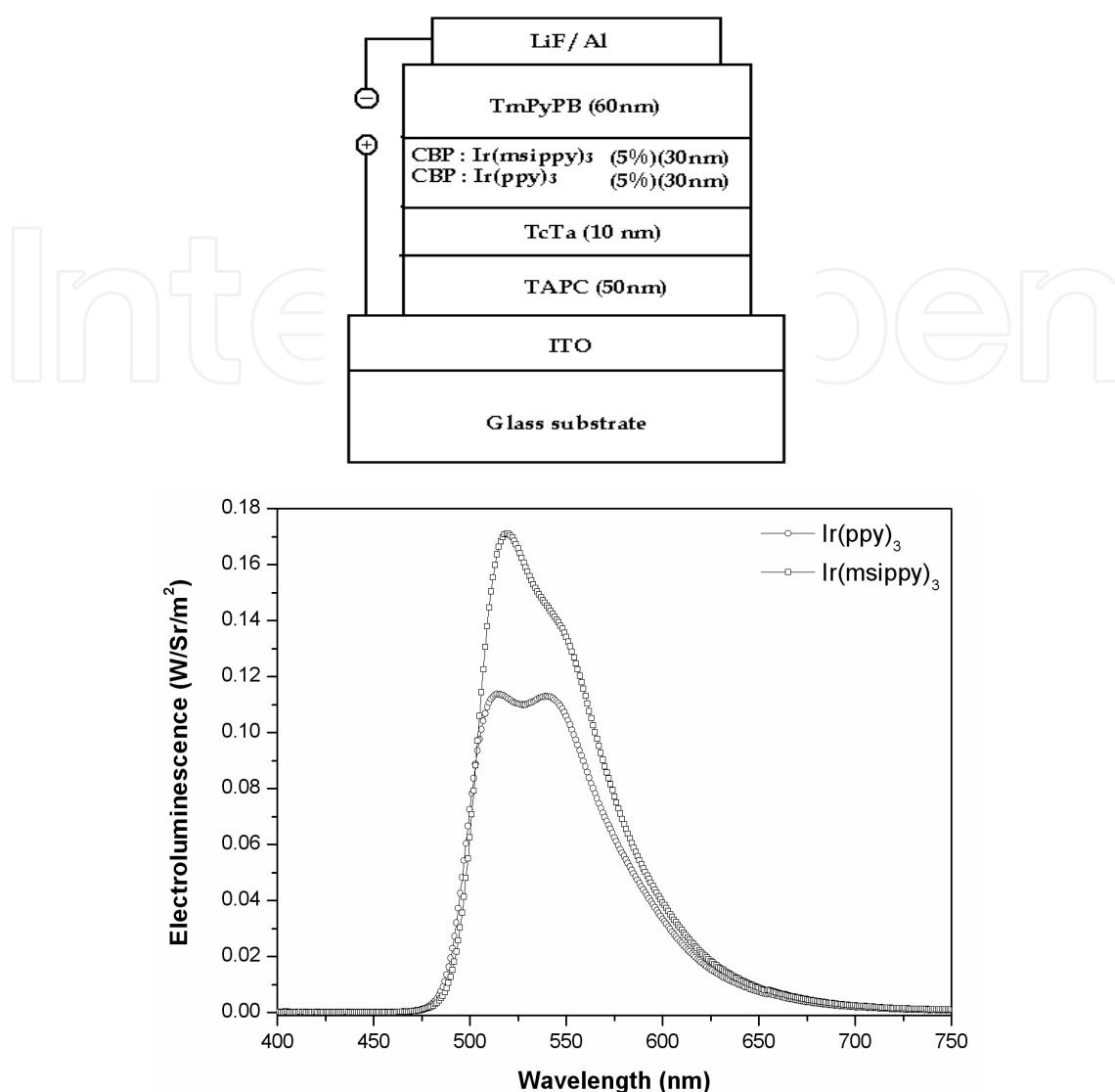


Fig. 8. The device structure (top), Electroluminescence spectra (bottom) of the fabricated PHOLEDs based on Ir(msippy)<sub>3</sub> and Ir(ppy)<sub>3</sub> complexes.

PHOLEDs based on	Luminescence (Cd/m <sup>2</sup> )	EQE (%)	Current efficiency (Cd/A)
Ir(msippy) <sub>3</sub>	77,910 (18V)	25.6	84.4
Ir(ppy) <sub>3</sub>	44,700 (18V)	18.7	60.3

Table 3. The device efficiencies of PHOLEDs based on Ir(msippy)<sub>3</sub> and Ir(ppy)<sub>3</sub> dopants.

#### 4. A narrow band green emitting bulky trimethylsilyl substituted Iridium(III) complex and PHOLED characteristics

The homoleptic iridium(III) complex, *fac*-tris[2-(3'-trimethylsilylphenyl)-5-trimethylsilylpyridinato]iridium [Ir(disppy)<sub>3</sub>], has been synthesized by Suzuki coupling reaction. The effect of the substitution of bulky silyl groups on the photophysical and electroluminescence properties of Ir(disppy)<sub>3</sub> based device has also been investigated (Jung

et al. 2009). The trimethyl functional groups provide to the molecules such higher vapour pressure, higher thermal stability, good solubility and steric bulk via higher volume. These properties of silyl moieties effectively hinder the aggregation and excimer formation of ppy based iridium(III) complex (Liu et al. 2005). Ir(disppy)<sub>3</sub> complex is highly soluble in common organic solvents and slightly soluble in hexane due to the introduction of bulky trimethylsilyl groups. This complex is very stable up to 290 °C without degradation under N<sub>2</sub> atmosphere. Differential scanning calorimetry (DSC) showed the glass transition temperature of 184 °C. The observed T<sub>g</sub> value of Ir(disppy)<sub>3</sub> complex is considerably higher than that of Ir(ppy)<sub>3</sub> complex. This suggests that the introduction of silyl moieties in the ppy ring leads to higher thermal stability.

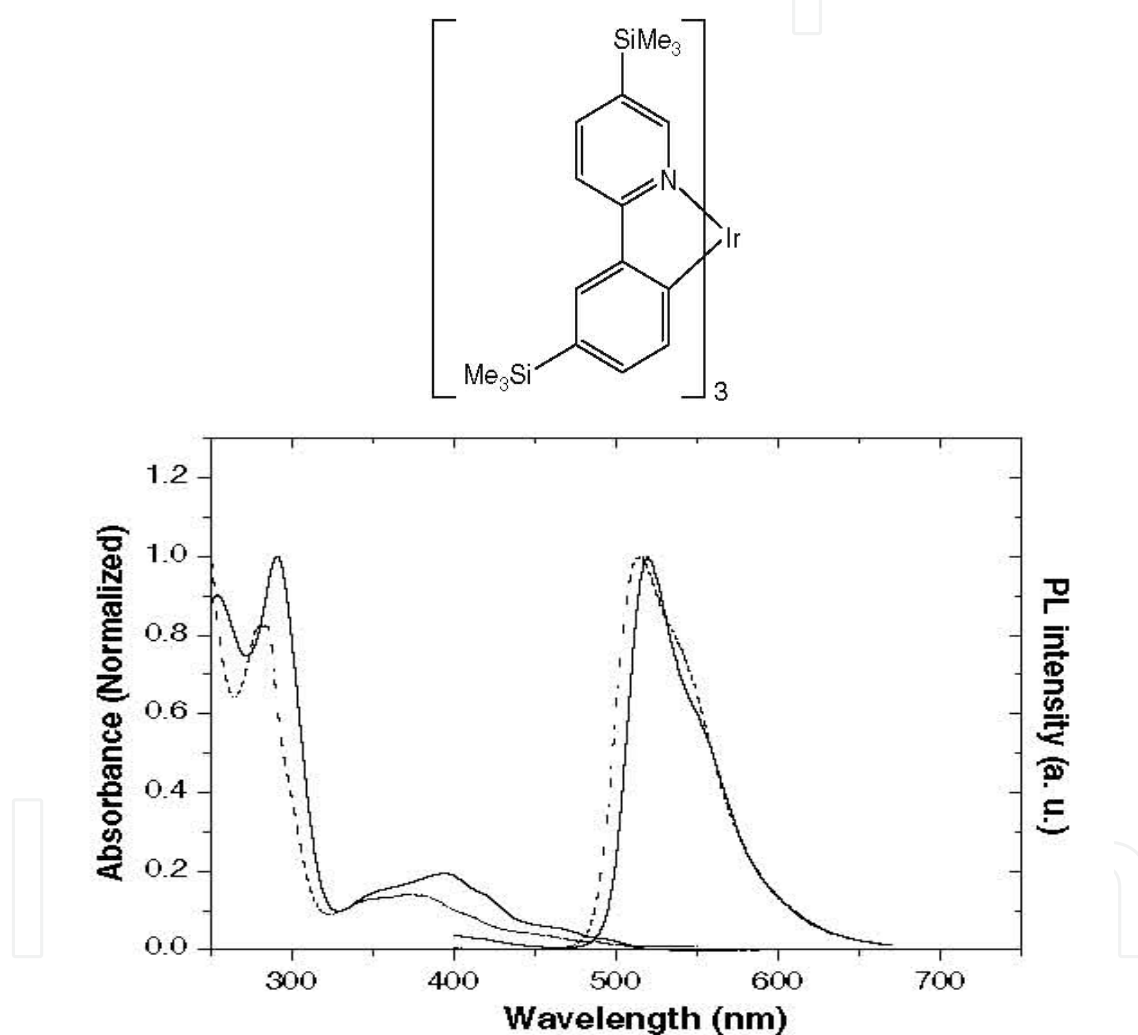


Fig. 9. The molecular structure (top), UV-Visible and photoluminescence spectra of Ir(disppy)<sub>3</sub> complex (bottom) in solution (solid line) and in film (dashed line).

The UV-Visible spectra of Ir(disppy)<sub>3</sub> and Ir(ppy)<sub>3</sub> complexes in solution show the absorption band around 288 nm corresponding to ligand centered (LC)  $\pi - \pi^*$  transitions and the absorption in the region of 350 to 480 nm corresponding to spin-allowed (singlet) and spin-forbidden (triplet) metal-to-ligand charge transfer (MLCT) transitions. The larger extinction coefficient of the singlet and triplet MLCT states of Ir(disppy)<sub>3</sub> complex relative to

that of Ir(ppy)<sub>3</sub> complex indicates the substituent silyl groups play a key role in the enhancement of the spin-orbit coupling. The PL spectra of Ir(disppy)<sub>3</sub> complex show the phosphorescence emission at 519 nm in solution and 513 nm in the film. Interestingly, the emission spectrum of Ir(disppy)<sub>3</sub> complex in the solid state is blue shifted in comparison to the diluted solution (10<sup>-5</sup>-10<sup>-6</sup> M) and the emission spectrum in solution shows the narrow band with a small full width at half maximum of 50 nm for solution spectrum and of 60 nm for film spectrum. The blue shifted emission of solution spectrum may indicate that bulky trimethylsilyl groups hamper intermolecular interactions even in the solid state. The molecular structure, UV-Vis and PL spectra of Ir(disppy)<sub>3</sub> complex are shown in Fig. 9. The HOMO level of Ir(disppy)<sub>3</sub> complex was estimated from cyclic voltametry to be -5.30 eV, which is compared with the value (-5.2 eV) obtained from ultraviolet photoelectron spectroscopy (UPS) and this is slightly higher than that of Ir(ppy)<sub>3</sub> complex. The LUMO level and optical band gap of Ir(disppy)<sub>3</sub> were estimated from its absorption data to be -2.71 eV and 2.59 eV, respectively. From the PL efficiency measurements, it is observed that the bulky silyl group on the ppy ring seems to play a key role in preventing self-quenching.

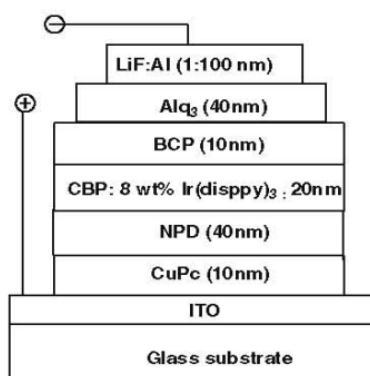


Fig. 10. The device structure of Ir(disppy)<sub>3</sub> or Ir(ppy)<sub>3</sub> based PHOLEDs.

The phosphorescent organic light emitting diodes (PHOLEDs) based on Ir(disppy)<sub>3</sub> complex were fabricated by the vacuum deposition process. The devices were made using ITO as anode/copper phthalocyanine (CuPc, 10 nm) as hole injection layer/4,4'-bis[(1-naphthyl)(phenyl)-amino]-1,1'-biphenyl (NPD, 40 nm) as hole transporting layer/CBP host : Ir(disppy)<sub>3</sub> or Ir(ppy)<sub>3</sub> (8%) (20 nm) as phosphorescent dopant/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm) as hole blocking layer/tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>, 40 nm) as electron transport layer/LiF (1 nm) as electron injection layer/Al (100 nm) as cathode. The device structure is shown in Fig. 10. The fabricated PHOLEDs show the yellowish green EL emission at 524 nm for Ir(disppy)<sub>3</sub> based device and at 516 nm for Ir(ppy)<sub>3</sub> based device, which are well matched with the solution photoluminescence (PL) spectra. Ir(disppy)<sub>3</sub> based PHOLED device exhibits the lower operating voltage (7.4 V), higher brightness and power efficiency compared with that of Ir(ppy)<sub>3</sub> based device as shown in Table 4. The higher device efficiencies observed for the Ir(disppy)<sub>3</sub> based device were compared with that of Ir(ppy)<sub>3</sub> device.

PHOLEDs based on	EL ( $\lambda_{\max}$ ) (nm)	Operating voltage (V)	Luminous efficiency (Cd/A)	Power efficiency (lm/W)
Ir(disppy) <sub>3</sub>	524	7.4	39.2	17.3
Ir(ppy) <sub>3</sub>	516	8.7	32.5	11.7

Table 4. The device performances (at 10 mA/cm<sup>2</sup>) of PHOLEDs based on Ir(disppy)<sub>3</sub> and Ir(ppy)<sub>3</sub> (reference) (8%) dopant in CBP host as EML.

## 5. Bulky cycloalkene substituted Iridium(III) complexes and PHOLED characteristics

The electroluminescence (EL) efficiency and the emission energy of iridium(III) complex based devices are greatly influenced by the organic ligand chromophores (Tang & VanSlyke 1987; Tang & VanSlyke 1989; Baldo et al. 1989). In the way to improve and tune the emission colors, we synthesized and reported the iridium(III) complexes using 2-cycloalkenylpyridine derivatives as cyclometalated ligands for OLEDs (Kang et al. 2008). Cyclic alkene is expected to give better stability than alkene in the complexes (Takiguchi et al. 2002). The molecular structures of the iridium complexes, tris-[2-(1-cyclohexenyl)pyridine]iridium [Ir(chpy)<sub>3</sub>] and tris-[2-(3-methyl-1-cyclohexenyl)pyridine]iridium [Ir(mchpy)<sub>3</sub>], are shown in Fig. 11.

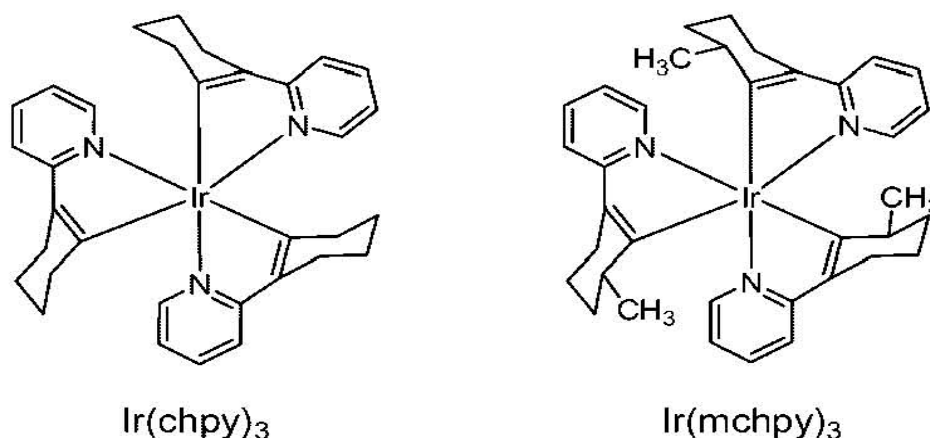


Fig. 11. The molecular structures of 2-cycloalkenylpyridine substituted iridium(III) complexes, Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub>.

The introduction of rigid and bulky cycloalkene unit in these iridium complexes is expected to provide high device efficiencies as well as the suppressed triplet-triplet (T-T) annihilation in the OLED devices. These iridium complexes, Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub>, with cycloalkenylpyridines have higher HOMO and lower LUMO energy levels than iridium(III) complex, Ir(ppy)<sub>3</sub>. We synthesized 2-cycloalkenylpyridine substituted iridium complexes, Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub>, in 44-74% yields and reported (Kang et al. 2008).

Ir(III) complex	UV-Vis Absorption ( $\lambda_{max}$ ) (nm)	PL		$\Phi_{PL}$	$(\tau_{ph})$ ( $\mu s$ )	HOMO/LUMO (eV)
		Sol	Film			
$Ir(chpy)_3$	336, 394, 447, 517	536	550	0.68	2.0	5.0/2.5
$Ir(mchpy)_3$	336, 394, 447, 517	535	543	0.61	1.3	5.1/2.6

Table 5. Photophysical and electrochemical data of  $Ir(chpy)_3$  and  $Ir(mchpy)_3$  complexes.

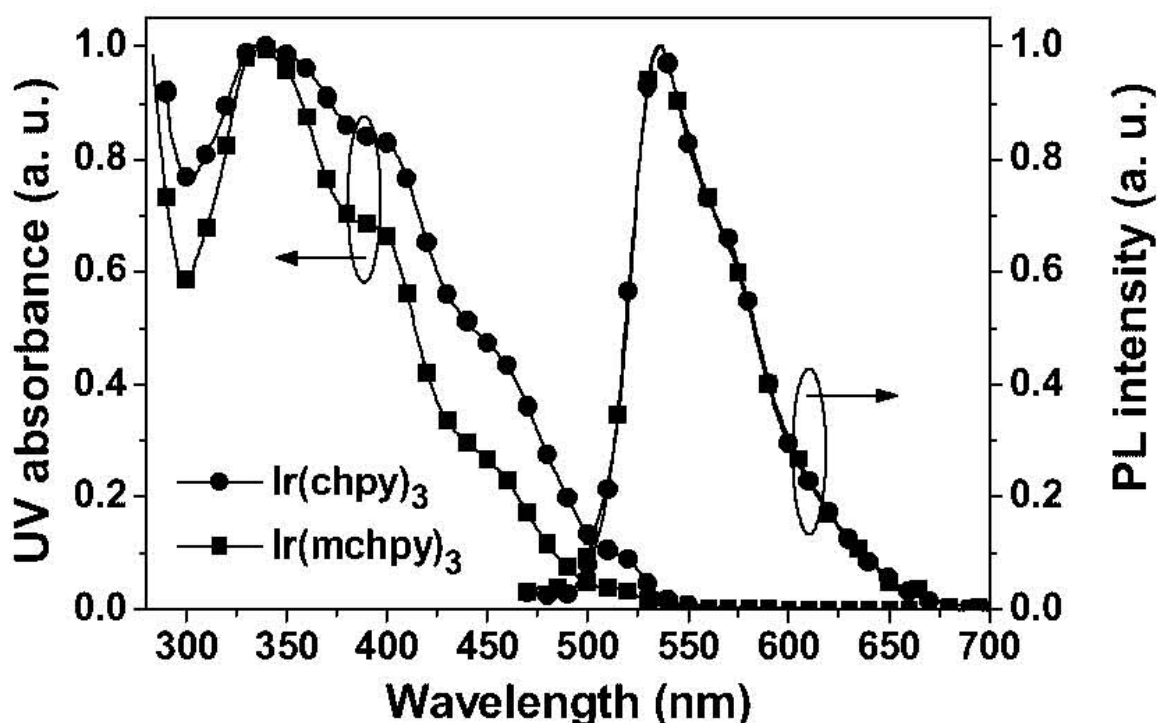


Fig. 12. The UV-Visible absorption and Photoluminescence spectra of iridium(III) complexes,  $Ir(chpy)_3$  or  $Ir(mchpy)_3$  in toluene.

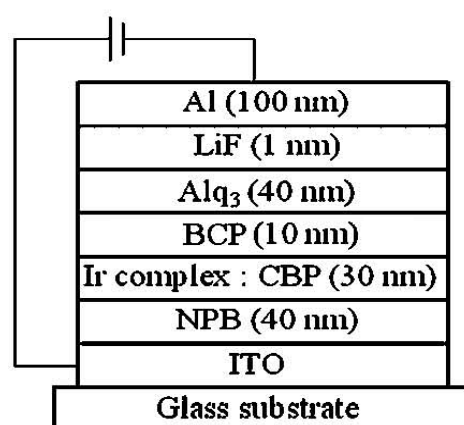


Fig. 13. The device structure of PHOLEDs based on Ir complex,  $Ir(chpy)_3$  or  $Ir(mchpy)_3$ .

The iridium(III) complexes,  $Ir(chpy)_3$  or  $Ir(mchpy)_3$ , show similar UV-Visible absorption and photoluminescence (PL) characteristics as can be seen in Fig. 12. The photophysical



properties of these complexes are summarized in Table 5. In UV-Vis absorption spectra, the absorption maxima were observed for both the complexes in solution at 336 nm and 394 nm, which are assigned to ligand based transitions and at 447 nm and 517 nm, assigned to spin allowed and spin forbidden metal-to-ligand charge transfer (MLCT) transitions. The photoluminescence (PL) spectra exhibited the emission at 536 nm (in solution) and 550 nm (in film) for Ir(chpy)<sub>3</sub> and at 535 nm (in solution) and 543 nm (in film) for Ir(mchpy)<sub>3</sub>. The photoluminescence lifetime ( $\tau_{ph}$ ) were measured in toluene solution to be 2.0  $\mu$ s for Ir(chpy)<sub>3</sub> and 1.3  $\mu$ s for Ir(mchpy)<sub>3</sub>, which are consistent with emission from a triplet excited state (Lamansky et al. 2001). The electrochemical properties were estimated by cyclic voltametry using Ag/AgCl with reference of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl (NPB) (HOMO) and estimated using absorption edge (LUMO). The determined HOMO and LUMO energy levels are -5.0 eV and -2.5 eV for Ir(chpy)<sub>3</sub> and -5.1 eV and -2.6 eV for Ir(mchpy)<sub>3</sub>, respectively. These HOMO and LUMO energy levels are higher than those of Ir(ppy)<sub>3</sub> (HOMO: -5.4 eV and LUMO: -2.9 eV).

The PHOLEDs were fabricated using Ir(chpy)<sub>3</sub> and Ir(mchpy)<sub>3</sub> complexes. The device structure has the following configuration: ITO (anode)/NPB (40 nm) as hole transporting layer/phosphorescent dopant Ir complex (6%), Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub> or Ir(ppy)<sub>3</sub> (for reference), doped in CBP host (30 nm) as EML/2,9-dimethyl-4,7-diphenylphenanthroline (BCP) (10 nm) as a hole blocking layer/Alq<sub>3</sub> (40 nm) as an electron transport layer/LiF (1 nm)/Al (100 nm) as cathode and the device structure can be seen in Fig. 13. The EL spectra of Ir complexes in devices are the same as the PL spectra of those iridium complexes, indicating that the most of the excitons recombine at the dopant Ir complex in the device. The Ir(chpy)<sub>3</sub> and Ir(mchpy)<sub>3</sub> complexes based devices exhibit yellow green emission with CIE color coordinates of (0.40, 0.59) for both Ir complexes. Ir(chpy)<sub>3</sub> based PHOLEDs showed a maximum external quantum efficiency (EQE) of 18.7%, a current efficiency of 69 cd/A, and a power efficiency of 62 lm/W, which is much higher than the Ir(ppy)<sub>3</sub> based device, while Ir(mchpy)<sub>3</sub> based device exhibited a little lower device performances than Ir(chpy)<sub>3</sub> based device but still it exhibited a much better performances than the Ir(ppy)<sub>3</sub> based device. The device performances are summarized in Table 6. The high efficiency of the Ir(chpy)<sub>3</sub> and Ir(mchpy)<sub>3</sub> based devices has been explained by more balanced injection and transport of electrons and holes in(to) the emitting layer. Because of the HOMO and

PHOLEDs With EML	Turn-on Voltage (V)	EQE (%)	Current efficiency (cd/A)	Power efficiency (lm/W)	CIE, 8 V, (x, y)
CBP:Ir(chpy) <sub>3</sub>	3.4	18.7	69.0	62.0	(0.40, 0.59)
CBP:Ir(mchpy) <sub>3</sub>	3.7	17.1	62.5	53.1	(0.41, 0.58)
CBP:Ir(ppy) <sub>3</sub>	3.7	14.6	50.2	47.8	(0.32, 0.61)

Table 6. PHOLED characteristics of Ir(chpy)<sub>3</sub>, Ir(mchpy)<sub>3</sub> and Ir(ppy)<sub>3</sub> (reference) (6%) doped in CBP host as EML.

LUMO levels of Ir(chpy)<sub>3</sub> and Ir(mchpy)<sub>3</sub> are higher than those of CBP host (HOMO/LUMO: 6.0 eV/2.9 eV), the dopants are behaving as hole traps and electron scattering centers so that both electron and hole mobility in the EML will be retarded by the doping. In contrast, Ir(ppy)<sub>3</sub> has almost the same LUMO level (2.9eV) as CBP so that Ir(ppy)<sub>3</sub> will have little

effect on electron mobility of EML. The better hole trapping and balanced hole and electron transporting ability in Ir(chpy)<sub>3</sub> in comparison with Ir(ppy)<sub>3</sub> resulted in better recombination of electrons and holes in EML, resulted in higher devices performances.

The substituents such as methyl, bulky trimethylsilyl, and cycloalkene groups substituted iridium(III) complexes have been investigated on their photophysical and electrochemical properties. The PHOLEDs based on these iridium(III) complexes have been presented. Among those, the methyl groups substituted Ir(dmppy)<sub>3</sub> based devices exhibited the green electroluminescence emission in the range of 508 nm to 520 nm, the bulky trimethyl substituted Ir(III) complexes based devices showed the yellowish green emission between 521 nm and 524 nm and the cycloalkene substituted iridium(III) complexes based devices showed the yellow green emission between 543 nm and 550 nm as summarized in Table 7.

PHOLEDs Based on	EL emission (nm)	PHOLEDs Based on	EL emission (nm)
Ir(dmppy) <sub>3</sub> complexes	508 -520	Ir(disppy) <sub>3</sub>	524
Ir(msippy) <sub>3</sub>	521	Ir(chpy) <sub>3</sub> & Ir(mchpy) <sub>3</sub>	550-543

Table 7. Electroluminescence data of PHOLED based on various substituents (methyl, bulky trimethylsilyl, and cycloalkene groups) substituted iridium(III) complexes.

## 6. Conclusion

We have presented the effect of various substituents on the photo-physical, electrochemical and electroluminescence properties of green emitting iridium(III) complexes and phosphorescent organic light emitting diodes.

- (a) The methyl groups were substituted on the ppy ligand of Ir(ppy)<sub>3</sub> and prepared a series of *fac*-[Ir(dmppy)<sub>3</sub>] complex derivatives. All Ir(dmppy)<sub>3</sub> derivatives are very stable up to 300°C without degradation in air. The crystal structures of Ir(4,4'dmppy)<sub>3</sub> and Ir(4,5'dmppy)<sub>3</sub> complexes exhibit only the *fac*- configuration with a distorted octahedral geometry around the Ir atom and indicated the decreased conjugation of 4,4'-ppy ligands. These derivatives show the emission between 509 nm and 534 nm in solution as well as in thin films at room temperature. The electroluminescence spectra of all derivatives in devices showed green emission between 508 nm and 520 nm. The device based on Ir(4,4'dmppy)<sub>3</sub> complex exhibited higher device external quantum efficiency of 10.9% at 4470 cd/m<sup>2</sup> compared with those of other devices.
- (b) The bulky trimethylsilyl substituted iridium(III) complex showed the PL emission at 510 nm in solution with higher PL quantum yield ( $\Phi = 0.43$ ). PHOLEDs exhibited the yellowish-green EL emission at 521 nm. The maximum external quantum efficiency (EQE) of 25.6% and current efficiency of 84.4 Cd/A were observed for Ir(msippy)<sub>3</sub> based device with CIE color coordinates of (0.31, 0.64). It has been reported that the charge carriers and excitons are confined within the EML of device and the energy and/or charge transfer from host to Ir(msippy)<sub>3</sub> dopant is efficient.

- (c) The homoleptic iridium(III) complex, *fac*-tris[2-(3'-trimethylsilylphenyl)-5-trimethylsilylpyridinato]iridium [Ir(disppy)<sub>3</sub>], is very stable up to 290 °C without degradation under N<sub>2</sub> atmosphere. Differential scanning calorimetry (DSC) showed the glass transition temperature of 184 °C. The introduction of silyl moieties in the ppy ring leads to higher thermal stability. The PL spectra of Ir(disppy)<sub>3</sub> complex showed the emission between 519 nm and 513 nm and showed the narrow band with FWHM of 50 nm. PHOLEDs based on Ir(disppy)<sub>3</sub> complex showed the yellowish green EL emission at 524 nm and exhibited the lower operating voltage (7.4 V), higher efficiencies of 39.2 cd/A and 17.3 lm/W.
- (d) Iridium(III) complexes using 2-cycloalkenylpyridine derivatives as cyclometalated ligands, Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub>, exhibited the PL emission between 536 nm (solution) and 550 nm (film) for Ir(chpy)<sub>3</sub> and 535 nm (Solution) and 543 nm (film) for Ir(mchpy)<sub>3</sub>. The Ir(chpy)<sub>3</sub> based PHOLED showed a maximum external quantum efficiency (EQE) of 18.7%, a current efficiency of 69 cd/A, and a power efficiency of 62 lm/W than Ir(mchpy)<sub>3</sub> device.

## 7. References

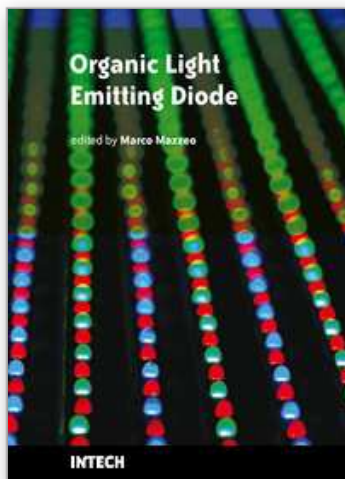
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## **Organic Light Emitting Diode**

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Organic light emitting diodes (OLEDs) have attracted enormous attention in the recent years because of their potential for flat panel displays and solid state lighting. This potential lies in the amazing flexibility offered by the synthesis of new organic compounds and by low-cost fabrication techniques, making these devices very promising for the market. The idea that flexible devices will replace standard objects such as television screens and lighting sources opens, indeed, a new scenario, where the research is very exciting and multidisciplinary. The aim of the present book is to give a comprehensive and up-to-date collection of contributions from leading experts in OLEDs. The subjects cover fields ranging from molecular and nanomaterials, used to increase the efficiency of the devices, to new technological perspectives in the realization of structures for high contrast organic displays and low-cost organic white light sources. The volume therefore presents a wide survey on the status and relevant trends in OLEDs research, thus being of interest to anyone active in this field. In addition, the present volume could also be used as a state-of-the-art introduction for young scientists.

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