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REGULAR ARTICLE

Synthesis, photophysical, electrochemical and electroluminescence studies of red emitting phosphorescent Ir(III) heteroleptic complexes

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Abstract. Five heteroleptic, cyclometalated (C^N) Iridium(III) complexes of acetylacetone (acac) and 1-phenyl-isoquinoline (piq) derivatives, Ir(acac)(piq)$_2$, Ir(acac)(2,4-difluoro-piq)$_2$, Ir(acac)(4-trifluoromethyl-piq)$_2$, Ir(acac)(4-N,N-dimethyl-piq)$_2$, Ir(acac)(4-acetyl-piq)$_2$, were synthesized and characterized. The (C^N)$_2$Ir(acac) complexes in toluene showed phosphorescence (λ_{max} = 598 nm to 658 nm) with quantum yields (0.1 to 0.32) and microsecond lifetimes (0.43 to 1.9 µs). The complexes were non-luminescent in thin films due to self-quenching but luminescent when lightly doped (5%) in a host organic material, 4,4′-Bis(N-carbazolyl)-1,1′-biphenyl (CBP). The HOMO levels determined using cyclic voltammetric oxidation potentials were in the range −5.48 to −5.80 eV. Electroluminescence properties and performance of the Ir complexes doped in CBP (active layer) were studied in a multilayer (ITO/F4TCNQ/TPD/doped CBP/BCP/LiF/Al) organic light emitting device (OLED). The electroluminescense (EL) spectra of the device matched with the phosphorescent spectra of the Ir complexes. The turn-on voltage at ∼4.5 V, maximum brightness of 7600 cd/m^2 and current efficiency of ∼7.0 cd/A at a brightness of ∼100 cd/m^2 indicate that these are promising OLED materials.

Keywords. 1-Phenyl-isoquinoline; Suzuki-Miyaura coupling; Iridium(III)complex; phosphorescence; red emitter; electroluminescence.

1. Introduction

Luminescent, homoleptic and heteroleptic Ir(III) complexes consisting of one or more cyclometalating (C^N) ligands are an important class of materials used in electro-phosphorescent organic light emitting devices (OLEDs).[1–5] The luminescence of the heavy metal complex is due to phosphorescence from the triplet state. The normally forbidden transition between Ground and Triplet state becomes permissible due to spin-orbit coupling strongly induced by the heavy metal. Often, the extinction coefficient (oscillator strength) for singlet-triplet transition becomes comparable to singlet-singlet transition. As a result, the radiative rate of phosphorescence from triplet to singlet is enhanced; resulting in decreased lifetime of the triplet state and enhanced luminescence quantum yield at room temperature.[6] In small molecule based OLEDs, recombination of electrons and holes produces singlet and triplet excitons in 1:3 ratio. The triplet excitons in most organic materials do not contribute to emission and go waste.[7] Highly phosphorescent molecules like Ir complexes are useful to harvest both singlet and triplet excitons and increase the electroluminescence efficiency.[8] In spite of these advantages, an Ir complex is rarely used as an active emitting layer because of self-quenching. The Ir complex is optimally doped in an active small molecule host material such that triplets of the host molecule are

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harvested and self-quenching is avoided. Doped electro-phosphorescent devices using Ir complexes have yielded nearly 100% internal efficiency.[9] Nearly 16% external efficiency has been reported in white light emitting devices using doped electro-phosphorescent material.[10]

The emission colour of an Ir Complex is tuneable in different ways like changing C^N ligand structure in a homoleptic complex and by changing ancillary ligand in a hetroleptic complex.[11–14] A number of studies have revealed a wealth of information on the photophysical, electrochemical, and electroluminescence properties of a large number of Ir complexes, apart from valuable information on synthetic routes and theoretical studies on these molecules.[15–17] Among the many cyclometalating ligands, it is shown that Ir complex of 1-phenyl isoquinoline (piq) has superior performance in electroluminescence. For example, PL quantum yield of Ir(piq)$_3$ was 0.32 in toluene[18] and in OLEDs using Ir(piq)$_3$ as dopant, EL brightness of 11,000 cd/m^2 has been reported.[19] The power efficiency and EQE are of 8.0 lm/W and 10.3% at a brightness of 100 cd/m^2 have been reported.[20] Similarly, good performance was observed in heteroleptic complex of Ir(piq)$_2$X.[21]

Another way of tuning emission colour of an Ir complex is by introducing electron donating and withdrawing group in the cyclometalating ligand.[22] A few derivatives of piq have been synthesized and PL and EL properties studied. In this work, we report the synthesis of five heteroleptic Ir complexes. The photophysical and electrochemical properties of these complexes are compared with Ir(piq)$_2$(acac). Electroluminescence of one Ir complex**(2)** is also reported.

2. Experimental

2.1 *Materials and measurements*

All the solvents, Na_2CO_3 and K_2CO_3 were obtained from SD Fine Chemicals (India). $IrCl_3$, 1-chloroisoqinoline, acetylacetone and 2-ethoxyethanol were purchased from Sigma-Aldrich and were used as received. F_4TCNQ, BCP, CBP, TPD, $Pd(PPh_3)_4$ and aryl boronic acids were purchased from Sigma-Aldrich. Reactions that require anhydrous conditions were carried out under an inert atmosphere of nitrogen. The progress of the reaction was monitored using Silica Gel TLC plates by UV detection (254 and 365 nm). Silica gel (100–200 mesh) was used for column chromatography. Melting points (uncorrected) were measured using a capillary melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded using Bruker spectrometer with working frequency 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. For ^{1}H NMR and ^{13}C NMR, the chemical shifts were referenced to CH_2Cl_2 or $CHCl_3$ present as an impurity in the deuterated solvent. Mass spectra were measured using a Thermo Finnigan LCQ Deca Electrospray quadrupole ion trap mass spectrometer (Thermo Electron Co., Hemel Hempstead, Herts, UK) or on MALDI-TOF (Micromass Tof Spec 2E). Photoluminescence was measured using SPEX Fluorolog 1681. Cyclic voltammetry was done using CH Instruments 600C.

2.2 *Synthesis*

2.2a *General method for the synthesis of ligands*: Compounds **6–10** (see Figure 1 for the synthetic scheme and structures of molecules **1–10**) were synthesized by the Suzuki-Miyaura coupling.[23,24] In a screw cap reaction vial charged with 1-chloroisoquinoline (1.0 mmol), aryl boronic acid (1.2 mmol), K_2CO_3 (5.0 mmol) and $Pd(PPh_3)_4$ (0.05 mmol), 1,2-dimethoxyethane (DME) (3.0 mL) and water (3.0 mL) were added and the reaction mixture was refluxed under nitrogen atmosphere for 20 h. On completion of the reaction, water was added and the organic phase was separated. The aqueous layer was washed thrice with ethyl acetate. All the organic layers were combined and washed with water, brine and dried over anhydrous sodium sulphate. The crude product was purified by column chromatography using hexanes and ethyl acetate as eluent. Pure compounds **6–10** were obtained as solid in 73–92% yield.

2.2.1a **6**: Yield: 0.19 g (92%); M.p.: 95°C.^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.54 (m, 4H), 7.69 (m, 4H), 7.89 (d, 1H, $J = 8$ Hz), 8.11 (d, 1H, $J = 8.5$ Hz), 8.61 (d, 1H, $J = 5.5$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 119.81, 120.00, 126.7, 126.88, 127.12, 127.52, 127.64, 128.32, 128.54, 129.79, 129.99, 136.84, 142.13, 142.28. ES-MS (m/z) for $C_{15}H_{11}N$ Calcd. 205.26; Obsd. 206.22 $(M+1)^+$.

2.2.1b **7**: Yield: 0.19 g (79%); M.p.: 80°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.0 (m, 2H), 7.57 (m, 2H), 7.71 (m, 2H), 7.78 (m,1H), 7.9 (d, 1H, $J = 8.5$ Hz), 8.63 (d, 1H, $J = 5.5$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 103.96, 104.17, 104.38, 111.66, 111.83, 120.8, 126.93, 126.98, 127.52, 130.29, 132.79, 132.82, 132.86, 142.32, 142.35. ES-MS (m/z) for $C_{15}H_9F_2N$ Calcd. 241.24; Obsd. 242.26 $(M+1)^+$.

2.2.1c **8**: Yield: 0.20 g (73%); M.p.: 120°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.57 (t, 1H, $J = 7.0$ Hz), 7.71 (m, 2H), 7.82 (m, 4H), 7.92 (d, 1H, $J = 8.0$ Hz), 8.02 (d, 1H, $J = 8.5$ Hz), 8.63 (d, 1H, $J = 5.0$ Hz).^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 28.81, 120.56, 125.31, 125.34, 126.53, 126.91, 127.18, 127.59, 130.25, 130.28, 136.84, 142.24, 142.28, 143.09, 159.13. ES-MS (m/z) for $C_{16}H_{10}F_3N$ Calcd. 273.26; Obsd. 274.27 $(M+1)^+$.

2.2.1d **9**: Yield: 0.22 g (83%); M.p.: 101°C. ^{1}H NMR (500 MHz, $CDCl_2$) δ ppm 3.04 (s, 6H), 6.87 (d, 2H, $J = 8.5$ Hz), 7.52 (m, 1H), 7.56 (d, 1H, $J = 6.0$ Hz), 7.65–7.67 (m, 3H), 7.85 (d, 1H, $J = 8.0$ Hz), 8.25 (d, 1H, $J = 8.0$ Hz), 8.6 (d, 1H, $J = 6.0$ Hz).^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 40.19, 111.67, 115.03, 115.88, 118.76, 126.60, 126.77, 126.84, 127.23, 127.69, 127.76, 129.69, 131.06, 137.01, 142.07, 150.82, 160.70. MALDI-TOF (m/z) for $C_{17}H_{16}$N2 Calcd. 248.33; Obsd. 248.43 (M^+).

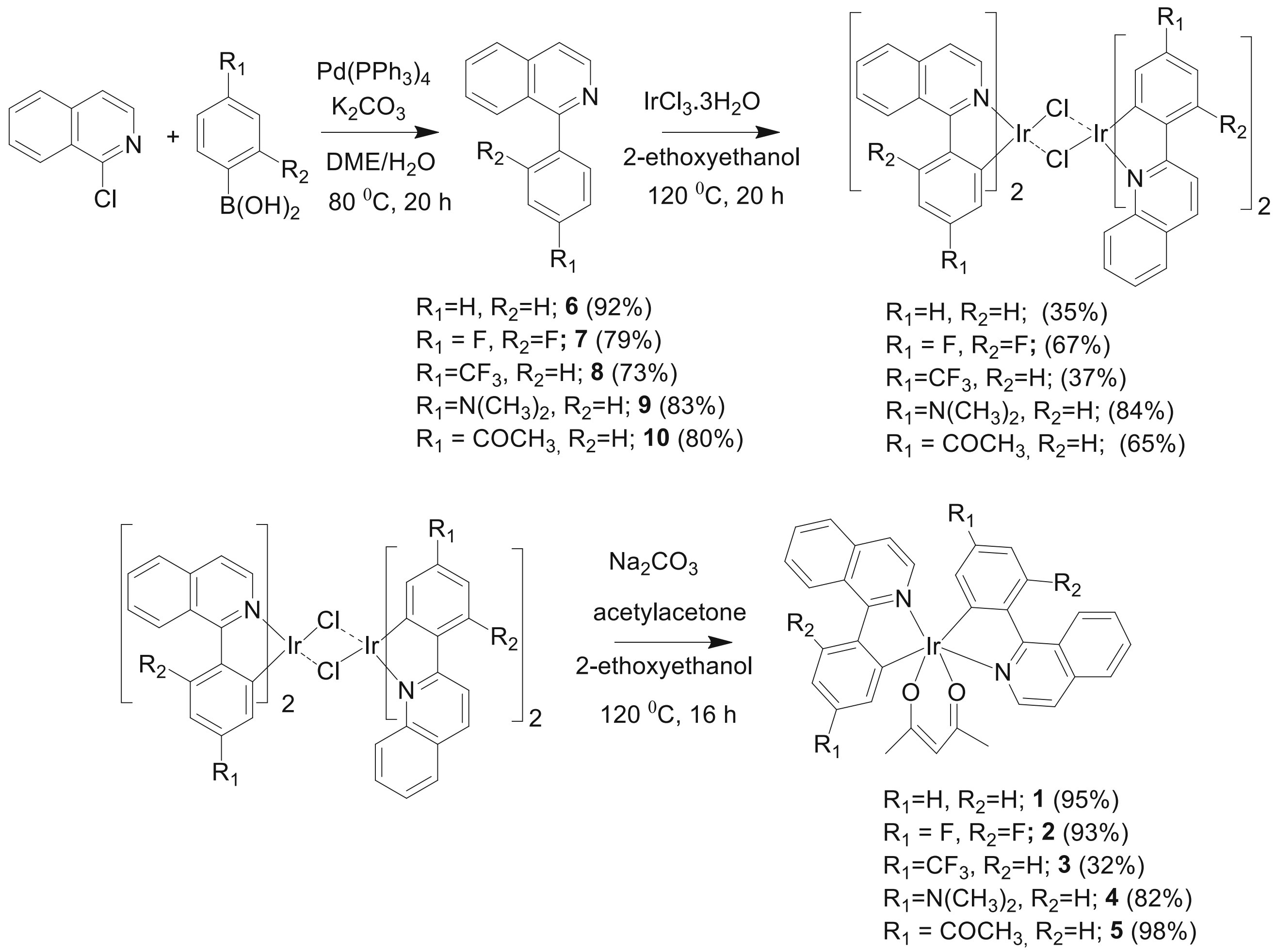

Figure 1. Synthetic route to prepare the Ir(III) complexes, **1**–**5**.

2.2.1e **10**: Yield: 0.20 g (80%); M.p.: 100°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.70 (s, 3H, CH_3), 7.56 (t, 1H, $J = 8.0$ Hz), 7.7 (m, 2H), 7.82 (d, 2H, $J = 8.0$ Hz), 7.91 (d, 1H, $J = 8.5$ Hz), 8.04 (d, 1H, $J = 8.5$ Hz), 8.13 (d, 2H, $J = 8.5$ Hz), 8.63 (d, 1H, $J = 5.5$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 26.76, 107.5, 120.46, 120.51, 126.95, 127.12, 127.51, 128.32, 128.38, 130.19, 136.83, 136.93, 142.23, 142.29, 144.14, 159.42, 197.97. ES-MS (m/z) for $C_{17}H_{13}NO$ Calcd. 248.30; Obsd. 248.26 (M^+).

2.2b *General method for the synthesis of Ir(III) heteroleptic complexes*: One of the ligands (**6**–**10**) (2.0 mmol), $IrCl_3$ (1.0 mmol) were dissolved in 2-ethoxyethanol (2.0 mL) and water (1.0 mL). The reaction mixture was refluxed at 120°C for 16 h. The solvent was evaporated under reduced pressure, and the solid residue was washed three times with methanol. The solid product (μ-chloro bridged dimer) was dried in vacuum. The μ-chloro dimer (1.0 mmol), acetylacetone (2.2 mmol), Na_2CO_3 (10.0 mmol) and 2-ethoxyethanol (3.0 mL) were mixed and refluxed for 16 h at 120°C. The solvent was evaporated under vacuum and the resulted solid residue was washed three times with methanol to afford pure **1**–**5** as coloured solid in 32–98% yields.

2.2.2a Characterization data for **1**: Yield: 0.33 g (95%).^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.25 (s, 6H, CH_3), 5.20 (s, 1H, CH), 6.38 (d, 2H, $J = 7.0$ Hz), 6.65 (t, 2H, $J = 7.5$ Hz), 6.89 (t, 2H, $J = 7.0$ Hz), 7.47 (d, 2H, $J = 6.5$ Hz), 7.71 (m, 4H), 7.94 (m, 2H), 8.20 (d, 2H, $J = 8.0$ Hz), 8.45 (d, 2H, $J = 6.5$ Hz), 8.98 (m, 2H). MALDI-TOF (m/z) for $C_{35}H_{27}N_2O_2Ir$ Calcd. 699.83; Obsd. 699.94 (M^+), 601.10 (M^+-acac).

2.2.2b Characterization data for **2**: Yield: 0.36 g (93%).^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.76 (s, 6H, CH_3), 5.22 (s, 1H, CH), 5.73 (d, 2H, $J = 8.5$ Hz), 6.41 (t, 2H, $J = 10.0$ Hz), 7.59 (d, 2H, $J = 6.5$ Hz), 7.66 (t, 2H, $J = 7.5$ Hz), 7.74 (t, 2H, $J = 8.0$ Hz), 7.91 (d, 2H, $J = 8.0$ Hz), 8.32 (d, 2H, $J = 6.0$ Hz), 8.41 (m, 2H). MALDI-TOF (m/z) for $C_{35}H_{23}N_2O_2F_4Ir$ Calcd. 771.79; Obsd. 772.30 (M^+), 673.34 (M^+-acac).

2.2.2c Characterization data for **3**: Yield: 0.13 g (32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.8 (s, 6H), 6.57 (s, 2H), 7.21 (d, 2H, $J = 8.5$ Hz), 7.69 (d, 2H, $J = 6.5$ Hz), 7.84 (m, 4H), 8.1 (m, 2H), 8.37 (d, 2H, $J = 8.5$ Hz), 8.48 (d, 2H, $J = 6.5$ Hz), 8.99 (m, 2H). MALDI-TOF (m/z) for $C_{37}H_{25}N_2O_2$ F_6Ir Calcd. 835.83; Obsd.836. 19 (M^+), 737.30 (M^+-acac).

2.2.2d Characterization data for **4**: Yield: 0.32 g (82%). ^{1}H NMR (500 MHz, $CDCl_3$ δ ppm 1.58 (s, 6H), 1.84 (s, 6H), 2.60 (s, 6H), 5.55 (s, 1H), 6.36–6.37 (m, 2H), 7.35 (m, 2H), 7.67 (m, 4H), 7.90 (d, 2H, J = 7.5 Hz), 8.04 (m, 4H), 8.36 (d, 2H, J = 6.0 Hz), 8.87 (d, 2H, J = 8.5 Hz). MALDI-TOF (m/z) for $C_{39}H_{37}N_4O_2Ir$ Calcd. 785.97; Obsd.785.40 (M^+), 686.62 (M^+-acac).

2.2.2e Characterization data for **5**: Yield: 0.40 g (98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.78 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 5.25 (s, 1H, CH), 6.86 (s, 2H), 7.47 (m, 2H), 7.62 (d, 2H, J = 6.0 Hz), 7.77 (m, 4H), 7.99 (m, 2H), 8.26 (d, 2H, J = 8.5 Hz), 8.52 (d, 2H, J = 6.0 Hz), 8.96 (m, 2H). MALDI-TOF (m/z) for $C_{39}H_{31}N_2O_4Ir$ Calcd. 783.90; Obsd. 783.76 (M^{n+}), 684.84 (M^+-acac).

2.3 *OLED fabrication and device measurements*

Multilayer structure OLED devices, namely, ITO/F_4TCNQ/TPD/CBP +Ir Complex/BCP/LiF/Al, were fabricated on pre-patterned, pre-cleaned ITO-coated glass substrates. The substrate was patterned using standard lithography and then cleaned by mechanical scrubbing with detergent, followed by ultrasonic cleaning in hot water. It was then blow dried using dry N_2 gas and was finally UV exposed for 10 min. Organic layers were deposited one after another by thermal evaporation of organic materials kept in separate quartz crucibles in a high vacuum ($\sim 10^{-6}$ torr) chamber. The doped layer of CBP with Ir complex (5% wt/wt) was deposited by simultaneously evaporating the CBP and Ir complex from their respective boats. The deposition rates were controlled with two independent quartz crystals near the respective sources and one near the substrate to monitor the film thickness. LiF and Al layers were deposited without breaking the vacuum. The thermal evaporation system was fitted with five evaporation sources. In one experiment, five different layers can be evaporated without breaking the vacuum. A thick layer of LiF (100 nm) was deposited on top of Al cathode as capping layer. After fabrication, the devices were transferred to another vacuum apparatus fitted with probes for measurements, which resulted in a brief exposure of the device to air. The current (I), voltage (V) and EL (L) characteristics of the OLEDs were measured in vacuum using a Keithley 617 programmable electrometer. EL intensity (cd/m^2) measurement was done using a large area calibrated silicon photodiode and fixed geometry of device and detector. EL spectra were measured using a monochromator and Photomultiplier Tube (S-20 response) operated at 720 V.

3. Results and Discussion

3.1 *Synthesis*

Iridium complexes **1–5** were synthesized as shown in Figure 1. The ligands **6–10** were synthesized by the Suzuki-Miyaura coupling.[23,24] 1-Chloroisoquinoline (1.0 mmol), aryl boronic acid (1.2 mmol), K_2CO_3 (5.0 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) were refluxed in DME/water under nitrogen atmosphere for 20 h. On completion of the reaction, the crude product was purified by column chromatography to get pure compounds **6–10** as solid in 73–92% yield. To synthesize the Iridium complexes, one of the ligands **6–10** and $IrCl_3$ (2:1 molar ratio) were refluxed in 2-ethoxyethanol (2.0 mL) and water (1.0 mL) mixture for 16 h.[19] On evaporation of the solvents and washing the solid residue with methanol, μ-chloro bridged dimer was obtained as solid. The μ-chloro dimer (1.0 mmol), acetylacetone (2.2 mmol), Na_2CO_3 were refluxed in 2-ethoxyethanol for 16 h. The solvent was evaporated under vacuum and the resulted solid residue was washed three times with methanol to afford pure **1–5** as coloured solid in 32–98% yields. The obtained solids were characterized by NMR, mass methods.

3.2 *Absorption and emission studies*

Absorption spectra of **1**–**5** in dichloromethane are shown in Figure 2. The emission spectra of **1**–**5** excited at the absorption peak are shown in Figure 3. The excitation

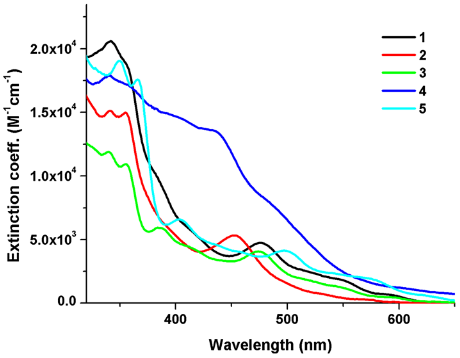

Figure 2. Absorption spectra of **1**–**5** reco rded in dichloromethane.

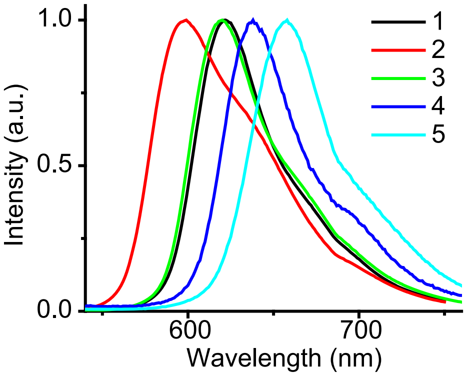

Figure 3. Peak normalized emission spec tra of Ir(III) complexes **1–5** in toluene.

spectra (not shown) were similar to the absorption spectra. The optical spectra of Ir complexes have been studied experimentally and theoretically.[11–16] The absorption spectra in the UV-Visible region consist singlet and triplet transitions of the type $\pi - \pi*$ and MLCT. The normally forbidden triplet transition is strongly allowed to such an extent that the extinction coefficients of $^3\pi - \pi*$ and ^{3}MLCT are comparable to the corresponding singlet transitions in some complexes.[15] The absorption spectra are thus broad and multiple peaks are commonly observed. Spectra of $\pi - \pi*$ transitions may have vibrational structures characteristic of the ligand whereas these are absent in MLCT transitions. The absorption spectra of **1–5** have the above common features. The spectral peaks were identified from the derivative spectra and the peak wavelengths and extinction coefficients are summarized in Table 1. The absorption spectrum of **4** (N,N-dimethyl derivative) is almost featureless and different from others whereas its emission spectrum was similar to that of others. The excitation spectrum was also similarly featureless indicating that the unusual absorption spectrum of **4** is not due to aggregates or impurities.

Ir complexes are weakly luminescent in aerated solution because of oxygen quenching of the long-lived (microseconds) triplet emitting state. Therefore, N_2 saturated dilute solutions of **1–5** in toluene were used to record the emission spectra (Figure 3). Phosphorescence spectra originating from ^{3}MLCT are generally broad and featureless in comparison to emission from $^{3\pi} - \pi*$ state.[11,15] Emission spectra of **1**–**5** were broad and featureless which indicate the ^{3}MLCT as the lowest excited state in these complexes. Though absorption and excitation spectra of **4** are different from those of other molecules, the emission spectra of all the molecules were similar except for the shift in the luminescence maxima. The parent molecule **1** has an emission peak at 622 nm, in **2** and **3** they are blue shifted by 24 and 3 nm, respectively, and in **4** and **5** they are red shifted by 18 and 36 nm, respectively.

The Ir(III) complexes are almost non-luminescent as solid thin films due to self-quenching. However, they are highly luminescent when doped lightly in 4,4-N,N'-dicarbazole-biphenyl (CBP) as the host material. Thin films of **1–5** were prepared on quartz plate using 5% (w/w) Ir(III) complexes in CBP by spin coating method. Figure 4 shows the emission spectra recorded by exciting CBP at 295 nm. The emission spectra of the thin films were identical to the spectra obtained during direct excitation of Ir complexes at their corresponding absorption peaks (see Figure 3) which indicate that efficient energy transfer occurs from the excited state of host CBP to the dopant Ir complex.

Table 1. Photophysical and electrochemical data of Ir complexes **1–5**

	λ_{abs} /nm^a log (ε/ M^{-1}cm^{-1})	λ_{em} /nm^b	λ_{em} / nm^c	$^d\phi_{Phos}$	$^b\tau/\mu s$	$k_r/10^6 s^{-1}$	$k_{nr}/10^6 s^{-1}$	$S_0 - T_1$/eV	$^eE_{HOMO}$ /eV
1	341 (4.3), 475 (3.7), 585 (2.9)	622	620	0.32	1.03	0.31	0.66	2.04	−5.48
2	341 (4.2), 355 (4.2), 453 (3.7)	598	595	0.29	1.9	0.15	0.37	2.13	−5.80
3	340 (4.1), 356 (4.03), 386 (3.8), 474 (3.6), 590 (2.7)	619	614	0.22	0.84	0.26	0.92	2.05	−5.75
4	340 (4.2), 435 (4.1)	640	633	0.20	0.60	0.33	1.33	2.04	−5.54
5	350 (4.3), 366 (4.2), 403 (3.8), 500 (3.6), 572 (3.3)	658	651	0.10	0.43	0.23	2.09	1.94	−5.65

^{a}In dichloromethane; ^{b}In toluene; ^{c} in thin films; ^{d}quantum yield in toluene; and $^eE_{HOMO} = -$ (oxidation potential with respect to Fc/Fc$^+$ at + 5.13 eV)

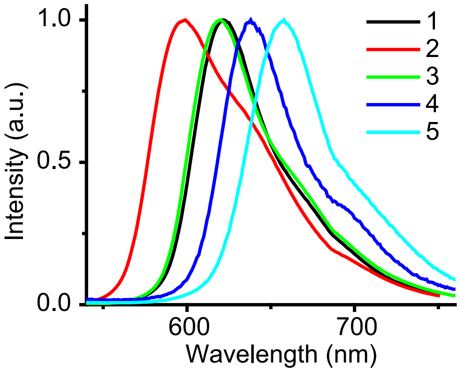

Figure 4. Peak normalized emission spec tra of Ir(III) complexes **1–5** in thin films.

The phosphorescence quantum yields (ϕ_{Phos}) of the Ir(III) complexes in toluene were obtained using rhodamine 6G as a standard.[27] The quantum yields varied from 0.1 to 0.32 for **1** to **5**. ϕ_{Phos} of **2** and **3** were higher as compared to **4** and **5**.

The Ir(III) complexes **1–5** showed single exponential photoluminescence decay in dry toluene with lifetime varying from 0.43 to 1.9 µs. These values are comparable to other heteroleptic Ir complexes.[18]

The radiative and non-radiative rate constants were calculated by using the following equations, assuming intersystem crossing yield, $\phi_{isc} = 1$. The value of ϕ_{Phos}, k_r, k_{nr} listed in Table 1 are comparable to the values reported for other Ir complexes.[18]

$$k_r = \phi_{Phos}/(\phi_{isc}\tau) \tag{1}$$

$$k_{nr} = (1/\tau) - k_r \tag{2}$$

3.3 *Electrochemical properties*

Cyclic voltammetric redox potentials provide insight into the HOMO and LUMO levels and stability of the radical anion/cation. Cyclic voltammetry of the molecules (~1 mM) were done in CH_2Cl_2 using tetrabutyl ammoniumhexafluorophosphate (0.1 M) as supporting electrolyte using $Ag/AgNO_3$ as a reference electrode and ferrocene as an internal reference molecule. Ir(III) complexes **1–5** showed characteristics of reversible oxidation process in cyclic voltammetry (Figure 5 and Figure S11 in Supplementary Information). The peak potentials were determined with respect to ferrocene as an internal standard. The HOMO levels of **1–5** were determined from the corresponding oxidation peak potentials using the reported equations[28–30] and the values are summarized in Table 1. The HOMO levels of these Ir(III) complexes lie in the range of -5.48 to -5.80 eV.

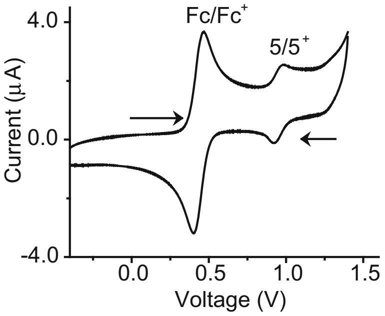

Figure 5. Cyclic voltammogram of **5** recorded in dichloromethane at a scan rate of 100 mV/s using tetrabutylammoniumhexafluorophosphate (TBAHFP) as supporting electrolyte; Ferrocene (Fc) is used as internal reference molecule; arrows show the sweep directions.

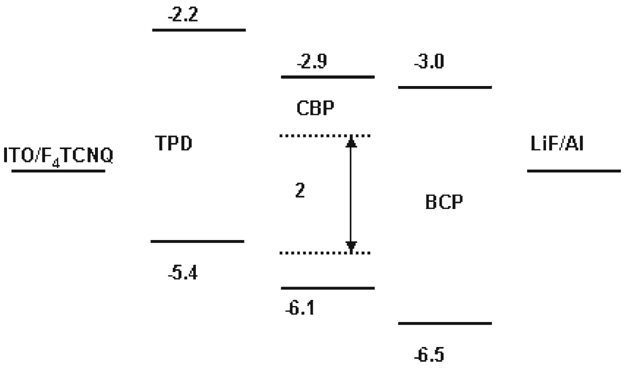

Figure 6. Energy level diagram of molecules used in multilayer OLED, ITO/F_4TCNQ/TPD/CBP+**2**/BCP/LIF/Al.

3.4 *Electroluminescence properties using Ir(III) complex as dopant molecules*

The electroluminescent properties and performance of **2** were studied in a multilayer OLED structure, ITO/F_4TCNQ(20Å)/TPD(500Å)/CBP+**2**(400Å)/BCP (60Å)/LiF(15Å)/Al. F_4TCNQ, TPD, BCP, LiF and Al were successively deposited onto the patterned ITO. The device area was 2 mm^2. The HOMO-LUMO energy levels of all the materials used in the device are shown in Figure 6 in the same order as arranged in the device. The dashed line shows the energy levels of the Ir complex **2**, which is the dopant in CBP. The functions of the various layers are as follows. F_4TCNQ facilitates hole injection from ITO into TPD. BCP and LiF facilitate electron injection and electron transport to the active layer of CBP doped with **2**. In addition, BCP serves as a hole blocking layer and TPD as an electron blocking layer. Thus, electron-hole recombination is expected to occur in the CBP.

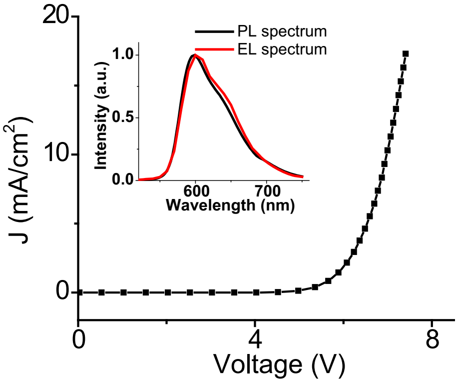

Figure 7. Current-Voltage characteristics of the device ITO/F_4TCNQ/TPD/CBP+**2**/BCP/LIF/Al. The inset shows the electroluminescence spectrum of the device and photoluminescence spectrum of Ir complex **2**.

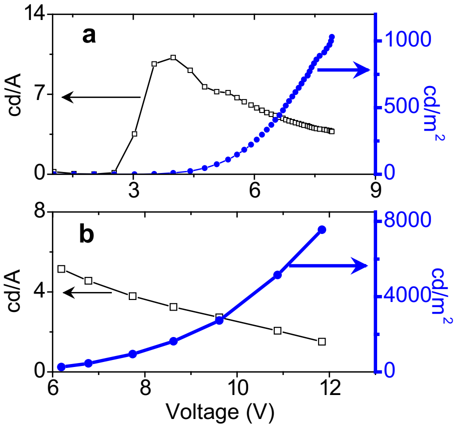

Figure 8. Light intensity (cd/m^2) and current efficiency (cd/A) behaviour of OLED device, ITO/F_4TCNQ/TPD/CBP+**2**/BCP/LIF/Al. (a) at low applied voltage; (b) at high applied voltage.

The I-V and electroluminescence characteristics of the phosphorescent OLED are shown in Figure 7. The inset shows the electroluminescence spectrum of the device and photoluminescence of **2** when doped in CBP as host. The electroluminescence spectrum overlaps onto the photoluminescence spectrum which suggests that all the emission is coming from the Iridium complex **2**. The turn-on voltage of the device was at 4.5 V. Figure 8 shows that the light intensity continuously increased with applied voltage whereas the current efficiency is ∼7.0 cd/A at a brightness of ∼100 cd/m^2. The highest brightness was measured to be 7600 cd/m^2.

It is worth mentioning that the performance of the device using **2** was not optimized for different doping ratios. This and the measurements of electroluminescence characteristics of other Ir complexes are in progress.

4. Conclusions

A series of new Ir(III) complexes of 1-phenylisoquinoline derivatives were synthesized and characterized. Photophysical studies of these complexes indicated emission in the orange to the deep red region. Electrochemical properties were used to determine the HOMO levels. The energy levels and emission quantum yields of these Ir complexes suggest that these molecules can serve as red emitting dopants in OLEDs. The OLED prepared using one of the molecules showed high brightness and current efficiency.

Supplementary information (SI)

^{1}H-NMR and ^{13}C-NMR spectra (Figures S1-S7), MALDI mass spectra (Figures S9 and S10), PL decays (Figure S8), and cyclic voltammograms of the Ir complexes (Figure S11) are available at www.ias.ac.in/chemsci.

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