

A Synthesis and Luminescence Study of Ir(ppz)₃ for Organic Light-Emitting Devices

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Tris(1-phenyl- κC^1 -pyrazolato- κN^2)iridium (Ir(ppz)₃) was prepared and its luminescence properties were investigated for the application to organic light-emitting devices (OLEDs). The photoluminescence (PL) spectra of Ir(ppz)₃ in dichloromethane showed a peak at 437 nm at room temperature. The luminescent lifetime of an Ir(ppz)₃ film doped in CBP was found to be 218 ns, which indicated that its emission is phosphorescent. OLEDs were fabricated with doped films of Ir(ppz)₃ in several hosts, and the electroluminescence (EL) peak was observed at 450 nm. The luminance of OLEDs was pure blue, with the CIE coordinates of $x = 0.158$, $y = 0.139$ at 100 cd/m², but luminous efficiencies were low since the LUMO of Ir(ppz)₃ is higher than those of the hosts used.

Since Tang and co-workers reported organic light-emitting devices (OLEDs) with a multi-layer structure, materials for the devices have been extensively studied over the past decade.^{1,2} Luminescent materials for these devices are generally classified into two types, fluorescent ones and phosphorescent ones. Fluorescent materials internally experience a quantum efficiency loss, however, due to non-emissive triplet exciton corresponding to 75% of the excited states. Recently, to achieve a high efficiency in OLED, electrophosphorescent devices were developed by Forrest and Thompson.³ An internal quantum efficiency approaching 100% was obtained by utilizing both singlet and triplet excitons occurring in the emitting layer doped with a phosphorescent dopant.

The heavy metal, such as Ir or Pt, in the complexes was known to induce the intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states.^{4,5} The spin-forbidden nature of radiative relaxation from the triplet excited state was then possible, resulting in high phosphorescence efficiencies. Thus, iridium complexes and platinum complexes have extensively been introduced to the emitting layer as dopants. In addition, iridium complexes were known to have high photoluminescence efficiency and relatively short excited state lifetime, which minimizes quenching of triplet emissive states.⁶

Color tuning of the emission of the iridium complexes can be achieved by a suitable choice of the ligand, and thus iridium complexes chelated with various kinds of ligands have been reported, demonstrating red, green, and blue phosphorescence. Suitable ligands can be designed from theoretical calculations and synthesized to be complexed with the Ir center, yielding Ir complexes displaying the desirable color emission.

Herein, we report the synthesis of an iridium complex, Ir(ppz)₃, and investigation of its luminescent properties. It

was reported that Ir(ppz)₃ was employed as an exciton blocking layer or as a dopant in the polymer host in other devices, but to best of our knowledge, this is the first time a device containing the emitting layer of Ir(ppz)₃ in monomer hosts was fabricated using a vacuum deposition method.⁷ A theoretical calculation indicated that the ligand, ppz, would lead to blue emission upon coordination with the iridium center. The excited state lifetime of Ir(ppz)₃ was found to be more than 200 ns, indicating that the emission was phosphorescence. Electroluminescent (EL) devices were fabricated with a doped film of Ir(ppz)₃ in several hosts, and their EL characteristics were discussed.

Experimental

General Methods. All the procedures for the synthesis of Ir(ppz)₃ were carried out in an N₂ or Ar atmosphere. Though the resulting complex was found to be air stable, the stability of the intermediate species was a concern, and thus precautions against air and water were taken during the synthesis. Solvents for the synthesis were pre-dried according to purification methods, or anhydrous solvents packaged under nitrogen were purchased and used with standard Schlenk techniques. The ligand, 1-phenylpyrazole (ppz), was purchased from Aldrich. UV-vis spectra were obtained on a 8452A Hewlett Packard spectrophotometer with 1×10^{-4} M ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) of Ir(ppz)₃ in CH₂Cl₂. PL spectra were obtained on a LS50B BSM spectrophotometer with an excitation wavelength of 350 nm. The concentration of Ir(ppz)₃ in CH₂Cl₂ for the PL solution spectra was 1×10^{-3} M. ¹H NMR spectra were obtained on Bruker 200 spectrometers. FAB/MS spectra were measured on a Jeol JMS-AX505WA at Seoul National University in Korea. Elemental analyses were also performed by an EA1110 of CE instruments at Seoul National University in Korea.

Synthesis of the Ir(ppz)₃. Ir(ppz)₃ was synthesized from reaction of ppz with Ir(acac)₃, according to the procedure previously

reported for Ir(ppy)₃ and its derivatives.⁸ Ir(acac)₃ (100 mg) and more than three molar amounts of ppz (0.95 mL) were dissolved in degassed glycerol (10 mL), and the mixture was heated at reflux under nitrogen for 10 h. After cooling, 1 M HCl (50 mL) was added to the reaction mixture resulting in the precipitation of the crude product. The precipitate was collected by filtration and dissolved in hot dichloromethane (30 mL). The volume of the dichloromethane solution was reduced, and the concentrated solution was flash-chromatographed on silica and eluted with CH₂Cl₂ to remove the dark impurities. The yellow solution was concentrated and recrystallized from a CH₂Cl₂/MeOH solution to give a yellow powder of Ir(ppz)₃ with a yield of 25%.

Ir(ppz)₃: Tris(1-phenyl- κ C¹-pyrazolato- κ N²)iridium, mp > 250 °C. UV-vis (λ /nm, (ϵ /M⁻¹ cm⁻¹): 242 (4.4 $\times$ 10⁴), 292 (1.7 $\times$ 10⁴), 325 (1.4 $\times$ 10⁴). ¹H NMR (200 MHz, CDCl₃) δ 6.76–7.96 (m, 18H), 6.37 (d, 3H). FAB/MS calcd for C₂₇H₂₁N₆Ir 621.7, found 622. Anal. Calcd for C₂₇H₂₁N₆Ir: C, 52.16; H, 3.40; N, 13.52%. Found: C, 52.05; H, 3.33; N, 12.82%.

Theoretical Calculation. Computationally, the electronic ground states of Ir(ppz)₃ and its host materials (CBP, MCP, BCP) were calculated using the B3LYP density functional method.⁹ LANL2DZ and 6-31G(d) basis sets were employed for Ir and other atoms, respectively. In the case of Ir(ppz)₃, time-dependent DFT (TD-DFT) calculations using the B3LYP functional method were performed at the respective ground-state geometry, while the basis set of ppz ligands were changed to 6-31+G(d) for the first excited-state calculation of the complex.^{10–12} Typically, the lowest 10 triplet and 10 singlet roots of the nonhermitian eigenvalue equations were obtained to get the vertical excitation energies and compared with the absorption spectrum to examine each peak.

Fabrication of OLED. OLEDs were fabricated by high vacuum ($\sim 1.3 \times 10^{-4}$ Pa) thermal deposition of organic materials onto the surface of an indium tin oxide (ITO, 30 $\Omega/\square$, 80 nm) coated glass substrate, chemically cleaned using acetone, methanol, distilled water, and isopropyl alcohol. The organic materials were deposited in the following sequence: 40 nm of *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) was used as a hole transporting layer, followed by a 20 nm thick emissive layer consisting of various hosts and Ir(ppz)₃ as a dopant. The hosts used were 4,4'-*N,N'*-dicarbazole-1,1'-biphenyl (CBP), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 1,3-bis(*N*-carbazolyl)benzene (MCP), and 1,3,5-tris(*N*-carbazolyl)benzene (TCP), and the doping concentration was 8 wt %. Ten nm thick BCP and 30 nm thick tris(8-quinolino)aluminum (Alq₃) layers were deposited as an exciton blocking layer and as an electron transporting layer, respectively. The typical organic deposition rate was 0.2 nm/s. Finally, 150 nm of Al:Li was deposited as a cathode. All organic materials used were supplied by Gracel Display Incorporation in Korea. The active area of the OLED was 0.09 cm². Current–voltage–light intensity of OLEDs was measured with a source measure unit (Keithley 236), an electrometer (Keithley 617), and a photodiode. The transient PL was measured with a photo-excitation at 337 nm from a pulsed nitrogen laser. The pulse width was 4 ns. The response was detected by a fast PMT and digitized by a 500 MHz digital storage oscilloscope (Tektronix TDS 654C).

Results and Discussion

Synthesis and Characterization of Ir(ppz)₃. Ir(ppz)₃ was prepared from the one-step reaction of Ir(acac)₃ with the ppz ligand as shown in Fig. 1. The yield of Ir(ppz)₃ was 25%, which was relatively low compared to those of Ir(ppy)₃ or other iridi-

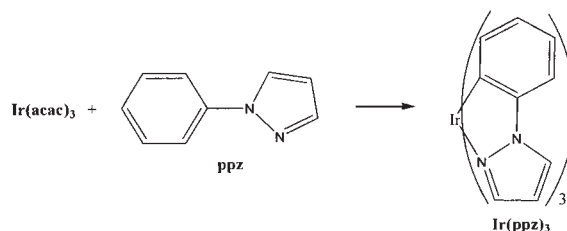


Fig. 1. A synthetic scheme of Ir(ppz)₃.

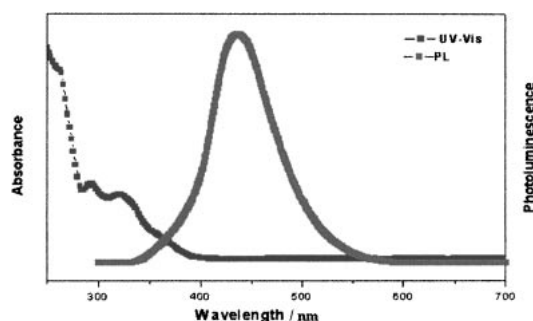


Fig. 2. UV-vis and PL spectra of Ir(ppz)₃.

um complexes. We think that it is due to extra nitrogen capable of a different coordination in ppz, and due to a lack of ligand stability under the reaction conditions.

The melting point of Ir(ppz)₃ was above 250 °C, while free ppz was liquid at room temperature. The ¹H NMR spectra of these complexes showed proton peaks of the coordinated ligand at 7.96–6.76, and 6.37 ppm, shifted upfield compared to those of the free ligand at 7.96–7.29, and 6.47 ppm, respectively. FAB/MS showed the molecular ion peak at *m/e* 622 for the complex. Elemental analysis results of Ir(ppz)₃ were also found to be satisfactory.

The photophysical properties of Ir(ppz)₃ were investigated using UV-vis absorption spectra and photoluminescence (PL) spectra. The absorption spectra for Ir(ppz)₃ are shown in Fig. 2. The absorption patterns of the spectra indicated that π – π^* ligand-centered (LC) transitions occurred below 250 nm, and metal-to-ligand charge transfer (MLCT) transitions occurred above 270 nm, similar to known cyclometallated iridium complexes.¹³

The results of the DFT calculation on the ground state of Ir(ppz)₃ indicated that 5d orbitals of Ir and orbitals of ppz ligands were strongly mixed in the three highest occupied molecular orbitals (HOMOs), which have been labeled as *d*₂, *d*_{1a} and *d*_{1b} following Hay's notation.¹⁴ The 5d character in those orbitals was 50% for *d*₂ and 48% for *d*_{1a} and *d*_{1b} from the population analysis. On the other hand, the three lowest unoccupied molecular orbitals (LUMOs), labeled as π_1^* , π_{2a}^* , and π_{2b}^* , did not show any 5d– π mixing, indicating the 5d character was 0% for π_1^* and 3% for π_{2a}^* and π_{2b}^* .

As shown in Table 1, the calculated excitation energy for the lowest excited triplet state (*T*₁) in Ir(ppz)₃ was 3.14 eV, with two higher triplet states extremely closed in energy. It was 0.55 eV higher than that of Ir(ppy)₃.¹⁴ All corresponded to excitations from an electron in an occupied orbital of *d*₂, *d*_{1a}, and *d*_{1b} containing significant Ir 5d character in the lowest π^* orbitals of ppz ligands. Because the ground states of *d*₂, *d*_{1a}, and *d*_{1b}

Table 1. Calculated Excitation Energies (E), Dominant Orbital Excitation, and Oscillator Strengths (f) from TD-DFT Calculations for $\text{Ir}(\text{ppz})_3$

Triplet states	Excitation	E/eV	Wavelength/nm	
$T_1(^3A)$	$d_2 \rightarrow \pi_1^*$	3.14	394.5	
$T_2(^3E)$	$d_{1a} \rightarrow \pi_1^*$	3.15	394.3	
	$d_{1b} \rightarrow \pi_1^*$	3.15	394.3	
$T_3(^3A)$	$d_2 \rightarrow \pi_1^*$	3.43	361.4	
$T_4(^3E)$	$d_2 \rightarrow \pi_{2a}^*$	3.45	359.2	
	$d_2 \rightarrow \pi_{2b}^*$	3.45	359.2	
$T_5(^3A)$	$d_2 \rightarrow \pi_1^*$	3.58	345.7	
$T_6(^3E)$	$d_{1a} \rightarrow \pi_1^*, d_2 \rightarrow \pi_{2a}^*$	3.59	345.3	
	$d_{1b} \rightarrow \pi_1^*, d_2 \rightarrow \pi_{2b}^*$	3.59	345.3	
$T_7(^3A)$	$d_2 \rightarrow \pi_{2a}^*, d_{1b} \rightarrow \pi_1^*$	3.64	340.2	
Singlet states	Excitation	E/eV	Wavelength/nm	f
$S_1(^1A)$	$d_2 \rightarrow \pi_1^*$	3.56	348.1	0.0141
$S_2(^1E)$	$d_{1b} \rightarrow \pi_1^*$	3.62	342.1	0.0275
	$d_{1a} \rightarrow \pi_1^*$	3.62	342.1	0.0277
$S_3(^1E)$	$d_2 \rightarrow \pi_{2a}^*$	3.66	338.8	0.0053
	$d_2 \rightarrow \pi_{2b}^*$	3.66	338.8	0.0052
$S_4(^1A)$	$d_{1a,1b} \rightarrow \pi_{2a,2b}^*$	3.70	335.5	0.0039
$S_5(^1A)$	$d_{1a,1b} \rightarrow \pi_{2a,2b}^*$	3.76	329.9	0.0556
	$d_{1a,1b} \rightarrow \pi_{2a,2b}^*$	3.76	329.9	0.0556
$S_6(^1A)$	$d_{1a,1b} \rightarrow \pi_{2a,2b}^*$	3.85	322.2	0.0622
$S_7(^1A)$	$d_2 \rightarrow \pi_{4a}^*$	4.56	271.8	0.0090

orbitals have very similar energy, it is thought that any excitation of an electron starts from one of them. Since the occupied orbital has a strong 5d component and the ligand π^* virtual orbital predominates in the unoccupied orbital, we assigned the triplet (T_1 – T_7) and the singlet (S_1 – S_7) states in Table 1 to MLCT (metal-to-ligand charge transfer) states.

It is known that an evidence for significant mixing of singlet and triplet excited states is seen in both absorption and emission spectra of phosphorescent materials which show strong spin–orbit coupling. The strong spin–orbit coupling on the Ir center thus allows for the formally spin-forbidden $^3\text{MLCT}$ transition with an intensity comparable to the allowed $^1\text{MLCT}$ transition.¹⁵

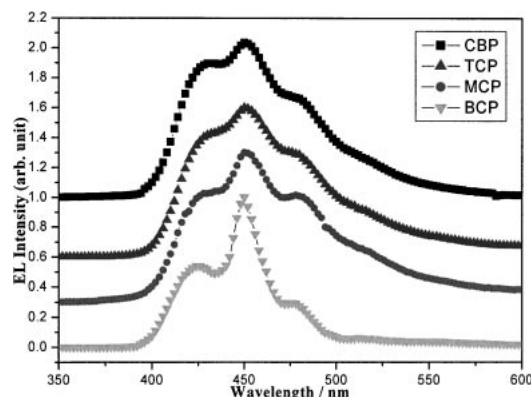
From the comparison with the absorption spectrum shown in Fig. 2, peaks distributed from 280 to 400 nm were assigned to MLCT absorptions. Singlet excited states (S_1 – S_7) and triplet excited states (T_1 – T_7) are separately located in the regions 270–350 nm and 340–400 nm, respectively. The peaks located at ca. 325 nm are believed to originate from S_5 and S_6 , whose oscillator strengths are dominant.

The powder of $\text{Ir}(\text{ppz})_3$ exhibited green luminescence under 365 nm light. On the other hand, the solid and solution PL spectra showed somewhat different results. The PL solution spectra of $\text{Ir}(\text{ppz})_3$ in dichloromethane were obtained, as shown in Fig. 2. $\text{Ir}(\text{ppz})_3$ showed an emission at 437 nm. The spin-coated neat solid film of $\text{Ir}(\text{ppz})_3$ on a quartz plate also exhibited PL peaks at 410 nm with broad and weak intensity, and at 485 nm with relatively strong intensity.

The solid film of the complex doped in CBP (4,4'- N,N' -dicarbazole-1,1'-biphenyl) was prepared by spin coating on a quartz plate, and its emission lifetime at 437 nm was obtained. The excited state lifetime was measured to be 218 ns, indicating that the emission from the film of $\text{Ir}(\text{ppz})_3$ doped in CBP was

blue phosphorescence.

Electroluminescent properties of $\text{Ir}(\text{ppz})_3$ in OLEDs were studied in detail by using $\text{Ir}(\text{ppz})_3$ as an emitter doped in various hosts. The device structure was ITO/NPB/host: $\text{Ir}(\text{ppz})_3$ /BCP/Alq/Al:Li. Hosts used were 4,4'- N,N' -dicarbazole-1,1'-biphenyl (CBP), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 1,3-bis(N -carbazolyl)benzene (MCP), and 1,3,5-tris(N -carbazolyl)benzene (TCP). The EL spectra of the OLEDs with various hosts are shown in Fig. 3. All spectra showed very similar features regardless of the host, which indicates that the emission spectra are from $\text{Ir}(\text{ppz})_3$. Furthermore, the emission must originate from $\text{Ir}(\text{ppz})_3$, not from the host, since the emission was found to be phosphorescence. The EL emission peak was shown at 450 nm, slightly shifted from the PL solution emission at 437 nm. The CIE coordinates for the device were measured to be $x = 0.158$, $y = 0.139$ at 100 cd/m^2 , which corresponds to pure blue.

Fig. 3. EL spectra of $\text{Ir}(\text{ppz})_3$ with various hosts.

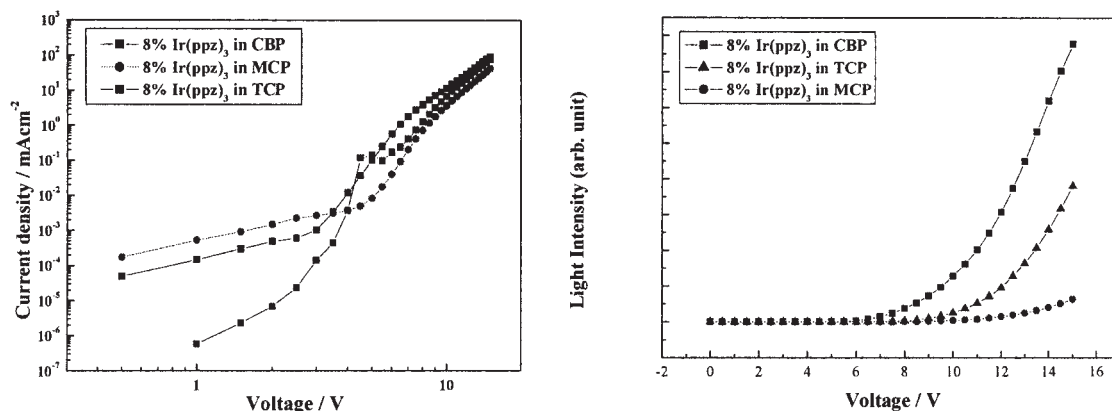


Fig. 4. J-V-L characteristics of OLEDs using 8% $\text{Ir}(\text{ppz})_3$:various hosts. The device structure is ITO/NPB/8% $\text{Ir}(\text{ppz})_3$:various hosts/BCP/Alq/Al:Li.

Table 2. HOMO, LUMO, and Energy Gap of $\text{Ir}(\text{ppz})_3$ and of Its Host Materials Calculated with B3LYP Density Functional

	$\text{Ir}(\text{ppz})_3$	CBP	MCP	BCP
LUMO	-0.5537	-1.2289	-0.7498	-1.2828
HOMO	-5.0251	-5.3167	-5.4555	-5.7863
Gap	4.4714	4.0878	4.7057	4.5035

There is a report that a device containing $\text{Ir}(\text{ppz})_3$ doped in a polymer film showed an emission at 547 nm.^{7c} This EL wavelength is significantly shifted from the PL wavelength of $\text{Ir}(\text{ppz})_3$. It is believed that the device structure influences the EL wavelength in that patent since the device structure is quite different from ours.

J-V-L characteristics of OLEDs of $\text{Ir}(\text{ppz})_3$ with various hosts are shown in Fig. 4. The device with CBP showed a maximum luminance of 365 cd/m^2 at 216 mA/cm^2 and a maximum luminous efficiency of 0.23 cd/A at 10 V.

It was considered that the low luminous efficiencies of OLEDs with $\text{Ir}(\text{ppz})_3$ were caused by the energy level mismatch between the hosts and $\text{Ir}(\text{ppz})_3$. The calculated LUMO of the hosts are shown in Table 2. There are two energy transfer mechanisms—Dexter transfer and Forster transfer. For the Forster transfer, the relevant energy gap is the excitation energy, while for the Dexter transfer the relative position of the excited state energy level of the host to that of the dopant is important. Since the LUMO of $\text{Ir}(\text{ppz})_3$ is higher than that of hosts as shown in Table 2, the Dexter energy transfer from the host to $\text{Ir}(\text{ppz})_3$ does not seem to be effective.

Since all of the hosts used were not proper for the Dexter energy transfer from the host to $\text{Ir}(\text{ppz})_3$, the main energy transfer mechanism would be a Forster transfer. In fact, the calculated triplet excitation energy of $\text{Ir}(\text{ppz})_3$ is 3.14 eV, while the singlet excitation energy of CBP is 3.50 eV, which means CBP could be used as a host for $\text{Ir}(\text{ppz})_3$. Forster transfer is known to be governed by the spectral overlapping between the absorption of the dopant and the emission of the host. The emission peaks of MCP, CBP, and BCP were 360 nm, 380 nm, and 450 nm, respectively. CBP and MCP show good energy overlapping, while BCP is not good enough to be used as a host. The reason why the device with CBP showed higher EL efficiency than the

one with MCP could be related to the better PL efficiency of CBP than that of MCP.

To develop an efficient blue electrophosphorescent device, it is really necessary to have a host material with proper energy levels and a wide band gap.

Conclusion

Tris(1-phenyl- κC^1 -pyrazolato- κN^2)iridium ($\text{Ir}(\text{ppz})_3$) was prepared and its luminescent characteristics were investigated. UV-vis spectra exhibited absorption below 400 nm. Theoretical calculations revealed that the absorption peak distributed from 270 to 400 nm originated from an MLCT transition of singlet and triplet states. PL solution spectra showed an emission peak at 437 nm and the excited state radiative lifetime of $\text{Ir}(\text{ppz})_3$ was 218 ns, which indicates the emission was blue phosphorescence. The luminance of OLED using $\text{Ir}(\text{ppz})_3$ was pure blue, but luminous efficiencies were low, considering the fact that the LUMO of $\text{Ir}(\text{ppz})_3$ is much higher than those of the hosts used. To develop an efficient blue electro-phosphorescent device, it is necessary to have a host material with proper energy levels and a wide band gap.

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