



Synthesis and Characterization of Novel Orange-emitting Iridium(III) Complex with Diphenylquinoline Ligands Containing Amino Substituent

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Abstract:

A new red emitting iridium complex with a amino-substituted 2,4diphenylquinoline, (A-DPQ) ligand has been synthesized. The synthesized iridium metal complex, Ir(A-DPQ)₂(acac) where A-DPQ= Amino-substituted,2,4diphenylquinoline,acac=acetyl acetone is characterized by elemental analysis (EA), ¹H NMR, and mass spectroscopy (MS)., DTA/TGA, XRD, and FTIR. The photophysical and electrophosphorescent properties of the complexes were briefly discussed.

Keywords: Iridium complexes, Amino-DPQ ,photoluminescence, electrophosphorescence.

Introduction:

Recently, the iridium complexes as phosphorescent emitter in organic light-emitting diodes (OLEDs) have attracted much attention since the realization of a high efficiency OLED device based on the complex *fac*tris(2-phenylpyridine)iridium [Ir(ppy)₃] [1-4.] The wavelength of emission of the iridium complexes can usually be tuned by modification or variation of cyclometalated ligands of 2-phenylpyridine or its analogical ligands, such as benzoisoquinolines[5], 2-phenylbenzothiazole [6], benzoimidazole [7] 2-4 Diphenylquinoline [8-11] etc.. In this paper, we report the synthesis and characterization of the novel diphenylquinoline based Ir complexes, Ir(Amino-DPQ)₂(acac), (DPQ=diphenylquinoline; acac=acetylacetone), where quinoline group is used to improve electron transport ability [12], consequently to facilitate the charge trapping across the bulk, and fluorinated substituent in the phenyl ring is introduced to tune the emission of the iridium complexes and increase the volatility for device processing [13]. The photoluminescence and electroluminescence of the complexes will be briefly discussed.

(b) Experimental

2.1 : Synthesis of 2-(4-Amino-phenyl)-4-phenyl-quinoline (A-DPQ) ligands:

The quinoline-derived ligand 2-(4- Amino-phenyl)-4 Phenyl quinoline (A-DPQ)], were synthesized conveniently according to Scheme 1 from the condensation of 2-Aminobenzophenone and 4-Amino acetophenone using the acid-catalyzed Friedlander reaction [14].

2-Aminobenzophenone (2gm), and 4-amino acetophenone (2gm), were added along with Di-phenyl Phosphate (DPP) (2 gm), and m-Cresol (3 ml), in a glass reactor fitted with mechanical stirrer, two glass inlets and one side arm. The reaction mixture was purged with argon for 20 min. and then the temperature was raised to 90 °C gradually under Argon atmosphere for 1 hour and subsequently to

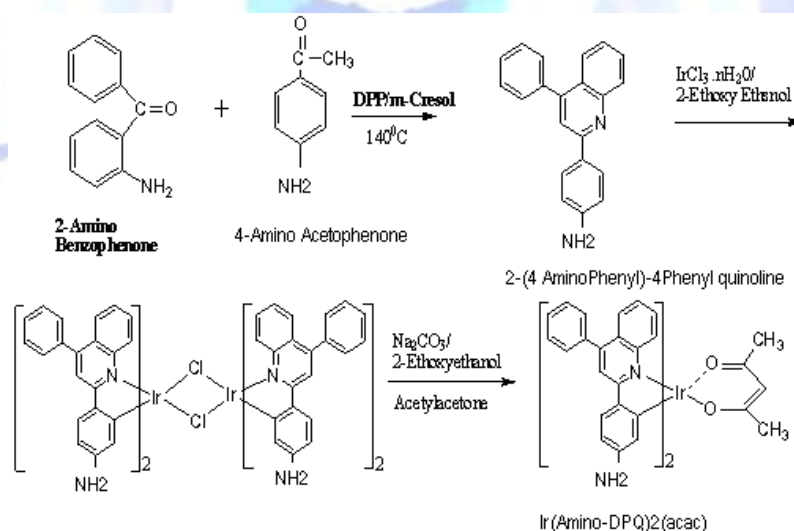


140 °C for 4 hours. After cooling, dichloromethane– CH₂Cl₂, (50 ml) and 10 % NaOH (50 ml) were added to the reaction mixture. The organic layer was separated and washed with distilled water (20 ml x 5) until it was neutral, then dried over MgSO₄ and evaporated under vacuum to yield an off- white solid with some radish liquid on top. The crude product was filtered and washed with hexane (5 ml x 3) to obtain crystalline solid of 2-(4-Aminophenyl)-4Phenylquinoline abbreviated as Amino-DPQ.to afford crystalline solid (2.78 g).

2.2 Synthesis of ofIr complex:

Amino-DPQ, (1.42 mmol) was dissolved in a mixed solvent of 2-ethoxyethanol (12 mL) and water (4 mL) in a 50 mL round-bottomed flask. Then IrCl₃•nH₂O (0.21 g, 0.59 mmol) was added. The mixture was stirred under argon at 120°C for 24 h. The mixture was cooled to room temperature and the precipitate was collected and washed with water, ethanol and hexane successively, and then dried in vacuum to give a cyclometallatedIr (III) μ -chloro-bridged dimer. In a 50 mL of flask, the dimer complex (0.12 g, 0.08 mmol), acetylacetonone (0.24 mmol) and Na₂CO₃ (86 mg, 0.8 mmol) were dissolved in 2-ethoxyethanol (8 mL) and the mixture was then refluxed under argon at 120°C for 16 h. After cooling to room temperature, the precipitate was filtered off and washed with water ,ethanol and ether give to to afford the desired Ir(III) complex.

¹H NMR (300 MHz, CDCl₃): d 1.64 (s, 6 H), 4.80 (s, 1 H), 6.70 (d, J = 7.0 Hz, 2 H), 6.74 (d, J = 7.5 Hz, 2 H), 6.82 (td, J = 2.2, 8.4 Hz, 2 H), 7.39–7.45 (m, 4 H), 7.53–7.68(m, 10 H), 7.77–7.86 (m, 4 H), 7.80 (s, 2 H), 8.58 (dd, J = 2.1, 7.8 Hz, 2 H). HRMS [M⁺] calcd. For C₄₇H₄₀O₂N₄Ir 885.34, found 885.41. Anal.Calcd. forC₄₇H₄₀O₂N₄Ir: C, 66.36; H, 4.24; N, 3.39. Found: C, 66.30; H,4.18; N, 3.46%.



(c) **Scheme1: Synthesis of (Amino-DPQ) ligand and Ir(Amino-DPQ)₂(acac) complex**



Result and Discussion:

3.1. Synthesis and structural characterizations

Phenylquinoline-based organic ligands were conveniently prepared from the condensation of 2 Aminobenzophenone and 4-Amino acetophenone using the acid-catalyzed Friedlander reaction [14]. The Ir (III) μ -chloro-bridged dimers were synthesized by the reaction of iridium trichloride hydrate with ligands according to the similar method reported by Nonoyama[15]. Then the diiridium complexes were converted to mononuclear iridium complex by replacing the two bridging chlorides with bidentate monoanionic acetylacetonate ligand in 50% -70% yields (Scheme 1). The structures and purity of the complex were characterized by ^1H NMR and elemental analysis. The complex is thermally stable up to 300–385 °C revealed by thermal gravimetric analysis (TGA). X-ray crystallographic studies have been carried out for (A-DPQ) and Ir(A-DPQ)₂ (acac)

3.2. FTIR analysis

The molecular confirmations of polymeric compound are done by FTIR spectra as shown in Figure 1. From the Figure 1, we can conclude that, the aromatic CH vibration stretch which appears at 3100–3000 cm^{-1} . A strong absorption band in the region around 1700 cm^{-1} is due to C=O stretching. There are aromatic C–C stretch bands for the carbon–carbon bonds in the aromatic ring at about 1500–1600 cm^{-1} . The substitution pattern in an aromatic is identified by looking at the C–H out of plane bending bands and also from the combination bands (overtone) between 1650–2000 cm^{-1} . The new strong bands between 1500 and 1400 cm^{-1} due to the imine (C=N) group and this is the characteristic of the quinoline ring. The C=N structure in the ligand gives the electron transporting characteristics. The N–H stretch appears at 3451–3200 cm^{-1} . C–N stretching absorption occurs at 1360–1250 cm^{-1} .

The characteristic peaks of FT-IR spectra of (A-DPQ) are 3110, 3080, 3035, 2998, 2928, 2590, 1952, 1840, 1813, 1614, 1545, 1488, 1445, 1418, 1330, 1294, 1234, 1123, 1094, 1014, 950, 927, 867, 843, 810, 742, 677, 639, 630, 581, 539, 486, 454 cm^{-1} .

The molecular structures of Ir(A-DPQ)₂(acac) complex was confirmed by FTIR spectra. The FTIR spectra of Ir(A-DPQ)₂(acac) were recorded using FTIR-8101 SHIMADZU is shown in Figure 2. The FTIR spectrum of the complex has been taken in KBr. FTIR Spectra of Ir(M-DPQ)₂(acac) is shown in Figure 2. The peaks at 3500–3560 cm^{-1} are due to O–H bonds. The peaks between 3500–3400 cm^{-1} are due to N–H bonds. The peaks at 3060 and 3040 cm^{-1} are due to the C–H stretching frequency of aromatic (C–H) ring. The peaks at 2925, 2870, 2840 cm^{-1} are attributed to the C–H stretching frequency of aliphatic CH₃, CH groups, etc. The peaks at 1550, 1500, 1450 cm^{-1} are due to the C=C of aromatic ring. The peak 1710 cm^{-1} due to C=O stretching frequency are noticed. The peak at 1266 cm^{-1} is due to aromatic C–N stretching. The peak at 1150 cm^{-1} is related to the C–O stretching frequency, while between 790–870 cm^{-1} are due to the >C=CH bending. The peak at 734 cm^{-1} is due to C–H out of plane bending in aromatic ring.





The characteristic peaks of FT-IR spectra of Ir(M-DPQ)₂(acac) are as follows: (FTIR film, cm⁻¹)

3533, 3500, 3407, 3100, 3060, 3040, 2960, 2925, 2870, 2840, 2533, 2500, 2450, 2300, 2166, 2050, 1710, 1650, 1550, 1500, 1450, 1380, 1260, 1150, 790-870, 734 cm⁻¹.

(d) 3.3 X-ray diffraction analysis:

The X-Ray diffraction pattern of Ir(A-DPQ)₂(acac) complex are shown in Figure 3. From the X-ray diffraction analysis, the powder Ir(A-DPQ)₂(acac) have many strong, sharp diffraction peaks and some diffused background. This indicates the crystalline character of the compound. These spacings correspond to the chain distances of a well-organized molecular layer structure. A much weaker diffraction peak indicates lower crystallinity or orientation. In addition, its higher volume fraction of insulating side chains may also contribute to its low field-effect mobility. However, too much crystallinity causes brittleness. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo).

(e) 3.4 Thermal properties analysis

3.4.1 Thermogravimetric (TGA) Analysis of Amino-DPQ:

The thermo gravimetric and differential thermal analysis (TG-DTA) curves of the amino-DPQ powder form as shown in Figure 3. TGA result of amino substituted DPQ shows the melting temperature at about 76.26 °C and glass transition temperature is at 156.96 °C. The DTA result reveals that the thermal stability of the polymeric compounds is around 302.80 °C, which indicate that the material is stable and no weight losses are observed at lower temperatures.

(f) 3.5 Optical Properties

3.5.1 Absorption and PL spectra of ligand:

The optical properties of asymmetric Amino-DPQ were measured in basic solvents i.e. dichloromethane and Tetrahydrofuran (THF) solutions and in acids i.e. acetic acid and formic acid. Figure 4 curve(a) shows the optical absorption spectra of Amino-DPQ in dichloromethane at room temperature. The polymeric compound have broad absorption peak at 264 nm (4.78 eV) due to π - π* transition and 334 nm (3.76 eV) due to intermolecular charge transfer in chloroform. The emission spectra of A-DPQ in CH₂Cl₂ showed emission peak at 408 nm [Figure 4 Curve (C)]

Figure 4 curve(b) shows the optical absorption spectra of Amino-DPQ in THF at room temperature. The polymeric compound have broad absorption peak at 265 nm (4.81 eV) due to π - π* transition and 332 nm (3.77 eV) due to intermolecular charge transfer in THF. The emission spectra of A-DPQ in THF showed emission peak at 428 nm [Figure 4 Curve (C)]

(g) Figure 5 (Curve (a)) shows absorption spectra of Amino-DPQ in acetic acid as a function molar concentration. The absorption spectra of the compound in the different solvents are characterized by two bands, one near 261 nm (4.82 eV) and the other at around 337 nm (3.70 eV) for Amino-DPQ. The former band can be assigned to π-π* transition whereas the lowest-energy band, which is less intense, is largely of charge transfer character. The absorbance spectrum of the compound is characterized by a strong absorption peak centered at 337nm and with a weak



shoulder at 261 nm. PL emission peak of (A-DPQ) ligand in acetic acid was located in the blue region with the λ_{\max} value at 420 nm. [Fig,5 Curve (c)]

(h) Figure 5 (curve (b). the absorption spectra of the Amino-DPQ compound in formic acid are characterized by two bands, one near 284 nm (4.64 eV) and the other at around 347 nm (3.66 eV) for Amino-DPQ. The former band can be assigned to π - π^* transition whereas the lowest-energy band, which is less intense, is largely of charge transfer character. PL emission peak of (A-DPQ) ligand in formic acid was located in the blue region with the λ_{\max} value at 431 nm. [Fig,5 Curve (d)]

3.5.2 Absorption and PL spectra of Ir Complex.

(i) The $\text{Ir}(\text{A-DPQ})_2(\text{acac})$ complex showed (Figure 6) absorption spectra with strong 1π - π^* transition of ligands between 250 and 350 nm and relative weak absorption bands in the range of 350-600 nm, assigned to metal-to-ligand charge transfer bands ($^1\text{MLCT}$ and $^3\text{MLCT}$) and $^3\pi$ - π^* transitions (**Figure 6**). The emission spectra of $\text{Ir}(\text{A-DPQ})_2(\text{acac})$ in CH_2Cl_2 showed emission peak at 630 nm, which were falling in orange region.

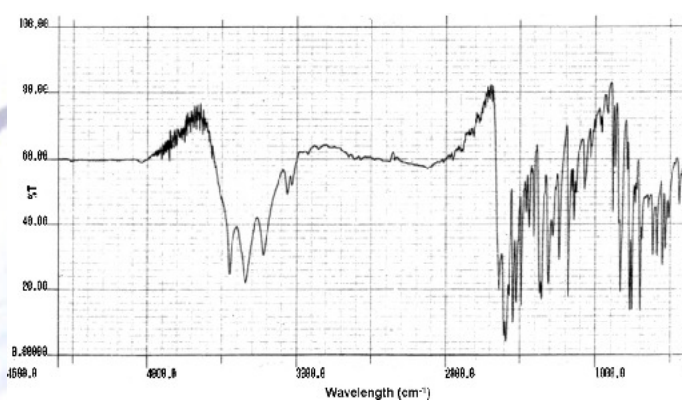


Figure.1- FTIR spectra of A-DPQ

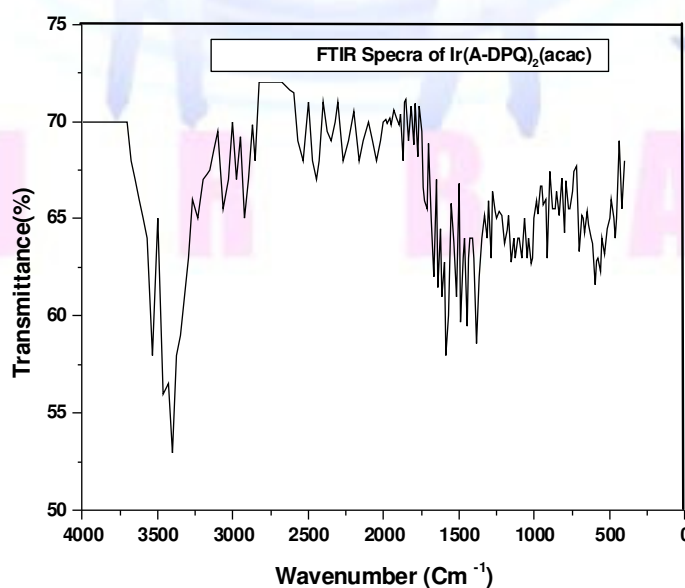


Figure. 2- FT-IR spectra of $\text{Ir}(\text{A-DPQ})_2(\text{acac})$

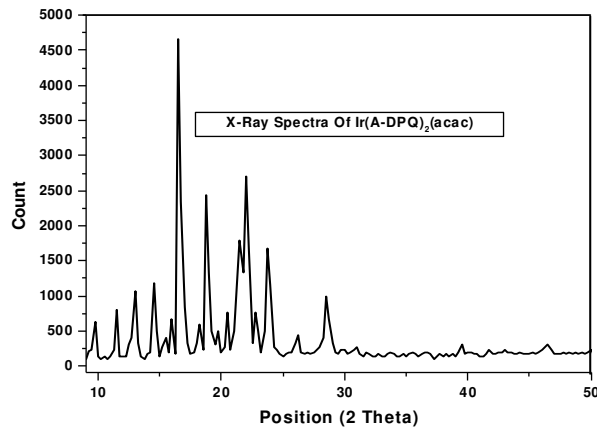


Figure. 3- XRD pattern of Ir(A-DPQ)₂(acac)

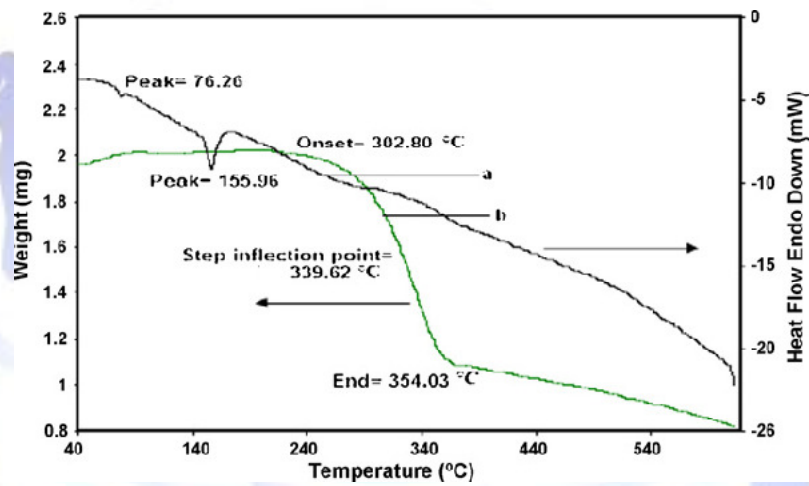


Figure. 3- Thermo gravimetric analysis curve.

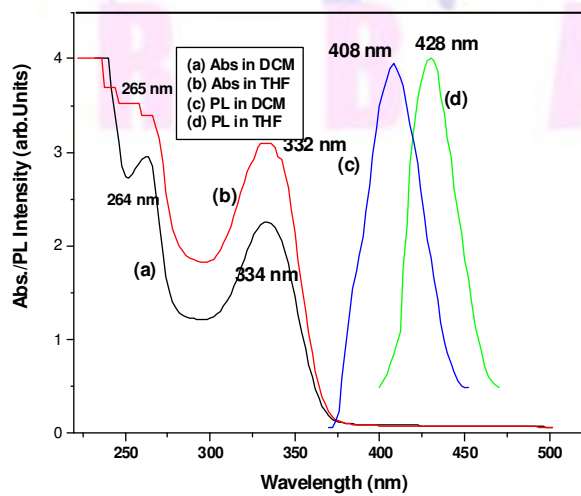


Figure. 4- Absorption spectra of Amino-DPQ in (a) DCM (b)THF solution



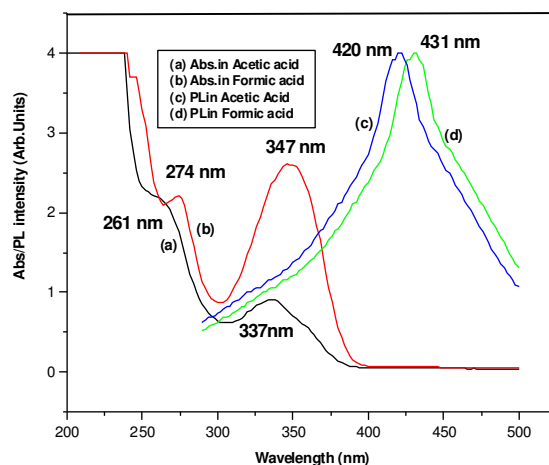


Figure. 5- :Absorption spectra of Amino-DPQ in (a) acetic acid (b)formic acid solution

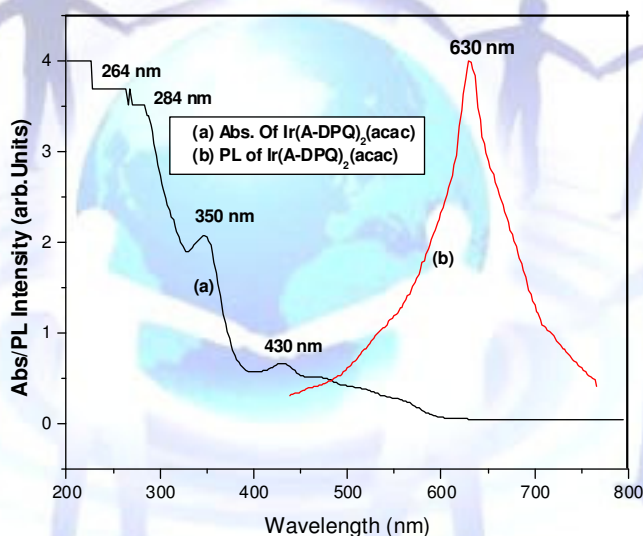


Figure. 6- Absorption and PL spectra of Ir(A-DPQ)₂(acac) complex in DCM solution

Conclusion:

In conclusion, we have synthesized and characterized three diphenylquinoline based iridium complexes. These complexes show strong orange emission, which can be tuned by the introduction of amino substituents on the ligand frame. A highly efficient OLED using complex Ir(A-DPQ)₂(acac) as the dopant has been preliminary demonstrated. Further studies on their electrophosphorescent properties are in progress.

We have also successfully synthesized a new blue emitting polymer(ligand) 2-(4-Amino-phenyl)-4-phenyl-quinoline (Amino -DPQ.. The synthesized polymer is thermally very stable over a wide range of temperature and suitable for the use as a blue-emissive material in solution processed organic devices. In conclusion, the



synthesized [(Amiono-DPQ) polymer with the emission in the blue region at 428 nm is very promising for applications in flexible organic devices.

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