RESEARCH ARTICLE



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Synthesis and characterization of a green-light-emitting (pbi-Br)₂Ir (acac) metal complex for OLEDs

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Abstract

We designed and synthesized a 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (pbi-Br) ligand, which was then employed to create an innovative phosphorescent cyclometallated iridium(III) (pbi-Br)₂Ir(acac) metal complex with acetyl acetone as an ancillary ligand using the Suzuki coupling reaction. The complex was then characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra and thermogravimetric analysis (TGA)/differential thermal analysis (DTA) for structural and thermal analysis, respectively. XRD confirmed its amorphous nature and the FTIR spectrum revealed the molecular structure confirmation of the metal complex. The TGA/DTA curve disclosed its thermal stability up to 310°C. Ultraviolet (UV)-vis absorption and photoluminescence (PL) spectra were measured to explore the photo-physical properties of the (pbi-Br)₂Ir(acac) complex in basic and acidic media respectively. With the variation in solvent from acidic to basic media, optical absorption peaks blue shifted with variation in optical densities. These results facilitated the calculation of various photo-physical parameters. When excited at 379 nm in the solid state, the synthesized complex gave out a green light emission, peaking at λ_{emi} = 552 nm. Staggering differences in optical density were observed in the PL spectra of the solvated complex. A Stokes' shift of 7140.45 cm⁻¹ and 7364.94 cm⁻¹ was observed when the complex was solvated in acetic acid and chloroform, respectively. Hence the synthesized iridium metal complex can be considered as promising green emissive material for optoelectronic applications.

KEYWORDS

iridium complex, Lippert–Mataga plot, molecular absorption cross-section, OLEDs, solid-state lighting, Suzuki coupling reaction

1 | INTRODUCTION

In recent years, phosphorescent iridium complexes with benzimidazole ligands have gained momentum in various optoelectronic applications such as organic light-emitting diodes (OLEDs), flat panel displays and solid-state lighting as they exhibit a broad range of emission colors in the green region of the visible spectrum. In particular, iridium-based complexes with benzimidazole ligand are envisioned to be superior green light emitters for the next generation of display and lighting technology.^[1-3] OLED technology, based on higher transition metal

complexes, have attracted much more attention due to the theoretical utilization of both singlet and triplet excitons for light emission to realize an internal quantum efficiency of 100%.^[4,5] Prior state of art illustrates phosphorescent heavy metal complexes such as Ru(II), Os(II), Re(III) and Ir(III) as green light-emitting photo-luminophores.^[6] Out of these, Ir(III) complexes have received more attention due to their broad color tunability, efficient emission and high thermal stability.^[7,8] Photo-physical properties of Ir(III) complexes are governed by the type of cyclometallated ligand.^[9] Among many, the benzimidazole ligand has been reported as an important component for the

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preparation of Ir(III) complexes in OLEDs due to its excellent electron mobility and flexible modification ability.^[10] It is also expected that iridium complexed with benzimidazole ligand can be employed in fabricating OLED devices and displays by either a vacuum deposition method or solution techniques due to good volatility and solubility. Keeping this in mind, we synthesized a (pbi-Br)₂Ir(acac) complex with 2-(4bromophenyI)-1-phenyI-1H-benzimidazole (pbi-Br) as the main ligand and acetyl acetone as an ancillary ligand to study the structural, thermal and photo-physical properties of this complex.

2 | EXPERIMENTAL

All reagents and solvents used were of analytical reagent grade. All reactions were performed under an argon atmosphere. A 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (pbi-Br) ligand was synthe-sized conveniently, according to Scheme 1, from the condensation of *N*-phenyl-O-phenylenediamine and 4-bromobenzaldehyde by the Suzuki coupling reaction^[11-13] as shown in Figure 1. *N*-Phenyl-O-phenylenediamine (1 equiv.) and 4-bromobenzaldehyde (1 equiv.) were dissolved in 50 ml of 2-methoxyethanol. The mixture was refluxed for 48 h and volatiles were removed under vacuum. The resulting organic solid was extracted by dichloromethane and washed with brine solution two or three times. It was then dried over MgSO₄ and evaporated under a natural environment to yield a brownish solid [C₁₉H₁₃BrN₂] with a 60% yield.



FIGURE 1 Synthesis route of 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (pbi-Br) ligand

2.1 | Synthesis of the [(pbi-Br)₂lr(acac)] complex

The (pbi-Br)₂Ir(acac) complex was synthesized according to Scheme 2 as shown in Figure 2. A mixture of 2-methoxyethanol (S) and water (3:1 v/v, 25 ml) was added to a flask containing $IrCl_3.nH_2O$ (176 mg, 0.5 mmol) and the ligand 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (pbi-Br) (700 mg, 2.0 equiv.). 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) dimmer, was mixed with Na2CO3 (0.30 g, 3.0 mmol), 2,4-pentanedione (0.30 g, 3.0 mmol), and 2methoxyethanol (20 ml) in a flask. The mixture was heated to react for 24 h. After cooling, the reaction was guenched with water and the mixture was extracted with dichloromethane. The combined extracts were then washed with brine, dried over MgSO₄, and evaporated to dehydrate it to produce a yellow solid compound with 65% yield.

3 | RESULTS AND DISCUSSION

X-ray diffraction was carried out on an X-ray Diffractometer System XPERT-PRO (PAN analytical), while Fourier transform infrared (FTIR) spectra were measured a on Bruker-Alpha instrument at room temperature over the range 4000–600 cm⁻¹ by averaging 64 scans at a maximum resolution of 4 cm⁻¹. Thermogravimetric analysis (TGA) was carried out on Perkin Elmer Diamond instrument. The optical absorption spectrum of the (pbi-Br)₂Ir(acac) complex in acetic acid was obtained on Perkin Elmer Lamda35 spectrophotometer and the photoluminescence (PL) spectrum was obtained using a Shimadzu RF 5301 spectrofluorometer. The Commission International d'Eclairage (CIE) coordinates of the synthesized complex were probed using a CIE1931 system.



FIGURE 2 Synthesis route of the (pbi-Br)₂Ir(acac) complex (Scheme 2)

3.1 | Fourier transform infrared spectroscopy

FTIR spectroscopy is an analytical technique employed to categorize molecular structures and validate the packing arrangements and chain conformational properties of polymeric compounds. This technique measures the absorption of a range of infrared light wavelengths of the material of interest. FTIR spectra of the (pbi-Br)₂Ir (acac) complex were measured over the range 4000–600 cm⁻¹ by averaging 64 scans at a maximum resolution of 4 cm⁻¹ as shown in Figure 3.

Numerous absorbance peaks were observed in the fingerprint region of the FTIR spectra, which may be attributed to C–H bending (690–900 cm⁻¹) and C–O stretching (970–1250 cm⁻¹). A peak at 1243.26 cm⁻¹ may be assigned to C–H bonding. A peak at 1547.18 cm⁻¹ may be attributed to C=C stretching and the peaks in the range 1500–1450 cm⁻¹ can be assigned to the aromatic ring stretch C–C. Variations in the range of2850–3000 cm⁻¹ may be due to double bonded =CH₂ stretching, peaking at 2843.71 and 2951.24 cm⁻¹ for –CH₃ stretching, while 3294–3950 cm⁻¹ can be assigned to single bond –N–H stretching vibrations showing peaks at 3631.37, 3555.21 and 3440.89 cm⁻¹.This result confirmed the formation of the cyclometallated iridium(III) (pbi-Br)₂Ir(acac) metal complex with acetyl acetone as the ancillary ligand.

3.2 | X-ray diffraction

X-ray diffraction (XRD) is one of the most promising techniques for structural analysis. The XRD pattern of the (pbi-Br)₂Ir(acac) complex in the solid state showed diffused diffraction peaks, revealing its amorphous nature. The peak with maximum relative intensity was observed at $2\theta = 40.593^{\circ}$ having interplanar distance 4.3048 Å as shown in Figure 4. Another three peaks with relative intensity of 44%, 23% and 12% were observed at $2\theta = 74.547^{\circ}$, 30.581° and 17.547° having interplanar distances as 1.26924 Å , 2.9209 Å and 5.05018 Å respectively.

3.3 | Thermogravimetric analysis and differential thermal analysis

TGA is used for precise measurement of specimen weight changes as a function of time and temperature in various gaseous environments. This analysis is very useful for investigation of reactivity and stability.



FIGURE 3 FTIR spectra of (pbi-Br)₂Ir(acac) complex





FIGURE 4 XRD pattern of the (pbi-Br)₂Ir(acac) complex

A thermogram of the (pbi-Br)₂Ir(acac) complex exhibited no weight loss in the temperature range below 310°C, indicating its thermal stability, as shown in Figure 5. With further increase in temperature, a weight loss of about 6.20% was observed up to 376°C. The DTA curve of the (pbi-Br)₂Ir(acac) complex shows a combination of endothermic and exothermic peaks.

The first endothermic peak was centered at 155.71°C, corresponds to the distortion of water from the synthesized complex, while the second peak at 381.94°C corresponded to the evaporation of residual moisture. However, no exothermic peaks were observed for the DTA curve. This result indicated that the synthesized Ir(III) complex is highly stable and cannot be distorted easily, even under high temperatures associated with heat generation during the operation of OLEDs, and leading to long device lifetimes.

3.4 | Photo-physical properties

Photo-physical properties such as absorbance, absorption maxima (λ_{abs}), molecular absorption cross-section, molar absorption coefficient, radiative life time, optical band gap (E_g), excitation maxima (λ_{exct}), emission maxima (λ_{emi}) and Stokes' shift ($\upsilon_{abs} - \upsilon_{em}$) of the molecules of the solvated (pbi-Br)₂Ir(acac) complex were established by UV-visible absorption and photoluminescence spectroscopy.



FIGURE 5 TGA and DTA curve of the (pbi-Br)₂Ir(acac) complex



FIGURE 6 UV-vis spectra of (pbi-Br)₂Ir(acac) complex in acetic acid



FIGURE 7 UV-vis spectra of (pbi-Br)₂Ir(acac) complex in chloroform

3.4.1 | UV-visible light absorption spectra

The UV-vis light absorption spectra of the (pbi-Br)₂Ir(acac) metal complex in acetic acid and chloroform at 10^{-3} M concentration, and recorded at room temperature is depicted in Figure 6 and Figure 7, respectively. The absorption spectra of the (pbi-Br)₂Ir(acac) complex displayed the characteristic vibration pattern of an iridium complex. The absorption peaks at 258, 272 and 308 nm in acetic acid and 265, 294 and 316 nm in chloroform could be assigned to the spin-allowed π - π * transition of the cyclometallated ligand.

The broad absorption bands in the range of 360–400 nm in acetic acid and 350–400 nm in chloroform can be assigned to spin-allowed metal-to-ligand charge-transfer (MLCT) transition and spin-forbidden MLCT transition, respectively, having peaks at 361, 376, nm in acetic acid and 364 and 376 nm in chloroform, respectively. Optical absorption parameters and the probability transition parameters of the (pbi-Br)₂Ir (acac) complex at 10^{-3} in acetic acid and chloroform are listed in Tables 1 and 2, respectively.

3.4.2 | Determination of energy band gap

By using the procedure described by Morita *et al.*,^[14] the optical band gap (E_g) of the solvated (pbi-Br)₂Ir(acac) metal complex was determined. The same measurement was found to be 2.35 eV and 2.42 eV in acetic acid and chloroform, as shown in Figure 8.

Theoretically, the energy is calculated using Einstein's equation given by.

$$E = hv = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda} = \frac{1239.83}{\lambda}$$

Where h = Planck's constant, c = velocity of light and λ is the absorption wavelength. The same analogy can be applied to calculate the amount of energy absorbed by phosphor when exposed to UV light. When the absorption wavelength is employed to the above equation, the amount of energy that is required by the phosphor to make transition from the highest occupied molecular orbital (HOMO)

TABLE 1 Optical absorption parameters of the $(pbi-Br)_2$ (acac) complex at 10^{-3} in acetic acid and chloroform

Complex	Solvent	Molar conc. mol/L	Band	λ _{max} (nm)	Transition	Optical density (a.u.)
(pbi-Br) ₂ Ir(acac)	Acetic acid	10 ⁻³	l	308	π-π*	2.926
	Chloroform	10 ⁻³		376 316	n−π* π−π*	2.777 2.703
			П	376	n-π*	2.536

TABLE 2 Transition probability parameters of $(pbi-Br)_2$ Ir (acac) complex at 10^{-3} in acetic acid and chloroform

Solvent	Absorption wavelength λ _{max} (nm)	Absorbance $A(\lambda) = \log \frac{I_{\lambda}^{0}}{I_{\lambda}}$ $= \epsilon_{\lambda} LC \text{ (a.u.)}$	Decadic absorption coefficient $a(\lambda) = \frac{A_{\lambda}}{I} = A(\lambda)$ (a.u.)	Naperian absorption coefficient $\alpha(\lambda) = a(\lambda)$ In 10 (cm ⁻¹)		Molecular absorption cross-section $\sigma(\lambda) = 0.382$ $\times 10^{-23}$. ε_{max} (cm)	Number density (N) $N = \frac{a(\lambda)}{\sigma}(\lambda)$	$\begin{array}{l} \mbox{Calculated} \\ \mbox{radiative} \\ \mbox{lifetime} \\ \mbox{$\tau_0=\frac{10^{-4}}{\epsilon_{max}}$ (µs)} \end{array}$
Acetic acid	272 308 376	2.47 2.92 2.77	2.47 2.92 2.77	5.6933 6.7233 6.3779	2474.6 2926.23 2777.21	$\begin{array}{l} 9.45 \times 10^{-21} \\ 0.117 \times 10^{-21} \\ 0.106 \times 10^{-21} \end{array}$	8.44 × 10 ²⁰	404 341 360
Chloroform	294 316 376	2.61 2.70 2.53	2.61 2.70 2.53	6.0095 6.2167 6.3779	2612.9 2703.6 2536.9	$\begin{array}{c} 9.98 \times 10^{-21} \\ 0.103 \times 10^{-21} \\ 9.69 \times 10^{-21} \end{array}$	3.78 × 10 ²⁰	382 369 394



FIGURE 8 Determination of band gap: (pbi-Br)₂Ir(acac) in (a) acetic acid and (b) chloroform

to the lowest unoccupied molecular orbital (LUMO), i.e. energy band gap, can be calculated.

The calculated values of the optical band gap were found to match with the theoretical values, as listed in Table 3.

3.4.3 | Photoluminescence spectra

The PL spectra of the (pbi-Br)₂Ir(acac) complex in the solid state exhibited intense green phosphorescence, peaking at 552 nm under an excitation wavelength of 379 nm, while in acetic acid and chloroform it peaked at λ_{emi} = 514 nm and 520 nm, respectively, as shown in Figures 9 and 10, respectively. This result reflected a noticeable bathochromic shift with a hyperchromic shift (increase in emission intensity) and a hypochromic shift (decrease in emission intensity) when (pbi-Br)₂Ir(acac) was solvated in chloroform and acetic acid respectively. These results can be attributed to the fact that chloroform is non-polar in nature, while acetic acid is polar protic solvent due in which there could be poor intermolecular interaction and dissociation of the complex.

3.4.4 | Stokes' shift

Stokes' shift (ν_{abs} - ν_{em}) indicates the difference in absorption and emission wavelengths. The Stokes' shift (cm⁻¹) can be determined by the formula:

$$\text{Stoke's shift} = \textbf{u}_{abs} - \textbf{u}_{emi} = \frac{1}{\lambda_{abs}} - \frac{1}{\lambda_{emi}} \times 10^7 cm^{-1}$$

Substituting the values of absorption and emission wavelength, the calculated values for Stokes' shift were found to be 7140.45 and

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FIGURE 9 Photoluminescence (a) excitation and (b) emission spectra of the (pbi-Br)₂Ir(acac) complex



FIGURE 10 Photoluminescence (a) excitation and (b) emission spectra of the (pbi-Br)₂Ir (acac) complex in various organic solvents

7364.94 cm⁻¹ in acetic acid and chloroform as shown in Figure 11 and Figure 12, respectively.

3.4.5 | Lippert-Mataga plot

This plot is between Stokes' shift ($\Delta \nu$) and solvent polarity function (Δf), which estimates the solvent sensitivity to chromophore.^[15] It is a known fact that the energy difference (ΔE) between the ground state and excited state is affected by the interaction between the

TABLE 3 Photo-physical properties of (pbi-Br)₂lr(acac) complex in solvated state

Photo-physical properties of complex											
Solvent	Nature of solvent	Polarity index	Solvent polarity function (∆f)	Dielectric constant (є)	Refractive index (n)	λ _{exe} (nm)	λ _{emi} (nm)	λ _{ab} (nm)	E _g (eV) (plot)	E _g (eV) (the.)	Stokes' shift (cm ⁻¹)
Acetic acid	Polar protic	6.2	0.2028	6.15	1.3716	455	514	376	2.35	2.724	7140.45
Chloroform	Non-polar	4.1	0.1483	4.81	1.4458	456	520	376	2.42	2.718	7364.94

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FIGURE 11 Stokes' shift of the $(pbi-Br)_2$ Ir (acac) complex in acetic acid



FIGURE 12 Stokes' shift of the $(\mbox{pbi-Br})_2\mbox{lr}$ (acac) complex in chloroform

considered solvent and chromophore. Stokes' shift of the complex versus solvent polarity function is shown in Figure 13. Photo-physical properties of the (pbi-Br)₂lr(acac) complex in the solvated state are listed in Table 3.

3.4.6 | 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 system.^[16] CIE coordinates of the (pbi-Br)2 Ir (acac) complex in the solid state were found to be (0.313, 0.680) with color correlating temperature (CCT) at 5778 K, indicating that the synthesized complex emitted deep green light, as shown in Figure 14. Whereas in the solvated complex, the same was found to be (0.035, 0.800), (0.073, 0.831) with 9607 and 8801 as CCT in acetic acid and chloroform,



FIGURE 13 Plot of Stokes' shift versus solvent polarity function

Δf (ε,n)



FIGURE 14 CIE 1931 (x, y) diagram of the (pbi-Br)₂lr(acac) complex

respectively. Correlated color temperature,^[17] a graphical method for correlating CIE coordinates using an RGB diagram was obtained based on the CIE 1931 system.

Correlated color temperature is the temperature of a black body whose chromaticity closely resembles that of a light source. For high quality white light (RGB) illumination the CCT should lie between 2500 K to 6500 K. Hence the same parameter for our complex fell inbetween these values. CIE coordinates and CCT values for the (pbi-Br)₂Ir (acac) complex in various environments are given in Table 4.

Figure 15 shows the plot of the solvent polarity function (Δf) versus CIE coordinates. The nature of the graph between polarity function (Δf) and CIE coordinates demonstrates its linear nature.

The absorption and emission spectra of phosphorescent metal complexes are in general influenced by various parameters such as

TABLE 4CIE coordinates and CCT values for the (pbi-Br)2Ir (acac)complex in various environments

Complex in	Emission wavelength (nm)	CIE coo	ordinates Cy	Co-related color temperature (K)
Solid state	552 nm	0.313	0.680	5778
Acetic acid	514 nm	0.035	0.800	9607
Chloroform	520 nm	0.073	0.831	8801



FIGURE 15 Plot of solvent polarity function (Δf) versus CIE coordinates

the valence electron configuration at the metal, the type of the electronic transitions or the correlation among lower lying electronic excited states.^[18-20] As in fluorescent small molecules, the photo-WILEY-LUMINESCENCE The Journal of Biological and Chemical Luminescence

physical behavior of transition metal complexes can be properly described with molecular orbitals, however the performance of accurate quantum mechanical calculations is far more complicated. It has been shown that frontier molecular orbitals are not equally delocalized in heavy metal complexes, resulting in different electronically excited states. Among these, metal-centered (MC) excited states are typically present in metal complexes with partially filled d shells at the metal center. The corresponding d-d transitions are Laporte forbidden and, consequently, exhibit very low transition probabilities. MLCT states involve electronic transitions from metal-based d orbitals to a ligandcentered π^* anti-bonding orbitals. Emissive MLCT states are particularly observed in d6 and d8 transition metal complexes and therefore play a major role in the photo-physics of iridium(III) compounds. Intraligand (IL) π - π^* excited states originate from the electronic transitions of the ligand.^[21-24] If the metal perturbation upon coordination is minimized, their spectral properties often closely resemble the free ligand states. Finally, ligand-to-metal charge-transfer (LMCT) excited states are occasionally observed in complexes with metal atoms in high oxidation states. All these transitions determine the photo-physical properties of transition metal complexes and can be used for the interpretation of experimentally observed spectra or the prediction of absorption and emission characteristics of novel compounds. Comparative analysis of our results with the results of W-S Huang et al.^[13] is shown in Table 5. This comparison revealed that our ligand and complex were synthesized at well defined temperature of about 130°C and 105°C respectively. In view of characterization, noticeable differences were observed in the absorption peak, energy gap and emission wavelength. Other important supporting characterizations such as FTIR spectra, which confirmed the structure formation, Stokes' shift, which reflected the difference between positions of the band maxima of the absorption and emission spectra and CIE coordinates, which helped to evaluate the quality of a color regardless

TABLE 5 Comparative analysis of our results with the results of W-S Huang et al.^[13]

S. no.	Characterization techniques	Parameters	Referred results	Obtained result
1.	FTIR	IR peaks	-	1243.26, 1547.18, 1500-1450, 2843.71, 2951.24,3631.37, 3555.21, 3440.89 cm ⁻¹
2.	XRD	Nature	-	Amorphous
3.	TGA-DTA	Thermal stability T _g T _d	- - 363°C	310°C 115.71 ℃ 381.94°C
4.	UV-vis absorption spectra	Abs. Peak in chloroform Abs. Peak in DCM Abs. Peak in acetic acid	- 303, 316, 388, 416, 450 a.u. -	265, 294, 316, 364, 376 - 258, 272, 308, 361,376 nm
5.	Energy band gap	By cyclic voltammetry By Morita <i>et al.</i> chloroform Acetic acid	3.02 eV - -	- 2.42 eV 2.32 ev
6.	Photoluminescence spectra	Solid state Chloroform DCM Acetic acid	- - λ _{emi} = 518 nm -	$\begin{array}{l} \lambda_{exc} = 379 \text{ nm and } \lambda_{ems} = 552 \text{ nm} \\ \lambda_{exc} = 456 \text{ nm and } \lambda_{ems} = 520 \text{ nm} \\ - \\ \lambda_{exc} = 454 \text{ nm and } \lambda_{ems} = 514 \text{ nm} \end{array}$
7.	CIE coordinates (x,y)	Solid state Chloroform DCM Acetic acid	- - -	(0.313, 0.680) (0.073, 0.831) - (0.035, 0.800)
8.	Stokes' shift	Chloroform Acetic acid	-	7364.94 7140.45 cm ⁻¹

of its luminance have also been measured to check the suitability of the complex for OLED applications.

4 | CONCLUSIONS

The synthesized green light-emitting Ir(III) phosphorescent complex, (pbi-Br)₂Ir(acac), bearing the 2-(4-bromophenyl)-1-phenyl-1H-benzimidazole (pbi-Br) ligand was proven to be amorphous in nature. FTIR spectrum results confirmed the formation of the (pbi-Br)₂Ir(acac) complex by indicating peaks at 1243.26 cm⁻¹, 1547.18 cm⁻¹,1500-1450 cm⁻¹, 2843.71 cm⁻¹, 2951.24 cm⁻¹, 3631.37 cm⁻¹, 3555.21 cm⁻¹ and 3440.89 cm⁻¹ attributed to C-H bonding, C=C stretching, aromatic C-C stretching, -CH₂ stretching, -CH₃ stretching and N-H stretching respectively. DTA/TGA curves inferred that the complex had the ability to maintain its properties unchanged upon heating up to 310°C. UV-vis spectra showed two prominent absorption bands in acetic acid (258 nm, 272 nm and 308 nm), (361 nm and 376 nm) and in chloroform (265 nm, 294 nm and 316 nm), (364 nm and 376 nm) attributed to $\pi \rightarrow \pi^*$ and spin-allowed ¹MLCT transition. The energy gap of the solvated (pbi-Br)₂Ir(acac) complex was found to be 2.35 eV and 2.42 eV in acetic acid and chloroform, respectively. When the metal complex was excited at 379 nm in the solid state, it displayed green emission, peaking at λ_{max} = 552 nm. However, the PL spectra of the solvated complex reflected noticeable bathochromic shift with hyperchromic shift (increase in emission intensity) and hypochromic shift (decrease in emission intensity) when (pbi-Br)₂Ir(acac) was in chloroform and acetic acid respectively. A Lippert-Mataga plot, established the relationship between Stokes' shift and solvent polarity function. Stokes' shifts of 7140.45 cm⁻¹ and 7364.94 cm⁻¹ were observed when the complex was solvated in acetic acid and chloroform. CIE coordinates of the (pbi-Br)₂Ir(acac) complex in the solid state were found to be (0.313, 0.680) with CCT at 5778 K, indicating that the synthesized complex emitted deep green light, which fell in the visible region of the electromagnetic spectrum. However, the same was found to be true (0.035, 0.800), (0.073, 0.831) with CCT at 9607 K and 8801 K in acetic acid and chloroform, respectively. These results reveal the potential of the synthesized iridium metal complex as a promising emissive material for OLEDs, light-emitting electrochemical cells and solid-state lightning applications due to its good thermal stability and intense emission wavelength.

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REFERENCES

- W. K. Hu, S. H. Li, X. F. Ma, S. X. Zhou, Q. F. Zhang, J. Y. Xu, P. Shi, B. H. Tong, M. K. Fung, L. Fu, Dyes Pigm, **2018**, 150, 284.
- [2] D. Chitnis, N. Thejokalyani, H. C. Swart, S. J. Dhoble, Renew. Sustain. Energy Rev. 2016, 64, 727.
- [3] C. Xiang, X. Fu, W. Wei, R. Liu, Y. Zhang, V. Balema, Adv. Funct. Mater. 2016, 26, 1463.
- [4] Q. Wang, J. Ding, D. Ma, Y. X. Cheng, L. X. Wang, X. B. Jing, F. S. Wang, Adv. Funct. Mater. 2009, 19, 84.
- [5] P. Tao, W. L. Li, J. Zhang, S. Guo, Q. Zhao, Adv. Funct. Mater. 2016, 26, 881.
- [6] A. Maity, D. Sinha, K. K. Rajak, J. Mol. Struct. 2018, 1158, 122.
- [7] G. Li, Y. Wu, G. Shan, W. Che, D. Zhu, B. Song, L. Yan, Z. Sua, M. R. Bryce, *Chem.Commun.* **2014**, *50*, 6977.
- [8] L. Donato, C. E. McCusker, F. N. Castellano, E. Zysman-Colman, Inorg. Chem. 2013, 52, 8495.
- [9] S. Lee, K.-H. Kim, D. Limbach, Y.-S. Park, J.-J. Kim, Adv. Funct. Mater. 2013, 23, 4105.
- [10] D. Liu, L. Deng, W. Li, R. Yao, D. Li, M. Wang, S. Zhang, Adv. Optical Mater. 2016, 04, 864.
- [11] S. Y. Mullemwar, G. D. Zade, N. Thejo Kalyani, S. J. Dhoble, Optik 2016, 127, 10546.
- [12] M. Ghate, H. K. Dahule, N. ThejoKalyani, S. J. Dhoble, Luminescence 2017, 1.
- [13] W.-S. Huang, Y.-H. Wu, Y.-C. Hsu, H. C. Lin, J. T. Lin, Polymer 2009, 50, 5945.
- [14] S. Morita, T. Akashi, A. Fujji, M. Yoshida, Y. Ohmori, K. Yoshimato, T. Kawai, A. A. Zakhidov, S. B. Lee, K. Yoshino, *Synth. Met.* **1995**, *69*, 433.
- [15] D. Chitnis, N. Thejokalyani, S. J. Dhoble, J. Lumin. 2017, 185, 61.
- [16] Color Calculator, Version 2, A software from Radiant Imaging, Inc 2007.
- [17] C. L. Ho, H. Li, W.-Y. Wong, J. Organomet. Chem. 2014, 751, 261.
- [18] F. Ito, T. Nagai, Y. Ono, K. Yamaguchi, H. Furuta, T. Nagamnra, Chem. Phys. Lett. 2007, 435, 283.
- [19] C. S. McCamy, Color Research and Application 1992, 17, 142.
- [20] P.-T. Chou, Y. Chi, Chem. A Eur. J. 2007, 13, 380.
- [21] J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* 2005, 44, 1713.
- [22] R. C. Evans, P. Douglas, C. J. Winscom, Chem. Rev. 2006, 250,2093.
- [23] D. Chitnis, N. Thejokalyani, S. J. Dhoble, Optik 2017, 130, 237.
- [24] G. Sarada, A. Maheshwaran, W. Cho, T. Lee, S. H. Han, J. Y. Lee, S. H. Jin, Dyes Pigm, **2018**, 150, 1.

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