Synthesis and Characterization of New Red Phosphorescent Iridium (III) Quinoline Complex for OLEDs

[1]H. K. Dahule, [2]Arelli Sridhar Goud

[1]*Dept. of Physics, Shivaji Science College, Congress Nagar,Nagpur-440012, R.T.M. Nagpur University, Nagpur. India*

[2]*Affiliation OPJS university, Churu, Rajasthan, India*

A new red emitting iridium complex bearing with 2,4-diphenylquinoline, (DPQ) ligand has been synthesized and characterized. The various techniques like mass spectrometry, [1]H-NMR, DTA/TGA, FTIR and XRD were employed to characterize the complex. A strong [1]MLCT (singlet metal-to-ligand charge-transfer) and [3]MLCT (triplet metal-to-ligand chargetransfer) absorption peaks at 267, 352, 441, 480, 522, and 564 nm in tetrahydrofuran (THF) are reported. In the photoluminescence (PL) spectra, the DPQ exhibits the luminescence peak at 418 nm when excited at 383 nm. The PL emission peak at 615 nm with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.68, 0.31) is reported in Ir(DPQ)$_2$ (acac) complex. The soluble red emitting Ir(DPQ)$_2$(acac) complex in common organic solvents is promising for flexible organic devices.

Keyword:- *Light emitting diode ,Iridium complex, photoluminescence, soluble red emitting Iridium complex.*

I.INTRODUCTION:

In recent years, considerable attention has been attached to organic light emitting diodes (OLEDs) due to their successful applications in solid-state lighting and full-color flat-panel display. To the present, cyclometalated iridium (Ir) (III) complexes are still the most promising phosphorescent guest materials for highly efficient OLEDs because of their short excited lifetime (microsecond time-scale), color tuning flexibility, high quantum yields and thermal stability[1–7]. Solution-processed organic light emitting-diode devices (OLEDs) are attaining the center stage as potential candidates for brightness applications for flat panel displays and solid state lighting owing to their simple processing route and low manufacturing cost.[8.] OLEDs fabricated by using solution processes such as spin coating and inkjet printing are promising for large fine-pixel devices. Mostly, soluble iridium organic complexes are used in the fabrication of solution-processed red-emitting OLEDs. [9-12]

In order to improve the efficiency and the color purity of full color displays,the red emitting Ir complexes are becoming increasingly important. Among different metal complexes, the cyclometallated iridium(III) complexes have been widely studied for decades because of their intriguing offer for developing a new field of applications in organic light-emitting diodes (OLEDs). [13-15]The iridium complexes are the most effective and show intense phosphorescence at room temperature.[16-17] .

The emission colors from these complexes, which range from blue to red, are strongly dependent on the choice of the cyclometalating ligand. [18], Thus, the design and synthesis of new organic ligands for Ir complexes is highly desirable. In this paper, we have demonstrated a pure red light emitting iridium complex and studied optical properties in various solvents. We have synthesized a 2,4-diphenyl quinoline and used as a ligand to synthesize the red iridium complex [Ir(DPQ)$_2$(acac)] DPQ= 2,4 diphenyl quinoline, acac = acetyl acetone), instead of common isoquinoline ligand. The absorption and emission of the ligand and the complex in the visible region was measured in different organic solvents such as acetic acid, formic acid, dichloromethane, and tetrahydrofuran (THF). The red light emission at 615 nm is reported in this complex.

II.EXPERIMENTAL DETAILS :

2.1Synthesis of 2, 4-Diphenyl quinoline (DPQ)

The 2, 4-diphenyl quinoline (DPQ) ligand was synthesized using the acid catalyzed Friedlander reaction according to Scheme 1 as shown in Fig. 1.The 2-Aminobenzophenone (0.32 gm, 8.1 mmol) and acetophenone (0.32 gm, 13.3 mmol) were added along with 2 gms of diphenyl phosphate (DPP) and 1.3 gm of m-cresol in a glass reactor fitted with the mechanical stirrer and two glass inlets.The 2 Aminobenzophenone reacts with the acetophenone in the presence of diphenyl phosphate at 140^0 C, in an argon atmosphere; the water vapors come out, and finally undergoes the crystallization,giving the 2, 4-diphenyl quinoline (DPQ) ligand.The reaction mixture was purged with an Argon gas (purity: 99.90%) for 20 min. and the temperature was then raised gradually to 90^0 C under the argon atmosphere for 1h and later to 140^0 C for 4h. After cooling to room temperature, the methylene chloride (20 ml) and 10% NaOH (20 ml) were added to the reaction mixture. The organic layer was separated and washed with the distilled water (10 ml x 5 times) until it was neutral (pH = 7). Finally it was dried over an MgSO4 and evaporated under the natural condition to yield an off-white solid. The

crude product was then washed with the hexane (5 ml x 2 times) to afford an off-white crystalline solid. [C_{21} H_{17} N] (1.952 gm, 93.4%), mol. wt. = 283.231 gm, m. p. = 114^{0}C , ^{1}H-NMR (300 MHz, CDCl): d 7.457.54 (m, 39H), 7.73 (t, J = 7.6 Hz,1H), 7.81 (S,1H), 7.90 (d, J =8.4 Hz, 1H), 8.22 (d, J = 7.4 Hz, 2H), 8.28 (d, J = 8.4Hz, 1H).

The characteristic peaks of FT-IR spectra of DPQ are:-(cm^{-1}): - 3069, 3053, 1964, 1911, 1853,1773, 1683, 1590, 1545, 1509, 1489, 1459, 1445, 1406,1357, 1231, 1145, 1074, 1030, 971, 922, 873, 732,684,589, 563, 543, 480, 457.

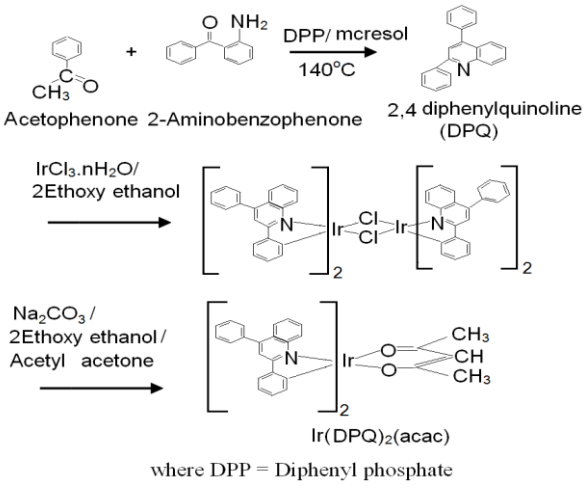

Fig. 1.Scheme 1 : Synthesis of Ir(DPQ)$_2$(acac)

2.2 Synthesis of Ir(DPQ) (acac) Complex

The Ir(DPQ) (acac) was synthesized according to the scheme-1, as shown in Fig. 1.The synthesized DPQ ligand (0.623g, 2.2mmol) was dissolved in ethoxy ethanol (10ml) in a 50ml round bottom flask. The Iridium trichloride hydrate [IrCl .3H O] (0.2984 gm, 1 mmol) and 3ml of water were then added to the flask. The mixture was stirred under an argon atmosphere at 120^0 C for 24hr. The mixture was then cooled to the room temperature and the precipitate was collected and finally dried to give a cyclometallated chloride bridged dimmer as a red powder. In a 50 ml flask, the synthesized complex, acetyl acetone (1.0 mmol) and Na CO2 (2.5 m mol) were dissolved in 2ethoxyetenol (15 ml) and the mixture was refluxed under an argon atmosphere for 12 hr. After cooling to the room temperature, the precipitate was filtered off and washed with the water, ethanol and ether to obtain the desired product. The yield of Ir(DPQ)$_2$ (acac) complex was 78.6%. Ir(DPQ)$_2$ (acac):

^{1}H-NMR (300 MHz,CDCl): d = 2 31.55 (S, 6H), 4.80 (S, 1H), 6.59 (d, J =7.0 Hz, 2H), 6.66 (d, J = 7.5 Hz, 2H), 6.95 (td, J = 2.2,8.4 Hz, 2 H), 7.407.45 (m, 4H), 7.507.70 (m, 10H),7.777.87 (m, 4H), 7.80 (S, 2 H), 8.60 (dd, J = 2.1, 7.813 Hz, 2H);

C-NMR (75 MHz, CDCl): d 28.2, 100.3, 3118.1, 121.9, 122.0, 125.7, 125.7, 126.0, 126.4, 127.0,128.7, 128.7, 129.0, 129.8, 130.2, 136.3, 137.6, 138.0,147.3, 148.3, 149.6, 150.0, 150.9, 169.6, 185.5;

MS[m/z]: 853(M+); Anal. calcd. for C_{47} H_{37} O_2 N_2 Ir = 853.22: C, 66.10; H, 4.33; N, 3.28. Found: C, 65.95; H,4.11; N, 3.01 %.

The characteristic peaks of FT-IR spectra Ir(DPQ) (acac) are: FT-IR (film, cm $^{-1}$) - 3060, 3040, 2960, 2935, 2880, 2840,1750, 1600, 1500, 1450, 1260 ,1150, 873, 870 , 790.

The FT-IR spectra were recorded on a SHIMADZU Model 8101A infrared spectrophotometer. The XRD pattern was obtained by using X-ray analytical diffractometer with Cu Ka radiation (l = 1.5418 Å) operated at 40 kV and 20 mA. The solid DPQ and Ir(DPQ) (acac) were dissolved in tetrahydrofuran media in different mol. concentration. The optical absorption spectra of solutions were obtained on an Analytik Specord-50 spectrophotometer. The photoluminescence spectra were obtained by using HITACHI F - 4000 spectrofluorometer, while TGA / DTA and DSC measurements were recorded on Mettler Tolledo System. All these measurements were carried at room temperature.

III.RESULTS AND DISCUSSION:

3.1X-Ray structural analysis

The crystallinity of polyquinolines was evaluated by a wide-angle X-ray diffraction experiments. The XRD pattern of 2, 4- Diphenyl Quinoline is as shown in Fig. 2(a), while the XRD pattern of Ir(DPQ)$_2$ (acac) is shown in Fig. 2(b). The X-ray diffraction analysis on powder 2, 4 DPQ and Ir(DPQ)$_2$(acac) have many strong, sharp diffraction peaks. This reveals the crystalline character of the polymeric material. The spacing corresponds to the chain distances of a well organized molecular layer structure, which is consistent with the literature reports. The much weaker diffraction peaks indicate the lower crystallinity or orientation. The crystallinity parts give sharp narrow diffraction peaks, while the amorphous component gives a very broad peak. The ratio between intensities of narrow and broad peaks can be used to calculate the amount of rystallinity in the material. However, too much crystallinity may cause brittleness of organic films in actual devices.

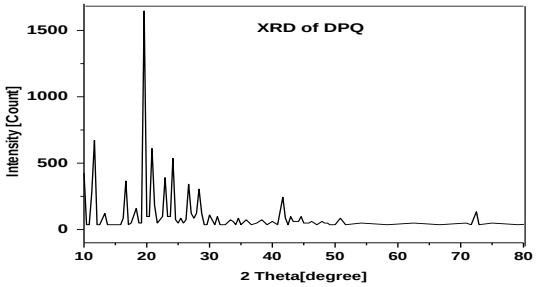

Fig. 2(a) The XRD Pattern of DPQ ligand

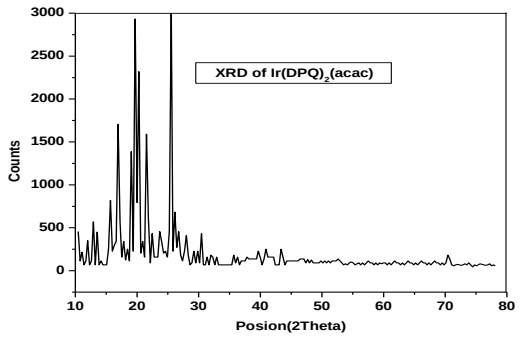

Fig. 2 (b) The XRD pattern of $Ir(DPQ)_2$ (acac) complex

3.2 Thermogravimetric analysis

We have investigated the thermal properties of DPQ and $Ir(DPQ)_2$(acac) complexes by using differential scanning calorimetry (DSC). The DSC second heating scans of the polymeric compounds are as shown in Fig. 3. The DPQ undergoes a glass O transition at 80^0 C, followed by a crystallization at 114^0 C and crystalline melting point at 380^0 C (Fig. 3,curve (a)). In contrast, no phase transition signal was observed for the $Ir(DPQ)_2$(acac) complex in the temperature range from 30 to 300^0 C (Fig. 3, curve(b))

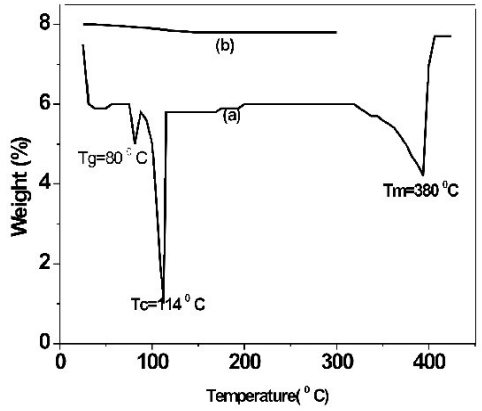

Fig. 3. DSC scan of (a) DPQ and (b) $Ir(DPQ)_2$(acac) complex.

The thermal stability, chemical reactivity and phase transitions properties of materials are evaluated by using TGA and DTA. The TGA is used for the precise measurement of the specimen weight changes as function of time and temperature in various gaseous environments. The DTA is employed for measuring the changes in specimen heat content during solid-state transformations and gas solid reactions. The TGA results reveal the onset decomposition temperatures of the polymeric compound around 300^0 C in nitrogen, indicating that the material is stable over a wide temperature range. The onset weight loss temperature of DPQ is found to be at 338^0 C. Indeed, the stability of the material is imperative for the fabrication of optoelectronic devices. The high thermal stability is closely related to the performance of these devices, which prevents morphological change, deformation, and degradation of the emitting layer.

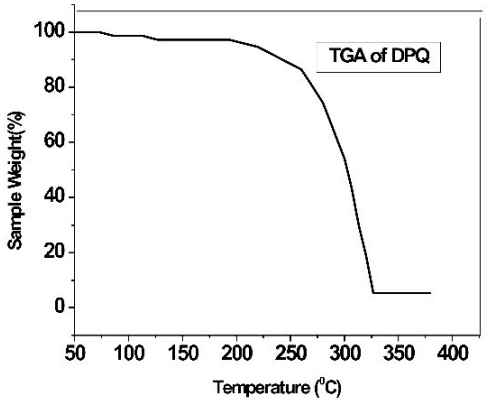

Fig. 4 Thermo gravimetric analysis (TGA) curve for DPQ ligand.

3.3 Optical properties

We have studied the optical properties of 2,4-diphenylquinoline (DPQ). The UVvis absorption spectra of 10^{-4} M DPQ in acetic acid, formic acid, dichlomethane (DCM), and chloroform at room temperature are shown in Fig. 5. The absorption of DPQ peaks are isolated by subtracting the contribution of solvent from the absorption of (DPQ + solvent). Pure acetic and formic acid solutions show absorption shoulders at 263 and 265, respectively, and no absorption above 320 nm. Whereas, the DPQ (10^{-4} M solutions) exhibits a strong absorption at 333 nm in acetic acid and 339 nm in formic acid. The shoulders at 263 and 265 nm also become prominent. A small red shift in the absorption peak position (333 nm and 339 nm) was noticed. Further, the intensity of various peaks is slightly higher in (DPQ + formic acid) solutions. However in both cases, the intensity of main absorption peak reduces to zero at 385 nm. On the other hand, the DPQ shows strong absorption in chloroform and dichloromethane solutions peaking at 254 nm and a broad shoulder at 327 nm. This red shift of the absorption spectrum in acids as compared to chloroform and dichloromethane of DPQ is due to protonation of the imine nitrogen of the quinoline ring to form the quinolinium ion. Such an effect of protonation on optical absorption has previously been observed in conjugated oligoquinolines. [19-20,] The lowest energy absorption bands are from the ð- ð* transitions by virtue of their large molar extinction coefficients. All solution absorption spectra of the polymer are structureless. The polymeric compound has nearly identical absorption maxima (ëmax) at 254 nm in both acids (curves (c) & (d)). However, no evident trend for this slight difference in absorption spectra and maxima is noticed, and no correlation can

be made between absorption maxima and molecular weight. The UV-vis absorption spectra could provide a good deal of information on the electronic structures of the polymeric compound. The two absorption peaks in polymeric compound are to the ð-ð* transitions of the conjugated polymer main chains in the visible region; and another in the UV region due to the conjugated side chains.

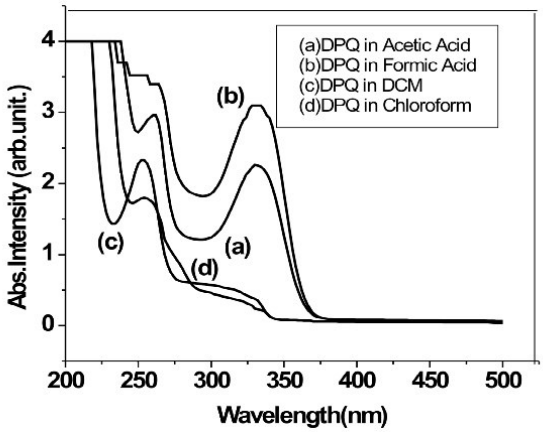

Fig. 5 Absorption spectra of 10 $^{-4}$M solutions of DPQ in acetic acid, formic acid, dichloromethane (DCM) and chloroform

From the UVvisible absorption spectra, the onset absorption of DPQ in acetic acid and DPQ in formic acid were measured to be 407 nm and 413 nm, respectively. Using the procedure described by Morita et al.[21.] for the optical energy gap determination, the energy gap Eg = 3.432 eV for DPQ in acetic acid and Eg = 3.418 eV in formic acid, as displayed in Fig. 6.

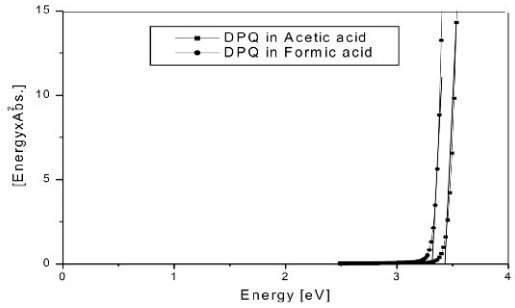

Fig. 6 Determination of optical band gap energy,Eg.of DPQ in acetic and formic acid.

The excitation and photoluminescence (PL) spectra of DPQ in Acetic acid (dilutesolution, 10^{-6} M) are shown in Fig. 7. The excitation band in Acetic acid is centered at 350 nm with a shoulder at 275 nm (curve (a)). The polymeric chromophore emits blue light with the emission maxima at 413 nm (curve (b)). Fig. 7 also shows the excitation and emission band of DPQ in Formic acid (dilute-solution, 10^{-6} M). The excitation band is centered at 376 nm (curve (c)) and the polymeric chromophore emits intense blue light at wavelength of 424 nm (curve (d)) when excited at 254and 376 nm. A small red shift between λ_{em} acetic acid and formic acid may be attributed to inductive effect caused by nitrogen loan pairs located on quinoline substituents.

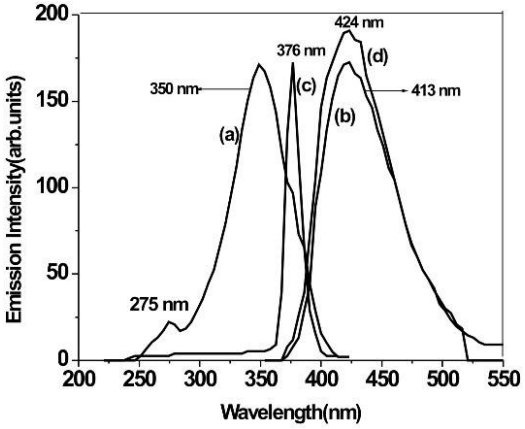

Fig. 7 (a) Excitation and (b) Emission spectra of DPQ in Acetic acid (10 $^{-6}$ M) ; (c) Excitation, (d) emission spectra of DPQ in Formic acid (10^{-6} M)

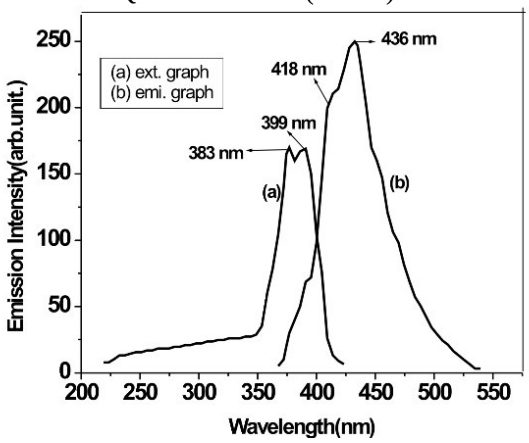

Fig. 8 Excitation & Emission spectra of DPQ in solid form

Figure 8 shows the excitation and photoluminescence (PL) spectra of DPQ in powder form. The excitation spectra DPQ crystalline powder shows two peaks at 383 nm and 399 nm. When the powder is excited at 383 nm, it emits intense blue light of wavelength 436 nm and a shoulder at 418 nm. The PL spectra of DPQ in acetic acid is blue shifted by about 23 nm and in formic acid by about 12 nm as compared to the powder. A substantial red shifts by 12-23 nm in the solid-state PL emission spectra of the chromophore relative to the dilute solutions is probably due to excimer formation rather than aggregation, judging by the lack of spectral shift in the absorption spectra for the solution with compared to the solid state. These results indicate a strong intermolecular interaction in the solid state.

Further, the PL emission spectra of the polymeric compound show a distinct solvent dependence. This effect was documented in the PL spectra presented for dilute solutions in solvents of varying polarity (Fig. 7). The Stokes' shift between absorption and emission spectrum in 10^{-5} M solution can be clearly observed in both acids (acetic and formic acid), as displayed in Fig. 9. This polymeric compound DPQ shows a broad band structured PL emission spectra with a large Stokes'

shift ranging from 70-89 nm (70 nm (0.17 eV) in acetic acid and 89 nm (0.139 eV) in formic acid). The broad, featureless PL emission spectra and the large Stokes' shifts of these diphenyl quinolines are the characteristic of intermolecular excimer emission, which has previously been observed in many conjugated polymers.

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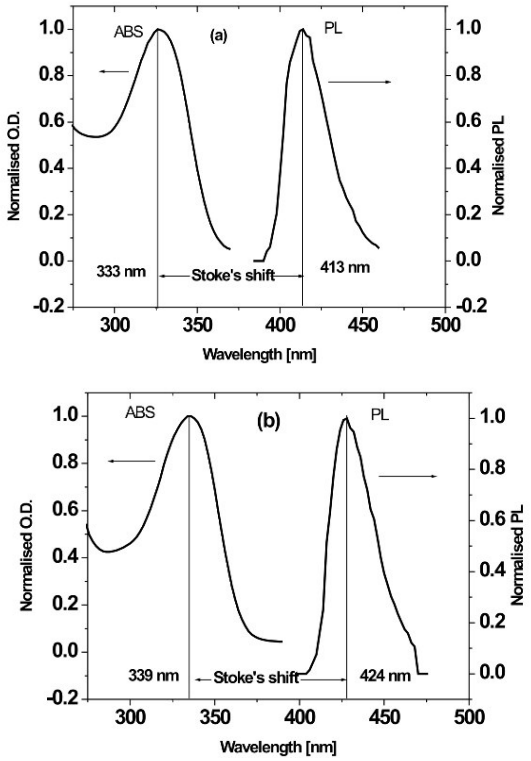

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Fig. 9 (a) Stokes' shift in Acetic acid and (b) Formic acid (10^{-5} M solution)

Figure 10 displays the absorption and emission spectra measured for $Ir(DPQ)_2$ (acac) in THF solution (10^{-4} M) of at room temperature. The absorption peaks of $Ir(DPQ)_2$ (acac) in THF solution appear at 267, 352, 441, 480, 522, and 564 nm. We assign the strong absorption bands in the UV region to the spin-allowed π-π^* transition of the cyclometalated quinoline ligands. The lowest energy absorption, with the peak wavelengths in the region 440-460 nm (inset of Fig. 10), can be ascribed to a typical spin-allowed metal-to-ligand charge transfer (^{1}MLCT) transition; we believe the weak bands at long wavelengths are associated with both spin orbit coupling enhanced $^3\pi$-π^* and ^{3}MLCT transitions. It is noteworthy that the formally spin forbidden ^{3}MLCT gains intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spinorbit coupling on Ir, which results in an intensity that is 1 comparable with the allowed ^{1}MLCT.

We observed highly intense photoluminescence (PL) for $Ir(DPQ)_2$ (acac) in THF with values of λmax located at 615 nm with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.68, 0.31). The broad, structureless spectral features lead us to conclude that the phosphorescence originates primarily from the ^{3}MLCT state

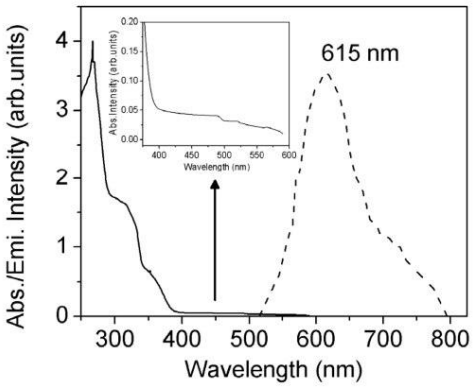

Fig. 10 Absorption and emission spectra of $Ir(DPQ)_2$(acac) in THF solution 10^{-5} at room temperature.

IV.CONCLUSION:

We have successfully synthesized a new red emitting soluble Ir(III) phosphorescent complexe $Ir(DPQ)_2$(acac), bearing a 2,4-diphenyl quinoline, (DPQ) ligand. The synthesized complex is thermally very stable over a wide range of temperature and suitable for the use as a red-emissive material in solution processed organic devices. In conclusion, the synthesized $Ir(DPQ)_2$(acac), complexes with the emission in the red region at 615 nm is very promising for applications in flexible organic devices.

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