



## A Green Light Emitting (Pbi-Cl)<sub>2</sub>Ir(Acac) Organic Metal Complex with PMMA Polymer Matrix for OLED's.

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### Abstract

We have synthesized an innovative phosphorescent cyclometalated iridium (III) (pbi-Cl)<sub>2</sub>Ir(acac) metal complex with acetyl acetone as ancillary ligand by Suzuki Coupling reaction and the blended thin films of (pbi-Cl)<sub>2</sub>Ir(acac) metal complex with PMMA at 1 wt% concentration have been prepared. The optical properties of blended thin film of synthesized (pbi-Cl)<sub>2</sub>Ir(acac) metal complex have been studied by using UV-vis optical absorption and photoluminescence (PL) spectra. UV-Vis measurements of (pbi-Cl)<sub>2</sub>Ir(acac) metal complex in thin film form shows two absorption bands at 303 and 313 nm related to π-π\* transitions. The absorption spectra of blended thin film is used to calculate the energy band gap (E<sub>g</sub>), which shows close resemblance with theoretical calculated value. The (pbi-Cl)<sub>2</sub>Ir(acac) metal complex emits intense green light having λ<sub>max</sub> = 543 nm. The blended thin films of (pbi-Cl)<sub>2</sub>Ir(acac) complex with PMMA at 1 wt% concentration show the emission peak at 514 and 545 nm respectively. The derivatives have high Stoke's shift value 13,550 cm<sup>-1</sup>, which is applicable for fabricating device. The (pbi-Cl)<sub>2</sub>Ir(acac) metal complex in powder form shows C.I.E. coordinates positioned in the green region, showing coordinates X=0.2521, Y=0.6139 in the chromaticity diagram.

The given iridium metal complex can be considered as promising emissive material in OLEDs, light-emitting electrochemical cells, visual presentations and solid state lighting.

**Keywords :** Iridium complex, Suzuki Coupling reaction, light-emitting electrochemical cells, solid state lighting, OLEDs.

### Introduction :

Recently, Industry and academia both pays extensive attention to organic light emitting diodes (OLEDs) due to its broad range of applicability to solid state lighting, light-emitting electrochemical cells, visual presentations and displays. [1-5]. More and more interest in the field of optoelectronics has been attracted towards synthesis of materials based on heavy metal (Ir(III), Pt(II), Os(II), Re(II)) complexes, used as phosphorescent dopants, due to their potential applications in organic light emitting devices (OLEDs) [6-10]. From the above heavy metal-containing phosphor emitters that have been reported in OLEDs, cyclometalated complexes of iridium(III) materials have shown the most promising applications due to their high quantum efficiency, short lifetime of triplet excited states and broad range of emission colors [11].

At present, many red organic dyes in use do not show a good comprise between device efficiency and color purity. [12-15]. By taking into consideration of the strong spin-orbit coupling which is induced by the central heavy metal atom, iridium (III) complex have been considered as a good phosphor with high quantum efficiency. [16-20]. The substituent effect can notably afford the versatile phosphorescence color tuning of the complexes from blue to red. [21-23].

Also, Purely red-emitting phosphorescent complexes of iridium(III) are common, whereas the purely blue-emitting and green emitting

complex dopants [24] are scarcely found. Hence, the current effort of scientists has been focused on the syntheses of green-emitting iridium(III)-based materials in solid crystalline powder as well as in blended thin film form.

In this paper we have synthesized new green light emitting phosphorescent cyclometalated iridium (III) (pbi-Cl)<sub>2</sub>Ir(acac) metal complex with acetyl acetone as ancillary ligand and the blended thin films of (pbi-Cl)<sub>2</sub>Ir(acac) metal complex with PMMA.

## 2. Experimental

### 2.1 Materials

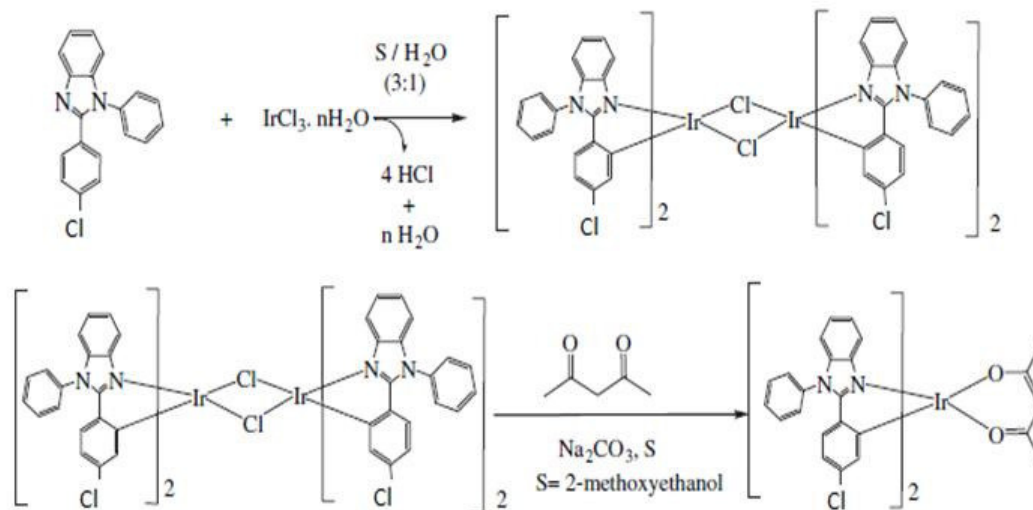
All reagents and solvents of AR grade were used as received without further purification. All reactions were performed under argon atmosphere.

### 2.2. Synthesis of [(pbi-Br)<sub>2</sub>Ir(acac)] Complex

(pbi-Cl)<sub>2</sub>Ir(acac) complex was synthesized according to scheme 1 as shown in Fig.1. To a flask containing IrCl<sub>3</sub>.nH<sub>2</sub>O (176 mg, 0.5 mmol) and ligand 2-(4-Chlorophenyl)-1-phenyl-1H-benzimidazole (pbi-Cl) (700 mg, 2.0 equiv.), a mixture of 2-methoxyethanol (S) and water (3:1 v/v, 25 mL) was added. The mixture was refluxed to react for 48 h and then cooled to room temperature. Later, the reaction was quenched with water, extracted with dichloromethane, and dried under vacuum. The solid yield was collected by filtration and evaporation to give the crude product. The crude product, i.e., m-chloro-bridged Ir(III) dimer, was mixed with Na<sub>2</sub>CO<sub>3</sub> (0.30 g, 3.0 mmol), 2,4-pentanedione (0.30 g, 3.0

mmol), and 2-methoxyethanol (20 mL) in a flask. The mixture was heated to react for 24 h. After cooling, the reaction was quenched with water and the mixture was extracted with

dichloromethane. The combined extracts were then washed with brine, dried over  $MgSO_4$ , and evaporated to dryness so as to afford pure compound as a yellow solid with a 65% yield.



**Fig. 1** :- Synthesis route of  $(pbi-Cl)_2Ir(acac)$  Complex (Scheme 1)

### 2.3 Preparation of Blended Films

Commercially available polymers PMMA were used for making blended films of the synthesized  $(pbi-Cl)_2Ir(acac)$  complex. Polymer PMMA matrix is prepared by dissolving 0.495 g of polymer PMMA in 15 ml of chloroform with vigorous stirring for 15 min at room temperature. Later 0.005 g of the synthesized  $(pbi-Cl)_2Ir(acac)$  complex was taken individually and dissolved in the same solvent in separate beakers. Later, the solution of  $(pbi-Cl)_2Ir(acac)$  complex was mixed with PMMA matrix at room temperature under vigorous stirring for 15 min to obtain the homogeneous mixture. The resulting homogeneous mixture is then poured on to a glass or good quality stainless steel substrate. The solvent is allowed to evaporate in air for 2–3 h at room temperature and then pilled up from the substrate. The obtained films are placed in vacuum dry oven at room temperature overnight to remove residual solvent left, if any. The obtained 1 wt% blended films are homogeneous and showed excellent optical transparency. No visible phase separation is detected.

### 3. Result and Discussion

The optical absorption spectrum of  $(pbi-Cl)_2Ir(acac)$  complex in blended thin film form obtained on PERKINELMER LAMDA 35 spectrophotometer and the photoluminescence (PL) spectrum was obtained by a SHIMADZU RF 5301 Spectrofluorometer.

#### 3.1. Photo-physical properties

To evaluate the functioning of organic materials in device applications, its important to analyze their photo-physical properties. Using UV-Vis absorption and photoluminescence (PL) spectroscopy, The basic photo-physical properties such as absorption maxima ( $\lambda_{abs}$ ), excitation maxima ( $\lambda_{exct}$ ), emission maxima ( $\lambda_{emi}$ ), optical band gap ( $E_g$ ), Stoke's shift ( $\nu_{abs} - \nu_{em}$ ), optical density and C.I.E. Co-ordinate of the molecules were determined [37] and summarized in Table 2.

##### 3.1.1 UV-vis. Absorption Spectra

To analyze the electronic transition in compound the UV-vis. Spectroscopy is used. The color arises from (i) d - d transitions within the metal ions (usually produce absorption of low intensity) and (ii) n -  $\pi^*$  and  $\pi - \pi^*$  transitions within the ligand. Another type of transition referred to as "charge transfer" may also be operative in which an electron is transferred between an orbital in the ligand and an unfilled orbital of the metal or vice versa (MLCT). These give rise to more intense absorption bands, which are analytical importance.

The absorption Spectra of  $(pbi-Cl)_2Ir(acac)$  complex in blended thin film form were taken at room temperature showing peaks at 303 nm and 313 nm as shown in fig.2. The intense absorption bands in the UV region for given complex was attributed to the intra-ligand (IL)  $\pi \rightarrow \pi^*$  and also spin -allowed metal-to-ligand charge transfer  $^1MLCT$  transition.

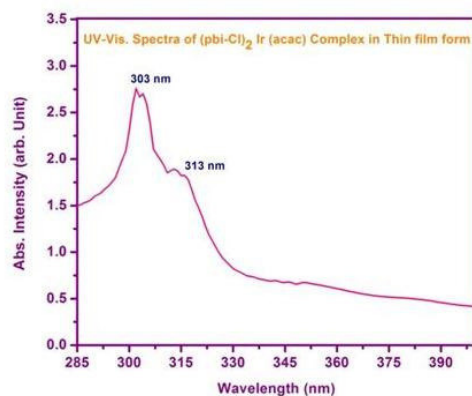


Fig. 2 : UV-vis spectra of (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form

**3.1.2 Determination of Energy band gap :**

Morita et al.[25] theory was used to determine the energy band gap of synthesized (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film from UV-Absorbance spectra. The intercept of the tangent

to the plots of [α hv]<sup>2</sup> versus photon energy as shown in Fig.3. The graphically calculated energy band gap for (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form found to be 4.35 eV.

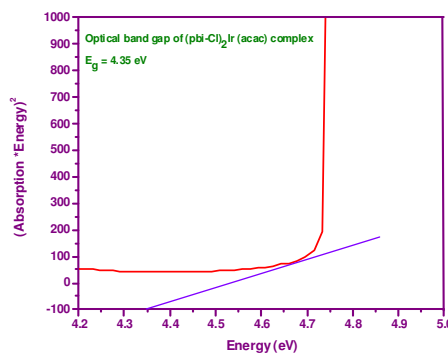


Fig. 3: Determination of band gap of (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form

Energy is theoretically commonly calculated using Einstein's equation given by ,  $E = h\nu = \frac{hc}{\lambda}$

.....(1). where h = Planck's constant , c = velocity of light in air and λ is the excitation wavelength. By using above equation , the energy band gap can be calculated as  $E = \frac{hc}{\lambda_g} = \frac{1239.83}{\lambda_g}$

.....(2)

Thus the theoretical value of optical band gap matches with the values obtained by employing the ASF plot for all the solvents as tabulated in the Table 2.

**3.1.3. Stokes Shift : -**

Stokes shift (u<sub>abs</sub>- u<sub>em</sub>) indicates the difference in absorption and emission wave lengths. The Stokes shifts (cm<sup>-1</sup>) can be determined by the formula (24)

$$\text{Stokes shift} = \nu_{abs} - \nu_{emi} = \frac{1}{\lambda_{abs}} - \frac{1}{\lambda_{emi}} \times 10^7 \text{ cm}^{-1}$$

..... (3)

Substituting the values of absorption wavelength and emission wavelength, it can be concluded that the molecules exhibits Stokes shifts of 13,550 cm<sup>-1</sup> as shown in fig.4.

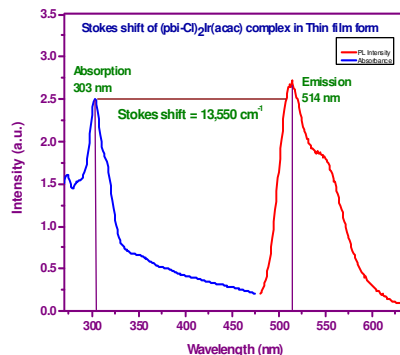


Fig. 4 : Stokes shift of (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form

**3.1.4. Photoluminescence Spectra**

The emission in iridium (III) complexes arises from metal-to-ligand charge transfer commonly . The (pbi-Cl)<sub>2</sub>Ir(acac) complex in powder form shows emission at 543 nm in powder form as

shown in Fig. 5 , it may be due to fact that the complex posses spin forbidden <sup>3</sup>MLCT excited states rather than ligand-based π→π\* transitions at room temperature .

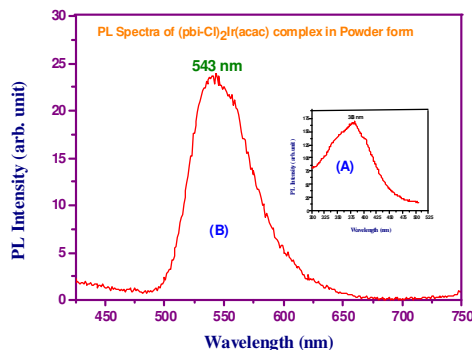


Fig. 5 : PL Spectar of (pbi-Cl)<sub>2</sub>Ir(acac) complex in powder form

Considering the emission spectra of (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form as shown in fig.6 , the slightly Blue shift is observed

, which shows that the emission considerably originating from the mixing of <sup>3</sup>MLCT excited states as well as ligand-based π→π\* transitions.

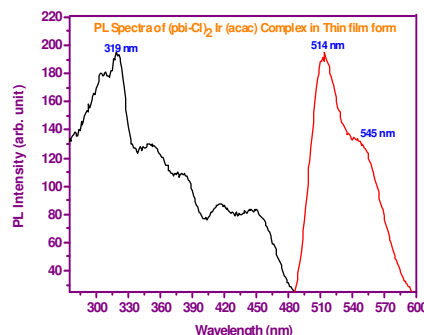


Fig. 6 : PL Spectar of (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form

**3.1.5. CIE coordinates**

The color of the phosphorescence is represented by color coordinates which could be calculated from the emission spectrum using the chromaticity

coordinate calculation method based on the CIE 1931 (Commission International d'Eclairage) system. The chromaticity diagram (Fig.7) shows , chromaticity coordinates of solid state(pbi-

Cl)<sub>2</sub>Ir(acac) complex and (pbi-Cl)<sub>2</sub>Ir(acac) complex in blended thin film form as mentioned in table 1.

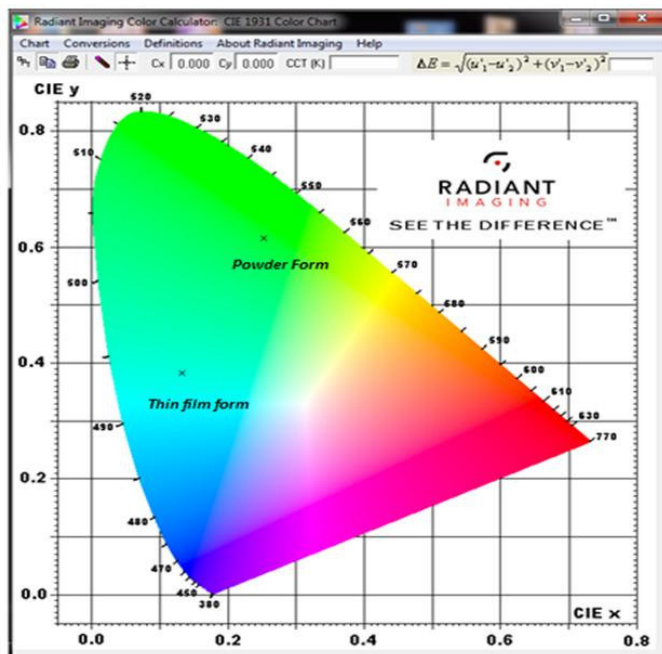


Fig. 7 : The C.I.E. chromaticity diagram of (pbi-Cl)<sub>2</sub>Ir(acac) complex.

**Table 1 :** C.I.E. co-ordinates of (pbi-Cl)<sub>2</sub>Ir(acac) complex in solid as well as in blended thin film form

Type of Complex	Emission Wavelength (nm)	C.I.E. Co-ordinates ( 1931 Chart )	
		Cx	Cy
<b>Powder Form</b>	543 nm	0.252	0.613
<b>Thin Film Form</b>	514 nm	0.382	0.139

**Table 2 :** Photo-physical properties of (pbi-Cl)<sub>2</sub>Ir(acac) complex in Blended Thin Film form

Complex	Molar Conc.	Band	$\lambda_{abs}$ (nm)	Optical Density (a.u.)	$\lambda_{exc}$ (nm)	$\lambda_{emi}$ (nm)	$E_g$ (eV) (ASF Plot)	$E_g$ (eV) (Theo.)	Stokes Shift (cm <sup>-1</sup> )
(pbi-Cl) <sub>2</sub> Ir(acac) Complex thin film	1 wt%	I	303	2.72825	319	514	4.35	4.10	13,550
		I	313	1.92784					

**4. Conclusion**

film shows emission at 514 and 545 nm with C.I.E. We have synthesized (pbi-Cl)<sub>2</sub>Ir(acac) Using UV-Vis absorption and photoluminescence phosphorescent complex in nearly quantitative yield (PL) spectroscopy, the basic photo-physical by Suzuki coupling reaction. In conclusion, (pbi-Cl)<sub>2</sub>Ir(acac) complex is new green light emitting excitation maxima ( $\lambda_{exc}$ ), emission maxima ( $\lambda_{emi}$ ), chromosphere in solid crystalline powder as well as optical band gap( $E_g$ ), Stoke's shift ( $\lambda_{abs} - \lambda_{emi}$ ), optical in blended thin film form. The synthesized (pbi-Cl)<sub>2</sub>Ir(acac) complex in powder form when excited at iridium metal complex can be considered as 383 nm show the emission in the green region at 543 nm and when excited at 319 nm the blended thin light emitting devices (OLEDs), light-emitting

electrochemical cells and solid state lightning due broad emission wavelength ranging from 514-545 nm.

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