

Efficient and Stable Deep-Red Phosphorescent Organic Light-Emitting Diodes Based on an Iridium Complex Containing a Benzoxazole-substituted Ancillary Ligand

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In the past two decades, organic light-emitting devices (OLEDs) have drawn considerable attention as a promising technology for practical optoelectronic applications.^[1] Cyclometalated iridium(III) complexes incorporated into OLEDs are one of the most studied class of compounds.^[2] Their heavy metal core results in the mixing of singlet and triplet manifolds, which enables harvesting of both singlet and triplet excitons.^[3] Furthermore, the iridium complexes are suitable for phosphorescent OLED (PHOLED) applications due to their relatively short phosphorescence lifetimes, easily sublimable feature, and excellent color tunability.^[4] For PHOLEDs to be useful in display and lighting applications, red, green, and blue emitters with sufficient luminous efficiencies, saturated color chromaticities, and adequate lifetimes are required.^[5] The advances in green phosphors achieved in the past couple of decades is particularly impressive.^[6] While the development of red phosphors has also gone through several evolutionary steps,^[7] their performances are still considerably behind those of green phosphors. For example, reports on high-performance red PHOLEDs with a Commission internationale de l'éclairage (CIE) coordinate $x \geq 0.67$ are still rare because the efficiency and brightness of saturated-red phosphorescent OLEDs are difficult to im-

prove due to the energy gap law and the drop in luminous flux in the saturated-red region.^[7a]

Okada et al. synthesized a widely used Ir^{III}(C-N)₃ complex using 1-phenylisoquinoline as a monoanionic cyclometalating ligand, [tris(1-phenylisoquinolinato-*N,C*²)iridium(III)] (Ir(piq)₃). A PHOLED device based on this complex exhibits a peak emission at 623 nm and a maximum power efficiency of 8.0 Lm W⁻¹ (9.3 cd A⁻¹) at 100 cd m⁻².^[8] Sun et al. reported an iridium complex, Ir(piq)₂acac, with 1-phenylisoquinoline as the main ligand and acetylacetonate as ancillary ligand. The reported Ir(piq)₂acac-based device exhibits a peak emission at 624 nm and a maximum current efficiency of 7.83 cd A⁻¹.^[9] In recent work, Kwon et al. reported an iridium complex using a new main ligand (2-(3,5-dimethylphenyl)-4-methylquinoline); a device based on this complex reached a maximum power efficiency of 32 Lm W⁻¹.^[10] So far, most red iridium complexes reported were obtained by changing the main ligands, and there are few reports on the modification of the ancillary ligands.^[11]

In this study, a deep-red emitter containing a new ancillary ligand, iridium(III) bis(1-phenylisoquinolinato-*N,C*²)(2-(benzo[d]oxazol-2-yl)phenol) (Ir(piq)₂bop) has been designed and synthesized. The use of a bulky 2-(benzo[d]oxazol-2-yl)phenol ancillary ligand is expected to suppress molecular aggregation and enhance the performance by reducing self-quenching.^[10] By doping Ir(piq)₂bop into Beq₂ (Beq₂ = bis(10-hydroxybenzo[h] quinolinato)beryllium), an efficient deep-red OLED with a luminous efficiency of 9.1 Lm W⁻¹ (10.3 cd A⁻¹) can be obtained at 100 cd m⁻², along with CIE coordinates of (0.67, 0.33). Furthermore, we found that the device has an extrapolated lifetime of over 30 000 h at an initial luminance of 100 cd m⁻². Due to the high efficiency and stability of the device, even in a simple device structure, we conclude that Ir(piq)₂bop is a promising organic phosphor for practical OLED applications.

The ligand 1-phenylisoquinoline was prepared through a Suzuki coupling reaction between 1-chloroisoquinoline and phenylboronic acid. Synthesis of the final Ir complex involved two key steps: In the first step, IrCl₃ was reacted with an excess of the synthesized ligand (1-phenylisoquinoline) to produce a chloro-bridged Ir dimer. This dimer can be easily converted into the monomeric complex Ir(piq)₂bop by replacing the bridging chlorides with 2-(benzo[d]oxazol-

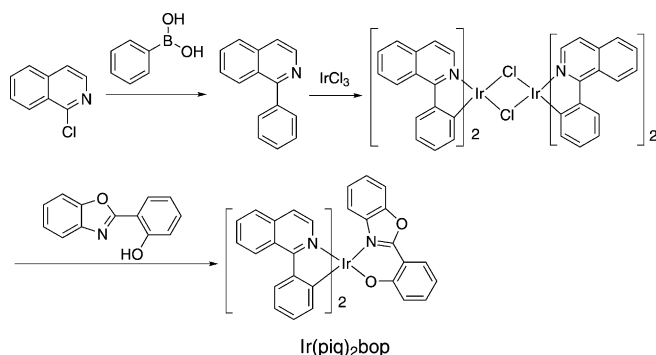
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2-yl)phenol in the presence of Na_2CO_3 . The synthetic pathway towards the preparation of $\text{Ir}(\text{piq})_2\text{bop}$ is outlined in Scheme 1. The molecular structure of $\text{Ir}(\text{piq})_2\text{bop}$ has been confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis.



Scheme 1. Synthesis of $\text{Ir}(\text{piq})_2\text{bop}$.

Figure 1 shows UV/Vis absorption and photoluminescence (PL) spectra of $\text{Ir}(\text{piq})_2\text{bop}$ in a dilute dichloromethane (CH_2Cl_2) solution at room temperature. From the absorp-

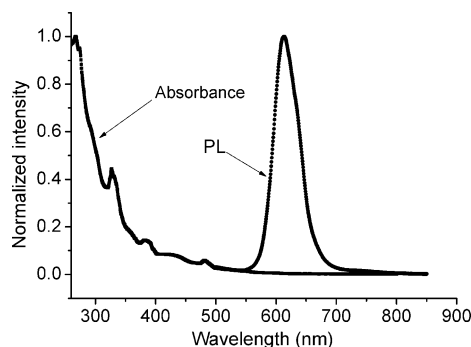


Figure 1. Absorption and photoluminescence (PL) spectra of $\text{Ir}(\text{piq})_2\text{bop}$ in dilute dichloromethane solution at room temperature. Inset: Structure of $\text{Ir}(\text{piq})_2\text{bop}$.

tion spectra, the high intensity peaks at 267 and 328 nm are attributed to the spin-allowed ligand centered $\pi-\pi^*$ transition localized on the 1-phenylisoquinoline ligand, while the weak, low-energy absorption shoulders located at 382 and 480 nm, respectively, likely originate from the $S_0 \rightarrow {}^1\text{MLCT}$ (metal-to-ligand charge transfer) and $S_0 \rightarrow {}^3\text{MLCT}$ transitions.^[12] These features are analogous to other $(\text{CN})_2\text{Ir}(\text{L})$ complexes as reported previously.^[13] Strong spin-orbital coupling was confirmed, where the oscillator strengths of singlet and triplet MLCTs are similar (i.e., less than a factor of 2 in their extinction coefficients), and thus result in strong phosphorescence.^[13c] $\text{Ir}(\text{piq})_2\text{bop}$ in a dilute CH_2Cl_2 solution exhibits a strong deep-red emission peaked at 614 nm, thus indicating that the lowest excited triplet state is dominated by the ${}^3\text{MLCT}$ excited state. The PL quantum efficiency in CH_2Cl_2 solution was determined to be 0.49, by using *fac*-

tris(2-phenylpyridine) iridium($\text{Ir}(\text{ppy})_3$, $\Phi_p=0.4$) as a standard.^[14] The HOMO level of $\text{Ir}(\text{piq})_2\text{bop}$, determined by using ultraviolet photospectroscopy (UPS), is 5.2 eV, while the LUMO level is 2.8 eV, as determined from the HOMO level and the optical absorption edge. It should be pointed out that the HOMO energy level of the iridium complex corresponds to the 5d orbital of the iridium atom with substantial mixing with the π orbitals of the 1-phenylisoquinoline ligands, while the LUMO level is determined by the π^* orbitals of the 1-phenylisoquinoline ligand and independent of the 2-(benzo[d]oxazol-2-yl)phenol ligand.^[15]

To understand the electroluminescent (EL) properties of $\text{Ir}(\text{piq})_2\text{bop}$, a red PHOLED with a configuration of ITO/NPB (40 nm)/Bebq₂:5% $\text{Ir}(\text{piq})_2\text{bop}$ (30 nm)/Bebq₂ (25 nm)/LiF (1 nm)/Al (100 nm) was fabricated, where ITO (indium tin oxide) and LiF/Al are the anode and the cathode respectively, 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl amino] biphenyl (NPB) is the hole-transporting layer (HTL), and Beq₂, which possesses LUMO and HOMO energy levels of 2.8 and 5.5 eV, respectively,^[16] was used as host material and the electron transporting layer (ETL) (Figure 2). The device shows almost unchanged EL spectra centered at 624 nm at different luminances, without any undesired emission (Figure 3), which indicates that an effective charge capture and complete energy transfer occurred between Beq₂ and $\text{Ir}(\text{piq})_2\text{bop}$. The similarity between the PL and the EL spectra suggests that the EL is indeed due to the emission from $\text{Ir}(\text{piq})_2\text{bop}$.

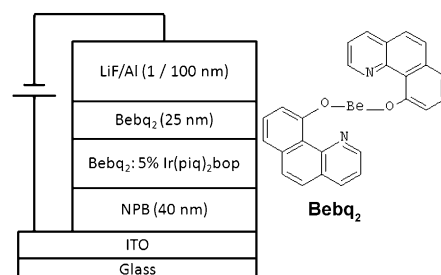


Figure 2. Schematic cross-section of the PHOLED device and molecular structure of Beq₂.

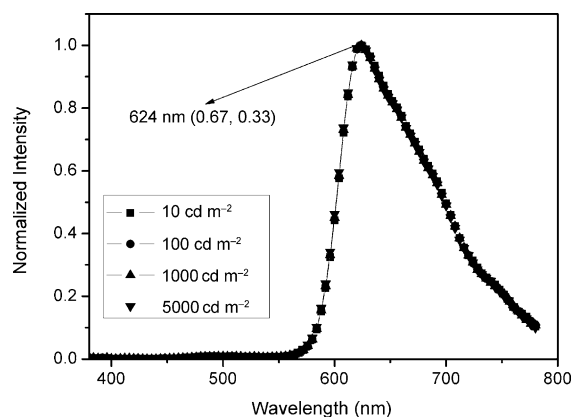


Figure 3. EL spectra of the PHOLED device at different luminances.

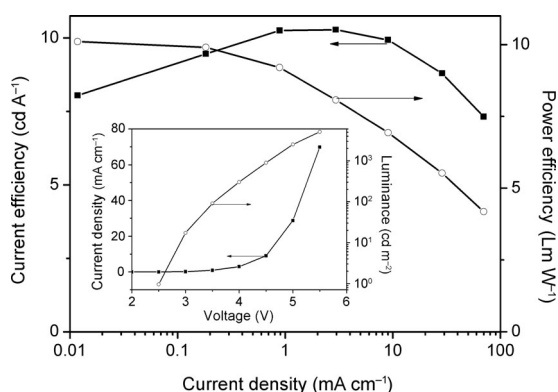


Figure 4. Current efficiency and power efficiency as a function of current density of the PHOLED with 5% Ir(piq)₂bop. The inset depicts the *J*-*V*-*L* characteristics of the device.

Figure 4 shows efficiencies and *J*-*V*-*L* (inset) characteristics of the PHOLED device with 5% Ir(piq)₂bop doped into Bebq₂. Owing to the matched energy levels, the energy barrier for hole injection from NPB to Bebq₂ is only 0.1 eV. The device exhibits low operating voltages of 2.6, 3.6, and 4.6 V to give luminance values of 1, 100, and 1000 cd m⁻², respectively. Considering that the HOMO and LUMO energy levels of Ir(piq)₂bop are embedded by those of Bebq₂, Ir(piq)₂bop can act as traps for both electrons and holes. This suggests that exciton formation on Ir(piq)₂bop can occur both through direct charge trapping and energy transfer from the host material, which may result in a high efficiency of the OLED. The device shows an efficiency of 9.1 Lm W⁻¹ (10.3 cd A⁻¹) at 100 cd m⁻². The device was then simply encapsulated by using a two-component epoxy glue and a cavity glass lid without using any desiccant. The encapsulated device shows a projected lifetime of over 30000 h and 600 h at an initial brightness of 100 cd m⁻² and 1000 cd m⁻², respectively (Figure 5.^[17]) Notably, the performance of the Ir(piq)₂bop-based device is better than that of the Ir(piq)₃-based device using a similar device structure. The efficiency of the Ir(piq)₃-based device is only 4.3 Lm W⁻¹ at 100 cd m⁻², and the efficiency roll-off is much more obvious in the Ir(piq)₃-based device. In addition, it shows a lifetime of about 150 h at 1000 cd m⁻².^[16]

In summary, a biscyclometalated deep-red phosphorescent dopant containing a new ancillary ligand, iridium(III) bis(1-

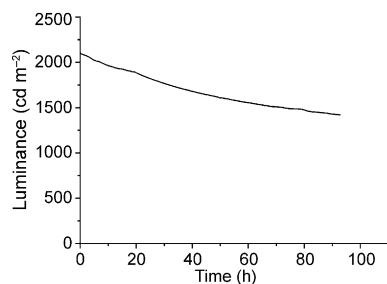


Figure 5. Reduction in luminance of the PHOLED device as a function of time.

phenylisoquinolinato-*N,C'*) (2-(benzo[*d*]oxazol-2-yl)phenol) (Ir(piq)₂bop) has been designed and synthesized. By doping the new complex into Bebq₂, a saturated red-emitting device was obtained. At a luminescence of 100 cd m⁻², the device shows efficiencies of 10.3 cd A⁻¹ and 9.1 Lm W⁻¹ with CIE coordinates of (0.67, 0.33). The device also shows a good projected lifetime of over 30000 h at an initial brightness of 100 cd m⁻². Due to the reasonable good efficiency and stability of the device even in a simple device configuration, we believe that Ir(piq)₂bop is a promising organic phosphor for applications in OLED technology.

Experimental Section

Absorption and fluorescence spectra were recorded with a Perkin-Elmer Lambda 2S UV-Vis spectrophotometer and a Perkin-Elmer LS50B luminescence spectrophotometer, respectively. The highest occupied molecular orbital (HOMO) value of the Ir complex was measured by ultraviolet photoelectron spectroscopy using a VG ESCALAB 220i-XL ultrahigh vacuum (UHV) surface analysis system. The lowest unoccupied molecular orbital (LUMO) value was determined from the difference between the HOMO energy and the energy gap determined from the optical absorption edge.

Indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 30 Ω/square were used as anodes for OLEDs, and all layers were deposited by vacuum thermal evaporation. Before successive deposition, the substrates were patterned by traditional lithography, cleaned and dried in an oven at 120 °C. The ITO substrates were then treated with UV light-ozone before loading into a deposition chamber. All organic layers and the cathode were sequentially deposited onto the ITO substrates under a pressure of 10⁻⁶ Torr. Immediately after preparation, the device was encapsulated under nitrogen atmosphere using a two-component epoxy glue and a glass lid. Current density-voltage-luminance (*J*-*V*-*L*) characteristics, CIE coordinates, and electroluminescent (EL) spectra were measured with a programmable Keithley model 237 source and a Photoresearch PR650 photometer.

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