Synthesis and Electrophosphorescent Properties of a Novel Iridium Complex with Arylamine Unit in the Polymer Light-emitting Devices

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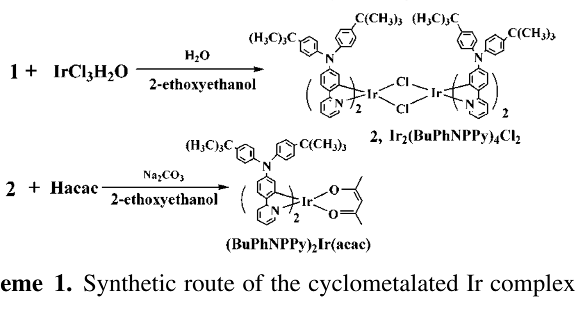
A novel Ir complex, $(BuPhNPPy)_2Ir(acac)$ with arylamine unit, was synthesized. A peak external quantum efficiency of 10.4% photons per electron at current density of 32 mA/cm^2 and a maximum luminance of 14610 cd/m^2 at drive voltage of 24 V were achieved in a single-layered polymer light-emitting device using this Ir complex as dopant with 4% dopant concentration and a blend of poly(vinylcarbazole) as host matrix. The highly efficient electrophosphorescence of the Ir complex was exhibited with green emission at 533 nm.

Cyclometalated iridium (Ir) complexes have been of considerable interest in electrophosphorescence (EPH) because they have strong spin–orbit coupling of the 5d orbit resulting in efficient intersystem crossing from the singlet excited state to the triplet excited state.[1–9] Most of these emissive cyclometalated Ir complexes with imine ligand were homoleptic complexes[1–4] and heteroleptic complexes[5–9] in the early studies. The strong ligand field of the imine ligand, along with the added stabilization of π donation from iridium into the aromatic ligand, helps to make these types of complexes very stable and exhibit significant optoelectronics properties in the phosphorescent polymeric and organic light-emitting devices (PLEDs and OLEDs).[10] Highly efficient phosphorescent OLEDs and PLEDs with Ir complexes as dopants and organic small molecules or polymers as hosts matrix were recently achieved. An external quantum efficiency (EQE) of 19% photons per electron (ph/el) in OLEDs and 10% ph/el in PLEDs using Ir complexes as green phosphorescent emitters were achieved by Ikai[11] and Gong,[12] respectively. Despite these developments, attempts to further expand the potential of Ir complexes for practical application in OLEDs and PLEDs have encountered some obstacles. For example, the high efficiency of the devices was obtained at low current density. EQE decreases with increased current density (J) in the devices after J passed a critical level. In addition, the molecular aggregation tendency of Ir complexes was enhanced in the higher J, which leads poor device efficiency. To realize the practical applicaton of Ir complexes in highly efficient PLEDs, it is critical to design the rational molecular structure of Ir complexes to effectively suppress the molecular aggregation effect.

In this paper, *N*,*N*-di(4-*tert*-butylphenyl)-4-(2-pyridyl)benzenamine (BuPhNPPy) is designed and chosen as the cyclometalating ligand with arylamine unit to prepare a novel bicyclometalated Ir complex. As a arylamine unit with bulky butyl group was incorporated into the Ir complex, the reduction of aggregating and self-quenching tendency of Ir complex should drastically occur, which results in highly luminous efficiency and the improved optoelectronic properties for Ir complex. Using this Ir complex as dopant with 4% weight concentration and a blend of poly(vinylcarbazole) (PVK) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) as host matrix, a single-layered PLED exhibits a high EQE of 10.4% and bright green emission at 533 nm. To the best of our knowledge, $(BuPhNPPy)_2Ir(acac)$ is the first example of triarylamine-containing Ir complex with highly luminous efficiency.

The synthetic route of this $(BuPhNPPy)_2Ir(acac)$ is shown in Scheme 1. BuPhNPPy ligand was prepared by the modified Ullmann reaction between 4-(2-pyridyl)phenylamine and 4-*tert*-butyliodobenzene in refluxing *o*-dichlorobenzene.[13] The chlorobridged dimer and the bicyclometalated $(BuPhNPPy)_2Ir$-(acac) complex were synthesized according to a improved method.[5] The typical synthetic experiment of this Ir complex was completed below.

Iridium trichloride hydrate (0.179 g, 0.0508 mmol) and BuPhNPPy (0.881 g, 2.03 mmol) in a mixture of 2-ethoxyethanol (15 mL) and water (5 mL) were refluxed for 25 h under nitrogen atmosphere. The yellow solid was isolated by filteration and washed with 10 mL of ethanol and 5 mL of acetone, respectively, to give chlorobridged dimer of $Ir_2(BuPhNPPy)_4Cl_2$ (**2**) after a majority of 2-ethoxyethanol was removed out under vacuum. Dimer **2** was crystallized from the mixed solvent of dichloromethane, toluene and hexane (1:1:1) to give 180 mg of yellow crystal of dimer **2**. Whereafter, dimer **2** (150 mg, 0.0685 mmol), acetyl acetone (180 mg, 0.018 mmol) and sodium carbonate (79 mg) in 2-ethoxyethanol (15 mL) were refluxed for 15 h under nitrogen atmospheres. Excess water was added in the residue after a majority of 2-ethoxyethanol was evaporated out under vacuum, and resulting residue was cooled to room temperature. The yielding yellow precipitate was filtered, dried, and chromatographed using aluminum oxide/dichloromethane column to give 100 mg of $(BuPhNPPy)_2Ir(acac)$ powder with a yield of 60.0%.



Scheme 1. Synthetic route of the cyclometalated Ir complex.

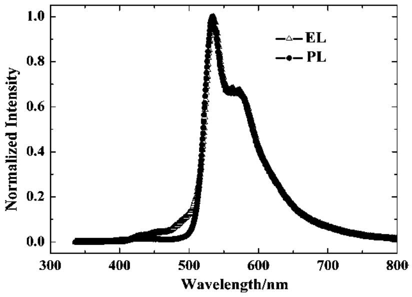


Figure 1. PL and EL spectra for 4% Ir complex-doped PLEDs.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ [ppm]: 8.25 (d, $J = 5.6$ Hz, 2H), 7.30 (t, $J = 8.4$ Hz, 4H), 7.12 (d, $J = 8.4$ Hz, 8H), 7.24 (m, 2H), 6.83 (d, $J = 8.4$ Hz, 8H), 6.45 (dd, $J = 2$ Hz, 2.4 Hz, 2H), 6.16 (t, $J = 8.4$ Hz, 2H), 5.85 (d, $J = 1.2$ Hz, 2H), 5.23 (s, 1H), 1.81 (s, 6H), 1.31 (s, 36H).

An initial study of photoluminescence (PL) and EPH properties of a single-layered $(BuPhNPPy)_2Ir(acac)$-doped PLEDs was carried out using a blend of PVK and PBD as host matrix. The configuration of this doped PLEDs is ITO/PEDOT, 70 nm/ $(BuPhNPPy)_2Ir(acac)$ (4.0 wt %) + PVK:PBD (40.0 wt %), 70 nm/Ba, 5 nm/Al, 200 nm. The weight concentrations of $(BuPhNPPy)_2Ir(acac)$ and PBD are 4 and 40 wt %, respectively. The intense green PL and electroluminescence (EL) was observed for the $(BuPhNPPy)_2Ir(acac)$-doped PLEDs. The EL spectrum is identical to the PL spectrum with a dominant peak at 533 nm and a shoulder peak of 560 nm, shown in the Figure 1. The Commission Internationale de I'Eclairage (CIE) coordinates is $X = 0.38$ and $Y = 0.53$.

No emission at 416 and 393 nm is observed under optoexcitation and electroexcitation for the device. The results indicate that the PL and EL of the device originate from the Ir complex rather than PVK or PBD, and PVK:PBD-based emission is annihilated. The fact that the peak PL quantum yield for the neat $(BuPhNPPy)_2Ir(acac)$ thin film and the thin film of 4.0 wt % $(BuPhNPPy)_2Ir(acac)$-doped with a blend of PVK and PBD (40.0 wt %) were found to be 1.4 and 42.0%, respectively, provides further a evidence of the efficient energy transfer from PVK:PBD to $(BuPhNPPy)_2Ir(acac)$.

The EPH data for the $(BuPhNPPy)_2Ir(acac)$-doped PLEDs are shown in Table 1. The current density–voltage–luminance feature of the device is recorded in Figure 2.

The doped device exhibits a light turn-on voltage of 9.6 V, a maximum luminance (L) of 14610 cd/m^2. A peak EQE = 10.4% and luminous efficiency (LE) of 17.1 cd/A were also achieved for the device at $J = 32$ mA/cm^2. The EQE first increased and then decreased with increasing J. This phenomena is similar to that for $Ir(DPF)_3$-doped PLEDs[12] and $Ir(BuPPy)_3$-doped PLEDs.[4]

However, EQE decreased sharply at a high J for the reported phosphorescent devices. For $Ir(DPF)_3$-doped PLEDs, a peak EQE was 10% at $J = 4$ mA/cm^2 and decayed sharply to approximately 6% at $J = 80$ mA/cm^2. For $(BuPhNPPy)_2Ir(acac)$-doped PLEDs, EQE still retained 9.1% when the $J = 80$ mA/cm^2. The reduced rate of EQE was efficiently restrained for the device under high J. This indicates that the EPH performance of Ir complex is improved by incorporating a arylamine into Ir complex. The bulky nonplannar *tert*-butyl and arylamine in Ir complex play an important role in improving miscibility and inhibiting aggregation of Ir complex. The related investigation is in progress to further identify the fact.

Table 1. The EPH data for $(BuPhNPPy)_2Ir(acac)$-doped PLEDs

J /mA·cm^{-2}	V /V	EQE /%	LE /cd·A^{-1}	L /cd·m^{-2}	CIE Corordinates
20	19.2	9.2	15.0	2910	$X = 0.38$
32	20.6	10.4	17.1	5449	$Y = 0.53$
80	23.0	9.1	14.9	11910	
100	23.7	8.2	12.3	13580	

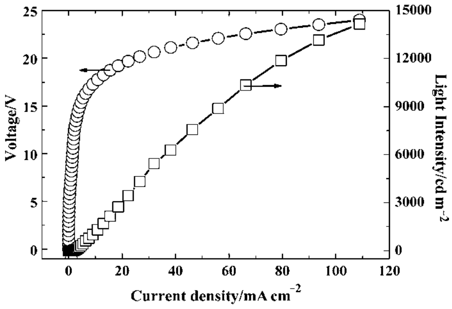


Figure 2. The current density–voltage–luminance feature of 4% $(BuPhNPPy)_2Ir(acac)$-doped PLED.

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